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PEACEFUL USES OF ATOMIC ENERGY

UNITED NATIONS

PROCEEDINGS
OF THE
INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY

Volume 15
APPLICATIONS OF RADIOACTIVE ISOTOPES AND FISSION PRODUCTS IN RESEARCH AND INDUSTRY

Proceedings of the International Conference on the Peaceful Uses of Atomic Energy

Held in Geneva
8 August-20 August 1955

Volume 15

Applications of Radioactive Isotopes and Fission Products in Research and Industry

UNITED NATIONS
New York
1958

UNITED NATIONS PUBLICATION

Sales No.: 1956. IX.1. Vol.15

A/CONF.8/15

Price: US$7.50.; 54/-stg.; 32.00 Sw. frs
(or equivalent in other currencies)

PREFACE

The Proceedings of the International Conference on the Peaceful Uses of Atomic Energy are published in a series of 16 volumes, as follows:

Volume Number	Title	Sessions Included
1	The World's Requirements for Energy; The Role of Nuclear Power	2, 3.2, 4.1, 4.2, 5, 24.2.
2	Physics; Research Reactors	6A, 7A, 8A, 9A, 10A.1.
3	Power Reactors	10A.2, 3.1, 11A, 12A, 13A, 14A.
4	Cross Sections Important to Reactor Design	15A, 16A, 17A, 18A.
5	Physics of Reactor Design	19A, 20A, 21A, 22A, 23A.
6	Geology of Uranium and Thorium	6B, 7B.
7	Nuclear Chemistry and the Effects of Irradiation	8B, 9B, 10B, 11B, 12B, 13B.
8	Production Technology of the Materials Used for Nuclear Energy	14B, 15B, 16B, 17B.
9	Reactor Technology and Chemical Processing	7.3, 18B, 19B, 20B, 21B, 22B, 23B.
10	Radioactive Isotopes and Nuclear Radiations in Medicine	7.2 (Med.), 8C, 9C, 10C.
11	Biological Effects of Radiation	6.1, 11C, 12C, 13C.1.
12	Radioactive Isotopes and Ionizing Radiations in Agriculture, Physiology and Biochemistry	7.2 (Agric.), 13C.2, 14C, 15C, 16C.
13	Legal, Administrative, Health and Safety Aspects of Large-Scale Use of Nuclear Energy	4.3, 6.2, 17C, 18C.
14	General Aspects of the Use of Radioactive Isotopes; Dosimetry	7.1, 19C, 20C.
15	Applications of Radioactive Isotopes and Fission Products in Research and Industry	21C, 22C, 23C.
16	Record of the Conference	1, 24.1, 24.3.

These volumes include all the papers submitted to the Geneva Conference, as edited by the Scientific Secretaries. The efforts of the Scientific Secretaries have been directed primarily towards scientific accuracy. Editing for style has been minimal in the interests of early publication. This may be noted especially in the English translations of certain papers submitted in French, Russian and Spanish. In a few instances, the titles of papers have been edited to reflect more accurately the content of those papers.

The editors principally responsible for the preparation of these volumes were: Robert A. Charpie, Donald J. Dewar, André Finkelstein, John Gaunt, Jacob A. Goedkoop, Elwyn O. Hughes, Leonard F. Lamerton, Aleksandar Milojević, Clifford Mosbacher, César A. Sastre, and Brian E. Urquhart.

The verbatim records of the Conference are included in the pertinent volumes. These verbatim records contain the author's corrections and, where necessary for scientific accuracy, the editing changes of the Scientific Secretaries, who have also been responsible for inserting slides, diagrams and sketches at appropriate points. In the record of each session, slides are numbered in numerical order through all presentations. Where the slide duplicates an illustration in the submitted paper, appropriate reference is made and the illustration does not appear in the record of the session.

Volume 16, "The Record of the Conference," includes the complete programme of the Conference, a numerical index of papers and an author's index, the list of delegates, the records of the opening and closing sessions and the complete texts of the evening lectures.

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Application of Tracer Atoms in the Study of the Mechanisms of Chemical Reactions

By V. N. Kondratyev, USSR

One of the principal objectives in studying the chemical transformations of substances is to gain an insight into the mechanism of chemical reactions which is a problem of commanding interest from both the theoretical and the practical point of view. Owing, however, to the complexity of the mechanism of most reactions, as well as to the frequent lack of sufficient data about the conditions under which the reaction proceeds, our knowledge of the subject is still very limited. Hence the value of every new method of studying the mechanism of chemical reactions. A method which in its possibilities and effectivity eclipses many employed up to now, whether purely chemical, physico-chemical or physical, is that of radioactive tracers. Their application on a large scale in various fields of science and engineering has been made possible by the discovery that nuclear energy can be put to practical uses. With the help of this method scientists in many countries have, in a short period of time, obtained extremely valuable results, which have considerably broadened and deepened our knowledge of the mechanism of chemical reactions.

The purpose of the present communication is to illustrate, by a limited number of examples taken from the investigations of scientists working in various research institutions of the Soviet Union, the high effectivity of tracer techniques and certain new possibilities offered by the application of this method to the study of the mechanism of chemical reactions.

The mechanism of a complex chemical reaction is actually a combination of a large number of reaction stages, by means of which the initial substances are ultimately converted into the reaction products. Therefore an understanding of the sequence in which some substances are converted into others in the course of a chemical reaction represents an important step towards understanding the chemical mechanism of the reaction. Of great importance in solving this problem is the kinetic method employing tracer techniques, evolved in connection with the new possibilities of investigation afforded by the discovery of radioactive tracers and originally applied to the study of biochemical processes associated with metabolism in the living organism.[1] M. B. Neiman and coworkers[2] applied the kinetic method to the study of the mechanism of chemical reactions. They demonstrated that the kinetic method not only makes it possible to establish the sequence of the transformation of some substances into others, but also offers the possibility of determining the rates of the formation and expenditure of the various substances involved in the reaction.

The essence of the kinetic method lies in the fact that by adding a substance labelled with an appropriate radioactive tracer at the initial or any other stage of the reaction and measuring the kinetics of the concentration and specific activity variation of both this substance and the substances which are the supposed products of the chemical transformation of the added substance, it is possible to establish the true sequence of the chemical transformation of the substances involved in the reaction and the rate of transformation of the substances being investigated at various stages of the reaction. For example, let the assumed sequence of reaction stages be such that some intermediate substance B, obtained from the substances A_1 and A_2 by two different routes, be in turn converted into the substance (or substances) C by one or several routes, as represented by the following scheme:

$$\begin{array}{l} \ldots \rightarrow A_1 \overset{w_1}{\searrow} \\ \qquad\qquad\quad B \overset{w'}{\rightarrow} C \rightarrow \ldots \\ \ldots \rightarrow A_2 \overset{w_2}{\nearrow} \end{array}$$

where w_1, w_2 and w' represent the rates of corresponding stages. Furthermore, let A_1 be the supposed precursor of the substance B. To check this assumption a small quantity of the substance A_1 labelled with a radioactive isotope (together with a small quantity of unlabelled B) is added to the initial mixture. In this case the specific activity of the substance will evidently decrease monotonously from the moment the radioactive isotope is introduced into the mixture, whereas the specific activity of the substance B will increase (if B is formed from A_1), at some moment reach a maximum and then begin to diminish. From the condition of the maximum for the relation of the specific activities of the substances B and A_1 (β and α_1) which must exist at the moment the maximum is reached, we obtain the following expression:

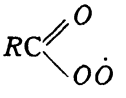
Original language: Russian.

$$\frac{\beta}{\alpha_1} = \frac{w_1}{w_1 + w_2}$$

On the basis of this relation it is possible to check the supposed scheme of the reaction by measuring the specific activities of A_1 and B in the course of the reaction. For instance, if the specific activities of A_1 and B in the maximum β are equal, which can only be if $w_2 = 0$, we conclude that in this reaction the substance B is formed exclusively as a result of the conversion of the substance A_1, which is thus its precursor. If, on the other hand, $\beta < \alpha_1$, then w_2 is not equal to 0 and the substance B is formed both via the substance A_1 and by other routes.

The data obtained by A. F. Lukovnikov and M. B. Neiman[3] while investigating the cold-flame oxidation of butane (at a temperature of 285°C) may be cited as an example of the application of the kinetic method to the study of the mechanism of complex chemical reactions. The question was posed whether carbon dioxide is obtained only owing to the oxidation of the carbon monoxide formed in the foregoing reaction stages or whether there are other routes by which CO_2 is formed. The answer to this question was found by adding a small quantity of carbon monoxide labelled with radioactive carbon, C^{14}, together with a small quantity of the usual CO_2, to the butane-oxygen mixture. The kinetic curves of the specific activities of CO (α) and CO_2 (β) are shown in Fig. 1. It is evident from this figure that the specific activity of CO_2 is always much less than the specific activity of CO, from which it follows that in the cold-flame oxidation of butane only an insignificant portion of the CO_2 is formed by the oxidation of CO. Measurements of the rate of the formation of CO_2 and of the rate of the formation of CO_2 from CO (w_1) revealed that at different stages of the reaction not more than 1–5% of the CO_2 is formed from CO.

In the opinion of A. F. Lukovnikov and M. B. Neiman, the main possible route of the formation of CO_2 in this reaction is that of the decay of the acyl peroxide radicals



which are formed in the course of butane oxidation; these radicals disintegrate into CO_2 and the alkoxyl radicals RO. It should be noted that a number of facts point to the presence of free radicals in oxidation reactions. In the experiments of A. F. Lukovnikov and M. B. Neiman in pentane oxidation, radical formation was proved by the following procedure. By oxidizing pentane at 305°C in the presence of 10% hydrogen containing HT, these authors observed a marked activity of the formaldehyde and acetaldehyde formed in the oxidation of C_5H_{12}. Since, in the conditions of the experiment, there is no exchange between pentane and molecular hydrogen, A. F. Lukovnikov and M. B. Neiman draw the conclusion that the exchange in the course of the oxidation reaction points to the presence of free radicals in the reaction zone.

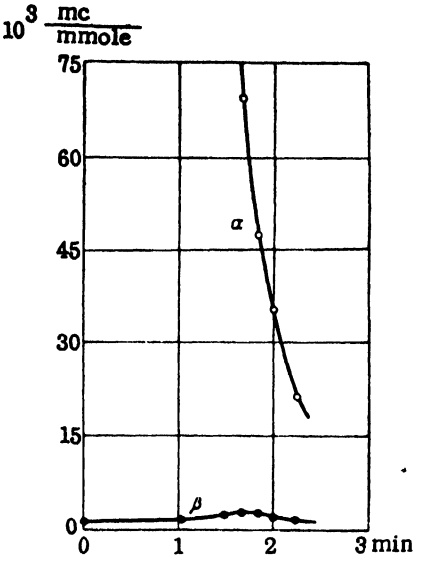


Figure 1. Kinetic curves of the specific activities of CO (α) and CO_2 (β) for the reaction of butane oxidation, with the addition of labelled carbon monoxide

Similar results were also obtained by L. Y. Margolis and S. Z. Roginsky,[4] who studied the catalytic oxidation of olefines over silver and active oxides by tracer techniques (C^{14}). Some of the results obtained by these authors are shown in Fig. 2 and Tables 1 and 2. Fig. 2 relates to ethylene oxidation over silver (at a temperature of 220°C). The products of this reaction, which is of practical importance, are ethylene oxide and carbon dioxide. The question was posed whether the CO_2 is formed as a result of the further oxidation of ethylene oxide or whether both reaction products are formed independently. In the former case the specific activity of the CO_2 formed in a mixture of labelled ethylene and common ethylene oxide should be close to the specific activity of ethylene oxide. It may be seen from Fig. 2 that the specific activity of CO_2 is practically many times

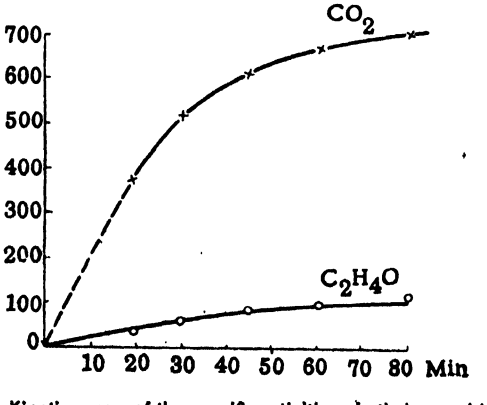


Figure 2. Kinetic curves of the specific activities of ethylene oxide and carbon dioxide for the reaction of the catalytic oxidation of ethylene, with the addition of labelled ethylene

greater than the specific activity of C_2H_4O, which means that the bulk of the CO_2 is formed not through ethylene oxide. The data of Table 1, which gives the rates of ethylene oxide formation and CO_2 formation in pure ethylene and in the case of the addition of aldehydes (the data were obtained by measuring the activity distribution of the reaction products when adding labelled ethylene or aldehyde), further show that the aldehyde exerts practically no influence on the rate of the formation of CO_2. Consequently, aldehydes cannot be the chief intermediate in the catalytic oxidation of ethylene. The products of C_2H_4 oxidation over silver contain practically no aldehydes, this being due not to their oxidation or degradation, but to the absence of processes of their formation.

Table 2 gives data for the rates of the formation of aldehydes and CO_2 in the oxidation of ethylene over V_2O_5.* The rate of the formation of CO_2 from ethylene undergoes no change when the aldehyde or ethylene oxide are present in the mixture. From this it follows that aldehydes cannot be the chief intermediate products of the exhaustive oxidation of ethylene.

L. Y. Margolis and S. Z. Roginsky also proved by similar experiments that CO and CO_2 are formed independently in the oxidation of olefines.† From the results obtained they draw the conclusion about the independent, parallel—and not consecutive—formation of oxides, aldehydes and acids in the catalytic oxidation of hydrocarbons. On the basis of these data S. Z. Roginsky has developed an electron-peroxide theory of mild catalytic oxidation, in which the active intermediates are O_2^-, RO_2^-, etc.[5]

It might also be mentioned that tracer techniques made it possible to answer the long unanswered question about the transfer of the oxygen atoms of the oxide catalyst in the course of the reaction of oxidation, a question of fundamental importance for the theory of oxidation catalysis. By applying the tracer method with the use of O^{18} to the low-temperature oxidation of carbon monoxide over MnO_2 G. Y. Turovsky and F. M. Weinstein, as well as V. N. Vasilyev, S. Y. Elovich and L. Y. Margolis,[6] unequivocally proved the absence of any transfer.

* In these, as in the previous experiments, either the ethylene or the aldehyde was labelled with the isotope C^{14}.

† The products of the oxidation of a mixture of ethylene labelled with the isotope C^{14} and common acetaldehyde were studied in these experiments. It was shown that the activity distribution between CO and CO_2 is practically equal. However, there is no oxidation of CO into CO_2 in these conditions.

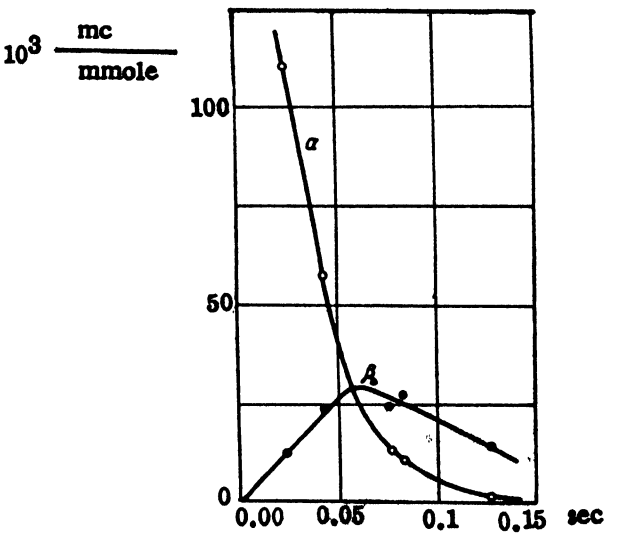


Figure 3. Kinetic curves of the specific activities of formaldehyde and carbon monoxide for the reaction of methane oxidation, with the addition of labelled HCHO

Still another example of the application of the kinetic method is afforded by the results obtained in studying the thermal oxidation of methane. In a paper on photochemical mercury-sensibilized methane oxidation, A. B. Nalbandyan[7] demonstrated that at high temperatures the principal products of this reaction are formaldehyde, carbon monoxide and carbon dioxide. An analysis of the kinetic curves of the accumulation of formaldehyde and carbon monoxide justified the assumption that the reaction sequence is the following:

$$CH_4 \xrightarrow{+O_2} HCHO \xrightarrow{+O_2} CO \xrightarrow{+O_2} CO_2$$

In view of the importance of this conclusion for establishing the mechanism of the thermal oxidation of methane, A. B. Nalbandyan, M. B. Neiman and co-workers[8] checked the correctness of this sequence of methane conversions for the case of the thermal reaction ($t^0 = 670°C$) by the kinetic method. Figure 3 shows the kinetic curves of the specific activities of formaldehyde (α) and carbon monoxide (β). The observed intersection of these curves points to the exclusive formation of carbon monoxide by the oxidation of the formaldehyde produced in the previous reaction stage. In this way the results of the study of methane thermal oxidation fully bear out the sequence of reaction stages established by photochemical enquiry. We see that unlike the reactions of butane oxidation and the catalytic oxidation of ole-

Table 1. Rates of Partial Reactions (in arbitrary units) in Oxidizing Ethylene Labelled with C^{14}, Pure Ethylene, and Ethylene Mixed with Aldehydes Over Ag at 220°C

Reaction	C_2H_4			Note
	Pure	HCHO	CH_3CHO	
1. Formation of ethylene oxide	0.30	0.40	0.45	Main reaction
2. Formation of carbon dioxide	0.20	0.17	0.20	Side reaction

Table 2. Rates of Partial Reactions (in arbitrary units) in the Oxidation of Ethylene Labelled with C^{14} Over V_2O_5 at 400°C

Reaction	C_2H_4			Note
	Pure	CH_3CHO	Ethylene Oxide	
1. Formation of aldehydes	0.022	—	0.006	Main reaction
2. Formation of carbon dioxide	0.04	0.04	0.03	Side reaction

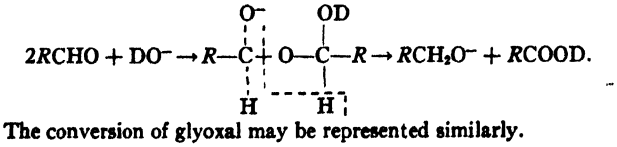
fines, considered above, the oxidation of methane is marked by a strict sequence of the separate stages.

The possibility of ascertaining whether any given reaction products are formed as a result of the consecutive conversion of one substance into another or whether these products appear in the course of the reaction by independent routes is of great practical significance, since it indicates ways of influencing the course of the reaction. For example, the establishment of the fact that the major portion of the losses as CO_2 and CO in the catalytic oxidation of ethylene is not associated with the further oxidation of ethylene oxide prompts us to seek a possibility of raising the yield of ethylene oxide by influencing the primary process of ethylene oxidation, i.e., by the choice of a proper catalyst. Similarly, the establishment of the consecutiveness of the formation of formaldehyde and carbon monoxide in the homogeneous oxidation of methane suggests that we concentrate our efforts on accomplishing a possible inhibition of the reaction of formaldehyde oxidation.

However, the kinetic method in the form in which it has been applied up to now does not yet furnish a key for solving the fundamental problem of the chemical reaction mechanism, the problem of the chemical nature of the elementary processes by which the reaction stages are effected. To solve this problem it is necessary to answer the following questions as well: is the reaction in question homolytic or heterolytic? what factors determine the type of the reaction? is it saturated molecules, radicals or ions that take part in the reaction? as well as the question —the rupture of which bonds is responsible for the intra- or inter-molecular rearrangements underlying the reaction? The tracer technique furnishes the most complete and exact answer to these questions. Following are separate examples of the application of isotopic tracers to the solution of these problems for chemical reactions of diverse classes.

Let us first examine the mechanism of certain oxidation-reduction reactions. It is a well-known fact that hydrogen in the O-H bonds undergoes acid dissociation with considerably greater ease than in C-H bonds. By analogy the difference in O-H and C-H bonds is often extended to chemical reactions on the assumption, for example, that reduction by alcohols is effected by the hydrogen of the hydroxyl group. However, as far back as 1938, H. Fredenhagen and K. F. Bonhoeffer[9] showed this analogy to be unjustified in the case of the Cannizzaro reaction: the products of the dismutation (disproportionation) of benzaldehyde, as well as of the intramolecular dismutation of glyoxal in heavy water, contained no deuterium bonded to carbon.‡

‡ According to the above-mentioned authors, the mechanism of the dismutation of aldehyde may be represented as follows:



$$2RCHO + DO^- \rightarrow R-C(O^-)(H)-O-C(OD)(H)-R \rightarrow RCH_2O^- + RCOOD.$$

The conversion of glyoxal may be represented similarly.

Table 3. Reduction of Aldehydes and Diazonium Salts by Ethanol Labelled with Deuterium in the Hydroxyl Group

Compound undergoing reduction	*Reduction product*	*Deuterium content in the hydroxyl group of alcohol*	*Deuterium content in reduction product*	
			Found	*Calculated*
Furfurol	Furfuryl alcohol	6770	21	1730
Benzaldehyde	Benzyl alcohol	6770	13	760
p-nitrophenyl-diazonium chloride	Nitro-benzene	2590	17	520
m-chlorophenyl-diazonium chloride	Chloro-benzene	2250	17	450
3-nitro-4-amino-toluene	3-nitro-toluene	3570	11	510

In a number of investigations G. P. Miklukhin and G. A. Razuvayev with co-workers found several new instances of reduction reactions (the Meerwein-Ponndorf reaction, the reduction of diazonium salts, the photochemical decomposition of phenylmercury) which proceed at the expense of the hydrogen of the C-H bond.

Some of the data obtained by G. P. Miklukhin and A. F. Rekasheva[10] are given in Table 3, giving data to the reaction of the reduction of aldehydes and diazonium salts by ethyl alcohol labelled with deuterium in the hydroxyl group.

Column 3 of the table gives the deuterium content in this group (γ); columns 4 and 5 give the deuterium content in the reduction product (column 2) of the corresponding initial compound (column 1). Column 4 gives the deuterium content found, experimentally and column 5, the deuterium content calculated on the assumption that the reduction is accomplished at the expense of the hydroxyl group hydrogen. It may be seen from these figures that the deuterium content in the reduction products is negligible compared with the calculated content; ergo the above assumption is erroneous.

These and other data enabled G. P. Miklukhin to assume that there occurs no transfer of a proton (deuton) in these reactions, but, instead, a hydrogen atom is transferred as a result of the homolytic cleavage of C-H bonds. This assumpion is corroborated by the fact that the C-H bond is weaker than the O-H bond, and therefore in reactions of the homolytic type we should observe the preferential cleavage of the carbon-hydrogen bond. We are led to the same conclusion by a study of the photochemical decomposition of phenylmercury hydroxide in methanol or ethanol labelled with deuterium in the hydroxyl group.[11] Here it is not the D atoms of the hydroxyl group of the alcohol, but the H atoms of the alkyl group of the alcohol that are transferred to the benzene formed as a result of the photolysis of the hydroxide, i.e., as in the previous cases, it is the C-H bond that is ruptured.

It might be added that similar results are obtained upon the reduction of diazonium salts with phos-

phorous acid or upon the oxidation of phenylhydrazine with copper sulphide and red prussiate of potash, in which case it is the P-H and N-H bonds of the reagents, and not the O-H bonds, that furnish the hydrogen.[12]

One of the factors determining the homolytic or heterolytic character of a reaction is the structure of the reactants. Some time ago B. V. Tronov[13] suggested that the frequently observed opposite action of the same substituent upon the reactivity of a given compound (determined by the chemical nature of the reagent with which this compound interacts) depends upon whether the reaction of that compound with that reagent is homolytic or heterolytic. This point of view was supported lately by the investigations of M. B. Neiman and co-workers[14] who studied the isotopic exchange reactions of halogen-containing compounds. These authors demonstrated that the same substituent exerts an opposite influence on the rate of isotopic exchange, depending upon whether the exchange reaction follows the ionic-molecular (heterolytic) or atomic (homolytic) mechanism.

The results of these investigations concerning the iodine exchange are shown in Table 4, where column 1 gives the compound in question, column 2, the rate constants of the exchange reaction (in 1 mole^{-1} sec^{-1} $\times$ 10^5) for the ionic mechanism of exchange (in the system RI + KI dissolved in 90% of ethyl alcohol + 10% of water at 30°C), and column 3 gives the relative values of the rate constants for the atomic mechanism (in the system RI + I_2 in cyclohexane solution, also at 30°C; the iodine atoms were produced photochemically by the dissociation of the I_2 molecules).

It is evident from the table that the lengthening of a normal aliphatic radical, as well as the branching of the carbon skeleton, causes a drastic decrease in the rate of the ionic reactions and an increase in the rate of the atomic reactions. Similarly opposite effects on the rates of reactions of both types are produced by making the SiR_3 radical more complicated and by substituting an I atom for an H atom.

An interesting example showing the influence of structural features upon reactivity is afforded by the reaction of the condensation of primary amines into a secondary amine which was studied by A. I.

Table 4. Rates of Atomic and Ionic Reactions of Isotopic Exchange of Iodine

Compound (RI)	*Ionic exchange*	*Atomic exchange*
CH_3I	890	0.02
CH_3CH_2I	56	0.04
$CH_3CH_2CH_2I$	33	0.056
H_3C / H_3C >CHI	3	1.6
$(CH_3)_3SiCH_2I$	13	0.8
$(C_2H_5)_3SiCH_2I$	4.5	1.2
CH_3I	890	0.02
CH_2I_2	0.3	34
CHI_3	0.1	1140

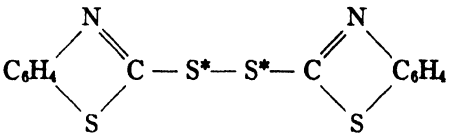
$$RNH_2 + R'NH_2 \rightarrow RNHR' + NH_3$$

Brodsky and co-workers[15] for different R and R', with the use of radioactive nitrogen N^{15}. As may be seen from Table 5, the site of the C-N bond rupture is determined by the ratio of the basicities of the two participating amines: the less basic amine (R' NH_2) yields ammonia, whereas the more basic produces a secondary amine.

Indeed, according to the data of this table, the strength of the C-N bond decreases in the following sequence: aniline > α — naphthylamin > benzamide. This series coincides with that founded on basicity. From this the authors conclude that the reaction proceeds through the nucleophilic addition of R' to nitrogen at R and a proton transfer from the amino group attached to R to the amino group at R'.

Examples were given above of the application of tracers to the study of the mechanism of oxidation and oxidation-reduction reactions. Another important class of reactions in the study of which the tracer method plays a substantial part is the class of reactions underlying the rubber vulcanization process.

The use of tracers has shed some light on the mechanism of the action of vulcanization accelerators. Here mention should be made first of the work of B. A. Dogadkin and co-workers,[16] who used dibenzothiazol disulphide labelled with radiosulphur S^{35} in the sulphide bridge as an accelerator



These authors found that dibenzothiazol disulphide is capable of producing the vulcanization effect in the absence of sulphur by partly entering into the structure of the vulcanizate and partly being reduced to mercaptan. The activity was found to be distributed evenly between the sulphur in the vulcanizate and the sulphur in free mercaptan. This justifies the conclusion that the accelerator decomposes into two identical radicals formed by the rupture of the —S*—S*— bond. D. Graig[17] has shown that in the

Table 5. Distribution of N^{15} in the Products of the Condensation of Primary Amines into a Secondary Amine†

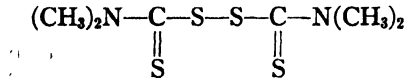
Primary amine		*Content of N^{15} (in %) in nitrogen*	
Labelled	*Unlabelled*	*of the condensation product*	*of the NH_4Cl formed in reaction*
$C_6H_5N^*H_2 \cdot HCl$	$C_6H_5NH_2$	1.62	1.47
$C_6H_5N^*H_2 \cdot HCl$	$C_{10}H_7NH_2$	2.15	0.67
$C_6H_5CON^*H_2$	$C_6H_5NH_2HCl$	0.51	2.07
$C_6H_5CON^*H_2$	$C_{10}H_7NH_2 \cdot HCl$	0.77	7.25

† It is pointed out by the authors that an excess of N^{15} over the content of this isotope in natural nitrogen (0.38%) by 0.29% in NH_4Cl (second line) and by 0.13% and 0.39% in the condensation products (third and fourth lines) is due to side reactions.

case of tetramethylthiuram disulphide the reaction mechanism is more complex.

As far as the mechanism of the action of radicals in vulcanization is concerned, it has been established[16] that the role of the radicals formed upon the decomposition of the accelerating agent is similar to the role of the initiating radicals in polymerization processes. It has been demonstrated that the radical, by splitting hydrogen from α-methylene groups or by joining the molecule across a double bond, converts the rubber molecule into a radical capable of adding a certain number of sulphur atoms, which form the sulphur bridges of the vulcanizate. This is accompanied by a parallel polymerization process forming —C—C— bond between the molecular chains of rubber.

Investigations of the isotopic exchange of sulphur in vulcanizates (as has been shown by chemical and thermo-mechanical investigations) have revealed that the vulcanizates, besides strong monosulphide linkages, contain easily ruptured polysulphide linkages. As has been shown by B. A. Dogadkin and co-workers,[18] the relative number of the two types of linkages is determined by the nature of the accelerator and the rubber, the ratio of the percentage of the sulphur and the accelerator, and also by the temperature of the vulcanization process.[19] These authors also showed that the heat treatment of vulcanizates causes an alteration in the structure of sulphur bonds towards the formation of bonds which contain fewer sulphur atoms, i.e., are stronger. Furthermore, both chemical analysis and the study of isotopic exchange with sulphur revealed[18] that in vulcanizates obtained with diphenylguanidine $(C_6H_5NH)_2CNH$ as an accelerator of vulcanization, the content of the polysulphide sulphur equals 34%, while vulcanizates obtained with thiuram contain no polysulphide sulphur.



An important contribution to interpreting these data was made by E. N. Guryanova,[20] who studied the isotopic exchange of sulphur between elementary sulphur and organic polysulphides, as well as the sulphur exchange between different polysulphides. This investigation established, for one thing, that in the case of disulphides the exchange with elementary sulphur proceeds with great reluctance; on the other hand, in polysulphides for instance in a polysulphide of the structure $R—S—S—S—R$ the exchange proceeds easily, but with the participation only of the middle sulphur atom.

By way of illustration Tables 6 and 7 list some of the results obtained in studying isotopic exchange in the sulphide-elementary sulphur (Table 6) and sulphide-sulphide (Table 7) systems. It may be seen from the first example in Table 6 that the measured specific activity of trisulphide after the attainment of exchange equilibrium practically coincides with the value calculated on the assumption that only one atom of the sulphide bridge enters the exchange. This conclusion is also supported by the absence of activity in the disulphide obtained upon the decomposition of trisulphide, as well as by the fact that upon the removal of the middle atoms of the sulphide bridge (in the form of Na_2S) the Na_2S has a triple specific activity (both examples of Table 6). In this way the exchange equilibrium in these cases may be set down as $R—S—S—S—R+S^* \rightleftharpoons R—S—S^*—S—R+S$. In the first example in Table 7 the equilibrium specific activity in the disulphide is equal to half the specific activity of the initial labelled disulphide. The specific activity of the trisulphide is equal to one-third, and of the disulphide obtained after the decomposition of the trisulphide, again to one-half of the specific activity of the initial disulphide. Hence: $R—S^*—S^*—R+R—S—S—S—R \rightleftharpoons R—S^*—S—S^*—R+R—S—S—R$.

In the second example in Table 7 the activity is distributed equally between the two components of the system.

As a result of her experiments, E. N. Guryanova arrives at the conclusion that the mechanism of the processes of sulphur exchange between elementary sulphur and polysulphides (Table 6) is based on sulphide dissociation across the —S—S— linkage, with only those sulphur atoms in the radicals formed participating in the exchange, which are not bound to carbon atoms. The correctness of this conclusion is borne out by the data obtained in studying the exchange of sulphur between polysulphides (Table 7), where RS groups (radicals) take part in the exchange, and not sulphur atoms.

As additional experimental proof of this conclusion, it may be pointed out that earlier J. A. Christiansen and A. W. Drost-Hansen[21] and Fava[22] found that the sulphur exchange between polythionates and thiosulphate likewise proceeds through the migration of sulphite and thiosulphate groups, and not

Table 6. Sulphur Exchange in Polysulphides. Exchange between Sulphide and Elementary Sulphur (activity in counts per minute=specific activity)

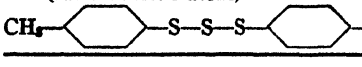
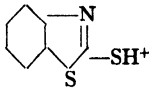
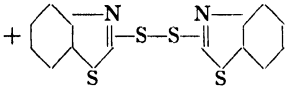
System	Activity of initial sulphur	Calculated activity of trisulphide: 3 atoms exchanged	Calculated activity of trisulphide: 1 atom exchanged	Found activity of trisulphide	Activity of sulphur in products of trisulphide decomposition: disulphide	Activity of sulphur in products of trisulphide decomposition: Na_2S
$C_2H_5—S—S—S—C_2H_5$ + S (ratio 1 mol: 1 atom)	11,960	2990	1993	1980	~ 0	5964
 + S*	—	—	—	2948	~ 0	8500

Table 7. Sulphur Exchange in Polysulphides; Exchange between Sulphides

System	Activity of initial disulphide or captax	Activity of disulphide or captax after exchange		Activity of trisulphide or altax after exchange		Activity of disulphide after decomposition of trisulphide	
		Calculated	Found	Calculated	Found	Calculated	Found
1	2	3	4	5	6	7	8
$C_2H_5—S^*—S^*—C_2 + H_5$ $+C_2H_5—S—S—S—C_2H_5$ (ratio 1:1)	1063	532	528	354	362	532	540
Captax	1216	608	596	608	608	—	—



Altax



(ratio 2:1)

atoms of sulphur. Somewhat later A. I. Brodsky and R. K. Eremenko,[23] by studying the mechanism of a number of typical reactions of obtaining and decomposing tri-, tetra- and pentathionate with the use of initial substances containing radiosulphur in set positions, found that these reactions proceed with the migration of sulphite or thiosulphate groups, with the sulphide and sulphite sulphur of the polythionate retaining its functions in the products of the polythionate decomposition. It should be added that the results of the latest work fully confirm the views concerning the structure of polythionates set out in detail by D. I. Mendeleev as far back as 1870.

By comparing their data with the results of E. N. Guryanova, B. A. Dogadkin and co-workers[18] arrive at the conclusion that in diphenylguanidine vulcanizates the sulphur bridges have a predominantly polysulphide structure of the $R—S—S_n—S—R$ type, while in thiuram vulcanizates the structure is mono- or disulphide, i.e., of the type $R—S—R$ or $R—S—S—R$. Besides the above-mentioned data of B. A. Dogadkin and co-workers, the presence of polysulphide sulphur in diphenylguanidine vulcanizates and its absence in thiuram vulcanizates is also confirmed by the data of the same authors on the kinetics of isotopic exchange with elementary sulphur and the kinetics of sulphur addition to the vulcanizate, given in Figs. 4 and 5. In keeping with the absence of the highly mobile polysulphide sulphur in thiuram vulcanizate, the activity of the vulcanizate in this case increases in parallel with the sulphur addition (Fig. 5), while in diphenylguanidine vulcanizate (Fig. 4) the exchange is observed in the absence of sulphur addition.

The question of the chemical nature of the radicals formed in the course of vulcanization is, of course, not exhausted by the above-mentioned idea of the mechanism of the action of accelerators being based on dissociation into RS radicals or radicals of a similar type. It may be assumed, for one thing, that the mechanism of the action of the same accelerator in the presence or absence of sulphur in the system is different. Some indications of this are contained in the works of S. E. Bresler and co-work-

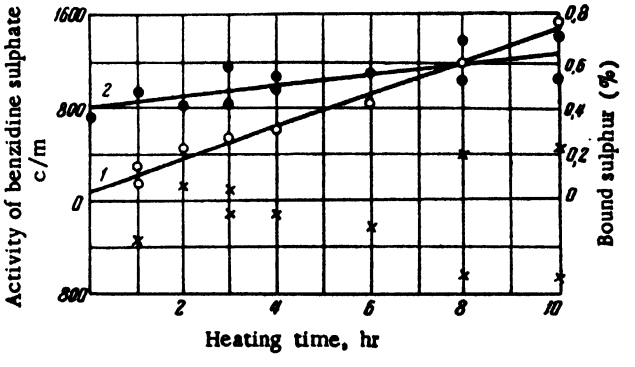


Figure 4. Kinetics of the exchange (1) and addition of sulphur (2) in vulcanizate with thiuram

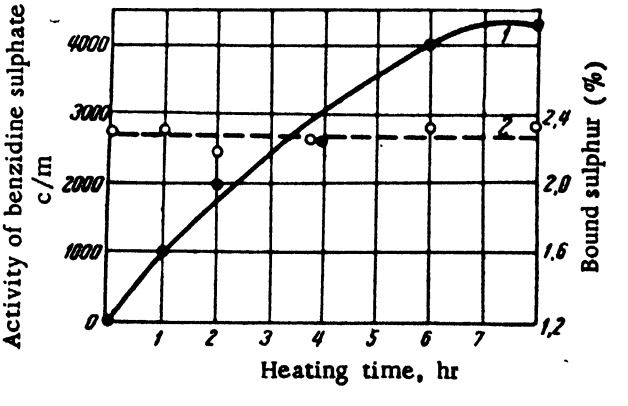


Figure 5. Kinetics of activity increase (1) and addition of sulphur (2) in vulcanizate with diphenylguanidine

ers,[24] who by studying the kinetics of sulphur binding by rubber in the presence of thiuram and the kinetics of the isotopic exchange of sulphur between elementary sulphur and this accelerator established the bimolecular law of these reactions (first order with respect to sulphur and thiuram) and the complete identity of their rate constants. It follows that in the conditions of their experiments the rate of the vulcanization process is determined by the interaction of sulphur with the accelerator. In the opinion of S. E. Bresler, the product of this interaction is the biradical S_2, whose adherence to the rubber molecule constitutes the initial stage of the process of the formation of the vulcanizate structure.

The above examples of the application of tracers to the study of the mechanism of various chemical reactions by no means exhaust the wealth of data accumulated in this field of chemistry and merely serve to illustrate the high effectivity of this method, which makes it possible to solve problems that present either great or insurmountable difficulties when other methods are employed. The deficiency of the investigations of the mechanism of chemical reactions by tracer techniques lies in the fact that this method was mostly employed apart from other methods (often without even taking into consideration the kinetics of the reaction). For further strides in this branch of science a complex approach to the study of the mechanism of chemical reactions is needed with the employment of diverse methods for the solution of concrete problems.

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Stable and Unstable Isotopes in Heterogeneous Catalytic Reactions

By John Turkevich,* USA

Heterogeneous catalysis is still an intriguing problem awaiting solution in terms of modern concepts of electronic structure of molecules and solids. It is now well established that in most cases the reaction takes place in the adsorbed phase on the catalyst and that the extent of surface is important. It is widely appreciated that for oxidation-reduction and hydrogenation-dehydrogenation reactions, elements and compounds of the transition type are particularly useful. On the other hand, for the reactions involving condensation, polymerization, cracking, and rearrangement, catalytic activity can best be correlated with acid-base properties. The quantitative formulation of these qualitative ideas still awaits a general and useful solution. The attainment of this solution will undoubtedly be facilitated by present studies on the structure of solid catalysts.

Activation of reacting molecules is another phase of the problem of heterogeneous catalysis. Do all of the reacting species have to be activated or does it suffice to activate only one of the reactants? What is the nature of the activation process? Are all the bonds in a complex molecule activated to the same extent or is the activation limited to those parts of the molecule spatially near the surface of the solid? Is the activation one of distortion or polarization in the adsorbed and reactive state or is it of a more profound nature: excitation to higher electronic states or dissociation into atoms, radicals or ions on the surface?

Techniques using stable and unstable isotopes have been of great help in increasing our knowledge of the activation process. In the present paper an attempt will be made to indicate the scope of these techniques and to cite examples from the work of the Princeton and Brookhaven group associated with the author in catalytic studies.

The number of radioactive isotopes useful to the catalytic chemist is limited to the exceptionally weak beta-emitting tritium, the weak beta-emitting carbon fourteen, a sulfur and a phosphorus isotope. There are no radioactive isotopes of convenient life of oxygen and nitrogen. Radioactive isotopes can be used in very high dilution and are detected by relatively inexpensive counting equipment. They are of particular advantage in studying reactions of simple molecules. When there are two or more atomic positions in the molecule that can undergo exchange, the use of radioactive isotopes gives only an over-all picture of the exchange process. The measurement of the specific activity of the sample is independent of the tracer atom distribution among the molecules in the sample. It will be the same if in the one case half the molecules have two tracer atoms per molecule and the other half have none and in the other case all the molecules have one tracer atom per molecule. Furthermore the specific activity is independent of the position of the tracer atoms in the molecule. To determine the distribution of tracer atoms in one molecule, one must chemically degrade the molecule in well-defined steps and determine in what fragment the radioactivity persists. Such chemical degradations may be subject to rearrangements and exchanges and are, at best, time consuming.

Stable isotopes such as deuterium, carbon thirteen, nitrogen fifteen and oxygen eighteen are available either in pure state or highly enriched with respect to normal isotopic composition. Infra-red absorption or mass spectrometry are used for analysis. The equipment for both types of work is much more expensive than for measuring radioactivity. The use of infra-red absorption methods is limited to the study of hydrogen exchanges since the deuterium shift is well marked to be easily detected. Not only can one determine the extent of the total exchange but in favorable cases such as that of the deuterated methanes, the distribution of the tracer among isotopic molecules.[1] It should be pointed out that proton and deuteron resonance techniques offer great promise in the field of analysis of tracer reactions.[2] This nuclear resonance absorption method will not suffer from the disadvantage of the infra-red absorption where Beer's law is often inapplicable.

Mass spectrometry has been used extensively to determine the distribution of tracer atoms among isotopic molecules and within a given molecule. In the spectrometer the molecule is broken down by electron impact at various valence bonds to give positive ions and neutral molecules and radicals. Intensity of the positive ions of various masses is characteristic of the molecule and constitutes its mass spectrum. The ion of highest mass is that of the parent molecule and can be used often to determine directly the number of isotopic molecules. In gen-

* Princeton University.

eral, peaks involving the loss of one or more hydrogen atoms from the parent molecule are sufficiently great to produce an overlap in the spectra of isotopic molecules containing hydrogen and deuterium. Thus for example, ions of mass sixteen in a deuteromethane mixture correspond to a CH_4^+ ion from a CH_4 molecule; a CH_2D^+ ion from CH_2D_2 and CDH_3 molecules; a CD_2 ion from CD_4, CD_3H and CD_2H_2 molecules. Therefore to translate the mass spectrum (intensities of positive ions of various masses) into per cent of various isotopic molecules involves a knowledge of mass spectra patterns of the different deuterocompounds involved. For this purpose a number of deuterium substituted compounds, not only chemically pure but also isotopically pure in hydrogen have been synthesized at Princeton University and the Brookhaven National Laboratory. Among them are CH_3D, CH_2D_2, CHD_3, CD_4, CH_3CH_2D, CH_3CHD_2, CH_3CD_3, CD_3CD_3, CHD =CHD, CD_2=CD_2, CD=CD, $CH_3CH_2CH_2D$, CH_3CHDCH_3, $CH_3CD_2CH_3$, C_3D_8, CH_3C=CD, CD_3C=CD, CD_3C=CH, $CH_2DCH_2CH_2CH_3$, $(CH_3)_3CD$, C_4D_8, CH_3OD, $CH_3CDOHCH_3$, $CH_3CDODCH_3$, $CH_3CHODCH_3$, ortho monodeuterotoluene, meta monodeuterotoluene, para monodeuterotoluene, omega monodeuterotoluene, etc.[3] To synthesize every possible deuterocompound in pure form is a long and arduous task. It is hoped that one can avoid this and be able to predict the mass spectrum of a deuterocompound from the knowledge of the corresponding proteum compound. This correlation can only be made on the basis of an understanding of the elementary processes taking place in a molecule under the influence of the disruptive electron bombardment whereby certain valence bonds are broken to a greater extent than others. It has been found that one can satisfactorily predict the mass spectrum of a deuterated compound from the knowledge of its proteum spectrum assuming that all bond breaking processes are the same for all isotopic molecules; that the breaking of carbon-hydrogen and carbon-deuterium bonds is governed by statistics; that the probability of a carbon-deuterium bond breakage is one half of that of the carbon-hydrogen bond and that the rupture of a carbon-hydrogen bond is slightly more favored when there are carbon-hydrogen bonds attached to the same carbon atom. One can calculate using these principles an approximate mass spectrum of any deuterated compound from the knowledge of the elementary processes involved in the formation of the positive ions by the electron bombardment of the analogous proteum compound. The mass spectrum of a mixture of various deuterocompounds can be resolved into per cent composition of the constituent isotopic molecules by subtraction of spectra of model compounds. Validity for such a procedure is assured by a small residue left for positive ion currents after subtraction of all possible deuterium and proteum compounds.[4] The distribution of tracer atoms within a molecule can be illustrated by considering the two monodeuteropropanes: $CH_3CH_2CH_2D$ and CH_3CH DCH_3. The first gives a mass of sixteen corresponding to a CH_2D fragment while the second one gives no ion of mass sixteen.

Examples will now be given of the use of specific isotopes as tracers for the elucidation of the activation process in heterogeneous catalytic reactions.

RADIOACTIVE ISOTOPES

Turkevich and Smith[5] used tritium containing materials to study both the migration of the double bond in butene-1—butene-2 system and the tritium exchange between the catalyst and the hydrocarbons. Since tritium has a low energy beta ray of only 0.0145 Mev, the tritium hydrocarbon was introduced with argon into the counter to determine each point on the exchange rate curve. The rate of double bond migration was determined by measurement of the vapor pressure of the hydrocarbon system. Turkevich and Smith established that catalysts for the migration of the double bond are also materials that readily exchange their hydrogens for the hydrogen of the butene. Furthermore the rates of exchange of the tritium and that of the double bond migration were comparable after proper correction had been made for the zero point energy difference between the hydrogen and the tritium. In addition it was found that propylene exchanged slowly and that ethylene did not exchange at all. On the basis of these experiments, it was postulated that in order for a substance to be a catalyst it had to have a hydrogen donor and a hydrogen acceptor separated by a distance of 3.5 Ångstroms. Sulfuric acid, phosphoric acid, alumina silicate, copper pyrophosphate and many metal catalysts partially loaded with hydrogen satisfy this criterion. The catalyst is not merely an acidic substance. It is a special kind of a hydrogen containing substance with acid and base sites separated by a definite distance and arranged perhaps in some cases in a definite geometrical pattern. Double bond migration takes place by a "hydrogen switch" mechanism wherein the catalyst gives one hydrogen to the substrate while abstracting another on the third carbon from the one to which the hydrogen had been added. The activation process consists in coupling energetically the two elementary acts of breaking a bond and forming a new chemical bond through the use of a catalyst that switches atoms. The hydrogen switch mechanism suggested by the tritium exchange studies can be extended to explain the activation of reacting molecules in most catalytic reactions involving the so-called acid catalysts, i.e., alkylation, polymerization and cracking of hydrocarbons.[6] It may be extended to cover also the hydrogen transfer reactions in biochemical systems catalyzed by enzymes containing phosphate groups.

Radiocarbon has been used by Turkevich and Bonner[7] to study the reduction of small amounts of radioactive carbon dioxide by charcoal of a large surface

area. The course of the reaction was followed by pressure measurements and changes in specific radioactivity of the carbon dioxide and carbon monoxide. At the relatively low temperature of 500°C there was no change in pressure or over-all radioactivity. However, a slow conversion was observed of the carbon dioxide into carbon monoxide of the same specific radioactivity as the original carbon dioxide. At the higher temperature of 735–848°C over 95% of the carbon dioxide was converted into carbon monoxide within four minutes of the introduction of the gas into the system. During this period there was no increase in pressure or change in total activity. This was followed by a slow pressure increase with an accompanying decrease in the specific radioactivity of the carbon monoxide. The mechanism for the interaction of carbon dioxide with carbon consists of two steps. In the first rapid step, the radioactive carbon dioxide approaches the carbon surface, deposits one of its oxygen atoms on the surface, and returns to the gas phase as radioactive carbon monoxide.

$$CO_2^* + \text{charcoal} = CO^* + \text{oxygenated charcoal}$$

In the next slow step the oxygenated charcoal decomposes by a reaction which consists of two unimolecular stages to give a second non-radioactive molecule of carbon monoxide.

$$\text{oxygenated charcoal} = CO + \text{charcoal}$$

This mechanism is supported by experiments carried out by Amick and Turkevich: small amounts of steam were introduced to charcoal of high surface area. At 700°C two steps were observed. In the first rapid step the water molecule approached the carbon surface, deposited its oxygen to form an oxygenated charcoal surface and returned in the gas phase as hydrogen.

$$H_2O + \text{charcoal} = H_2 + \text{oxygenated charcoal}$$

The product in the gas phase was then pure hydrogen. In the second slow step the oxygenated carbon surface decomposed into carbon monoxide and carbon at a rate similar to that of the carbon dioxide-charcoal reaction.

It is significant that for both reactions, the surface reaction is the rate controlling one and that it follows unimolecular kinetics.

Emmett and his co-workers[8] have used radiocarbon to study the Fischer-Tropsch reaction between carbon monoxide and hydrogen on an iron catalyst at one atmosphere pressure to produce hydrocarbons. They showed that a catalyst previously carbided with radiocarbon did not produce radioactive hydrocarbons on subsequent reaction with ordinary carbon monoxide and thus showing that ordinary carbide does not serve as an intermediate in the reaction. By adding small amounts of methane containing radiocarbon to ordinary carbon monoxide and hydrogen mixture and not finding any radioactivity in the product higher hydrocarbons, they proved that methane plays a negligible role in the synthesis. When, however, small amounts of various radioactive alcohols were added to the starting material, it was found that all the product hydrocarbons had a specific radioactivity of about one-third to one-half of the alcohol used. This was taken as evidence that the primary alcohol served as a nucleus for the formation of the higher alcohols. It was presumed that during the usual synthesis, carbon monoxide and hydrogen are activated to form a complex similar to that formed by the admixed alcohols.

STABLE ISOTOPES

There have been numerous studies on the reaction of H_2 and D_2 to form HD ever since the discovery of deuterium. These studies were used to indicate whether the activation of the adsorbed hydrogen leads to dissociation of the molecule into atoms. These finds are not going to be discussed in the present paper.

One of the simplest catalytic reactions is the addition of hydrogen to a carbon-carbon double bond. This reaction has been a subject of studies of deuterium exchange almost immediately after the discovery of deuterium. However, these studies were limited by the inadequacy of the experimental technique: the extent of the addition reaction was determined by the pressure drop while the depth of exchange was measured by the production of HD. Schissler and Turkevich[9] first applied the use of the mass spectrographic technique to analyze the products of the reaction between ethylene and deuterium determining during the course of the reaction the amounts of the various seven ethanes: C_2H_6, C_2H_5D, $C_2H_4D_2$, $C_2H_3D_3$, $C_2H_2D_4$, C_2HD_5, C_2D_6 and the five ethylenes: C_2H_4, C_2H_3D, $C_2H_2D_2$, C_2HD_3, C_2D_4 and H_2, HD, D_2. The results for a typical run on nickel wire for a two to one mixture are shown in Figs. 1 and 2.

It is seen from Fig. 1 that the C_2H_4 concentration drops during the course of the reaction while that of C_2H_2D, $C_2H_2D_2$, etc., rises and then drops to zero. Figure 2 indicates the way the concentration of the various deuteroethanes changes during the course of addition. The striking result is the appearance of completely light ethane C_2H_6 at the early stages of the reaction between deuterium and ethylene. At the completion of the reaction the products are in the order of monodeuteroethane, dideuteroethane light ethane, trideuteroethane, tetradeuteroethane, etc. It was also shown that under the conditions of the experiment ethane exchanged neither with deuterium nor with deuteroethane C_2D_6. Furthermore it was established that ethylene C_2H_4 and deuteroethylene C_2D_4 did not exchange unless hydrogen or deuterium were present. It was further shown by Thompson and Turkevich[10] that at a ratio of two parts of deuterium to one part of ethylene the distribution of deuteroethanes was the same in the condensed phase

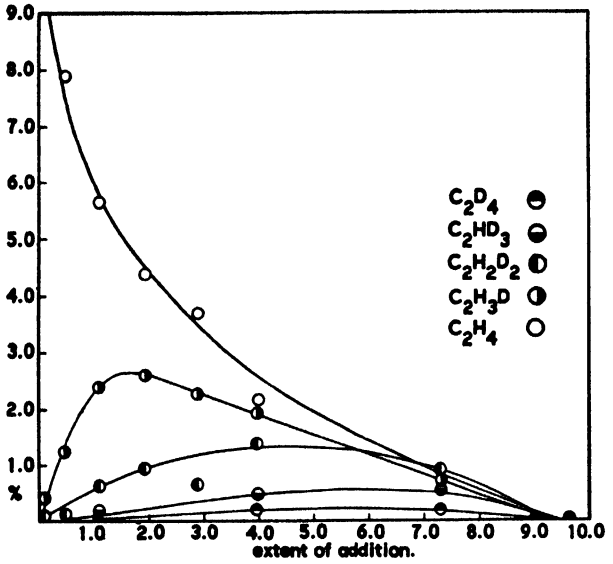

Figure 1. Behavior of ethylenes during the course of the reaction between ethylene and deuterium

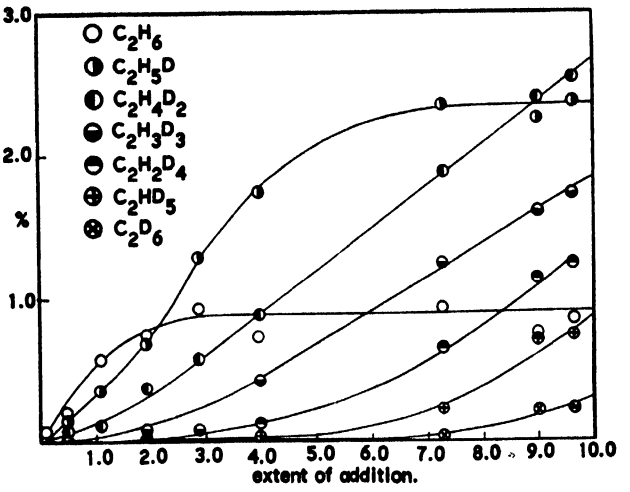

Figure 2. The formation of ethanes during the course of the reaction between ethylene and deuterium

at 100 atmospheres as at 10 mm pressure and that it was invariant to catalyst type and support.

Bond and Turkevich[11] studied in a similar fashion the kinetics of the propylene reaction with deuterium. Again a wide distribution of deuteropropanes was found and this distribution could be varied with the ratio of deuterium to propylene. No exchange was observed between propylene and deuteropropylene unless hydrogen was present.

In a further investigation Bond and Turkevich[12] studied the reaction of cyclopropane and deuterium. Again the distribution of deuteropropanes was found to depend on the ratio of deuterium to cyclopropane. The surprising result was that the distribution was not the same as that obtained for the propylene-deuterium reaction.

The catalytic reaction of the butenes and deuterium has been studied by T. I. Taylor, Wilson and others.[13]

The above experimental findings definitely eliminate many of the mechanisms that have been proposed for the reaction of hydrogen with an olefin on a catalyst:

1. The dissociative mechanism[14]

$$C_2H_4\ (ads) = C_2H_3\ (ads) + H\ (ads)$$

is untenable because the exchange between ethylene and deuteroethylene in one case and between propylene and deuteropropylene in the other case takes place only in the presence of hydrogen.

2. The reaction of a molecule of gaseous hydrogen with a molecule of adsorbed activated ethylene should produce only a deuteroethane with two deuteriums in it. This does not happen.

3. The reaction of a molecule of gaseous ethylene with a molecule of adsorbed deuterium should again lead to the production of only a dideuteroethane. This is contrary to the findings.

4. A reaction of one molecule of adsorbed ethylene with one molecule of adsorbed deuterium would also lead to a dideuteroethane and this is contrary to experimental findings.

One must therefore postulate the following reactions[15]

$$C_2H_4\ (ads) + H\ (ads) = C_2H_5\ (ads)$$

$$C_2H_5\ (ads) + C_2H_5\ (ads) = C_2H_4\ (ads) + C_2H_6$$

In the "half-hydrogenated" complex the hydrogens or deuteriums are transferred from one C_2H_4 (ads) molecule to another by a mechanism similar to the "hydrogen-switch" mechanism proposed earlier in the paper. It is thus seen that by means of tracer experiments one has been able to show that the reaction between the olefin and hydrogen involves the activation of a *large number* of molecules on the surface.

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Tritium as a Tool for Industrial and Chemical Research

By W. G. Brown, L. Kaplan, A. R. Van Dyken, and K. E. Wilzbach,* USA

Of the radioactive isotopes that can be produced in quantity in nuclear reactors, tritium, produced by the (n, α) reaction on Li^6, is one of the most interesting because of the variety of potential research applications for which it is suitable. Though progress in the utilization of tritium has thus far not been spectacular, it requires no great foresight to anticipate experimentation on a scale surpassing that of any other radioactive isotope in such diverse fields as hydrology, atmospheric pollution, petroleum exploration, and industrial process control.

In laboratory research, tritium may be considered to be in competition with the already widely used isotopes, deuterium and carbon-14. The case for tritium rests largely upon the enormous dilution ratios (10^{12} or greater) which can be tolerated, a factor which is more frequently critical in biological[1] than in chemical applications. Where this factor is not decisive, the choice between tritium and deuterium as a tracer for hydrogen atoms is likely to be determined by such considerations as the availability of the isotopes, simplicity and reliability of measurement, and ease of preparing labeled materials, factors which will vary with the nature of the problem and with the available laboratory facilities. As a molecular label, or for tracing intact groups, tritium may offer certain advantages over carbon-14 with respect to ease of incorporation of the isotope, cost, and activity levels attainable. Presently available assay procedures for tritium have, in large part, eliminated the advantage with respect to ease of counting formerly attributed to carbon-14. In some applications, multiple labeling[2] with two, or even all three, of the isotopes may be used effectively.

Tritium has a half-life of 12.4 years. It emits a beta particle with an average energy of 5.7 kev and a maximum energy of 18.9 kev, which corresponds to a range of about 0.9 mg per cm^2. The short range of the radiation, together with the high specific activities available, have made tritium an important source of accurately known radiation dosage, both for biological[1] and for chemical[3] studies.

The absence of gamma rays, the low energy of the beta particles and the rapid turnover of hydrogen in the body combine to make the health hazards associated with tritium less serious than those for many other radioactive materials. Conservative tolerance levels have been set[4] at 10^4 μc in the body, 0.2 μc per ml in water, and 2×10^{-5} μc per ml in air. The disposal of waste tritiated water is readily accomplished by dilution to tolerable levels; disposal of tritiated organic compounds is probably best accomplished by combustion before dilution.

A consequence of tritium radiation which must be considered in planning experiments with this isotope, particularly at high specific activities, is self-decomposition. This factor effectively prevents studies with completely tritiated organic compounds but is not a serious deterrent to tracer studies. Although little has been reported directly on the radiation-stability of tritium compounds, the extent of self-decomposition can be estimated from the results of studies[5] with carbon-14. As with the latter isotope, the amount of decomposition can be minimized by storing the labeled compound at as low a specific activity as is compatible with its subsequent use, or, in some cases, by diluting it with an inert solvent. Also of significance in the use of tritium is the possible effect of its radiation on reaction rates. Such an effect may become important at high activity levels; this effect has been suggested[6] as an explanation for the observation that the catalytic reduction of dienestrol with hydrogen containing 500 mc of tritium occurred faster than with ordinary hydrogen.

In the use of tritium-labeled organic molecules it is always necessary to consider the possibility of loss of isotope by exchange. Such exchange reactions, which are, of course, equally important for deuterium, have been studied[7] extensively with the latter isotope. On the basis of these studies it is often possible to predict with considerable confidence whether a particular hydrogen atom will be labile under given conditions. Among the many well-verified generalizations are the rapid exchange of O-H and N-H groups with water, the exchange of the α-hydrogen atoms of ketones in bases, the exchange of the *ortho* and *para* hydrogen atoms of aromatic amines in acid, and the stability toward exchange of saturated aliphatic hydrocarbons. The application of such generalizations will not only aid in the selection of a suitable position for labeling, but may, in some cases, facilitate the identification of the labeled positions within a complex molecule, as exemplified in a study of the distribution of tritium in labeled cortisone.[8]

The results of tracer studies with tritium, like those with deuterium, must be interpreted with due con-

* Argonne National Laboratory.

sideration for the differences in chemical and physical properties produced by isotopic substitution. Differences in physical properties are generally small, but may be magnified many-fold in such processes as fractional distillation or chromatography. Differences in chemical reactivity, however, may be much larger if the isotopic atom participates in the reaction. The difficulties which may sometimes be caused by such differences in reactivity are offset by the insight into reaction mechanisms which they often provide.

The methods available for the synthesis of deuterium compounds can also be applied to the introduction of tritium. These include homogeneous and heterogeneous exchange, catalytic reduction, hydrolysis of organo-metallic compounds, and reduction with complex metal hydrides. The procedures are frequently simpler in the case of tritium, since the problem of complete replacement of hydrogen by its isotope does not arise. In addition to such methods, common to the isotopes, there is currently under evaluation a technique[9] for tritium labeling based on the *in situ* production of tritons by nuclear transformation.

The determination of tritium is no longer seriously impeded by the limited range of its radiation. Efficient measurement is made possible by permitting the disintegration to occur within the active volume of the detector. For nonvolatile materials scintillation counting[10] of solutions containing soluble scintillators offers considerable promise as a method for routine analysis that is both sensitive and rapid, but additional experience and development appear to be required to establish the reliability of the method. At present, reliable results are best obtained on gaseous samples by measurement of the radiation-induced ionization with counters, operating in either the Geiger[11] or proportional region,[12] or with ionization chambers.[13] (A simple method of obtaining the gaseous samples is described later in this paper.) By the use of such procedures, on a routine basis, one part of tritium can be determined accurately in 10^{13} parts of hydrogen; more elaborate procedures, such as those used in studies on natural tritium,[14, 15] extend the range to one part in 10^{18}.

The low cost of tritium and the high dilutions which are permissible should lead to widespread use in industry. The scarcity of reported applications may be attributed to the fact that the commercial availability of the isotope and techniques for its utilization are of relatively recent origin. An obvious application of tritium is in the analysis, by means of isotopic dilution techniques, of complex mixtures produced in industrial processes. The low cost of the isotope and the simplicity of preparing labeled compounds should make the routine use of such procedures economically feasible. The use of tritium-labeled materials should also facilitate studies of the efficacy of such industrially-important decontamination procedures as laundering, cleaning of dairy equipment, and the removal of insecticides from food, as well as of other processes involving the separation of hydrogen-containing material. Tritium may be used similarly in measuring such properties as the thickness of surface films and the retention of dyes by fabrics. The short range of tritium beta particles should prove of value in the investigation of surface phenomena by radioautography, as suggested by Beischer's studies[16] with tritiated stearic acid monolayers. Additional applications are suggested by reports of the use of tritiated water in measuring the solubility of water in hydrocarbons[17] and the diffusion of water through surface films.[18] In the field of high polymers, potential uses include end-group analysis and molecular weight determination. In the petroleum industry the use of tritium may be expected in studies of combustion processes and of catalysis.

The utility of tritium in the study of chemical reactions was demonstrated soon after its discovery. Among the earliest such studies were those on the oxidation of fumaric acid by Allen and Ruben[19] and on the Menschutkin reaction by Harman, Stewart and Ruben;[20] many chemical investigations and even more numerous biological studies[1] utilizing tritium have subsequently been reported.

In the balance of this paper, some specific chemical applications from work at Argonne National Laboratory are discussed to illustrate the techniques employed and to indicate the usefulness of tritium.

ANALYTICAL PROCEDURES

Samples of gas suitable for assay of tritium are readily obtained from 5–10 mg samples of water or of organic compounds by a zinc fusion method.[21] In this procedure water is reduced to hydrogen by heating with zinc at 650°C for one hour in a sealed glass tube;[22] the hydrogen in organic compounds is converted to a mixture of methane and hydrogen by heating for two hours at 650°C with zinc metal to which small amounts of nickelic oxide and water have been added. Under these conditions 99% of the tritium in the sample appears in the gas phase; 1% is retained in the subsequently discarded reaction vessel. Results obtained by this simple one-step method are as accurate and reproducible as those obtained by older two-step methods based on combustion. The absence of a "memory effect" eliminates the need for pre-conditioning of the equipment between analyses of successive samples of widely different activity.

In the special case of compounds containing both carbon-14 and tritium, a two-step procedure must be employed: a 5 to 10-mg sample is oxidized[23] by heating with a mixture of copper and copper oxide in a sealed glass tube at 650°C for 30 minutes, the carbon dioxide and water are isolated by fractional condensation *in vacuo*, and the water is reduced to hydrogen by the zinc fusion method.

At Argonne, the preferred method of determining activity in the resulting gas sample is to transfer the sample, or a known fraction of it, to an ionization chamber (cf. Fig. 1) and to measure the ioniza-

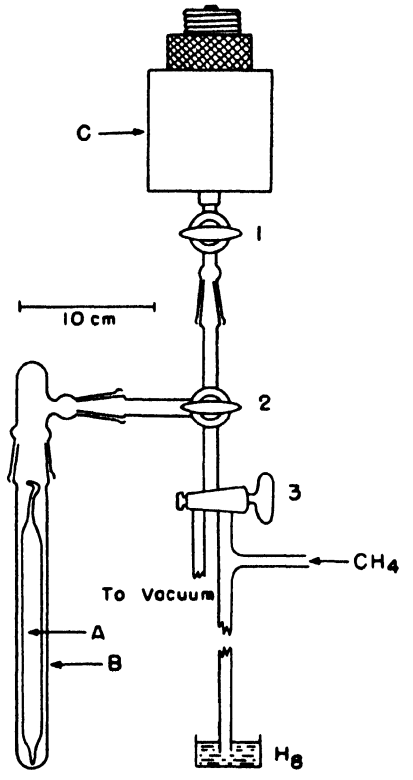

Figure 1. Introduction of sample into ion chamber; reaction tube (A) is opened by rotating tube (B); gas expands through stopcocks (2) and (1) into evacuated ion chamber (C), which is then filled to atmospheric pressure with CH_4

tion current,[13] under appropriately standardized conditions, by means of a vibrating reed electrometer. Currents corresponding to quantities of tritium ranging from 10^{-10} to 10^{-2} curie can be measured with an accuracy and reproducibility of 1%. In the higher ranges satisfactory results can also be obtained with the less sensitive and less expensive types of electronic current measuring devices.

SYNTHETIC METHODS

Hydride Reductions

The introduction of tritium at specific positions in organic molecules can be accomplished conveniently by reductions with tritiated lithium aluminum hydride, lithium borohydride, and sodium borohydride. The introduction of tritium into the borohydrides is accomplished by direct exchange[24] with tritium-hydrogen gas at elevated temperatures. Lithium aluminum hydride does not exchange with hydrogen gas below its decomposition point, but the tritiated reagent is available by synthesis[25] from tritiated lithium hydride, which can be prepared by exchange. A number of compounds, prepared by reduction of appropriate starting materials with lithium aluminum hydride-*t*, have been degraded to determine the specificity of labeling. In all of these compounds, including ethanol-1-*t*, 2-propanol-2-*t*, benzyl-α-*t* alcohol, and triphenyl-silane-*t*, more than 99.9% of the tritium was in the specified position. The applicability of hydride reductions to the synthesis of high-activity materials is illustrated by the preparation[26] of methyl iodide containing two atom per cent of tritium by reduction of methyl formate with tritiated lithium borohydride, followed by treatment with hydriodic acid. The over-all radiochemical yield, based on the initial tritium gas, was 40%.

Labeling with Recoil Tritons

In this method, an organic compound admixed with a lithium salt is irradiated with thermal neutrons in a nuclear reactor. Wolfgang, Rowland and Turton,[9] in the first application of this technique, irradiated powdered mixtures of glucose and lithium carbonate and found about 10% of the tritons from the (n, α) reaction on lithium-6 incorporated into the non-labile positions of glucose, with a specific activity of 2 μc per gram. More recently[27] they have obtained activities up to 100 μc per gram for glucose, as well as for several other natural products, before radiation damage became excessive.

At Argonne, several simple aromatic compounds have been investigated in the expectation that their comparative radiation stability would lead to maximum attainable incorporation of tritium. The samples were intimately mixed with powdered lithium sulfate, the amount of the latter beieng kept small (about 3% by weight) to minimize self-shadowing. Monitor solutions of lithium sulfate in water were used to permit the reliable estimation of total triton production. With the compounds studied, specific activities of 100 to 200 μc per gram were obtained with very little evidence of decomposition; higher specific activities could undoubtedly have been reached by longer irradiation. Recoveries of product, purified to constant specific activity, were greater than 50%. The fractions of the total tritons incorporated into non-labile positions of the parent molecules were, for benzoic acid, 25%, for *o*-toluic acid, 25%, and for anthracene, 37%. Partial degradations, carried out to establish whether the position of the tritium label was completely random, gave the following results: In anthracene, the concentration of tritium in the *meso* positions was not significantly different from the average for the other positions. The *meta* hydrogen atoms of benzoic acid were found to be 20% less radioactive than the average of the *ortho* and *para* hydrogens. On the average, the specific activity of a ring hydrogen of *o*-toluic acid was twice that of a methyl hydrogen. The more efficient labeling of aromatic than of aliphatic groups has been further demonstrated by the observation[28] that the hydrolysis of irradiated isopropyl benzoate yielded benzoic acid having a tritium-to-hydrogen ratio more than three times that of the isopropyl alcohol. The observed selectivity need not be associated with a preferential cleavage of certain C-H bonds; the stability of the various radicals formed by loss of a hydrogen atom probably plays an important role.

If sufficiently high specific activities can be produced, this method of labeling should prove of value

in applications not requiring a knowledge of the position of tritium within the molecule. The maximum specific activity attainable for a given compound is limited by the radiation damage produced by gamma rays, fast neutrons, and the recoil alpha particles and tritons from the reaction. The effect of gamma rays and fast neutrons can be controlled by suitable shielding within the thermal column of the pile. The probably more important damage from the energetic recoil particles can, to some extent, be alleviated by using particles of the lithium salt large enough to absorb some of the energy. As an example, irradiation of cholesterol[29] admixed with 60-micron particles of lithium oxalate resulted in good recovery of material having a specific activity of 200 μc per gram; equivalent irradiation using 30-micron particles produced more decomposition, and the use of a lithium myristate gel caused the formation of insoluble material from which no cholesterol whatever could be isolated.

Fragmentation of the parent molecule by radiation may lead to the formation of small amounts of very high specific activity impurities, necessitating more rigorous purification procedures than are required by other labeling techniques. In certain industrial applications, however, the presence of such impurities might not be a serious handicap.

COMPETITIVE T-METHYLATION AS A TOOL IN CARBOHYDRATE STUDIES[30]

The classical methylation procedure, as applied to the problem of locating free hydroxyl groups in polysaccharides, requires (*a*) that complete methylation be accomplished without rupture of glycosidic linkages, and (*b*) that a quantitative separation of the mixture of partially methylated monosaccharides by hydrolysis of the fully methylated material be achieved. In the special, but important, case of polysaccharides based upon glucose, the limitations imposed by these requirements can be eliminated by an application of tracer methodology. If the polysaccharide contains more than one type of monosaccharide unit, a separation cannot be avoided but the use of tracers will reduce the number of components to be resolved.

In this scheme, the polysaccharide is subjected to methylation by a reagent, for example methyl iodide, which is labeled by a suitable isotope, not necessarily but preferably a radioactive isotope. Factors such as cost, ease of preparation, and tolerable dilution ratios favor the use of a tritium-labeled methylating agent. The methylation need not be complete; the requirement is that a detectable amount of activity be introduced at each free position and hence a single treatment, as contrasted to the multiple treatments generally required to effect complete methylation, will suffice. The polymer is then hydrolyzed and the resulting mixture of partially methylated monosaccharides is then fully methylated with inactive reagents. In the case of a polysaccharide based upon glucose, this treatment will produce a single product, tetramethyl methylglucoside. The problem then becomes one of determining which carbon atoms in this product carry labeled methoxyl groups.

Should there be large differences in the reactivity of the different hydroxyl groups in the polysaccharide, as for example in the highly preferential triphenylmethylation of primary hydroxyl groups, certain types of free hydroxyl groups might escape detection. The available evidence indicates that the degree of selectivity in methylation is relatively small, but does result in significant departures from uniform labeling. The distribution of radioactivity among the labeled positions does, in fact, if the extent of T-methylation is kept small, provide a measure of the relative reactivity at the various hydroxyl groups.

With a view toward the eventual application of this technique to glucose polymers of the dextran type the problem of degrading tetramethylglucose in such a way as to reveal the activity in methoxyl groups at positions 2, 3, 4, and 6 has been studied. The preparation of an active material by a preliminary partial T-methylation of α-methyl-D-glucoside, followed by ordinary methylation to completion, provided the opportunity to evaluate the relative reactivity of the different positions in this prototype molecule. The reactions employed and the information developed thus far are shown in Fig. 2.

Degradation of tetramethylglucose by nitric acid oxidation following the procedure used by Hirst[31] in the classical determination of the structure of glucose, produces a mixture of trimethoxyglutaric and dimethoxysuccinic acids, the former predominating; methoxyacetic acid, if formed at all, has not been isolated from such oxidations. Since the dimethoxysuccinic acid has a configuration such that its methoxyl groups are those at the C-2 and C-3 positions in the tetramethylglucose, its activity is a measure of the extent of T-methylation at these positions. The activities of the methoxyl groups at the C-4 and at the C-6 positions must be obtained by difference. If the tetramethylglucose is degraded by chromic acid oxidation, however, the activity of the methoxyl group at the C-6 position, a point of considerable interest, can be determined directly. The principal products in this case are methoxyacetic and dimethoxysuccinic acids and, hence, rupture between C-4 and C-5 is the predominant (but not exclusive) path in chromic acid oxidation. The methoxyl groups in dimethoxysuccinic acid are thus derived mainly from the C-2 and C-3 substituents in the original molecule; the methoxyl group in methoxyacetic acid is derived from the substituent at the C-6 position. On the basis of this reasoning the specific activity of the methoxyacetic acid is a measure of the T-methylation at the C-6 position; that of dimethoxysuccinic acid provides a measure of the average T-methylation at the C-2 and C-3 positions, and a value for the C-4 position is obtained by differ-

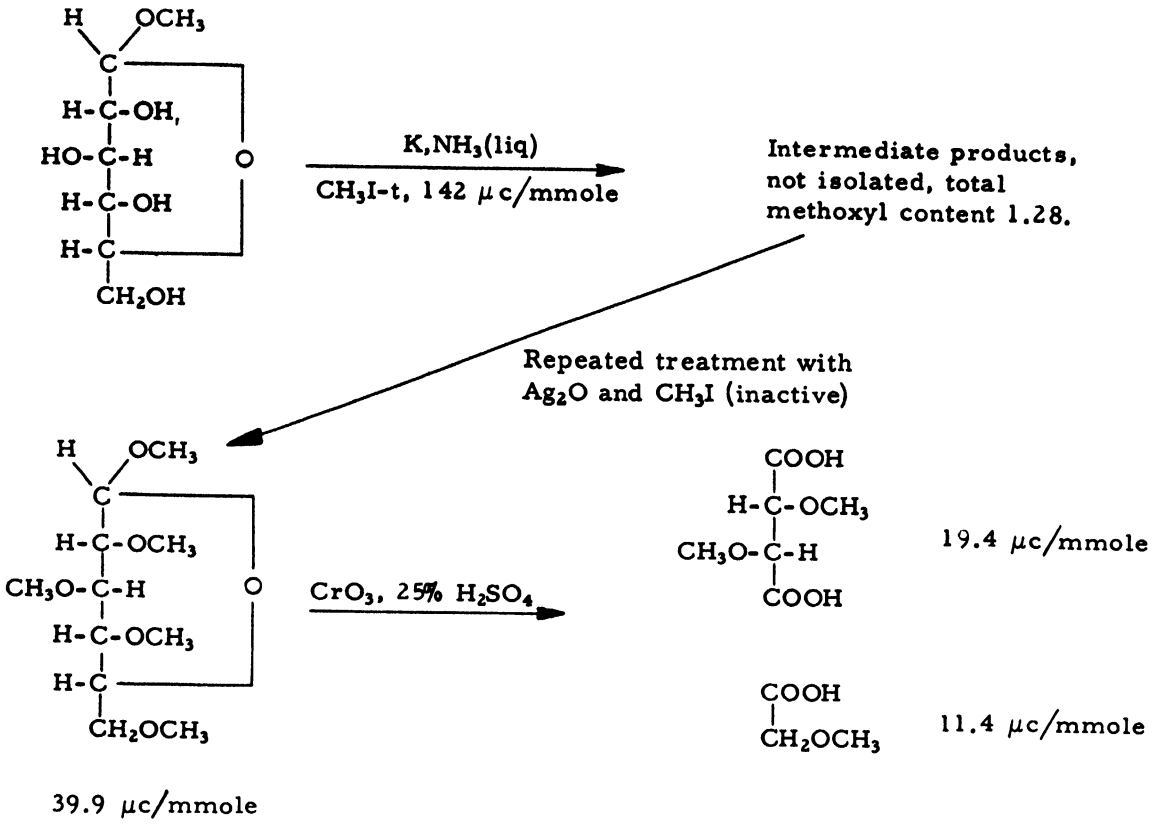

Figure 2

ence. The conclusion is reached that the extent of T-methylation at the C-6 position, is somewhat greater than at the 2, 3, and 4 positions (averaged) and, tentatively, that the extent of methylation at the C-4 position is not significantly different from the average of that at the C-2 and C-3 positions. This conclusion is of interest since Wolfram and El-Taraboulsi,[32] under somewhat different conditions of methylation and on the basis of actual isolation of the 2-methoxy compound in low yield, concluded that reaction occurs in the main at the 2-position. The conversion of tetramethylglucose to trimethylarabinose, now in progress, will permit an unambiguous determination, by difference, of the activity at C-2.

FRACTIONATION OF HYDROGEN ISOTOPES IN CHROMATOGRAPHIC SEPARATIONS

In the prosecution of the work described in the foregoing section extensive use was made of partition chromatography to separate the mixtures of aliphatic acids resulting from chromic acid or nitric acid oxidation of methylated sugars. The procedures employed were essentially those described by Isherwood[33] and by Marvel and Rands[34] in which the mobile solvent is a butanol-chloroform mixture, and the stationary solvent, supported on silica gel, is water. With T-labeled methoxyacetic acid and dimethoxysuccinic acid it was observed that the elution peaks based upon activity measurements tended to trail behind the peaks based upon titration. By refractionation of cuts, with added carrier, the possibility of an effect due to impurities was eliminated.

It was apparent, therefore, that the effect was caused by isotopic fractionation, and it seems worthwhile to draw attention to this effect as a possible source of error in tracer work with tritium. If a narrow cut is taken at the stoichiometrical peak, the specific activity found in the cut will be too low; if the cut is taken at the radioactivity peak, the specific activity found will be too high. That the effect can be quite large is shown by the behavior of formic acid. When tritium-labeled formic acid, TCOOH (5.8 μc/mmole), was eluted from a 40–cm column with butanolchloroform (1:9), the activities at 10% and 90% elution were 2.9 and 9.4 μc/mmole, respectively. Analysis of the elution curves, making use of the theoretical relationships derived by Martin and Synge[35] and by Mayer and Tompkins,[36] led to estimates of 420 for the number of theoretical plates and of 1.024 for the isotopic separation factor. For tritium-labeled methoxyacetic acid eluted with butanol-chloroform (1:40), the value of the separation factor was between 1.01 and 1.02.

The possibility that the observed separations could be attributed simply to a mass factor was evaluated by a study of C^{14}-labeled formic acid under conditions comparable with the experiments on the T-labeled acid. An effect bordering on the uncertainty of the experimental measurements was observed: the specific activity at 95% elution was only 1.5% greater than the average. An earlier study of some C^{14}-labeled acids of higher molecular weight by Garrison *et al.*[37] likewise had not revealed measur-

able isotopic discrimination in partition chromatography.

The origin of the relatively large effects observed in the T-labeled compounds is at present obscure; further experiments are in progress to determine whether the effect is dependent on the presence of an oxygen atom on the same carbon atom as tritium.

TRITIUM ISOTOPE EFFECTS ON REACTION RATES

Differences in rates of reaction produced by the substitution of deuterium for hydrogen have been extensively studied to provide information as to the participation of a particular hydrogen atom in a chemical reaction. Most such studies have involved separate rate measurements on the normal compound and on the compound deuterated at the position of interest. Although rate measurements using fully tritiated compounds are not practicable, the use of tritiated compounds at tracer concentrations is convenient for the measurement of isotopic rate ratios competitively, by observing changes in the tritium content of the reactant or of a product during the course of a reaction. The information developed by such competitive measurements does not necessarily duplicate that obtained by direct rate measurements; in some cases insight may be obtained into reaction steps which are not kinetically significant to the over-all reaction.

An early demonstration of the value of tritium in isotope effect studies was provided by Melander's investigation of the nitration of aromatic compounds.[38] The absence of a measurable isotope effect in the replacement of hydrogen by the nitro group provided evidence for a two-step mechanism, in which addition of the nitrating species to the aromatic system is rate-determining. Some recent studies of tritium isotope effects at Argonne are discussed below.

Chromic Acid Oxidation of 2-Propanol

A reaction for which complementary information has been obtained by the study of both deuterium and tritium isotope effects is the chromic acid oxidation of 2-propanol to acetone. The rate of oxidation of the pure 2-deutero-compound was shown[39] by Westheimer and co-workers to be one-seventh that of the protium compound, proving that the carbinol C-H bond is broken in the rate-determining step. Since for each molecule oxidized by acid chromate ion in the rate-determining step, two additional molecules of 2-propanol are oxidized in subsequent fast reactions initiated by chromium (IV), there remained the possibility that the more reactive intermediate oxidation states of chromium might attack the alcohol at the O-H rather than at the C-H bond. In a study of the tritium isotope effect in a competitive system, it has been found that the ratio of the rate of consumption of 2-propanol-2-*t* to that of 2-propanol varies from 0.13 in 0.3 *M* perchloric acid to 0.26 in 2 *M* acid. In the presence of manganous ion, which removes Cr(IV) and thereby isolates the chromium(VI) reaction, the observed ratio of 0.04 ± 0.02 is consistent with Westheimer's value for the deuterium isotope effect. The magnitude of the isotope ratio in the absence of manganous ion is such that in the dilute acid not more than about 7% of the alcohol can have been oxidized by a process, such as O-H bond rupture, which would not be affected by isotopic substitution on carbon. The dependence of isotopic rate ratio on acid concentration suggests that the oxidations initiated by chromium(IV) may take more than one reaction path, with that mechanism which is least affected by isotopic substitution becoming relatively more important at higher acidity.

Oxidation of Ethanol by Bromine

In another study[40] it has been shown that a methylene C-H bond is broken about seven times as fast as a C-T bond in the bromine oxidation of ethanol to acetaldehyde. If, as has been postulated, the formation of ethyl hypobromite were the rate determining step, followed by a rapid decomposition to acetaldehyde and HBr, little or no isotope effect would be observed. Since the formation of ethyl hypobromite in any but the rate-determining step of the reaction is inconsistent with the reaction kinetics, the observed isotope effect rules out the hypobromite as a precursor of acetaldehyde and leaves, as a plausible alternative, the direct transfer of a hydride ion from carbon to bromine. One of the kinetically indistinguishable formulations of such a mechanism is the following:

$$CH_3CH_2OH + Br_2 \rightarrow [CH_3CHOH]^+ + [HBr_2]^-$$

$$[CH_3CHOH]^+ \rightarrow CH_3CHO + H^+$$

$$[HBr_2]^- \rightarrow H^+ + 2Br^-$$

Hydrolysis of Silanes

The measurement of hydrogen isotope effects has been helpful in the investigation[41] of the alkaline cleavage of triorganosilanes. In basic solution molecular hydrogen is evolved according to the reaction:

$$R_3SiH + OH^- + HSol \rightarrow R_3SiOH + H_2 + Sol^-$$

one atom of hydrogen coming from the silane and the other from the solvent, *HSol*. The effects of substituting deuterium and tritium for protium, both in the silane and in the solvent, were measured. The ratio of the rate of hydrolysis of R_3SiH to that of R_3SiT, k_H/k_T, varied from 1.26 to 1.49, depending both on the nature of the radical *R* and on the solvent (aqueous piperidine or ethanol). The effects of tritium substitution in the reacting solvent molecule were greater; values of k_H/k_T for the reaction with triphenylsilane were 3.0 for piperidine and 7.0 for ethanol. These isotope effects indicate that the slow step in the reaction involves the simultaneous rupture of both silicon-hydrogen and solvent-hydrogen bonds, with the two hydrogen atoms strongly

bonded together in the transition state. If no such bond were formed, much larger values of k_H/k_T, about 8 for Si-H bond rupture and 21 for O-H bond rupture, would be expected from zero-point energy considerations.

THE MECHANISM OF SOME NITROBENZYL HALIDE REACTIONS

The combined use of deuterium and tritium as tracers for hydrogen has proved advantageous in an investigation of some reactions which are characteristic of nitrobenzyl halides and have been suspected to proceed by loss of a proton from the methylene group of the benzyl moiety. A study of these reactions, which are shown schematically in Equations 1–3, with methylene-labeled *p*-nitrobenzyl chloride, where R = *p*-nitrophenyl, *o*-nitrophenyl, *o,p*-dinitrophenyl, has established that a prototropic mechanism does apply to the formation of stilbene by self-condensation and to the formation of epoxides by condensation with aldehydes, but cannot explain the carbon alkylation of 2-nitropropane.

$$RCH_2Cl + HC(CH_3)_2NO_2 + OEt^- \rightarrow RCH_2C(CH_3)_2NO_2 + EtOH + Cl^- \quad (1)$$

$$2RCH_2Cl + 2OEt^- \rightarrow RCH = CHR + 2EtOH + 2Cl^- \quad (2)$$

$$RCH_2Cl + RCHO + OH^- \rightarrow RCH\!-\!\!-\!CHR + Cl^- + HOH \quad (3)$$

(O bridge between the two CH groups)

Previously the anomalous C-alkylation of 2-nitropropane had been attributed[42] to the formation of a nitronic ester by O-alkylation followed by loss of a proton from the methylene group and a migration of the benzyl moiety to carbon. If this mechanism were correct the formation of product from methylene-labeled nitrobenzyl halide would be accompanied by a loss, either partial or complete, of isotope from the methylene position. Actually, *p*-nitrobenzyl chloride labeled with tritium (11.4 μc per mmole) in the methylene group yielded a product containing a somewhat greater concentration of tritium (12.1 μc per mmole). This result could be reconciled with the proposed mechanism, however, if the loss of a proton occurred with a large isotope effect and if, in addition, the concentration of tritium in the chloride was increased by occurrence of a side reaction with a large isotope effect. The final proof that the reaction cannot proceed by a prototropic mechanism was established by the fact that *p*-nitrobenzyl chloride containing 1.9 atoms of deuterium in the methylene group formed a product containing the same amount of deuterium.

Likewise, although perhaps with greater justification, it has been assumed that the reactions of nitrobenzyl halides to form stilbenes,[43] by self-condensation, and epoxides,[44] by condensation with aldehydes, require an initial loss of a proton from the methylene group. If this assumption is correct, an exchange of hydrogen between a nitrobenzyl halide and a hydroxylic solvent might be anticipated under the appropriate conditions of basicity. The concurrent displacement of halide in such media complicates the study of an exchange reaction, but it has been determined that the displacement reaction with methylene-labeled *p*-nitrobenzyl chloride is accompanied by the appearance of isotopic hydrogen in the solvent. A similar treatment of normal *p*-nitrobenzyl chloride in hydroxyl-labeled solvent resulted in the appearance of isotope in unreacted chloride, as well as in the product of the displacement reaction. The exchange reaction was found to have the same concentration dependence as the displacement reaction, first order with respect to hydroxide ion and nitrobenzyl chloride, and, in the case of tritium exchange, to occur at a comparable rate. The rate of the exchange reaction for the deuterium-labeled compound is greater, by a factor of 2, than that for the tritium-labeled compound, whereas the displacement reaction is unaffected by deuterium substitution. It is clear, therefore, that the hydrogen exchange process proceeds independently of the displacement reaction and involves rupture of a methylenic carbon-hydrogen bond, presumably to form an anion of the nitrobenzyl halide.

When aldehyde is present and the predominant reaction is that leading to the epoxide, the transfer of D or T from labeled *p*-nitrobenzyl halide to the solvent occurs at the same rate as in the absence of aldehyde. The conversion of ordinary chloride to the epoxide occurs at a rate which is greater than the rate at which a labeled chloride loses D or T to the solvent; it is of the correct magnitude for the rate (unobservable) at which anions would be formed by loss of H. The fully deuterated chloride gives rise to epoxide at a rate equal to the observed rate of D exchange.

Participation of the same anion in the formation of *p,p'*-dinitrostilbene is suggested by the fact that isotopic enrichment of recovered *p*-nitrobenzyl chloride is observed when the reaction is not carried to completion.

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Applications of Radioisotopes in Chemical Research and Analysis

By John E. Willard,* USA

Radioisotopes applied to chemical research and analysis are proving to be one of the important scientific benefits to mankind from the development of atomic energy. Their usefulness is based on three features: (1) they furnish "tagged" atoms which make it possible to study in detail reactions and reaction steps which were previously unobservable; (2) they can often be detected by their radiations with much greater sensitivity than the same element can be detected by other means; (3) they can serve as efficient and economical sources of ionizing radiation for use in the study of radiation chemistry.

Radioisotopes have made accessible to investigation a whole new group of reactions, the so-called "exchange" reactions. Prior to the availability of isotopes one could only guess as to whether atoms of the same element in mixtures such as Cl_2 and CCl_4, $SO_3^=$ and $S_2O_3^=$, Fe^{++} and Fe^{+++}, HCl and C_6H_6 undergo interchange between the two molecular or ionic species. Now it is possible not only to determine whether exchange occurs but, when it does so, to study the kinetics. Such reactions are apt to be particularly rewarding in the basic information which they yield about reaction mechanisms because of their unique simplicity in that they occur with no change in chemical composition of the reaction system.

Just as the "tag" furnished by the radioactivity of radioisotopes makes it possible to observe exchange reactions it also furnishes a means of distinguishing the fate of a particular type of molecule or chemical group entering a chemical reaction from that of other types of molecules containing the same element. A dramatic illustration of this use is the elucidation by Calvin and coworkers[1] of the path of carbon in photosynthesis, starting with $C^{14}O_2$.

Radioisotopes of many elements are now readily available with specific activities of 10^4 disintegrations per minute per microgram or higher. Because such small amounts of material give easily measurable counting rates, radioisotopes have made possible determination of trace amounts of impurities in complex mixtures, investigations of chemical reactions occurring in monolayers, the measurement of the rates of extremely slow reactions, and studies of other phenomena requiring great sensitivity of detection.

* Department of Chemistry, University of Wisconsin.

Because radioisotopes produced by nuclear reactors may cost less than one thousandth as much per curie as radium, and because isotopes with a wide variety of radiation characteristics are available to suit specialized needs they are finding extensive use as radiation sources for radiation chemistry.

It is the purpose of this paper to illustrate the versatility and effectiveness of radioisotopes as a research and analytical tool. This will be done by a series of examples chosen both from work done in the author's laboratory and in other laboratories. It is not the purpose of the paper to deal with the detailed chemical findings in the fields used for illustration nor to present an extensive bibliography. A bibliography of work prior to 1949 has been published by the United Nations.[2a] A comprehensive discussion of applications of radioisotopes to chemical problems, with a bibliography covering such applications through 1949 has been prepared under the editorship of Wahl and Bonner[2b] and a summary and review of tracer applications during 1950 has been written by Edwards.[2c]

APPLICATIONS IN FREE RADICAL CHEMISTRY

Activation Energies of Radical Reactions from the Study of Exchange Reactions

Among the seemingly simplest reactions which can be chosen for fundamental kinetics studies are the exchange reactions of halogen with completely halogenated methanes. A number of such reactions have been shown to take place by free radical mechanisms. In such systems only two moleculars species need be present. The number of possible elementary reaction steps involving atoms and free radicals is smaller than in systems containing more species, and consequently the possibility of certainty in assigning activation energies to these steps is greater. Comparison of the activation energies of the thermal and photochemical reactions allows a check on postulated mechanisms and comparison of the rates and activation energies for reaction in the gas phase and solution can give information on the effect of solvent on the reaction. Probably the most thoroughly studied[3, 4] reaction of this type is the exchange of bromine between CCl_3Br and Br_2. It has been shown to take place by the steps:

$$\underset{(1)}{Br_2 \rightleftarrows 2Br}$$

$$\underset{(2)}{}$$

$$\underset{(3)}{CCl_3Br + Br \rightleftarrows CCl_3 + Br_2}$$

$$\underset{(4)}{}$$

The bromine atoms of reaction (1) may be produced either by the thermal dissociation of Br_2 at elevated temperatures, or by the absorption of light. If the initial Br_2 contains Br^{82} (36-hr) the rate of reaction (4) can be deduced from the rate of CCl_3Br^{82} formation, and this rate is equal to the rate of (3). The experimental techniques are quite simple since the distribution of activity can be determined by extracting the Br_2 from the organic layer with an aqueous reducing agent such as sulfite and then counting the aqueous and organic layers in solution counter tubes. These studies have shown that the activation energy of (3) is 8–10 kcal/mole and that the over-all rate constant and activation energy for the $CCl_3Br + Br_2^* \rightarrow CCl_3Br^* + Br_2$ reaction are essentially the same in the gas phase, in liquid CCl_3Br, and in CCl_4 solution. Further examples of such reactions have been given elsewhere.[5]

In the above reaction systems essentially every CCl_3 radical reacts with Br_2, because of the low activation energy of this process and the very low probability of encountering another CCl_3. When the reaction is carried out in the presence of a large excess of CCl_4, however, a very small fraction of the radicals abstract Cl from the latter. Using CCl_3Br containing $CCl_2Cl^{36}Br$ as a tracer it is possible to study the reaction $CCl_3^* + CCl_4 \rightarrow CCl_4^* + CCl_3$. By such means this chlorine abstraction reaction has been found[6] to have an activation energy about 10 kcal/mole higher than the $CCl_3 + Br_2 \rightarrow CCl_3Br + Br$ reaction and a frequency factor 10^{-4} of the latter. In similar work in which $C^{14}H_3$ radicals were produced by the photochemical dissociation of $C^{14}H_3I$ it has been possible to study the reaction $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$.[7]

Identification of Free Radicals

Although free radicals are known to be important intermediates in the mechanisms of many reactions they are so reactive that they are rarely present in any system in macroscopic concentrations. Consequently it is often very difficult to identify them. Radioiodine has offered a uniquely useful tool for such determinations. This is because the activation energy for reaction of radicals with I_2 is very low. If radioactive I_2^* is added to a system in which radicals are being produced they are converted to chemically stable radioactively labelled iodide molecules before they have opportunity to undergo any other reaction. The identity and relative amounts of the radicals may then be deduced by adding nonradioactive iodides as carriers, fractionally distilling and determining the specific activity of each separated carrier. By this means Gevantman and Williams[8] identified the radicals produced in the radiolysis of four alkyl iodides and of six liquid hydrocarbons.

Hamill and Schuler[9] have photolyzed methyl iodide in the presence of I_2^* in order to obtain evidence on the primary quantum yield of the $CH_3I \xrightarrow{h\mu} CH_3 + I$ reaction, which had been thought to be low because of caging effects. The observed quantum yield of 0.9 for CH_3I^* formation (by the reaction $CH_3 + I_2^* \rightarrow CH_3I^* + I$) indicates a relatively small caging effect. By similar techniques the quantum yield of the same reaction in the gas phase has been shown to be unity.[7] This gas phase exchange between CH_3I and I_2^* is well suited to serve as an actinometer for 2537 Å light.

A specialized but effective example of the power of tagged atoms in identifying radicals and radical reactions is found in investigations of the mechanisms of chemical reactions activated by radiative neutron capture (the Szilard-Chalmers process). If *n*-propyl bromide is irradiated with neutrons the naturally occurring Br^{81} isotope is converted to Br^{82} (36-hr), the latter being born with a recoil energy of thousands of kcal/mole. In liquid systems part of this energy is dissipated in breaking chemical bonds with the resultant formation of radicals. There is evidence[10] that some of the Br^{82} atoms which have been moderated to energies where they can enter stable combination do so immediately, that is before diffusing as thermal atoms. They do so by high activation energy reactions with molecules of the medium or by combining with radicals they have just formed. Other Br^{82} atoms diffuse in thermal equilibrium with the medium for some time but eventually encounter a radical (formed during the energy losing process) with which to combine. The formation of organic compounds by this latter process is eliminated if 5 mole % or so of Br_2 is present during the neutron irradiation because the Br_2 "scavenges" both the diffusing radicals and the Br^{82}. The extent of the processes which produce organically bound Br^{82} after diffusion of the thermalized radicals as contrasted to those where reaction occurs before diffusion may be determined by comparing the "organic yields" with and without Br_2 present. This has been done not only for the total yield but for eleven separate products formed from different radicals. The results[11] are given in Table 1. The method used was to add to the irradiated *n*-propyl bromide carriers for the suspected products and distill while continuously recording the distillation temperature and the level of radioactivity in the distillate.

The organic yield observed in the presence of 5×10^{-2} mole per cent Br_2 is all attributable to reactions which occur to "hot" Br^{82} atoms while the difference between this yield and that in the absence of bromine is attributable to reactions between thermal Br atoms and radicals.

Table 1. Products of the Br^{81} (n,γ) Br^{82} Reaction in *n*-Propyl Bromide and the Effect of Added Bromine[11]

Product	*Organic yield in % no bromine added**			*Organic yield in % $5 \times 10^{-}$ mole fraction of bromine added*		
Methyl bromide	2.01	2 05		1.29	1.19	1.28
Ethyl bromide	0.50	0.52	0.7	0.31	0.29	0 32
i-Propyl bromide	1.87	1.94	1.7	0.68	0.80	0.71
n-Propyl bromide	18.0	17.9	17.1	7.42	7.96	7.58
Methylene bromide	1.27	1.31	1.8	0.90	0.99	1.07
Ethylene bromide	1.68	1 61	3.1	1.39	1 36	1.41
1,2-Dibromopropane	2.35	2.50	2.8	2.30	2.28	2.21
n-Hexyl bromide		0 31			0.31	
1,3-Dibromopropane	2.35	2 44	2.7	2.32	2.17	2.19
1,1,2-Tribromoethane	0 28	0.27		1.05	0.89	0.88
Polymer	1.05	1.16	1.5	3.27	3.45	3.40
Total organic yield	32.4	32.0	34.7	20.9	20.9	21.1

* The results in the first two columns of figures are duplicate determinations[11] without added bromine, those in the third column were obtained by Fox and Libby,[12] those in columns 4, 5 and 6 are duplicate determinations[11] with added bromine.

Polymerization Studies

Radiosulfur makes it possible to achieve high sensitivity in determining the ratio of sulfur to total polymer in systems where sulfur-containing initiators start polymerization chains. It also allows identification of the source of the bound sulfur when different sulfur-containing compounds are present in the reaction mixture.

Two examples will be cited. The rate of incorporation of S^{35} into polystyrene when S^{35}-labelled persulfate is used as a chain initiator for the emulsion polymerization has been used by Smith[13] as a measure of the rate of chain initiation. Mochel and Peterson[14] have used similar techniques in the determination of the end groups in Neoprene type GN.

APPLICATIONS IN INORGANIC CHEMISTRY

A multitude of applications of radioisotopes to problems of exchange, structure and reaction mechanisms in inorganic chemistry have been made. The examples given below serve to illustrate some of their unique contributions to this field.

Intermolecular Exchange

Sometimes structural evidence suggests that two atoms of the same element in a certain type of ion or molecule are chemically different and would not be expected to exchange with each other. In some of these cases radiotracers make it possible to determine whether the prediction is valid. For example, thiosulfate ion may be synthesized, by reacting alkaline sulfite with radiosulfur ($SO_3^= + S^* \rightarrow S_2{}^*O_3^=$), and later decomposed with acid ($S_2{}^*O_3^= \rightarrow SO_3^= + S^*$). When this is done[15] the elemental sulfur from the decomposition contains nearly all the radioactivity, thus showing that while in the thiosulfate ion it is chemically different from the sulfur derived from sulfite. No exchange of the two forms occurs even when the thiosulfate is heated at 125° for several hours, or subjected to precipitation as triethylenediamine nickel thiosulfate and redissolved in acid.

Recently Downs and Johnson[16] have presented evidence on the exchange of Cl_2 with PCl_5 which suggests that the three equatorial Cl atoms do not exchange rapidly with the two apical Cl atoms but do exchange readily with Cl_2.

Exchange Reactions between Ions

Radioisotopes have greatly advanced knowledge in the field of kinetics of ionic reactions. Among the types of reactions studied with their aid (with single examples of each) have been electron transfer[17] ($Fe^{++*} + Fe^{+++} \rightarrow Fe^{+++*} + Fe^{++}$), atom transfer ($S^*O_3^= + S_2O_3^= \rightarrow SS^*O_3^= + SO_3^=$),[15] the exchange of metal ions with coordinated metal complexes,[18] the exchange of anions with coordinated metal complexes ($(Co\ en_2\ CO_3)Cl + C^{14}O_3^= \rightarrow (Co\ en_2\ C^{14}O_3)\ Cl + CO_3^=$);[19] the thermal and photochemical electron transfer between the species in the two oxidation states of an optical interaction dimer ($SnCl_6^{=*} + SnCl_4^= \rightarrow Sn_2Cl_{10}^{-4} \rightarrow SnCl_6^= + SnCl_4^{=*}$).[20] It is of interest that in the cobalt complex-carbonate exchange cited it was possible to draw conclusions as to the mechanism of the racemization process from the exchange data.

Intermolecular Exchange

Among the reactions between rather simple molecules about which one could only speculate before the availability of radioisotopes but which have now been investigated in some detail are the exchange reactions between HBr and Br_2,[21] HCl and Cl_2,[22] $SnCl_4$ and HCl.[23] Unfortunately all these pairs prove to undergo so rapid exchange (demonstrated to be surface catalyzed in the case of the latter two) that it has been impossible to investigate the mechanisms of the homogeneous gas phase reactions, which would be of considerable theoretical interest.

The exchange between HF and liquid or gaseous ClF_3, BrF_5 and other interhalogen compounds has been shown[24] to go to completion in 10 min or less at room temperature. By contrast the rate of exchange between F_2 and the interhalogen compounds is essen-

tially zero[25] below 100°C but is rapid at 300°. HF and F_2 do not exchange at room temperature.[26]

Properties of Monatomic Sulfur

By irradiation of KCl with neutrons S^{35} atoms are produced in the crystal by the $Cl^{35}(n,p)S^{35}$ process. Several workers have investigated the chemical properties of the monatomic sulfur thus produced, which would be expected to be very different from the usual S_8 molecular form. There is evidence which is consistent with the conclusion that part of the S^{35} occurs in the crystal as neutral S atoms which are oxidized to $SO_4^=$ by the reaction $S + 4H_2O \rightarrow H_2SO_4^= + 3H_2$ when the KCl is dissolved in water.[27]

SURFACE STUDIES

Surfaces are two dimensional, or very thin three dimensional systems. As such their chemical content per square centimeter is extremely small, i.e., of the order of 10^{-7} gm or 10^{-8} mole. Yet it is the properties of this thin layer which, in many cases, make a substance scientifically interesting or practically useful.

Radioisotopes with specific activities high enough to give thousands of counts per minute from the number of atoms in a square centimeter of surface area are now available for a majority of the elements. These have made it possible to study conveniently and quantitatively many chemical reactions of surfaces which it was previously impossible even to detect.

Such studies may be designed to yield new information on surface forces and the kinetics of reactions involving surface atoms, and to aid in the solution of problems in fields such as metal plating, detergent action, mirror formation, corrosion prevention, catalysis, adhesion of protective coatings, degassing of surfaces, classification of minerals and others.

A survey of applications of radiotracers to the study of surfaces, together with references is given in a recent paper.[28] Among the subjects of investigation by various workers which are discussed are: (1) reactions of glass with ions in aqueous solution; (2) the reaction of bromine vapor with glass; (3) the determination of sticking coefficients for atoms striking surfaces; (4) reaction of surfaces with the unsaturated vapors of compounds of low volatility; (5) determination of the adsorption of surface-active agents at a solution-air interface; (6) chlorine exchange reactions between solid $AlCl_3$ and HCl, Cl_2 and organic chlorides.

Beischer[29] has developed a unique and ingenious technique for studying surfaces by preparing C^{14}-labelled stearic acid monolayers on a variety of surfaces by the Langmuir-Blodgett method. By means of radioautographs of these he has been able to investigate the homogeneity of distribution of the monolayers, their "melting points," their chemical reactions with the substrate material, surface diffusion, the effect of substrate on backscattering, and other properties.

GENERAL APPLICATIONS TO DETERMINATION OF MECHANISMS

Mechanisms of Organic Reactions

By specific synthetic techniques it is often possible to make organic molecules in which any desired carbon atom is labelled. Products formed by the reactions of such molecules may be selectively degraded in a manner which will show the new position of the C^{14}. This information on the fate of carbon atoms from individual positions in the molecule is often sufficient to allow a decision between alternate reaction mechanisms. Recent examples of this powerful use of C^{14} are given in papers by Bonner and Collins[30] who have studied molecular rearrangements of derivatives of triphenyl ethyl. Earlier examples may be found in references 2(*a*), (*b*) and (*c*).

Labelling of Complex Molecules

Of both practical importance in the labelling of compounds for mechanism studies and of theoretical interest are recent demonstrations that a usable efficiency may be achieved in radioactively tagging aliphatic and aromatic hydrocarbons and sugars with the aid of high energy atoms produced by nuclear processes.

Neutron irradiation of a 5 mole per cent solution of aniline or methyl amine in *n*-pentane leads to 25 per cent of the C^{14} from the $N^{14}(n,p)C^{14}$ process as n-C_5H_{12}, 1 per cent as i-C_5H_{12}, 12 per cent as n-C_6H_{14}, 6 per cent as other hexanes and 39 per cent as higher boiling hydrocarbons (Schrodt and Libby).[31] Anthracene-C^{14} has been produced in 0.2 per cent yield by neutron irradiation of its nitrogen homologue, acridene, while 3 per cent of the C^{14} was found as acridene (Wolf and Anderson).[32]

Using a process which they term "heterogeneous recoil tagging," Wolfgang, Rowland and Turton[33] have subjected finely ground mixtures of $LiCO_3$ and glucose to neutron irradiation to produce the $Li^6(n,\alpha)T$ reaction. The diameter of the $LiCO_3$ particles was about 1 micron and the range of the tritons is about 50 microns in organic material. About 10 per cent of the tritons stopped in the organic phase were incorporated into non-labile positions in glucose, giving a specific activity of about 2 μc/gm. This remained essentially constant through five recrystallizations as the penta-acetate. Specific activities 100-fold higher appear practicable for glucose, with still higher levels possible for compounds less sensitive to radiation decomposition. The same authors[33] report that in an independent check of this labelling technique L. Kaplan has found that 25 per cent of all the tritons produced in a mixture of Li_2SO_4 and benzoic acid result in benzoic acid labelled in the ring hydrogens, 96 μc/gm being obtained with little radiation decomposition.

Mechanism Studies on Fischer-Tropsch Synthesis

Carbon-14 has proved a valuable tool in answering the question as to whether a metallic carbide is an

intermediate in the synthesis of hydrocarbons from carbon monoxide and hydrogen over iron, nickel and cobalt catalysts.[34] By carbiding the catalyst surface with C^{14} before carrying out a hydrocarbon synthesis and then measuring the radioactivity in the hydrocarbon after synthesis it was shown that the majority of the product is formed by some process not involving the reduction of a carbide intermediate.

Carburization and Diffusion Processes in Iron

Bokros and Rosenthal[35] have enclosed amorphous carbon labelled with C^{14} in iron capsules heated to various temperatures and quenched and annealed in various ways. Following heat treatment the capsules were sectioned, etched, and coated with a very thin layer of vinyl resin to protect them from corrosion and then with a thin layer of nuclear track emulsion. After 10 days standing, to expose the emulsion to the C^{14} beta particles from the carbon which had migrated into the iron, the emulsion was developed. Photomicrographs of the developed samples were used to show both the etching pattern of the surface and the distribution of radiocarbon. Certain conditions of annealing were found to lead to slow diffusion of the carbon to grain boundaries.

Friedel-Crafts Reactions

Several exchange reactions of interest in connection with theories as to the mechanisms of the alkylation of aromatic compounds with alkyl chlorides, using aluminum chloride as a catalyst, have recently been studied. With the aid of Cl^{36} it has been found[36] that gaseous HCl and a variety of chlorinated hydrocarbons[37, 38, 39] exchange readily with solid $AlCl_3$. Using H^3Cl it has been shown[40] that the tritium does not exchange with the hydrogens of liquid toluene in 10 hours at 140°.

Isotope Effects

For most tracer applications of radioisotopes the fact that the latter are different in mass from the stable isotopes of the same element, and therefore may react at a slightly different rate is undesirable. Fortunately the mass effect is small except for elements of low atomic weight. When the effect is detectable it may be employed as an aid in elucidating reaction mechanisms. Because of their lower zero point energy C^{12}–C^{14} bonds break less readily than C^{12}–C^{12} bonds. Thus if the rate determining step of a reaction is suspected to be the rupture of a certain C–C bond the hypothesis may be tested by determining whether the rate is slower when the bond is C^{12}–C^{14} than when it is C^{12}–C^{12}. Furthermore, since the relative rates of isotopic reactions are predictable from rate theory they may be used to provide experimental test of the theory. Applications of this type have been discussed and examples and references given in recent review articles.[2b, 41]

Measurement of Very Slow Reaction Rates

Many chemical reactions of potential interest undoubtedly take place at rates too slow to allow detection by ordinary methods within feasible lengths of time. If the reacting material is labelled with a radioactive isotope at a moderately high specific activity the rate may, however, be easily determined. For example, when $C^{14}H_3I$ is dissociated by 2537Å light in the presence of CH_4 at room temperature a very small fraction of the methyl radicals formed reacts by the step $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$.[7] Although the abstraction occurs at the rate of only 4×10^{-8} moles per day in a typical reaction system it may easily be measured in a day's time, and with higher efficiency counting methods than used in the work cited could be measured after only a few minutes of reaction, i.e., 10^{-10} moles.

Reactions of Atoms with Abnormally High Energy or Charge

Nuclear transformations yield product atoms which have abnormally high kinetic energy, or charge, or both, and which may be radioactively tagged. For example, a Br^{82} atom which has just been formed by the $Br^{81}(n, \gamma)Br^{82}$ (36-hr) reaction with the emission of a 7 Mev γ-ray will have a recoil energy of 322 ev or about 7400 kcal/mole, while an S^{35} atom formed by emission of a 0.59 Mev proton in the $Cl^{35}(n,p)S^{35}$ (87d) process is born with an energy of some 16,400 ev. Br^{80} (18) min produced by the isomeric transition of Br^{80m} has a minimum charge of plus 1 and an average charge of plus 10.

Since chemical bond energies are rarely in excess of 5 ev, the recoil energies and charges resulting from many nuclear processes are sufficient to rupture the parent bond of the atom, and allow it to break many bonds in neighboring molecules, before being slowed to thermal energies. The products may be identified by their radioactivity after separation with the aid of specific carriers or chemical procedures. With a knowledge of the product species, there is a possibility of deducing the nature of the bond rupture processes by which the highly activated atoms lose their energy and finally achieve new stable chemical combination. For the kineticist this method of activation has the unique advantage that the particular atom which is activated is tagged with radioactivity by the same act which activates it.

Detailed discussions and examples of work in this field have been given earlier.[10, 42] One example of many that might be cited is the reaction of CH_4 with I atoms activated by the $I^{127}(n, \gamma)I^{128}$ process. Whereas photochemically produced I atoms are unreactive to methane approximately 50% of the I^{128} species freshly formed by the (n, γ) process undergo a bimolecular reaction of the type $I + CH_4 \rightarrow ICH_3 + H$.[43]

APPLICATIONS IN ANALYTICAL CHEMISTRY

Activation Analysis

In activation analysis a sample to be analyzed for traces of an element is irradiated in an intense neutron flux. Radioisotopes of the trace constituent may be formed by the (n, γ) process. A weighed amount

of the non-radioactive naturally occurring form of the element is then mixed with the sample in such a way that the radioactive atoms will become chemically indistinguishable from it. A known weight of the element is then isolated from the mixture and carried through procedures to insure radiochemical purity. From the observed radioactivity in this portion and the per cent recovery of the added carrier the total radioactivity attributable to the trace element in the irradiated sample can be computed. By comparison of this activity with that induced by the same neutron exposure in a sample of known weight of the element sought the weight of the trace element may be determined.

For elements which have high neutron absorption cross sections such analyses are extremely sensitive if high neutron fluxes are used. For example it may be estimated that in a flux of 10^{13} neutrons/cm^2/sec, such as is now available at several nuclear reactors, 10^{-12} grams/ml of Dy can be detected, while many elements can be detected at a level of 10^{-9} grams/ml or less.[44a] In addition to its sensitivity the method has the advantages that it can be carried out on very small samples of almost any type, that the results are not invalidated by small contamination with the element sought if this occurs during separation after irradiation, and that quantitative recovery is not required. With the rapidly increasing availability throughout the world of nuclear reactors providing high neutron fluxes, activation analysis may be expected to become a more and more generally used analytical tool. Many good discussions of the subject are available.[44]

Isotope Dilution Technique

When it is desired to determine the amount of a substance in a complex mixture from which it is difficult to separate it quantitatively the method of isotope dilution may often be used effectively. A radioactively tagged sample of the substance, of known specific activity, is first prepared. A known amount of this is mixed homogeneously with a weighed amount of the sample to be analyzed. Part of the substance is then separated from the mixture. From the decrease in specific activity resulting from dilution of the active material by the inactive material in the mixture the original amount in the mixture may be computed. The procedure is essentially one of using the fractional recovery of the added radioactivity to indicate the fractional recovery of the inactive compound originally present in the sample.

Keston[45] and co-workers have effectively applied this technique to the separation of complex mixtures of amino acids and have extended its sensitivity by ingenious modifications. As the initial step in analyzing such a mixture they convert all of the amino acids to the *p*-iodo-benzensulfonyl derivatives ("pipsyl" derivatives) using pipsyl chloride labelled with I^{131}. Next, known weights of unlabelled pipsyl derivatives of the amino acids are added as carriers and separated by fractional crystallization, solvent extraction and other methods. The amount of each amino acid present in the original mixture is calculated from the I^{131} specific activity of a pure sample of the carrier isolated from the mixture and does not depend on complete recovery. The method is capable of determining amino acids present in less than microgram quantities. In order to use paper chromatography for the separation and purification of the I^{131} labelled pipsyl derivatives in place of the more tedious and less certain processes such as fractional crystallization a further modification was made. In this procedure small amounts of S^{35} labelled pipsyl amino acid derivatives are added in place of the unlabelled pipsyl amino acid carriers. These serve as "indicators." The mixture of derivatives is then separated by paper chromatography and radioautograms of the chromatogram are taken with and without an aluminum filter, which cuts out the S^{35} radiation but allows the more penetrating I^{131} radiation to pass. After the addition of the "indicator" further manipulations need not be quantitative. A constant ratio of S^{35} to I^{131} activity in successive strips cut from a spot on the chromatogram demonstrates purity. The ratio of the S^{35} to I^{131} activity in any such strip together with a knowledge of the specific activity of the original S^{35} and I^{131} pipsyl chlorides can be used to calculate the amount of the particular amino acid on the strip in the original mixture.

Carrier Techniques

Examples of the use of carriers to separate the I^{131} and Br^{82} derivatives of free radicals from complex reaction mixtures have been given in the section of this paper dealing with free radical chemistry. In the section on isotopic dilution techniques an example of the use of unlabelled pipsyl derivatives of amino acids as carriers for I^{131} labelled derivatives was given. As a third and different type of example the work of Heidelberger, Hadler and Wolf[46] on the identification of the metabolic products of a carcinogenic compound, 1,2,5,6-dibenzathracene-9,10-C^{14}, applied to the skin of mice, may be cited. Known weights of suspected metabolites were added to the desired tissue fractions and then portions of these carriers were separated, purified and counted. By the presence of activity in the purified fractions three new metabolites were identified.

Other Analytical Applications

Opportunities for the application of radiotracers in analytical problems are many and varied. In any separation procedure where the component of interest is radioactively tagged its distribution at each step may be determined by the distribution of the radioactivity, whether it be precipitation, solvent extraction, fractional condensation in the trap of a vacuum line, column chromatography, paper chromatography, electrolysis or other separation process. If it is desired to know the extent to which a procedure purifies a substance *A* with respect to *B* a small amount of

high specific activity B may be added before processing and the fractional decrease in radioactivity noted at each step in the process. Radioactive tracers are an attractive tool for determination of the solubility of relatively insoluble salts.[47] For example, radiobromine is readily available with a specific activity sufficient to give 1000 counts/min per milliliter of saturated silver bromide solution.

RADIOISOTOPES AS RADIATION SOURCES

Investigations of the mechanisms of chemical reactions initiated by high energy radiations are now being conducted in many laboratories.[42] Many of these investigations are made possible because of the availability and convenience of Co^{60} as a source of gamma radiation. The simplicity with which multicurie sources may be housed and used is illustrated by equipment employed in our laboratory.[48] The housing for experimental work consists of a lead turret on a low table, the volume below the table being shielded on three sides by stationary shielding and on the fourth by a rolling lead door. The capsule containing the Co^{60} is screwed on to the end of a rod which passes through vertical holes in the turret and the table. The source can be positioned in the center of the turret when not in use and, when desired, lowered to any position adjacent to experimental equipment below the table. Using a 400 curie Co^{60} source 1 cm in diameter and 2 cm high in a cylindrical aluminum capsule an average gamma ray intensity of 2×10^6 roentgens/hr is obtained in 5 ml of liquid held in an annular glass irradiation vessel around the capsule.

Many radioisotopes besides Co^{60} may find use as radiation sources for specialized applications. One of particular interest is tritium. It can be used as the element to study the radiation chemistry of hydrogen[49] in mixtures with other substances or can be used to synthesize hydrogen compounds. Radiolysis rates should be easily measurable in a milliliter of most liquids containing a curie of tritium. The very weak beta radiation from tritium offers the advantages that protective shielding is not required, darkening of glass vessels by the radiation is minimized, and the radiation dose may be accurately calculated if the tritium assay of the sample is known.

For the study of chemical reactions initiated by neutron capture,[10] antimony-beryllium photoneutron sources utilizing Sb^{124} are useful if more intense sources such as provided by nuclear reactors are not available.

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Radioactive Isotopes in Petroleum-Production Research

By J. W. Watkins and H. N. Dunning,* USA

The injection of water to restore pressure and to force petroleum to production wells has become an important method of petroleum production. Petroleum commonly occurs in the fine pores and interstices of sandstone and limestone formations. Heterogeneous conditions that often exist within productive formations decrease production efficiency. The efficiency of petroleum production by water flooding may be increased appreciably by early detection and correction of formation heterogeneities and by improving the characteristics of the water as a flooding medium.

Characteristics of petroleum-productive formations may be determined by analysis of cores cut during drilling operations, by subsurface measurements, and by wellhead tests. However, calculations involving these data are based on the assumption that conditions between wells are comparable to those at well bores. Tracers added to water injected into input wells and detected in water entering production wells afford a means of evaluating certain reservoir conditions between wells.

The use of additives to improve the properties of the water, in addition to the usual treatment of injection water to minimize its corrosive and plugging characteristics, is desirable. Detergents are among the more promising additives investigated recently. Extensive laboratory tests have shown that dilute detergent solutions are effective for removing petroleum from consolidated and unconsolidated sands and increasing the injectivity of water into sandstone cores. A recent field test has shown that the injectivity of brines into productive formations may be increased appreciably by the use of nonionic detergents.

Many promising water tracers are limited in their usefulness by adsorption on the solid surfaces of petroleum reservoirs. Adsorption of detergents at solid-solution interfaces is a major economic factor influencing their use in water flooding. However, application of chromatographic theories has shown that such adsorption may not be the limiting factor previously supposed. According to these theories, it should be possible to move a detergent zone through the reservoir in the same manner as a zone is moved through a chromatographic column. The basic data for calculations based on these theories are obtained from adsorption isotherms.

RADIOACTIVE ISOTOPES AS TRACERS FOR INJECTION WATER

The usual practice in water flooding is to inject water into and produce petroleum from alternate wells. The well pattern most often employed is the "5-spot," in which there are 4 water-input wells at the corners of a square and a petroleum-production well at the center. Similarly, 4 production wells surround each input well when this pattern is repeated. Water is injected and petroleum is produced throughout the entire vertical section of the formation susceptible to water flooding.

Data commonly employed in reservoir-engineering calculations are obtained by three general methods: (1) core analysis, (2) wellhead measurements, and (3) subsurface measurements. Although much useful information may be derived from such data, some errors are inherent to core analysis, and extrapolations of wellhead-test data to include the area between wells frequently introduce indeterminate errors.

Subsurface measurements include electrical logs, gamma-ray and neutron logs, and water-input profiles (the rate at which water enters vertical segments of the productive formation at the sand face of input wells). Some of the methods for determining input profiles are comparatively rapid; others are slow and require elaborate and cumbersome equipment. In general, agreement of the results obtained by different methods is not satisfactory. Hence, the use of an efficient water tracer should provide two general types of information needed to supplement that available from other test methods: (1) the rates of movement and distribution of water and (2) the zones through which water moves between wells. This information then may be correlated with profiles made in input wells.

Efforts to use tracers for determining the flow of water on and below the surface of the ground have been made for more than 50 years. However, comparatively few technical papers describing the methods employed and results obtained have been published. One of the earliest reports on the use of water tracers was published in 1906.[1] Several papers

* Including work by F. E. Armstrong, H. N. Dunning, R. J. Heemstra, L. Hsiao and J. W. Watkins, Bureau of Mines, Bartlesville, Okla.

have presented information pertaining to the use of stable tracers,[2-6] and results of laboratory and field surface or pipeline flow studies made with radioactive tracers.[7-12] Some recent publications [13-16] have described the use of radiotracers for determining the zones through which water leaves input wells (water-input profiles). Many other current, and some proposed uses of radioisotopes as tools of petroleum-production research have been listed.[17-20] US patents granted to French[21] and Hinson[22] describe the use of radiotracers for following the subsurface flow of fluids. However, nothing had been published concerning the use of radiotracers for following the flow of water between wells or for detecting the entry of water into production wells until Watkins and Mardock[23] reported the results of preliminary field tests in 1954.

An ideal water tracer should have the following characteristics, listed in order of relative importance:

1. High aqueous solubility of its common compounds and low or negligible solubility in crude petroleum.
2. Low adsorption on solid reservoir surfaces.
3. High detectability in low concentrations by portable apparatus.
4. General availability at low cost.
5. Nonhazardous nature under normal working conditions.
6. Detectability in the well bore and at the surface.

From the beginning of intensive work with water tracers in Bureau of Mines laboratories in 1951, radioactive isotopes have appeared to offer several advantages over stable substances. Consequently, essentially all work was done either with radioactive substances or with elements that also were available in radioactive form.

Radioactive isotopes are superior to stable ones as water tracers in the following respects:

1. Higher detectability in low concentrations.
2. Detectability in the well bore with subsurface instruments if the emitted radiation is gamma.
3. Detectability with portable, durable, automatic, and recording equipment.

Laboratory Evaluation of Potential Tracers

Numerous substances have been tested in the laboratory to determine their suitability as water tracers on the basis of the above criteria. Most of the tracers were selected primarily because of the aqueous solubility of their common compounds and probable low adsorption characteristics. However, fluorescein was compared to other potential tracers because some of the earliest work and many occasional field tests have been made with fluorescent dyes.

The first laboratory tracer-evaluation tests were made by comparing the adsorption of fluorescein to that of a yellow dye occurring in some oil-field brines and a similar substance extracted from petroleum. The adsorbents were cores cut from petroleum sands. All three substances were appreciably adsorbed by the cores, but small quantities of each of the three eventually appeared in the effluent.

In later tests, cores with substantially greater surface areas permitted the use of higher and more detectable concentrations of stable materials. These cores were cut parallel to the bedding planes from a sandstone outcrop. The sandstone was comparatively homogeneous and similar in physical characteristics to many petroleum sandstones. The cores, approximately 2 inches in diameter and 24 inches in length, were sealed in plastic tubes.

Stable isotopes were used in the preliminary laboratory tracer tests because of the great number of substances that might be tested. However, the elements tested were those that were readily available as radioactive isotopes. Cesium and selenium were tested because their common compound are water-soluble and because both were available as gamma-emitting radioisotopes (cesium-134 and selenium-75). Multiphase-flow studies employing cesium as a tracer had been reported by Josendal *et al.*[12] prior to this work.

The first test of the series was made by injecting 50 milliliters (ml) of distilled water containing 160 parts per million (ppm) of stable cesium chloride into one of the water-saturated cores. The core had a permeability to air of 310 millidarcys (md), a porosity of 26.5 per cent, and a pore volume of 388 ml. The tracer was injected and was followed by tap water at the rate of 15 ml per minute at a pressure of 50 pounds per square inch, gage (psig). The cesium content of the effluent was determined with a Beckman DU flame spectrophotometer. No cesium was detected in the effluent, although 1.8 liters of water, about 4.6 pore volumes, had flowed through the core. A second tracer "slug," consisting of 50 ppm of cesium chloride and 10,000 ppm of sodium chloride in 50 ml of water was injected into the core under the conditions of the previous experiment except that the core now was saturated with brine. No cesium was detected in the effluent, although 600 ml, about 1.5 pore volumes, were displaced.

A slug containing 200 ppm of cesium chloride and 10,000 ppm of sodium chloride in 50 ml of water then was injected into the core; this was followed by brine injected at the same rate and pressure as those used in the two previous tests. Essentially no cesium was detected in 1.5 liters or about 3.9 pore volumes that had passed through the core. It was concluded that cesium was too highly adsorbed to be useful as a tracer either in fresh waters or in brines.

Selenium oxide was tested as a tracer by injecting 50 ml of solution containing 60 ppm of selenium oxide and 10,000 ppm of sodium chloride into a second core having an air permeability of 300 md, a porosity of 26.0 per cent, and a pore volume of 315 ml. The slug, followed by brine, was injected at the rate of 4 ml per minute at a pressure of 50 psig. The effluent was tested for selenium content by a colorimetric method employing potassium iodide as an indicator. No selenium was detected in testing aliquot samples totaling 570 ml, or about 1.8 pore volumes.

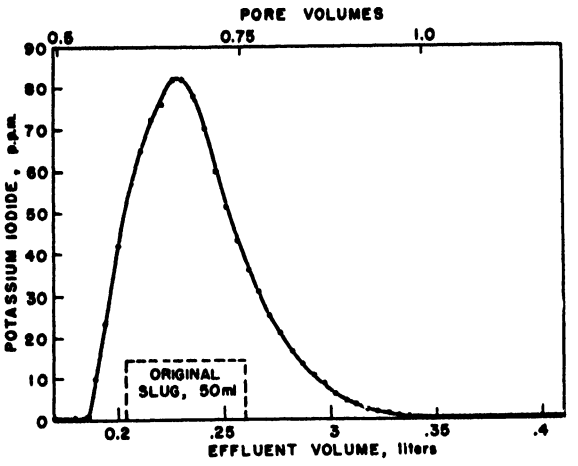

Figure 1. Elution of potassium iodide from sandstone core

It was concluded that selenium was strongly adsorbed by the core.

The next laboratory test was made with stable potassium iodide. A tracer slug containing 10 ppm of potassium iodide and 10,000 ppm of sodium chloride in 50 ml of water, followed by brine, was injected into a core at a rate of 1.5 ml per minute and at a pressure of 50 psig. The core had an air permeability of 180 md, a porosity of 22.9 per cent, and a pore volume of 343 ml. Iodine was determined in the effluent by a colorimetric method. Results of this test are shown in Fig. 1. Iodine was first detected in the effluent after the injection of 185 ml, reached a peak of 80 ppm after 200 ml, and decreased almost to zero after 340 ml, or about 1 pore volume of water had been passed through the core. Summation of the area under the curve indicated that about 98 per cent of the potassium iodide injected was recovered. A second test made with a concentration of 200 ppm potassium iodide yielded comparable results.

A third laboratory test was made in which a solution containing 0.1 millicurie (mc) of potassium iodide-131 in tap water without added carrier was continuously recycled for 550 hours through a sandstone core. This core had an air permeability of 181 md, a porosity of 22.0 per cent, and a pore volume of 344 ml. A steel, water-filled jacket was fitted over the plastic-mounted core to permit the use of higher pressure and to provide some radiation protection. A differential pressure of 125 psig was maintained across the core during the test; the flow rate averaged 1.5 ml per minute. Radioactivity of the effluent was measured with a dipping-type Geiger-Mueller tube.

Figure 2 shows the adsorption of potassium iodide-131 by the sandstone core. Radioactive iodine was first detected after 340 ml (about 1 pore volume) of effluent had been produced. A total of about 109 pore volumes of fluid was circulated through the core. The plotted data indicate a loss of about 80 per cent of the radioactive iodine during the flow test. They also indicate that iodine, as the iodide ion, may be used as a water tracer even under conditions of extended contact with reservoir surfaces. The continued loss of tracer with continuous recycling suggested that incomplete contact caused by intricate pore distribution or clay minerals may affect apparent adsorption rates. Potassium iodide-131 was used as a tracer in several field tests because the laboratory tests indicated comparatively low adsorption.

The short half-life of iodine-131 makes it unsuitable for uses in which the transit time between wells may exceed 3 to 4 weeks. Therefore, it was desirable to select another radioactive tracer having a suitable gamma emission, a somewhat longer half-life, stable aqueous solubility, and low adsorption characteristics. Two isotopes of the platinum-metals group, ruthenium-103 and iridium-192, were selected for laboratory tests. These tests are not complete enough to permit the release of results obtained. However, the value of further laboratory and field experiments has been indicated.

Field Tracer Tests

The methods used in making field tracer tests with radioactive iodine were described in detail in a previous publication.[23] All obtainable information concerning the production property and well performance was correlated before field tests were made. Results of core analyses, water-injection rates and pressures, and petroleum- and water-production rates were studied and wellhead tests were made to evaluate input-well performance. If the wells had been "shot" with explosives, diameters of the shot holes were determined by calipering.

After a group of wells had been selected for a tracer test, gamma-ray background and neutron logs were made in all of the wells by conventional methods. A water-input profile then was determined in the selected input well by a method using radioactive iodine adsorbed on a resin.[14, 15] The resin, of a suitable particle-size range, was injected with water at normal rate and pressure. After injection, repeated gamma-ray logs were made in the well to detect the zones into which most of the water entered. These zones were indicated by the highest residual radioactivity above background.

The water-soluble tracer then was injected into the input well while standard injection conditions were maintained. The radioactivities of fluids produced

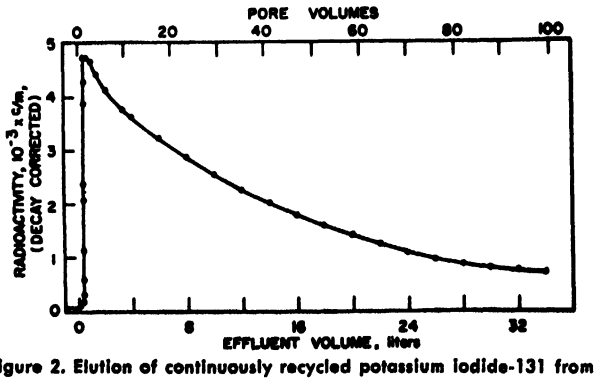

Figure 2. Elution of continuously recycled potassium iodide-131 from sandstone core

from wells surrounding the input well were recorded continuously with Geiger-Mueller tubes inserted into each wellhead, count-rate meters, and strip-chart recorders. Usually two slugs of tracer were injected at intervals of about 72 hours. Detection of the first slug of tracer at the production wells gave comparative information on transit time, as well as relative distribution of water between wells. This information permitted positioning the gamma-ray logging instrument opposite the productive formation in the production wells in time to log the radioactivity of the wells as the second slug of tracer flowed into them. In this manner water-production profiles were made to determine the zones of excessive water entry into the wells. Figure 3 is an isometric diagram illustrating the correlation of water-input and water-production profiles obtained by the use of radioactive tracers. Gamma-ray background logs in this figure are indicated as dashed lines opposite each of the two production wells and on either side of the center input well. Gamma-ray logs showing the principal zones of exit of water from the input well and entry of water into the production wells are indicated by the solid lines. The log recordings of necessity have been exaggerated horizontally to illustrate adequately differences in radioactivity. The distance from the input well to each of the production wells was approximately 500 feet.

The principal point of exit of water from the input well is shown to be at the bottom of the hole, or at a depth of 722 to 725 feet (all depths have been corrected to a common surface elevation). A minor zone of water exit was indicated at about 709 feet. The principal zones of water entry into production well H-16 were indicated at about 724 and 728 feet. Lesser zones of entry were observed at about 705 and 715 feet. Most of the water was shown to enter well F-16 at the bottom, or at a depth of about 723 feet.

The principal zone of water transmission, indicated by correlation of the logs shown in Fig. 3, was the lower 3 to 4 feet of the formation, which extended a short distance into a shale bed below the sandstone. This information was used by the operator of the project to plug the lower section of the formation at the input well, thereby materially reducing both water-injection and water-production rates and increasing the petroleum-production rate.

Detergent Adsorption

The determination of detergent adsorption at interfaces is a fundamental problem of detergency in oil production as well as in other applications. Salley *et al.*[24] have used a radiotracer technique to measure detergent adsorption directly at the solution-air interface. Sulfur-35 was used in these studies. Judson *et al.*[25] extended the method to measure selective adsorption of detergent molecules at the solution-air interface. Aniansson[26] used a similar method to investigate the adsorption of a detergent containing sulfur-35 at the air-solution interface. Hutchison[27] measured the adsorption of sodium dodecyl sulfate

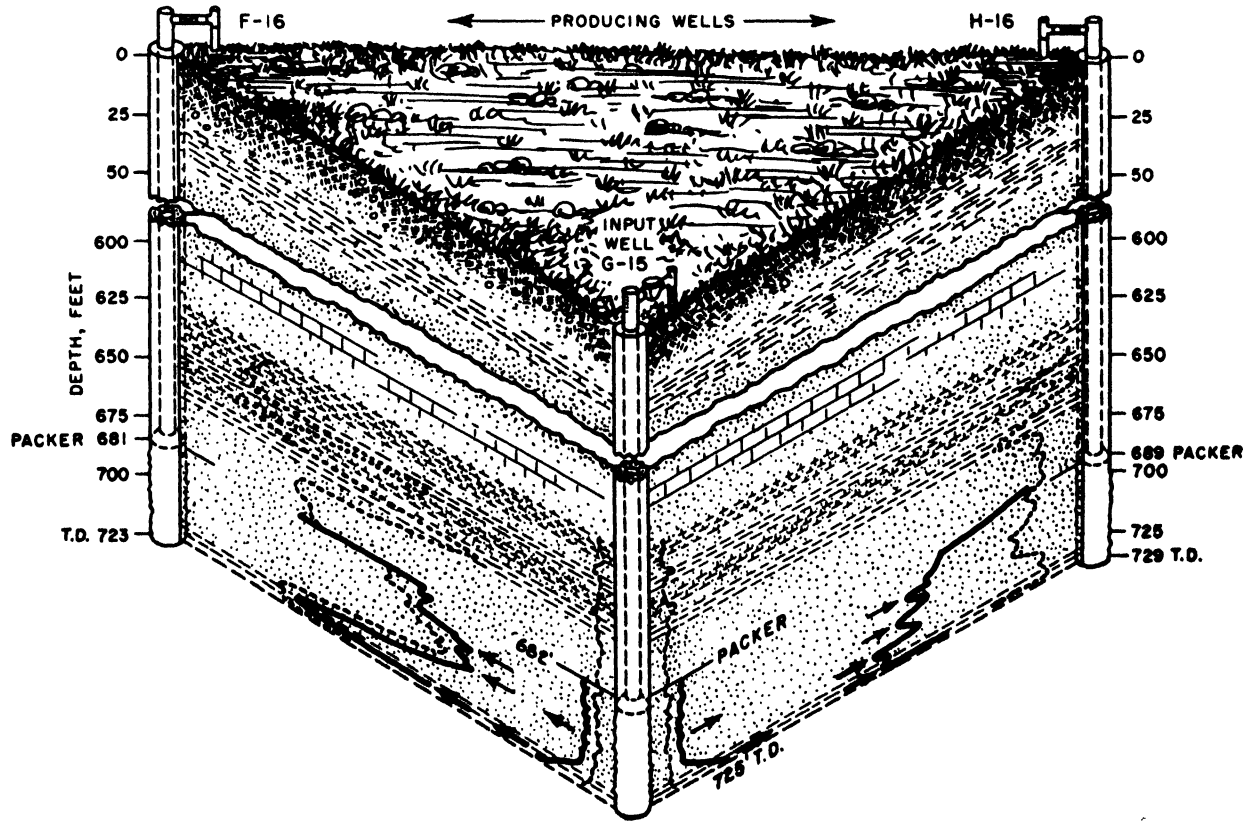

Figure 3. Correlation of radioactivity water-input and water-production profiles

at the air-solution interface by removing the surface film with a platinum ring and counting the emission of sodium-22. Meader and Fries[28] determined the adsorption of an alkyl aryl sulfonate tagged with sulfur-35 and of sodium palmitate tagged with carbon-14. These investigators measured adsorption directly by counting radioactivity of detergents adsorbed on cotton. Other workers have studied detergency by using radiotracers in artificially prepared soils.[29]

Hsiao and Dunning[30] recently made a comparative study of the adsorption of nonionic polyoxyethylated detergents on sand in an attempt to determine the fundamental mechanisms of adsorption. Three methods of analysis were used, including a radiotracer technique. Few earlier studies of nonionic detergent adsorption have been reported, and none of these studies involved radiotracers.

Adsorption at the solid-solution interface usually is determined indirectly from decreases in concentration of the active or distinctive groups within homogeneous solute molecules. The condensation of ethylene oxide with an alkyl phenol results in polyoxyethylene side chains whose lengths may be described by the Poisson distribution function.[31, 32] Because the detergents do not consist of a single molecular species, analysis for either the hydrophilic or lipophilic elements alone does not furnish exact information on the behavior of the other group. Furthermore, analysis by surface-tension methods does not indicate clearly the behavior of the bulk of the molecules because the species vary in their surface activities.[33] The radiotracer method was used to analyze for the carbon-14-tagged polyoxyethylene chain (hydrophilic), and the surface-tension method to follow the hydrophilic-lipophilic balance of the polyoxyethylated phenol which determines the surface activities of the molecules. The availability of detergents containing ethylene oxide chains tagged with carbon-14 permits observation of the behavior of the hydrophilic side chain during the adsorption process—the first time this has been possible.

The radiotracer method alone was suitable for analyzing detergent solutions when adsorption on oily sand was being investigated. The aromatic hydrocarbon content of petroleum and the appreciable amounts of interfacially active constituents[34] invalidate results of photometric and surface-tension methods commonly used.

Ottawa sand, 140- to 200-mesh, cleaned with chromic acid was used as the substrate in these studies. The surface area of the sand was about 300 square centimeters per gram, determined by microscopic measurements and sieve analysis. A commercial nonionic polyoxyethylated alkyl phenol, Igepal CO-710, and an experimental detergent of similar composition, RLS-3066-90, both stable and radioactive, were used as received from General Aniline and Film Corp. The radioactive detergents were synthesized by mixing carbon-14-tagged ethylene oxide with inactive ethylene oxide before the condensation reaction. The petroleum sample, obtained from the Oklahoma City Wilcox field, Oklahoma County, Okla., was light and relatively nonviscous and had an unusual tendency to cause sand with which it came in contact to become preferentially oil-wet.

The general procedures for the three methods were identical. Detergent solutions of known concentrations and volumes were agitated by a wrist-action shaker for several hours with known volumes of sand and then were centrifuged to remove fine suspended sand. The supernatant liquids then were analyzed to determine residual detergent concentrations. The amounts of adsorption were calculated from the observed changes in concentration. Tests were conducted in an air-conditioned room maintained at 25° ± 1°C. Details of the radiotracer techniques were described recently.[30] The only modification required for measuring adsorption on oily sand by the radiotracer method was in sampling. The detergent solution to be counted was withdrawn from the aqueous phase with a mircropipet, taking care at all times to avoid contamination with petroleum.

The comparative study of nonionic detergent adsorption[30] showed that the more surface-active species in each of the detergents were selectively adsorbed at the sand-solution interface from detergent solutions of low concentration. At higher concentrations adsorption was less specific. The extent of adsorption determined by the surface-tension method was greater than that determined by spectrophotometry which, in turn, was greater than that determined by the radiotracer method for both detergents at equilibrium concentrations below 450 micromolar. The adsorption determined by the photometric method was about 20 per cent greater than that determined by the radiotracer method in this low concentration range. This difference was maintained at higher concentrations of RLS. The adsorption isotherm of Igepal deviates from theoretical forms at higher concentrations. A decrease in adsorption at higher concentrations was observed with each of the three methods. The radiotracer and photometric isotherms of Igepal were about equal at concentrations of more than 550 micromolar.

Adsorption isotherms of Igepal and RLS on clean Ottawa sand are presented in Fig. 4. These isotherms were obtained from the radiotracer data of Hsiao and Dunning[30] and are plotted on a molar, rather than a weight, basis. Implications of the shape of these isotherms regarding the selectivity of adsorption have been discussed previously.[30] If an adsorption isotherm can be described by the Langmuir equation, a plot of $C/(x/m)$ versus C takes the form of a straight line. The RLS isotherm and the low-concentration portion of the Igepal isotherm may be described in this manner. The most probable position of these lines was calculated by the method of least squares. These calculations indicate that the adsorption of these detergents may be expressed as follows:

$$\text{(Igepal) } x/m = 10^{-3}C/\ (0.0093\ C + 0.827)$$

$$\text{and (RLS) } x/m = 10^{-3}C/\ (0.0224\ C + 0.083)$$

where C is expressed in micromolarity and x/m is micromoles of detergent adsorbed per gram of sand.

The adsorption isotherms of these detergents on Ottawa sand saturated with Oklahoma City Wilcox petroleum are presented in Fig. 5. In these systems detergent is removed from solution by adsorption on the sand and by absorption in the oil and in the emulsion phase that forms between the oil and water layers. The distribution of the detergents between oil and water can be determined with a fair degree of reproducibility. However, the amount of detergent removed from solution to form the emulsion phase depends on several interrelated variables, including agitation, concentration, and rate of oil displacement. Therefore, attempts to relate these sorption isotherms to adsorption on clean sand would be of doubtful value. However, the total sorption at the higher concentrations is 2 to 3 times that observed with clean sand. Furthermore, total sorption of Igepal and RLS on oily sand does not become equal to the respective values of adsorption on clean sand until equilibrium concentrations of 575 and 420 micromolarity are reached. The lowest concentration portions of these isotherms are of considerable interest because the sorption is less than adsorption on clean sand. Apparently this fact indicates that the detergent solutions at these concentrations do not displace all of the oil from the sand surface. Hence, the surface would not be available for adsorption of the detergent. If this reasoning is valid, the use of radiotracers to measure detergent adsorption in oil-sand systems may be a means of determining the wettability of reservoir surfaces, a problem that generally is considered to be incapable of solution by accepted methods.

CONCLUSIONS

Radioactive tracers offer several advantages over stable tracers in many petroleum-production research studies. Measurements of adsorption in water-tracer and detergent studies that cannot be made by using

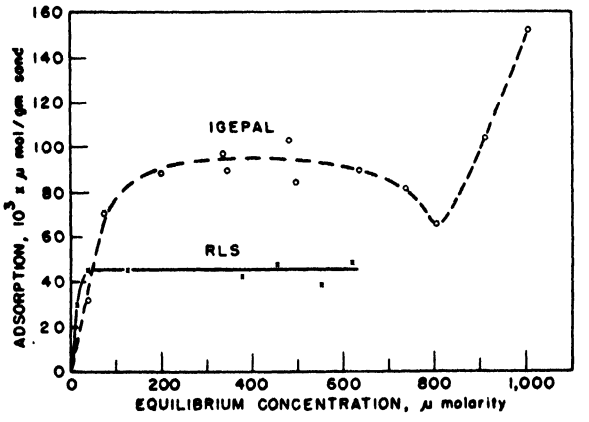

Figure 4. Adsorption isotherms of nonionic detergents on sand

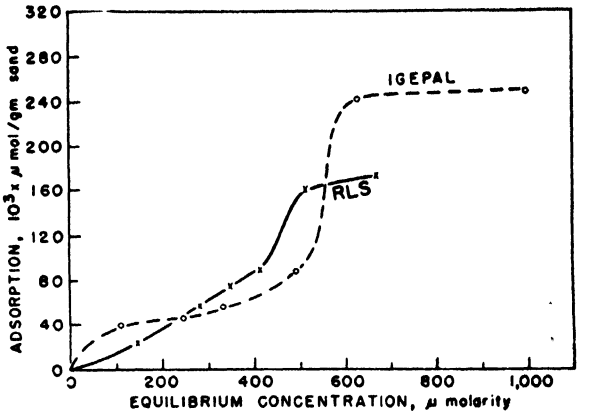

Figure 5. Sorption isotherms of nonionic detergents on oily sand

stable isotopes as tracers may be made rapidly and accurately by using radioisotopes.

Fluorescein and other dyes, cesium, and selenium proved to be poor water tracers because of excessive adsorption on solid surfaces. Conversely, iodine-131 and iridium-192 were found to have low adsorption characteristics and to be suitable for use as tracers for water injected through petroleum-productive formations. The gamma radiation emitted by these two isotopes makes possible the positive determination of the points of water entry into production wells.

The adsorption of nonionic detergents RLS and Igepal on clean sand surfaces is extensive but reversible. The RLS isotherm and the low-concentration portion of the Igepal isotherm may be described by the Langmuir equation. The extent of sorption of these detergents by sand saturated with petroleum is 2 to 3 times as great as the adsorption on clean sand at concentrations of 500 to 1000 micromolarity. Sorption of the detergents by oily sand is less than adsorption on clean sand at low concentrations. The sorption of Igepal and RLS by oily sand equals the adsorption of that detergent on clean sand at equilibrium concentrations of 575 and 420 micromolarity, respectively.

ACKNOWLEDGEMENT

The cooperation of Well Surveys, Inc., Tulsa, Okla., in making water-input profiles, gamma-ray and neutron logs, and in otherwise assisting with the field-tracer tests described herein and that of General Aniline and Film Corp. in synthesizing the radioactive detergents is gratefully acknowledged.

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The Use of Radioactive Tracers for Studying Absorption from Solution by Fibrous Materials

By Howard J. White, Jr.,* USA

The partitioning of the various components of a multicomponent solution between the solution and a fibrous sample is fundamental to a number of processes in the textile industry, especially dyeing. Related partitioning processes occur in fibrous plants and in fibrous materials such as muscle. The study of such processes is thus of importance for several reasons.

If a fibrous sample is immersed in a bath and removed for analysis, the separation of the fibrous sample from the solution is a major experimental problem. Because of the physical nature of the fibers, entrainment of large amounts of solution between the fibers occurs when the sample is removed from the solution. It is logical to expect that separation of entrained and absorbed material would be easier with single fiber samples, and such a separation can be made in favorable cases.

The use of single fiber samples of a convenient length imposes microanalytical problems which are conveniently solved through the use of radioactive tracers. It is the purpose of this paper to discuss the technique of using tracers for such measurements and to present examples of some of the various types of results that can be obtained.

DESCRIPTION OF METHOD

The experimental method consists of immersing a fiber in a radioactive solution and measuring the amount of radioactivity taken up by the fiber. The process can be conveniently broken into four parts: preparation and treatment, washing, counting, and calibration. These four parts will be discussed briefly in order. Exact experimental details can be obtained from Barnard, Palm, Stam, Underwood, and White.[1]

Preparation and Treatment

Sections of human hair, 10 cm in length and weighing 300 μg on the average, were purified, dried, and weighed. Human hairs were selected for two reasons. They are keratin fibers and may be expected to be similar in properties to wool. They are comparatively large and strong, which facilitates handling. They are also fairly round, which facilitates collateral measurements such as swelling and simplifies interpretation of rate data.

The hairs were attached to stainless steel spring clamps for identification and treated with solutions containing the radioactive species. The isotopes used were Na^{22}, S^{35}, and Br^{82}. They were used in the form of simple salts, such as NaBr, LiBr, and Na_2SO_4, which were easily prepared by standard processes such as ion exchange from the forms in which the isotopes were obtained. The fibers were immersed in the radioactive solutions in test tubes.

Washing

The fibers were removed from the solution, shaken to remove excess droplets insofar as possible, washed for a predetermined period of time, and air dried. The selection of the wash liquid and the time of washing was made in the following way. First the surfaces of fibers which had been washed and dried were examined using a microscope. The absence of salt crystals was taken as an indication that contaminating surface salt had been removed. Then fibers were washed for varying periods of time to determine the rate of loss of radioactivity, and the results were plotted in terms of fiber radioactivity against the logarithm of the time of washing. Figure 1 shows such curves. The existence of a plateau in the short-time region of the curve was taken to mean that, over the interval of time covered by the plateau, surface contamination had been removed and absorbed material within the fiber had not yet started to be lost by the fiber. Thus, the existence of a plateau was taken to mean that the liquid in

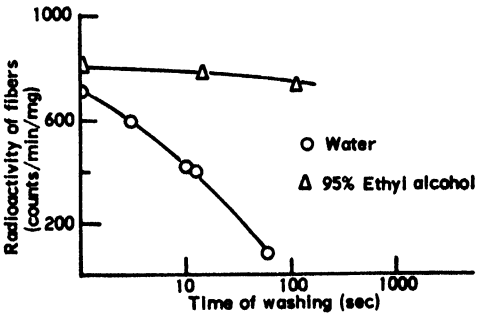

Figure 1. Rate of removal of Na^{22} Br from hair by various wash liquids

* Associate Director of Research, Textile Research Institute, Princeton, New Jersey. Including work by William S. Barnard (present address: Chicopee Manufacturing Corporation, Chicopee Falls, Massachusetts), Paul B. Stam (present address: Dan River Mills, Danville, Virginia), Donald L. Underwood (present address: The Toni Company, Chicago, Illinois), Research Fellows, Textile Research Institute; Howard J. White, Jr.

question was a satisfactory wash liquid over the interval of time covered by the plateau.

Examples of satisfactory wash liquids are ethyl alcohol for hairs containing alkali halides and water for hairs containing Na_2SO_4. A solution identical with the treating solution but containing no radioactive isotope was also a satisfactory wash liquid.

Counting

The fibers were coiled in a loose spiral on a disc that had been smeared with a very thin layer of albumin fixative which served to hold the fiber in place. The disc was then heated to drive off water and denature the albumin fixative thus anchoring the fiber firmly in place. The radioactivity of the fiber was then determined using an internal flow counter.

The choice of metal for the backing discs was dictated by the calibration method which will be described next. However, the discs were always made of resistant metals, either stainless steel or tantalum.

Calibration

The calibration was effected by correlating the radioactivity of the sample with that of a standard. The standard was formed by evaporating a known amount (usually 1 ml) of a solution of known concentration on a disc similar to that containing the fiber. The concentration of the solution was chosen so that the average thickness of the resulting salt layer was considerably less than 1 $\mu g/cm^2$.

It was necessary to apply a calibration factor in correlating the radioactivities of a sample and a standard. This factor compensated for such things as self-absorption of radiation within the fiber, changes in the characteristics of the backing disc caused by the thin layer of albumin, and differences in geometry between sample and standard. The factor was determined in the following way. A fiber sample which had been counted was dissolved in a volatile solvent, usually nitric acid, and reprecipitated in a thin film by drying. The apparent change in radioactivity was determined. A standard was prepared on a disc containing a layer of albumin, and the apparent change in radioactivity resulting from the albumin layer was noted. A hair was then dissolved in nitric acid on top of the standard and the apparent change in radioactivity again noted. The factors which affected the fraction of the total radiation counted were now assumed to be the same for the sample and for the standard. The sum of the three apparent changes was used to prepare the calibration factor. The factors vary with isotope and fiber weight but, once determined for a given isotope and a range of fiber weights, they can be applied to all fibers containing the isotope.

RESULTS

Uptake of Alkali Bromides by Hair

The uptake of alkali bromides by hair has been studied by Barnard, Palm, Stam, Underwood, and White.[1] Figure 2 shows the absorption isotherm they obtained. The concentrations of the alkali bromide solutions have been converted to activities. In the case of NaBr the amount of salt taken up has been measured using both Na^{22} and Br^{82} as tracers; only Br^{82} was used for KBr and LiBr.

It is evident from inspection of Fig. 2 that considerable amounts of alkali bromides are absorbed by hair from concentrated salt solutions. The amount absorbed depends on the activity of the salt regardless of the identity of the cation. This fact suggests that some common process is dominant for each salt. Such a common process would be the absorption of the bromide ion by the polymer.

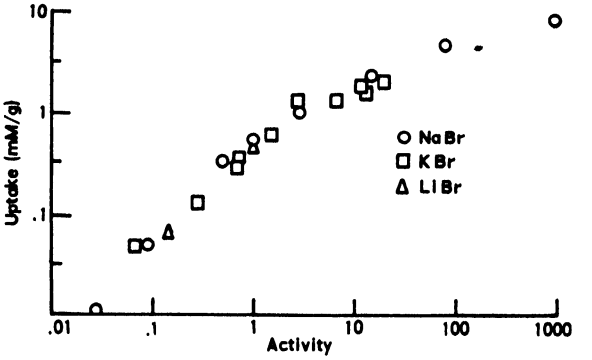

Figure 2. Uptake of alkali bromides as a function of thermodynamic activity

It is also possible to study the effect of temperature on the amount of salt absorbed. The amount of salt absorbed from a solution of constant activity decreases as the temperature increases, showing that the transfer of salt from solution to fiber is an exothermic process.

The rate of absorption of salt by hair cannot usually be accurately described by the use of Fick's law. However, by approximately fitting Fick's equation to the experimental results, a diffusion constant can be obtained which gives a qualitative description of the diffusion process. This has been done for several sets of absorption results involving alkali bromides at room temperature. It was found that the rate was markedly dependent on salt concentration, becoming slower as the concentration of the external solution increased. However, for the most dilute solutions for which the rate was measured ($\sim 1\ N$), the diffusion constant was smaller than $D = 10^{-9}$ cm^2/sec. Since diffusion constants in aqueous solutions are considerably larger ($D \cong 10^{-5}$ cm^2/sec), it is evident that the diffusional properties of the salt in hair differ from those in aqueous solutions.

It is evident from this brief survey that the polymer network of hair exerts a marked influence on the properties of ions within its boundaries. This is true for both equilibrium and rate properties for ions such as Na^+ and Br^- which do not interact chemically with any specific groups within the fiber.

Uptake of Na_2SO_4 by Hair

So far no mention has been made of the well-

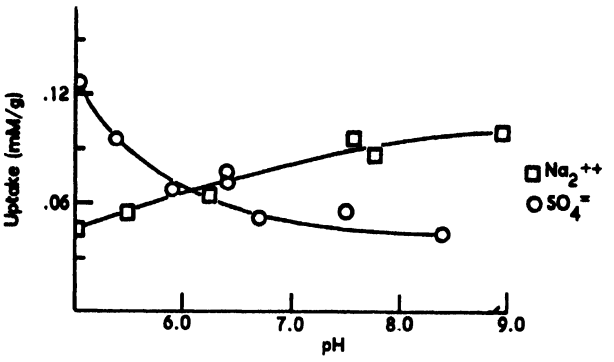

Figure 3. Uptake of Na_2^{++} and $SO^=$ by hair as a function of pH

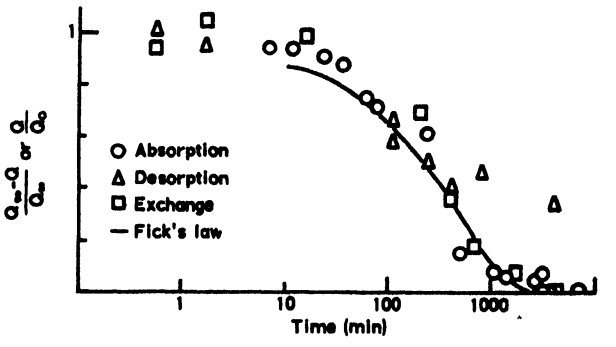

Figure 4. Rates of absorption, desorption and exchange of Na_2SO_4 by hair

known amphoteric properties of proteins. Since both ions of Na_2SO_4 can be tagged by using Na^{22} and S^{35} as tracers, it is an ideal salt for following changes in the uptake of ions with changes in pH. Such results are shown in Fig. 3. The Na_2SO_4 concentration in the solution was kept constant at 0.77 *M*/l. The uptake is expressed in terms of divalent units; in other words, the actual amount of Na^+ absorbed has been halved.

The pH at the intersection of the two curves is the isoionic point. To the left the difference between the two curves represent the amount of H_2SO_4 absorbed; to the right the difference represents the amount of NaOH absorbed. The distance from the lower curve to the abscissa represents the amount of Na_2SO_4 absorbed. It is evident that the absorption of salt is inhibited by either absorbed base or absorbed acid.

The kinetics of the absorption and desorption of Na_2SO_4 have been studied by Underwood and White.[2] The results are shown in Fig. 4. Three types of measurement—absorption, desorption and exchange—are shown. The absorption results are plotted as the function $(Q_\infty - Q)/Q_\infty$ against time, where Q is the amount absorbed at the time indicated by the abscissa and Q_∞ is the amount absorbed at equilibrium. The desorption and exchange results are plotted as Q/Q_0, where Q_0 is the amount present in the fiber at the start of the desorption or exchange experiment. The exchange results were obtained by placing fibers, which had been brought to equilibrium with a radioactive solution and then washed, in a nonradioactive solution of the same composition and concentration. The rate of loss of radioactive salt by the fiber was then followed. In every case the gain or loss of $SO_4^=$ by the fiber was followed.

Certain features of these experiments should be emphasized. In every case the external bath was enough larger than the fibrous sample that it was effectively unchanged in concentration throughout the experiment. For a sample following Fick's law with these boundary conditions, absorption and desorption results should coincide when plotted as in Fig. 4. If the diffusion of the $SO_4^=$ ion is the rate-controlling factor, the exchange results should nearly coincide with the others because the exchange experiment measures the rate of diffusion of the $SO_4^=$ ion alone.

It is evident from Fig 4 that the absorption and exchange results coincide with each other, and they also coincide moderately well with the solid line which was obtained by using Fick's law. The desorption results are different. Complete desorption is very slowly attained, and the shape of the curve cannot be explained in terms of Fick's law. Desorption is thus probably a composite process. The following mechanism can be suggested to account for the slow desorption.

When desorption starts, the water desorption bath contains a few H^+ ions. Two processes are thus possible, desorption of salt and exchange of Na^+ ions for H^+ ions. The second process would mean that part of the $SO_4^=$ ions would be desorbed as H_2SO_4 rather than Na_2SO_4, and the desorption of H_2SO_4 is known to be very slow.

CONCLUSIONS

Under favorable conditions, absorption by fibers may be studied using radioactive tracer techniques with facility and accuracy unattainable using more conventional chemical methods. This holds for equilibrium measurements and particularly for kinetic measurements where simple boundary conditions are readily attained and where measurements involving only the transfer of radioactive ions can be used in addition to conventional measurements involving a net change in composition of the system.

ACKNOWLEDGEMENT

This work was done as part of the Dyeing Research Project of Textile Research Institute. The author appreciates the guidance of the Project's Advisory Committee, representing the textile and chemical manufacturing firms who sponsored this work.

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Radioactive Isotopes as Tools in Sanitary Engineering Research

By Harold A. Thomas, Jr.,* USA

A series of investigations at Harvard University since 1946 has been made to ascertain the utility of radioactive materials as tracers in a variety of sanitary engineering applications. The results of these studies presented in graduate theses and in technical publications show the practicability of a number of new techniques useful in the design of water and sewage treatment plants and in the investigation of self-purification of wastes in streams and soils.

Radioisotopes have shown many advantages over older tracer materials such as dyes and salts. The foremost advantage of radiotracers is the ability to detect them in small concentrations, eliminating misleading density currents that may occur when brine is used. In addition precise quantitative methods of detection are available. In some instances it is not necessary to take samples of the fluid being tested. This eliminates an often vexing source of error in model testing.

Of primary significance in sanitary engineering research is the fact that radiotracers have made possible a precise evaluation of the magnitude and effect of horizontal mixing of fluids in pipes, tanks, streams, and in ground-water flow. The importance of longitudinal mixing is due to the circumstance that many dangerous and objectionable substances in water, such as pathogenic bacteria, human excrement, putrescible solids, and hazardous radioactive wastes are destroyed (or removed) at rates nearly proportional to their concentrations. In still water and in laboratory jar tests the rate of disappearance (or decay or die-away) of such substances may be calculated approximately by an exponential-decay law. When wastes of these types are faced in streams, pipes, tanks, or in the soil, the downstream concentrations may be considerably higher than predicted from the simple exponential-decay law. This is caused by the short circuiting of the flow. This phenomenon is due to three factors: (1) the non-uniform distribution of velocity caused by the curvature of and shear at the solid boundaries of the flow; (2) eddy diffusion associated with the turbulence of the moving stream; and (3) irregular displacements such as those due to wind, to thermal and other density currents, and to sludge removal mechanisms.

The efficiency of sewage treatment water purification and disinfection systems, the capacity of streams and ponds for handling pollutional loads depend to a large extent on the amount of longitudinal mixing occurring in the flow. The greater the amount of mixing the higher the concentrations of pollutant found downstream. Failure to take into account the influence of longitudinal flow dispersion may result in grossly inadequate design. The concepts are explained by a description and analysis of a typical tracer test.

Mohawk River Tracer Test

On August 9 to 17, 1954, in a joint project of the United States Geological Survey, the Knolls Atomic Power Laboratory (KAPL) at Schenectady, New York, the New York State Department of Health, and the research group at Harvard, a tracer test with radiophosphorus, P^{32}, was made on the lower reaches of the Mohawk River from the KAPL outfall to the confluence with the Hudson River fifteen miles downstream. The objectives of the test were to assess the health hazards associated with accidental spillage of radioactive contaminants and to ascertain the amounts of certain low-level wastes that might safely be discharged into the Mohawk River. Of particular interest in this connection was the existence of a water supply intake for the filtration plant of the town of Cohoes, New York, on the Mohawk River just upstream from the junction with the Hudson River.

The drainage area of the Mohawk River at Troy, New York, is 3462 square miles; at the time of the test the average rate of flow was 1100 cubic feet per second. The river depth is variable; the average depth at KAPL is 20 feet, with a maximum of 36 feet. At Vischer Ferry Dam (VF), the first downstream sampling station from the outfall (1.7 miles), the depth is 36 feet, and the river width is 1900 feet. There are hydroelectric stations at this dam and at Crescent Dam, 1.5 miles upstream from the Cohoes intake.

A dose of 4.5 curies of phosphorus-32 was introduced into the stream through the KAPL outfall during a 3-hour period starting at 10:00 am August

* Associate Professor of Sanitary Engineering, Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts. Including work by R. S. Archibald, Pipe Founders Corporation; C. G. Bell, Northwestern University; F. L. Parker, Harvard University; D. R. Stanley, D. R. Stanley & Associates Ltd.; H. A. Thomas, Jr., Harvard University.

9, 1954. The effluent of the sewer (68°F) was cooler than the river water (76°F); accordingly for several hundred feet the outfall flow remained close to the bottom of the river. However during the travel to the first sampling station the vertical concentration distribution became more nearly uniform.

The test procedure consisted in the periodic collection of samples at downstream stations. One-liter samples were evaporated and the residue (about 70 milligrams) transferred to stainless steel cup-planchets and counted with thin end-window Geiger-Muller counting equipment. Conversion from the observed count rates to disintegration rates was based upon comparison with a calibrated P^{32} source.

Results for the first three sampling stations are shown in Fig. 1; at the remaining downstream stations the measurements were obscured by fluctuation in background and natural activity. The curves of time versus activity concentration (disintegrations per minute per liter) exhibit certain characteristic features of tracer tests of this type: (1) a diminution of the peak activity with passage downstream; (2) an increasing amount of longitudinal spread of the tracer-cloud at the downstream stations; and (3) a reduction in the downstream direction of the total amount of activity-flux passing each sampling station (the area under each curve is proportional to the total activity passing the station). The latter effect is characteristic of tracer substances such as radiophosphorus that are readily absorbed by the stream bed or are removed by other self-purification processes such as biological uptake or precipitation and deposition. The results of longitudinal mixing, dilution, and removal are quantitatively expressed in Table I. Details pertaining to the computations and analytical procedures have been described by Parker[1] and Bell *et al.*[2]

MATHEMATICAL MODEL OF THE DISPERSION—SELF-PURIFICATION PROCESS

It has been found that concentration-time distributions for tracer tests of the "sudden injection" type in streams, lakes, pipelines and treatment basins may often be formulated satisfactorily by the following equation:

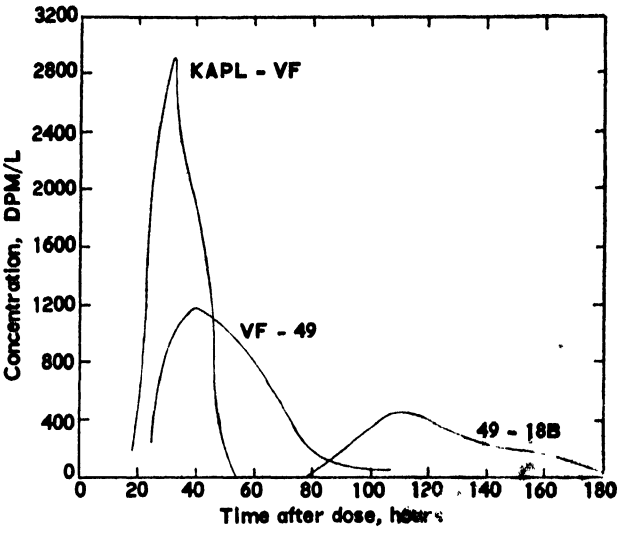

Figure 1. Activity concentration versus time at three sampling stations, Mohawk River Aug. 9–18, 1954

$$u = \frac{W}{2A\sqrt{\pi K t}} \exp\left[-(\lambda+\mu)t - (X-\bar{v}t)^2/4Kt\right] \quad (1)$$

where u = the tracer concentration at time, t, at a downstream station, X, below the point of dosage; A = the area of the cross section of the stream at X; W = the amount of activity in the initial dose of tracer; K = the coefficient of longitudinal dispersion reflecting the shape and dimensions of the fluid boundaries, the mean velocity, roughness, wind action, etc.; $\bar{v}$ = the mean flow velocity; λ = the nuclear decay constant = 0.693/half-life of the tracer isotope = 0.048 per day for P^{32}; and μ = the self-purification decay constant.

Taylor[3] has presented a theoretical analysis of the mixing phenomena for turbulent flow in straight circular pipes that yields time-concentration and space-concentration distributions according with Equation 1 with $\lambda = \mu = 0$, and with the coefficient of longitudinal dispersion given by the following relationship:

Table I. Results of Tracer Test, Mohawk River, August 9–18, 1954

Station	River miles from KAPL outfall	Time of observed peak, hr	Mean flow-time, hr	Observed peak activity-concentration, dpm/liter	Per cent of initial dose (4.5 curies) passing: Observed	Corrected for nuclear decay	Corrected for nuclear decay and for self-purification	Coefficient of longitudinal dispersion K, ft²/sec
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
KAPL	0.0	0.0	0 0	—	100	100	100	—
Vischer Ferry Dam	1.7	34.0	35.1	2900	58.2	62.1	100	14
Buoy 49	2.8	48.7	50.9	1200	50.4	54.2	100	49
Buoy 18B	7.5	118.5	118.5	450	19.7	24.5	100	67
Cohoes Water Treatment Plant	13.0	—	217*	—	3.3*	—	100	

* Extrapolated value.

$$K = 7.14\, r\, \bar{v}\, f^{\frac{1}{2}} \qquad (2)$$

where r = the hydraulic radius of the pipe (diameter/4), and f = the Weisbach-Darcy pipe friction coefficient. Values of K obtained from Equation 2 by substituting appropriate values of r, $\bar{v}$, and f for the Mohawk River are smaller by an order of magnitude than those obtained by evaluating the parameters of Equation 1 from the observed concentration history at each station. This is to be expected in as much as Taylor's theory pertains to straight, uniform circular conduits, whereas the river is extremely non-uniform in cross-section and is obstructed by dams.

The percentage of the initial dose of activity, P, passing a sampling station (fixed value of X) is given by the following equation.

$$P = \frac{100}{W} Q \int_{\theta}^{\infty} u\, dt = \frac{100 \exp\left[-\frac{X\bar{v}}{2K}\left(\sqrt{1 + 4K(\lambda+\mu)/\bar{v}^2} - 1\right)\right]}{\sqrt{1 + 4K(\lambda+\mu)/\bar{v}^2}} \qquad (3)$$

Using Equations 1 and 3, the parameters $\bar{v}$, μ and K for each of the three curves of Fig. 1 were calculated. Results of these computations are shown in Table I, columns 4, 6, 7, 8 and 9. Column 4 is obtained from the mean velocity and the distance downstream, $X/\bar{v}$, and gives the time abscissae to the centroid of the concentration-time distributions (flow-through curves) after correction for the activity loss due to nuclear decay and self-purification. These times correspond to the arithmetic mean time of flow that would have been obtained using an "ideal" tracer with no decay ($\lambda = \mu = 0$); they approximate closely the "theoretical" detention period (Volume of river between the dosing point and the sampling station divided by the discharge). The obtaining of flow-times from radio-tracer tests constitutes one of the chief advantages of the method. Flow-times are needed in order to establish the capacity of streams for handling many types of industrial and domestic wastes; precise determination of flow-times by other methods is often difficult or impossible in streams and lakes of irregular shape when adequate hydrographic surveys are not available.

Columns 6, 7 and 8 of Table I indicate the activity removals of P^{32} in the Mohawk River under the conditions of August 1954 that were attributable to nuclear decay and to self-purification respectively. With this particular isotope the removal due to self-purification is especially large ($\lambda \ll \mu$).[2] Certain isotopes present in the wastes of chemical processing plants for nuclear power reactors such as strontium and ruthenium have been found to be much more resistant to stream self-purification processes.

In Fig. 2 the logarithm of the proportion of the initial dose that passed the successive downstream sampling stations is plotted against the mean flow-time (Table I, columns 4 and 6). The points fall approximately on a straight line as predicated in the mathematical model (Equation 3). By extrapolation it is found that at the intake of the water treatment plant 0.15 curies or 3.3% of the initial activity remained in the flowing stream; 96.7% had disappeared due to nuclear decay and to absorption and biological uptake in the stream. If the assumption were made that with the conditions in the stream in August 1954 a removal of 96.7% of P^{32} could be obtained in a *steady state* rate of application, it is readily computed that 1600 curies of this isotope could be added daily at KAPL such that the water at the Cohoes plant intake would not exceed an activity concentration of ten per cent of the "maximum permissible concentration" for drinking water (2×10^{-4} microcuries per milliliter).[4] Under such an assumption it appears that the stream has a substantial capacity for handling waste radiophosphorus; however pending long-term experimentation the assumption must be regarded as being tenuous. It is true that most streams in the northeastern region of the United States have a large unsatisfied chemical and biochemical demand for phosphorus and for other less common elements such as rubidium, zirconium, molybdenum, cesium, and the rare earths. The uptake of these elements in inland waterways has been found to depend critically upon the amounts of non-radioactive elements of the same chemical species added in the tracer and also upon the concentration of these naturally occurring in the stream. Pending further experimentation, the storage of long-lived radioisotopes adsorbed or otherwise transferred from the flowing water to the stream bed must be regarded as being precarious and unreliable. Substantial release from storage of hazardous contaminants such as strontium could conceivably occur dur-

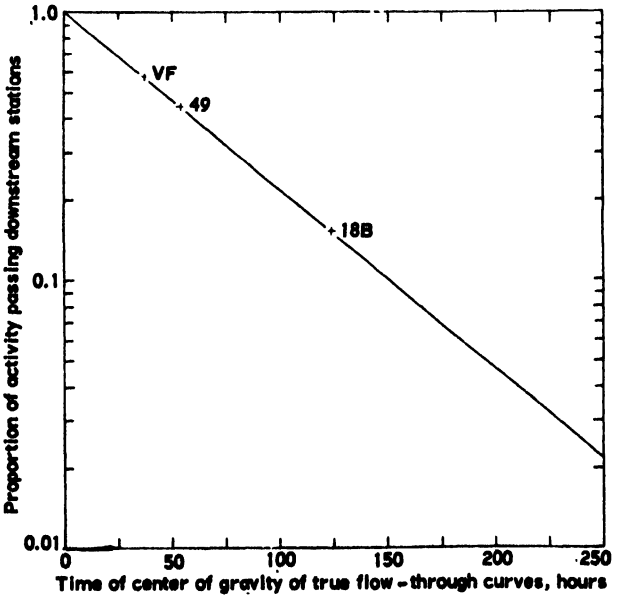

Figure 2. Proportion of initial dose flowing past downstream stations, Mohawk River, Aug. 9–18, 1954

ing a period of unusual stream conditions—for example, during an extended drought during a high temperature period or during exceptionally violent thermal "overturns" in reservoirs in spring or autumn. On the other hand under favorable conditions prevailing at some sites, it is not unreasonable to expect that health hazards of this type will be minimal and that for certain isotopes at least, it will be found economical to take advantage of the substantial capacity for self-purification of streams for the disposal of low-level wastes.

It should be emphasized that the degree of self-purification for a given isotope may be expected to vary over a wide range with different flow rates in the stream and during different seasons of the year At low flow rates the dilution is small but flow-times and biochemical activity are apt to be large; during times of high flow the relatively large dilution afforded may be offset by the shorter times available for self-purification and nuclear decay.

The coefficients of longitudinal dispersion for the Mohawk River (Table I, column 9) reflect marked differences in the cross section and degree of turbulence in different reaches of the stream. The parameter for longitudinal mixing, K, like the other self-purification parameters, $\bar{v}$ and μ, have been found to vary considerably in different streams and in a given stream during the various seasons of the year. As is the case with other hydro-meteorological and biochemical stream parameters, they should be regarded as statistical variates and it should be the object of further experimentation to establish norms, in order that the capacity of streams for safely handling both radioactive and other types of liquid wastes may be delimited more precisely.

SMALL-SCALE EXPERIMENTS AND MODEL TESTING

Prior to production of radioisotopes in large quantities from nuclear piles tracer tests on flowing liquids in sanitary engineering treatment devices were made with salts and dyes. These materials had disadvantages that under some conditions seriously impaired the value of the test results. In testing a sedimentation tank, for example, a brine solution introduced at the inlet would cause density currents that disrupted normal patterns of flow; dyes were apt to be partly adsorbed on solid surfaces or else react with other substances in the water to an extent as to cause a color change. In general both salts and dyes may conveniently be detected in water if their concentration exceeds $\frac{1}{10}$ milligram per liter, but in many flow systems the mixing is so marked that initial doses of tracer of convenient size are so dispersed that a considerable proportion of the tracer cloud is diluted to concentrations below the threshold of detectability (less than $\frac{1}{10}$ milligram per liter). The amount of tracer "recovered" at the downstream sampling station was often found to be considerably smaller than that added to the flow. With suitable radiotracers and sensitive counting equipment and under carefully controlled conditions it has been found possible to "recover" substantially all of the initial dose.

In investigation of eddy diffusion, longitudinal dispersion and other hydrodynamic characteristics of a flow system, the following are desirable properties for a radiotracer:

1. The isotope should possess a moderately long half-life, $\lambda = 1.0$ per week.
2. Relative freedom from absorption on solid boundaries is important; this may be controlled partly by adding suitable amounts of carrier. Also the isotope should not readily be precipitated by the water or substances dissolved therein.
3. The energy of beta radiation should preferably exceed 0.6 Mev. In model testing it is often convenient to employ a moderately strong gamma emitter so that dip counters may be used or so that radiation may be detected outside of pipe walls, thereby eliminating the collection of samples.
4. The isotope should be nonvolatile if samples are to be evaporated.
5. The cost should be low; pile irradiated units often provide the least expensive source.
6. The isotope should not have radioactive daughters; these may complicate the interpretation of the count-rates if elemental separation occurs in the flow.
7. The tracer should be relatively non-hazardous if accidentally spilled or ingested (the maximum permissible concentration for drinking water should preferably not exceed 10^{-4} microcuries per milliliter). The use of strontium-89, which in many respects has the attributes of a good tracer, may be unsuitable for tracer tests in a water treatment plant. Ordinarily, however, it is feasible to use radiotracer in quantities such that adequate counting rates above background and natural water-borne radioactivity are obtained, yet yielding concentrations well below hazardous levels for ingestion or immersion.

The most generally satisfactory tracer isotopes for the measurement of the hydrodynamic characteristics of flow systems have been found to be rubidium-86, scandium-46, and iodine-131.

Various tracer tests in pipelines, treatment tanks and hydraulic models have been described.[5]

In an investigation by Stanley[6] the depth of penetration of floc into rapid sand filters was determined using a coagulant tagged with radioiodine. This was accomplished by the mutual coagulation between negatively charged, colloidal silver iodide and positively charged hydrous ferric oxide. The measurements of the depth of penetration into the sand column filter were made by making a gamma-ray profile along the column with a high-efficiency gamma-ray Geiger tube. The principal objective of the investigation was to determine the effect of the rate of filtration and the sand size upon the rate of penetration of the floc. Heretofore, there has been a paucity of data on the extent of floc penetration in filters owing to the labor and analytic detail involved in model and pilot plant studies. The designer of a filter bed must specify filter media of proper size and

depth, yet he must avoid the uneconomic consequences of overdesign. The experimental results with radiotracers indicated that many filters have been designed too conservatively and that unnecessary head losses and wash water flows have been accepted. With the ease, sensitivity, and reproducibility of the new technique, data have been obtained that make possible the development of a rational theory of the mechanism of water filtration in sand beds that supersedes the older, largely empirical and sometimes wasteful principles of filter design.

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Use of Carbon-14 to Study Organic Adsorption Properties of Activated Carbon

By A. S. Goldin, R. C. Kroner, A. A. Rosen and M. B. Ettinger,* USA

The use of activated carbon for concentrating organic impurities in water and wastes[1, 2] has opened new avenues for investigation of water quality and pollution problems. The technique includes: (1) adsorption of organic impurities from water or waste streams by passing them through a column of selected activated carbon; (2) air-drying the carbon; and (3) elution of the adsorbed material from the carbon by an appropriate solvent.

While adsorption of organic materials from aqueous solution by activated carbon has been extensively studied, there are but scant data concerning the elution of adsorbed material from activated carbon. Such knowledge is required to put the interpretation of results obtained by the "carbon filter" technique on a firm basis.

Factors of interest relative to the use of the technique include: (1) rate of elution by solvents; (2) recoverability of adsorbed materials without chemical change; (3) efficiency of recovery; and (4) a possible basis for prediction of recovery efficiency.

Using phenol as a test chemical, preliminary studies reconfirmed general knowledge and showed that:

1. Phenol could be quantitatively removed from highly dilute aqueous solution by treatment consisting of percolating the solution through activated carbon in columns.

2. Batch adsorption of phenol by activated carbon from solution was variable, depending on quantity of carbon, phenol concentration, etc.

Attempts to elute phenol adsorbed on activated carbon with various solvents gave variable and incomplete recovery even with protracted extraction in Soxhlet type apparatus. Table I shows data on the rate of desorption of phenol from activated carbon by chloroform. Table II indicates recoveries obtained using other solvents.

Table I. Rate of Desorption of 1.0 gm of Phenol from 15.0 gm of C-190 Carbon

Hours extracted	*Approx. no. of cycles*	*gm of phenol extracted*	*% of phenol recovered*
4.2	50	0.688	68.8
6.5	78	0.0258	71.4
7.2	86	0.0073	72.1
14.5	174	0.0036	72.5
21.5	336	0.0019	72.7

* US Public Health Service, Robert A. Taft Sanitary Engineering Center.

These data suggest that a portion of the phenol might undergo a chemical change during the process of adsorption, drying, or elution, or that it might be irreversibly adsorbed.

Using chloroform extracts of phenol adsorbed on activated carbon, search was made by use of infrared and ultraviolet adsorption spectra for evidence of chemical compounds formed from the adsorbed phenol. No indication of such compounds was found; both types of spectra gave no hint of significant quantities of impurities. Since approximately 25% of the adsorbed phenol was unrecoverable by the eluent it is believed that any major amount of chemical compounds derived from phenol by reaction would have been noted.

Studies of serial adsorption and desorption treatments using aqueous phenol, followed by protracted extraction with chloroform in a Soxhlet apparatus hinted that irreversible adsorption might not be involved. Accordingly the use of tagged phenol was employed to determine whether phenol, adsorbed on carbon, and extracted extensively with chloroform might be subject to recovery in a second cycle of operations as outlined at the beginning of this paper.

ADSORPTION AND ELUTION OF RADIOACTIVE PHENOL

Procedure

Step 1. Quintuplicate 1 gm lots of activated carbon were weighed into 500 ml Erlenmeyer flasks. 10 ml of the stock radioactive phenol solution (50 mg phenol per ml) and 90 ml of water were added to each flask. The flasks were shaken at frequent intervals for two hours and allowed to stand overnight.

Table II. Recovery of Phenol from Carbon Using Various Solvents

Solvent	*Recovery procedure used*	*Hours extracted*	*% phenol recovered*
Cyclohexane	Soxhlet	12	50
Isooctane	Soxhlet	12	>50
Sodium hydroxide, $N/10$*	Soxhlet	16	58
Sodium hydroxide, $N/10$	Reflux	18	60
Benzene	Reflux	18	66
Alcoholic sodium hydroxide	Reflux	18	67
Alcohol-benzene-sodium hydroxide	Reflux	18	70

* Water actual solvent, presumably slightly alkaline due to entrainment of NaOH.

Table III-A. Material Balance, Based on Chemical Measurement of Phenol

1 Run no.	2 Carbon	3 Phenol added step 1	4 Phenol not adsorbed step 1	5 Phenol extracted step 2	6 Phenol on carbon step 2	7 Phenol added step 3	8 Total phenol step 3	9 Phenol not adsorbed step 3	10 Phenol on carbon step 3	11 Phenol extracted step 4
	gm	mg	mg	mg	mg	mg	mg	mg	mg	mg
1	1.0	500	218	216	66	60	126	1.3	125	49.6
2	1.0	500	213	224	63	60	123	1.5	122	53.2
3	1.0	500	207	214	79	60	139	2.0	137	56.8
4	1.0	500	190	224	86	60	146	1.5	144	54.0
5	1.0	500	204	226	70	60	130	1.6	128	56.8

Table III-B. Elution of Radioactive Phenol in Second Cycle Based on Radioactive Estimates of Phenol Derived from First Cycle and Chemical Data

Run no.	Estimated total phenol on carbon step 3, col 10 (Table III-A)	Estimated radiophenol on carbon step 2 (col. 6)	Radiophenol recovered step 4*	Non-radioactive phenol recovered step 4†
1	125 mg	66 mg	8.3 mg	41 3 mg
2	122	63	— lost	
3	137	79	11 3	45.5
4	144	86	8.2	45.8
5	188	70	11.6	45.2

* Based on direct measurement of activity.
† By difference (total phenol recovered minus radioactive phenol recovered).

The carbon was then filtered off and air-dried. The filtrates were kept for phenol determination (4-aminoantipyrine method).

Step 2. The air-dried activated carbons were extracted for seven hours in a Soxhlet apparatus with chloroform. This was believed to give essentially complete extraction. (See Table I.) The chloroform extracts were saved for phenol and radioactivity determinations. The carbons were air-dried for step 3.

Step 3. The activated carbons were placed in 125-ml Erlenmeyer flasks with 50 ml of water containing 60 mg of non-radioactive phenol. The flasks were shaken at frequent intervals and let stand overnight. The carbon was then filtered off and air-dried. The filtrates were kept for phenol determination. Although the presence of radioactive phenol in the water would have been of interest, the total quantity of phenol not adsorbed was small. Attempts to detect active phenol were not made for this reason.

Step 4. The air-dried carbon was extracted for twelve hours in a Soxhlet apparatus with chloroform. The quantity of phenol and radioactivity of the eluted phenol were determined.

Radioactive phenol was estimated by preparing from it tribromphenol and counting an "infinitely thick" sample of tribromphenol on a planchet in an end window counter. Counts were used on a relative basis to estimate quantities of radioactive phenol.

DISCUSSION

The data make it quite clear that some of the radioactive phenol retained by the carbon after the first cycle was neither chemically altered nor irreversibly retained. It was, in fact, recovered to the extent of about 13% in the elution phase of the second cycle. While the total recovery of phenol in the second cycle was 92% of the adsorbed phenol, only 76% of the applied phenol per se was actually recovered, the rest of the recovered phenol being radioactive phenol applied in the first cycle. This figure (76% recovery) is very similar to the 75% recovery of phenol obtained in the first elution operation (Table III-A) applied to the radioactive phenol.

It would be possible to speculate at length on the phenomena involved. The observations presented make only two facts clear:

1. Under the study conditions, phenol is not subject to appreciable loss as the result of chemical reaction.

2. At least part of the "irreversibly adsorbed" phenol is subject to recovery when a second adsorption and elution cycle is applied.

It is plain that carbon used for recovery of organic materials from water or waste should not be reused, that "blank" determinations on new carbon should be carefully examined, and that the carbon filter technique should carefully avoid over-runs since they are equivalent to adsorption and elution cycles.

Many questions remain unanswered. However, the use of tagged organic materials is suggested as a valuable tool for study of the mechanism of adsorption and desorption.

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Radiometric Methods for Drinking Water Analysis

By D. W. Moeller, J. G. Terrill, Jr., and M. S. Seal,* USA

The use of radioactive materials as isotopic tracers or indicators has many applications in analytical chemistry. Yet, at present, radiochemical techniques are generally absent from the field of water analysis. This report describes radiometric techniques for the determination of chlorides and sulfates, and suggests several possible applications for these techniques. It is believed that such applications will lead to a saving in time and labor, and will give laboratory personnel an opportunity to gain valuable experience in handling radioactive materials.

Radioactive materials serve as tracers or indicators because of three important properties. First, their chemical behavior is identical with that of the non-radioactive isotopes of the same element. Second, their radiations permit indication of their location and quantity.[1] Third, detectable quantities are so minute that, even in quantitative chemical determinations, their mass may, for practical purposes, be neglected.

It has been demonstrated[2, 3] that the end point of a precipitation reaction can be determined by radiometric titration, the rate of change of the radioactivity of the solution serving to establish the equivalence point of the titration. The substance to be titrated, or the titrating reagent, can be "tagged" with a radioactive indicator.

CHLORIDE DETERMINATION

The chloride test is an example of the titration technique where the titrating reagent contains a radioactive indicator.

Silver nitrate precipitates chlorides in acid solution as silver chloride[4] according to the following reaction:

$$XCl + AgNO_3 \xrightarrow{H^+} XNO_3 + \underline{AgCl}$$

If silver nitrate reagent containing trace amounts of radioactive silver is added in excess, the end (equivalence) point can be determined by radiometric analysis. The determination of the end point is based upon two facts: (1) the reaction is regularly progressive, and (2) radioactive silver will not appear in substantial quantities in solution until after all the chlorides have been precipitated. A typical plot of solution activity and radioactive reagent added is shown in Fig. 1.

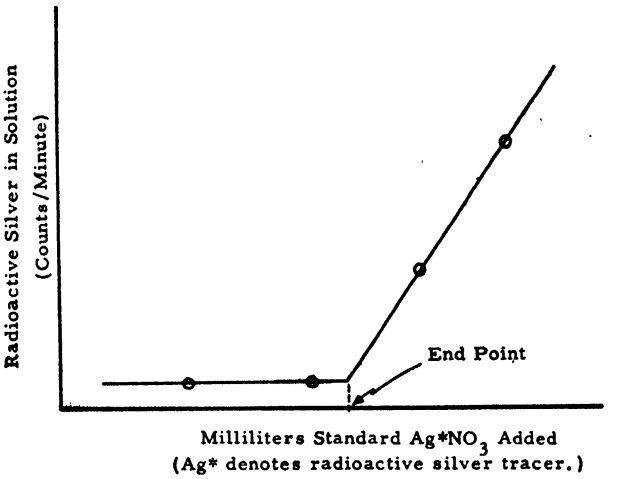

Figure 1. Precipitation reaction in which the reagent added contains the radioactive tracer

Analytical Procedure

(*a*) To a 100 ml sample, add 5 ml of 1:1 HNO_3.

(*b*) Add, with stirring, a known quantity† of 0.01711 *N* Ag^*NO_3. Record the volume in milliliters added as *R*. (The standard silver nitrate solution should contain approximately 60 microcuries ($\sim$ 0.1 mg) per liter of Ag^*NO_3 tracer.)

(*c*) Filter the sample through filter paper (Whatman No. 40 or equivalent).

(*d*) Evaporate a 3 ml portion of the filtrate in a stainless steel counting cup, and determine its radioactivity. The counting rate should be adjusted for the volume change due to the added nitric acid and silver nitrate reagent, by multiplying by the factor $(105 + R)/100$.‡

(*e*) Repeat steps (*a*), (*b*), (*c*), and (*d*) until sufficient points have been established for plotting the characteristic curve (see Fig. 1). Because of the linear nature of the reaction, the investigator must know at least three points on the curve, one just prior to reaching the end point and at least two after the end point.

* Radiological Health Program, Public Health Service, Dept. of Health, Education and Welfare, Washington 25, D. C.

† A general knowledge of the amount of chloride present in the samples will give an indication of the volume of reagent required to establish points before and after equivalence.

‡ Only a relative counting rate is needed. The absolute quantity of radioactive material in the sample need not be determined. However, all count rate determinations on a single series must be performed under similar conditions; otherwise they will not be comparable. In each case, the background must be subtracted from the gross counts to obtain the net counting rate.

Table I. Typical Titration and Counting Data from Which the Curves for 0, 20, and 50 ppm Cl^- in Fig. 2 Were Developed

Sample	*ppm Cl^-*	*ml Ag^*NO_3 added*	*Radioactivity in solution, counts/minute/ml*
1A	0	2.0	813
B	0	4.0	1595
C	0	6.0	2404
5A	20	3.0	42
B	20	5.0	709
C	20	7.0	1488
6A	50	8.0	39
B	50	10.0	730
C	50	12.0	1568

(*f*) Plot the characteristic curve and determine the end point as in Fig. 1.

ppm Cl^- = (ml Ag^*NO_3 required to reach end point) = (6.066)

Results

As an initial step in applying the outlined analytical procedure to the determination of chlorides in water, several samples of distilled water to which known quantities of chloride as sodium chloride had been added were analyzed. Typical data are presented in Table I.

The data for all determinations plot as shown in the upper portion of Fig. 2. Obtaining the end points from the curves, the concentrations of chlorides in the samples can be calculated as suggested in the analytical procedure. Calculated values are given in Table II.

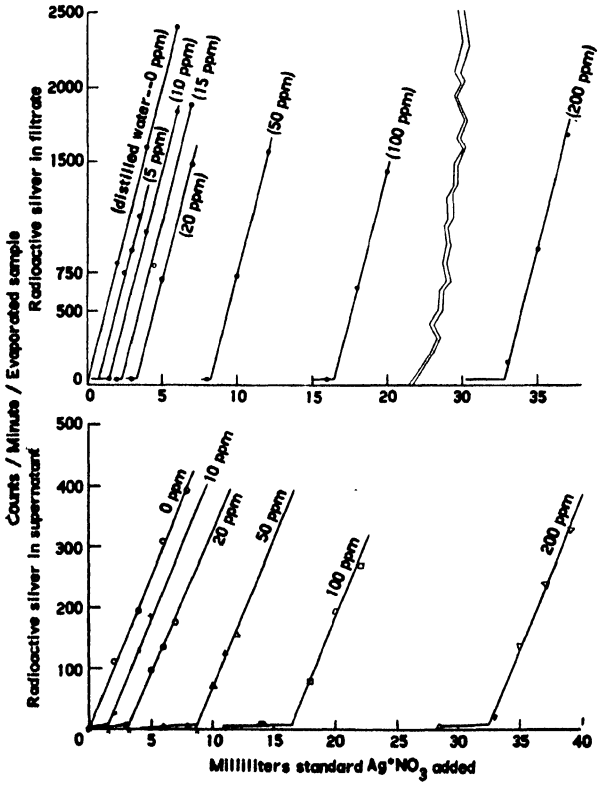

Figure 2. The determination of chloride in synthetic samples

Table II. Chloride Concentrations of Standards as Determined by Radiometric Titration with Filtration

Known ppm	*Experimentally determined ppm*
5.0	4.85
10.0	9.1
15.0	14.3
20.0	20.3
50.0	49.9
100.0	99.9
200.0	199.3

Several modifications of the given analytical procedure are apparent. One such modification would be to count the filtrate samples in liquid form. However, the danger of spillage and necessity for increased concentrations of radioactive silver in such a procedure outweigh the advantages. A second modification would be to substitute centrifugation for filtration in step (*c*) of the given analytical procedure. This modification was tested on one set of samples in the laboratory. After the addition of each successive increment of reagent, 10 milliliter samples were withdrawn and centrifuged for 5 minutes in a standard clinical centrifuge. Successive 3 milliliter samples of the supernatant liquid were removed for evaporation and counting, the remaining supernatant being returned to the titration vessel and the titration continued. This process was repeated until a sufficient number of results were obtained to yield characteristic curves. Data obtained applying this method to synthetic solutions containing 0 to 200 ppm chloride are indicated in the lower portion of Fig. 2, and summarized in Table III.

The radiometric technique, using filtration, was applied also to five natural-water samples representing a variety of sources. For comparison, each sample was run in triplicate by the standard Volhard method.[4] The data for these samples are presented in Fig. 3 and Table IV.

As may be observed from Fig. 3, for a given sample, the radioactivity in solution, prior to reaching

Table III. Chloride Concentration of Standards as Determined by Radiometric Titration with Centrifugation

Parts per million chloride	
Known	*Experimentally determined*
10	9.4
20	19.4
50	52.6
100	99.5
200	197.0

Table IV. Chloride Concentrations of Natural Waters as Determined by Radiometric Titration Using Filtration and by the Volhard Method

Sample	*Parts per million chloride*	
	Radiometric method	*Volhard method*
1. Potomac River	6.5	6.6
2. Well 1 (250 ft)	5.0	5.3
3. Well 2 (300 ft)	52.3	52.2
4. Stream	7.8	6.4
5. Tapwater	8.8	7.4

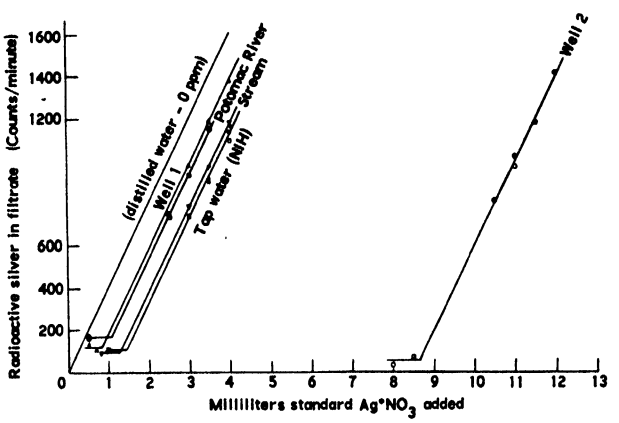

Figure 3. The determination of chloride in natural waters

the end point, is almost constant and, once the end point is passed, the increase in radioactivity of the filtrate per unit quantity of silver nitrate added is linear for all concentrations of chlorides tested. Thus, if the nature of the curve is established *for a given set of conditions,* a simplified analytical procedure can be followed for subsequent chloride determinations on the same or similar samples. The radioactivity in the solution prior to the end point and the slope of the curve after equivalence are required. The simplified procedure would consist of a repetition of steps (*a*), (*b*), (*c*), and (*d*) as given, except that in step (*b*) a measured quantity of 0.01711 *N* Ag^*NO_3 known to be in excess by several milliliters of that quantity required to reach the end point should be added. *Graphically,* the end point for the titration could then be determined by plotting the counting rate value thus obtained, and sketching in the characteristic curve, using the previously determined value for the counting rate prior to the end point and the previously determined slope for the curve after the end point. *Mathematically,* the end point, in terms of milliliters of Ag^*NO_3, is:

$$\text{End point (ml of } Ag^*NO_3) = Ag^*NO_3 \text{ added, (ml)} \left[\frac{\text{Final activity (cpm)} - \text{Activity prior to end point (cpm)}}{\text{Slope of activity curve after end point (cpm/ml)}}\right]$$

where cpm means the counts per minute of the evaporated sample.

SULFATE DETERMINATION

In an acid solution, barium chloride precipitates sulfates as barium sulfate. Sulfites and large amounts of silica and iron should be absent.§

$$XSO_4 + BaCl_2 \xrightarrow{H^+} XCl_2 + \underline{BaSO_4}$$

§ The interference of these substances is lessened in this test since, before sufficient reagent has been added to produce complete precipitation, an almost negligible amount of foreign ions will be absorbed and carried down. Furthermore, the precipitate is not weighed.

To determine the sulfate concentration, a trace amount of radioactive sulfur as the sulfate is added to the unknown solution. A known amount of standard barium chloride solution, sufficient to precipitate a portion (~ 50%) of the sulfate present, is then added. The percentage of the total sulfate precipitated can be determined, using the radioactive sulfur as an indicator. The total sulfate in the original solution can then be calculated graphically or mathematically.

A typical plot of solution activity and reagent added is shown in Fig. 4.

Analytical Procedure

(*a*) To a 100 ml sample, add 1 ml of 1:1 HCl.

(*b*) Add 3 ml S^*O_4 tracer. The use of volumetric pipette is recommended. (The tracer should contain approximately 60 microcuries (< 0.1 mg) S^*O_4 per liter.)

(*c*) Stir sample well.

(*d*) Add a known amount of standard $BaCl_2$ solution, with stirring. Record the volume of $BaCl_2$ added as *R*.

(*e*) Filter the sample through filter paper (Whatman No. 40 or equivalent).

(*f*) Evaporate a 3 ml portion of the filtrate in a stainless steel counting cup and determine its radioactivity. The net counting rate should be adjusted for the volume change due to the added reagents, by multiplying by the factor, $(104 + R)/100$.

As in the chloride determination, after the nature of the precipitation curve is established for a given set of conditions, a simplified analytical procedure can be followed on subsequent similar samples.

Results

Sulfuric acid was added to distilled water to make up a solution containing approximately 200 ppm sulfate. This sample was analyzed by both gravimetric and radiometric methods. Typical data are presented in Fig. 5. One milliliter of the barium chloride solution was equivalent to 0.819 milligrams of sulfate.

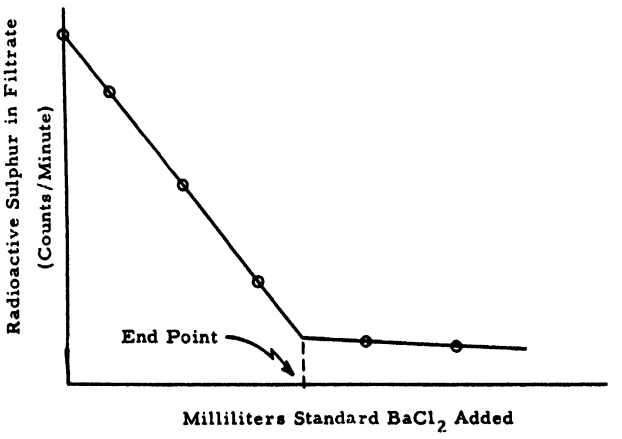

Figure 4. Precipitation reaction in which the unknown sample contains the radioactive tracer

Obtaining the end point from curve *A*, Fig. 5, the sulfate concentration in the sample can be calculated:

$$\text{ppm } SO_4^{=} = (\text{ml}BaCl_2)\ (0.819\ \text{mg/ml})\ (10) = (22.25)(0.819)(10) = 182\ \text{ppm}$$

The determination was repeated, utilizing the same technique, except that the samples were filtered through Whatman No. 42 filter paper. The different slopes of curves *A* and *B*, Fig. 5, can be explained by the different types of filter paper used. As can be expected, Whatman No. 42 paper exhibited a greater degree of retentiveness for the $BaSO_4$ precipitate than did Whatman No. 40. The results are indicated by curve *B*, Fig. 5.

Obtaining the end point as before, the sulfate concentration in the sample can be calculated:

$$\text{ppm } SO_4^{=} = (\text{ml}BaCl_2)\ (0.819\ \text{mg/ml})\ (10) = (22.1)(0.819)(10) = 181\ \text{ppm}$$

Duplicate gravimetric analyses of this same sample revealed sulfate concentrations of 182 and 178 ppm.

Applications of this same procedure to well and stream samples yielded inconclusive results. The sulfate concentration in these samples was known to be low (15–50 ppm), and it is probable that, at these concentrations, either the precipitation reaction was not complete, due to solubility considerations, or the barium sulfate precipitate was too fine to be removed adequately by the filter paper. Boiling the samples had little effect. The radioactivity in the filtrate was reduced only if several times the amount of barium necessary to precipitate all the sulfate completely was added.

The above condition could, perhaps, be overcome by evaporating the original sample, as suggested in the standard gravimetric procedure, until it contained roughly 250 ppm. The sulfate content could then be determined radiometrically. Any of the accepted methods for aging the precipitate would also contribute to the success of the test for low sulfate concentrations.

DISCUSSION AND CONCLUSIONS

Radiometric titration techniques for the quantitative determination of chlorides and sulfates have been investigated in the laboratory. It is hoped that publication of the results of these efforts will stimulate research workers to conduct similar investigations directed towards the refinement of such techniques. As radiometric procedures become familiar to the laboratory worker, he will undoubtedly discover many other applications for them. Possible applications include, for example, the determination of lead, silver, zinc, and magnesium, radioactive phosphorus serving as the indicator; or calcium might be determined as the oxalate, using radioactive calcium as the indicator.

In contemplating the use of radiometric titration techniques, an attempt should be made to choose radioactive materials which meet certain basic criteria. *First,* the technique should utilize a radioactive material which is the source of an easily detectable radiation. A strong beta emitter is preferable. *Second,* a radioactive material should be chosen, where possible, which has a sufficiently long half-life that prepared stock solutions can be used for a reasonable length of time. The two examples cited in this report make use of Ag^{110} and S^{35}, having half-lives of 270 and 87 days, respectively. Stock solutions of either could be used for several months. If the outlined analytical procedure is followed, one millicurie of either of these radioactive isotopes would be sufficient to run a thousand or more separate analyses. Radioactive phosphorus, suggested as an indicator in several possible applications cited above, has a half-life of only 14 days. However, it is believed that the fact that radioactive phosphorus is readily available, is economical, and is a pure beta emitter tends to overcome this disadvantage. *Third,* any use of radioactive materials involves a potential health hazard. In the dilutions needed in radiochemical analyses, this hazard is usually minor. However, since it does exist, an attempt should always be made to use materials which are relatively nonhazardous. For similar reasons, a radiochemical technique should be used only where it is superior to present methods, or where it enables determinations to be made which are otherwise unobtainable.

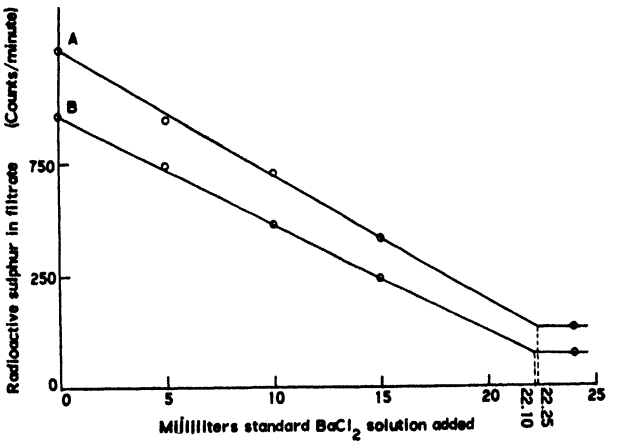

Figure 5. The determination of sulfate in synthetic samples

The present-day standard (Volhard) method[4] for the determination of chlorides in drinking water requires adding an excess of standard silver nitrate reagent, coagulating the silver chloride precipitate formed, and back-titrating the excess silver nitrate with a second standard reagent. The end point is difficult to observe, especially in samples which contain a considerable amount of chloride, or which are highly colored. It is believed that the radiometric titration technique described herein, by eliminating the need for (and inherent inaccuracies of) visual observation of the end point, results in a superior test. The standard gravimetric method[4] for the determination of sulfate in water requires that it be carefully precipitated, dried, ignited, and weighed. Such a procedure normally necessitates a delay of

approximately 24 hours before data are available. The preliminary investigations reported herein indicate that, using radioactive sulfur, a greatly shortened and simplified technique can be perfected.

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Quantitative Determination of Impurities in High-Purity Metals Through Radioactivation Analysis

By J. V. Jakovlev, USSR

I. INTRODUCTION

The method of radioactivation analysis was first employed by G. Hevesy and H. Levi,[1] then by G. T. Seaborg and J. J. Livingood,[2] and by Grinberg.[3] A large number of papers have now been published on its application to various problems.[4, 5, 6]

The method is based upon the irradiation of the samples under investigation by nuclear particles (in most cases by slow neutrons) and the formation, owing to nuclear reactions, of radioisotopes, their activity being a measure of the content of the elements. The sensitivity of radioactivation analysis depends primarily on the activation cross section of the element being determined, the flux of bombarding particles, and also upon the time of irradiation and the half-life of the radionuclides obtained. Figure 1 illustrates the minimum quantities of elements determined by this method upon irradiation with a 5×10^{11} n/cm^2/sec slow neutron flux for one month (in the case of long-lived isotopes) or for saturation time (in the case of short-lived isotopes), i.e., the quantities of elements which under given conditions yield amounts of radioisotopes (with a half-life of not less than 25 minutes) corresponding to 40 disintegrations per second at the end of irradiation time. The figure gives the isotopes on the basis of which activity the determination is carried out.

For different elements the sensitivity of the method in the conditions described varies from 10^{-5} to 10^{-11} gm, which makes it possible to determine a large number of elements (43) at concentrations $\sim n \times 10^{-6}$ per cent. The sensitivity of the method can be considerably enhanced by using neutron fluxes of greater intensity (10^{13}–10^{14} n/cm^2/sec). Therefore radioactivation analysis may be employed for determining trace quantities of elements present as admixtures in metals, alloys, salts, oxides or in natural objects. As compared with other methods of analysis, the present method has the advantages of being sensitive and specific.

In a number of cases radioactivation analysis makes it possible to determine the content of elements of high activation cross section by direct measurement of the activity of the irradiated sample. This may be done provided the half-life or radiation energy of the radioactive isotope of the element being determined differs sharply from the corresponding values for the radioactive isotopes of the other elements present in the sample. Furthermore, the activation cross sections of these elements must be considerably lower.

However, the application of this mode of radioactivation analysis is limited, and therefore in most cases, particularly when determining trace impurities, it is necessary to resort to the chemical separation of the element being determined. This renders possible the simultaneous determination of a large number of elements in the samples. The use of isotopic carriers for separating radioactivities makes it possible to introduce a correction for losses in the course of chemical processing. What is more, this makes it unnecessary to take into account the purity of the carriers and reagents used.

The purpose of the present investigation was to evaluate the precision and sensitivity of the radioactivation method of determining trace quantities of elements in various substances in cases where direct determination without chemical separation could not be effected. The author sought to establish the possibility of attaining the maximum sensitivity of the method, calculated theoretically for the determination of the pure element, as well as for the case of analyzing complex objects.

A comparison of some of the experimental data obtained in analyzing a number of different substances shows that the method of radioactivation analysis is the most expedient and advantageous method (in relation to other methods of analytical chemistry) in determining impurities in high-purity substances. These substances have in recent years acquired great scientific and practical importance in various fields of industry and nuclear physics.

Examples are given, in the present communication, of the application of the method of radioactivation analysis to determine rare-earth impurities in graphite, beryllium, bismuth and lead, as well as to determine rare-earth elements, antimony, molybdenum, copper and zinc in germanium. The determination of impurities in beryllium, bismuth and lead was carried out by P. D. Gorbachov.

II. DETERMINATION OF RARE-EARTH IMPURITIES

Rare-earth impurities, which have a high neutron absorption cross section, are detrimental to the quality

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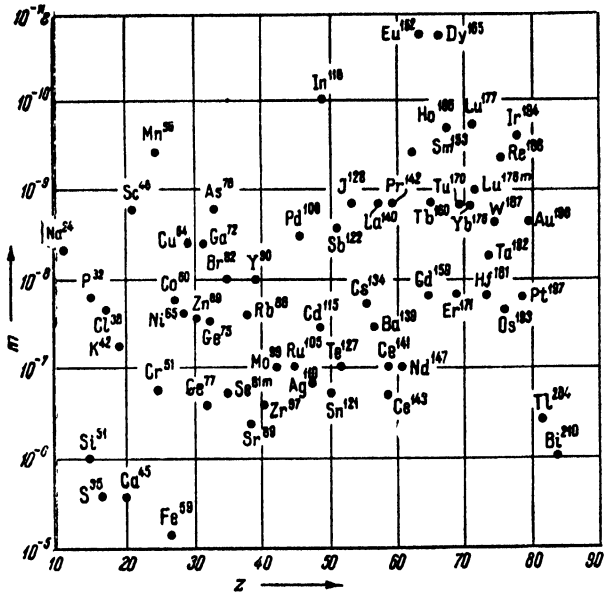

Figure 1. Radioactivation analysis sensitivity

of such materials as graphite, beryllium, bismuth, lead, zirconium, and sodium, used for the construction of nuclear reactors.

The determination of trace impurities of rare-earth elements is an extremely difficult problem of analytical chemistry. Radioactivation analysis offers a solution of this problem. Thus W. A. Brooksbank and G. W. Leddicotte[7] determined the content of a number of rare-earth elements in biological materials, making use of the chromatographic separation of these elements after irradiation of the sample.

The author of the present paper explored the possibility of determining the total content of rare-earth elements on the basis of the activity of certain radioactive isotopes without resorting to chromatographic separation.

The choice of isotopes whose activity could serve as a measure of the total content of rare-earth elements was based on the data given in Table 1.[8, 9, 10] It is evident from this table that following not very prolonged bombardment, say 48 hours, the activity of the rare-earth elements will in the main be due to the activity of Dy^{165}, Eu^{152}, Sm^{153}, and La^{140}.

An analysis of the decay curve of an irradiated mixture corresponding approximately in composition to the content of rare-earth elements in a natural mixture lent proof to this supposition. The following half-lives were established: 3 hours, 10 hours, 46 hours and 12.5 days (Fig. 2), which can be attributed to the presence of Dy^{165}, Eu^{152}, Er^{171}, Sm^{153}, La^{140}, and a number of long-lived rare-earth isotopes (see Table 1).

Owing to the fact that the procedure of isolating the rare-earth elements is a time-consuming one, activity measurements can begin not earlier than 15–16 hours after the end of the irradiation period. By this time the activity of Dy^{165} practically disappears. The activity of Er^{171}, which comprises but 0.5 per cent of the activity of Eu^{152}, may be neglected. The half-lives of Sm^{153} and La^{140} are too close to be resolved in analyzing the decay curve, the activity of La^{140} being about 30 per cent of the total activity of the samarium and lanthanum. Therefore the amount of rare-earth elements may be estimated on the basis of Eu^{152} activity or Sm^{153} activity, with a correction for the La^{140} content. In the latter case measurements should begin not earlier than 3 days after the end of the irradiation period.

Knowing the amount of europium or samarium, it is possible to calculate the total content of rare-earth elements in the sample. This calculation may introduce a systematic error, which, however, plays an insignificant role in determining minute traces of rare-earth elements.

Preliminary calculations showed that in the conditions of our experiments (neutron flux 2–3 $\times$ 10^{11} n/cm^2/sec; time of irradiation 48 hours; time from

Table 1. Activation Cross Sections of Main Isotopes of Rare-Earth Elements

Element	*Relative content in natural mixture, %*	*Radioisotope*	*Half-life*	*Atomic activation cross section in barns*	*Activation cross section considering content in natural mixture*
Y	17.8	Y^{90}	61 hr	1.2	0.214
La	11.45	La^{140}	40 hr	8.4	0.963
Ce	28.6	Ce^{141}	33.1 d	0.265	0.076
		Ce^{143}	36 hr	0.11	0.031
Pr	4.45	Pr^{142}	19.1 hr	11	0.49
Nd	15.9	Nd^{147}	11.9 d	0.31	0.049
		Nd^{149}	1.8 hr	0 21	0.033
Sm	4.45	Sm^{153}	47 hr	40	1.78
Eu	0.76	Eu^{152}	9.3 hr	669	5.09
Gd	6.36	Gd^{159}	18 hr	0.99	0.063
Tb	0.95	Tb^{160}	73.5 d	22	0.209
Dy	2.86	Dy^{165}	2.32 hr	1014	29.0
Ho	0.83	Ho^{166}	27.4 hr	60	0 498
Er	2.55	Er^{171}	7.5 hr	1.02	0.026
Tu	0.51	Tu^{170}	120 d	130	0.663
Yb	1.91	Yb^{175}	4.2 d	19.1	0.365
		Yb^{177}	1.8 hr	0.7	0.013
Lu	0.64	Lu^{176m}	3.67 hr	34.4	0.22
		Lu^{177}	6.98 d	104	0.665

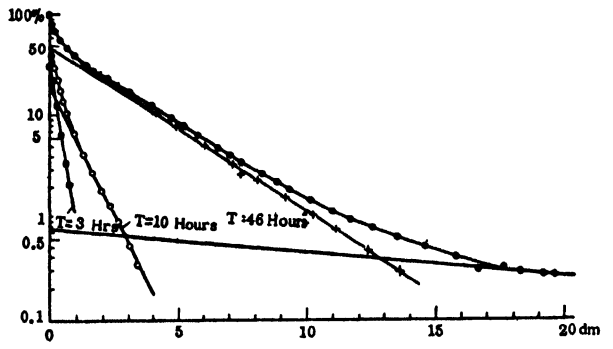

Figure 2. Decay curve for irradiated mixture of rare-earth elements

the end of irradiation to the commencement of measurements for europium samples 15–16 hours, and for samarium samples, 3 days; activity of samples ~ 100 counts per minute) it is possible to determine ~ 10^{-10} gm of Eu and ~ 10^{-9} gm of Sm.

In the present investigation the sum of rare-earth elements was determined both on the basis of europium (in graphite and germanium) and on the basis of samarium (in beryllium, bismuth and lead).

Determination of Rare-Earth Impurities in Graphite

To determine the content of rare-earth elements in graphite a finely pulverized 300 mg sample was placed in a quartz container. Standards were prepared by introducing europium (10^{-8} to 10^{-10} gm) in the form of a solution of its salt in an identical weighing bottle. The solution was evaporated to dryness; the weighing bottles containing the sample and the standard were placed in an aluminium container and subjected to neutron bombardment at a flux of 2–3 $\times$ 10^{11} n/cm^2/sec for 48 hours.

After irradiation the graphite was decomposed by boiling in 200 ml of H_2SO_4 (1:1), containing 8 gm of chromium trioxide and 15 mg of a mixture of rare-earth elements as a carrier. The solution was neutralized with ammonia to a weakly acidic reaction and diluted with water to a 800 ml volume. Then, heating the solution, we added 200 mg of $AgNO_3$ and ammonium persulphate (portion-wise) to oxidize the chromium completely. After this 30–40 mg of $Fe_2(SO_4)_3$ were added to the solution and precipitated with ammonium hydroxide. The rare-earth elements were twice precipitated as fluorides, hydroxides and oxalates. The oxalates were ignited to form oxides, which were mounted on a target of tracing paper for activity measurements and weighed.

The sample activity was measured in a type B counter with a TM-20 end-window-type tube. The target was placed at a distance of 1 cm from the end window. The reproducibility of the counting circuit was checked with a β-emitting standard (RaD + RaE). The statistical error of the count was below 3 per cent.

Experiments showed the europium content in graphite to be below the sensitivity of the measurements. Therefore subsequent analyses were carried out after preliminary enrichment accomplished by burning the graphite in platinum cups at 1100°C. Since the ash content of the graphite samples is very low, the enrichment factor is sufficiently high.

Ten mg of ash were taken for analysis. Irradiation was conducted in the same conditions as in the case of graphite. After irradiation the ash was transferred to a platinum cup and 10 mg of a carrier and several millilitres of hydrofluoric acid were added. The ash was then dissolved on heating, and the solution, with a precipitate of fluorides, was evaporated to a 0.5 ml volume; a mixture of boric and nitric acids was added, and the solution was boiled to remove BF_3. Thereupon the rare-earth elements were separated according to the procedure described above. The decay curve for one of the samples is shown in Fig. 3.

The europium content in the graphite ash samples, determined by this method (calculated for graphite), proved the same: 5.0 $\times$ 10^{-9} % for the first run and 5.3 $\times$ 10^{-9} % and 5.0 $\times$ 10^{-9} % for the second.

Determination of Rare-Earth Impurities in Beryllium Oxide and in Beryllium

To determine rare-earth impurities in these materials use was made of preliminary enrichment founded upon dissolution of the basic beryllium acetate in chloroform and the extraction of admixtures with 6*N* hydrochloric acid. The use of radioactive tracers showed the extraction to be almost complete (95–98%). The enrichment factor equals 20.

The hydrochloric acid solutions were evaporated several times with concentrated nitric acid. The nitrates were ignited at a temperature of about 300°C to give oxides, which were transferred to an aluminium container. The weight of the enriched samples obtained in this way equalled about 100 mg.

The samarium standards were prepared on the basis of "radioactivation-pure" beryllium oxide obtained by repeated washing of the chloroform solution of the basic acetate of beryllium with hydrochloric acid. A definite volume of a standard solution of samarium nitrate was added to 100–150 mg of beryllium oxide. The precipitate was thoroughly dried and transferred to a container. The enriched samples and standards were placed in an aluminium container and subjected to irradiation in the same conditions as the samples of graphite.

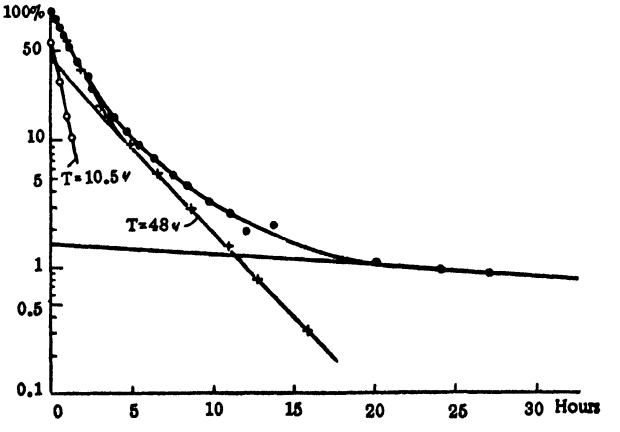

Figure 3. Decay curve for rare-earth samples separated from graphite ash

After irradiation the enriched samples and standards were dissolved in 5 ml of 6*N* hydrochloric acid, with the addition of 15–20 mg of neodymium as a carrier; the oxalates of the rare-earth elements were precipitated from a 0.3*N* hydrochloric solution with oxalic acid. The oxalate precipitate, after standing for 12 hours, was filtered and ignited to oxides. The dissolution of these in 6*N* HCl was followed by the precipitation of first the hydroxides and then again the oxalates, which were ignited once more to oxides.

The activity of the samples was measured three days after the end of irradiation. The measurements were made by means of a B-type counter with an aluminium B-1 tube. Decay curves for the samples of rare-earth elements separated from the beryllium oxide of various runs and of the samarium standard are represented in Fig. 4, from which it is apparent that the half-life values for the different samples vary in the interval of 46.5 to 48.3 hours. To determine the sensitivity of the method and check the purity of the beryllium oxide used for the preparation of the standards, experiments were performed with an addition of differing quantities of samarium (from 0.001 to 1 μg). The results of these experiments are shown in Fig. 5, from which it follows that purified beryllium oxide contains no rare-earth impurities and the sensitivity of the method makes it possible to determine 10^{-9} gm of samarium.

The total content of rare-earth elements in the sample was calculated from the samarium content in the natural mixture on the basis of the amount of samarium determined from the ratio of the activities of the standard and the prepared sample; the latter was corrected for the lanthanum content.

The results of the determination of rare-earth impurities in some of the samples of beryllium oxide and beryllium are shown in Table 2.

Determination of Rare-Earth Impurities in Bismuth and Lead

The method of determining the content of rare-earth elements on the basis of samarium was also applied to analyzing bismuth and lead. Preliminary enrichment was effected by precipitating the bulk of the bismuth as oxychloride, while the rest was removed by hydrogen sulphide precipitation. The bulk

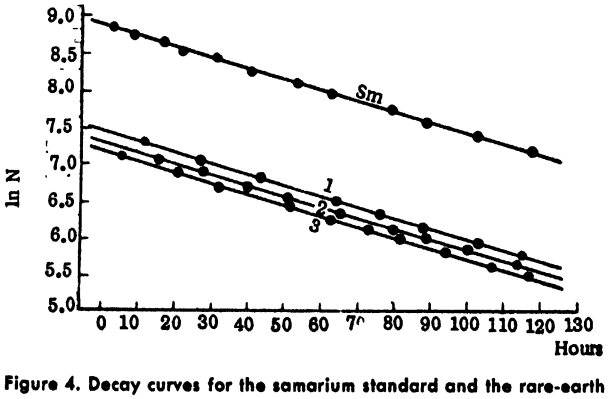

Figure 4. Decay curves for the samarium standard and the rare-earth samples obtained from beryllium oxide

Table 2. Determined Content of Rare-Earth Elements in Beryllium Oxide and Beryllium

Sample	*Content of rare-earth elements (in percentage to Be)*
1. Beryllium oxide	2.3×10^{5}
1. Beryllium oxide	2.5×10^{5}
2. Beryllium oxide	4.9×10^{5}
3. Beryllium oxide	2.0×10^{5}
4. Beryllium oxide	5.4×10^{5}
1. Pure beryllium	5.8×10^{5}
2. Pure beryllium	7.8×10^{5}
3. Pure beryllium	6.2×10^{5}
4. Pure beryllium	1.5×10^{4}

Table 3. Determined Content of Rare-Earth Elements in Bismuth and Lead

No. of Sample	*Metal*	*Content of rare-earth elements in percentage*
1	Bismuth	2.5×10^{-6}
2	Bismuth	3.7×10^{-6}
3	Bismuth	2.1×10^{-6}
4	Bismuth	2×10^{-7}
5	Bismuth	1.5×10^{-7}
6	Bismuth	1×10^{-7}
7	Bismuth	1.7×10^{-6}
8	Lead	1×10^{-7}

of the lead was separated in the form of chloride, and the rest was precipitated as sulphide. Experiments with radioactive tracers demonstrated that losses of rare-earth elements in the course of such enrichment do not exceed 5–10%. The filtrates were evaporated with 100–150 mg of "radioactivation-pure" beryllium oxide and subjected to the same irradiation procedure as described in the analysis of beryllium. A blank experiment with the addition of all the reagents to beryllium oxide pointed to the absence of activity corresponding to the rare-earth elements. The half-life of the samples obtained from lead and bismuth proved equal to 46.5 hours. The results of analyzing certain samples of bismuth and lead in respect to the content of rare-earth elements are shown in Table 3.

III. DETERMINATION OF IMPURITIES OF RARE-EARTH ELEMENTS, ANTIMONY, MOLYBDENUM, COPPER AND ZINC IN GERMANIUM DIOXIDE AND GERMANIUM

Germanium has lately found extensive employment in radio engineering as a semi-conductor.

The electrical characteristics of germanium are affected by various factors, the most important being the presence of contaminants in the germanium lattice. Thus the presence of elements of the I–III groups of the periodic system makes the germanium a p-type conductor, whereas contamination with elements of the V–VI groups gives rise to electron conductivity.

Radioactivation analysis was also applied to determining impurities in germanium. A. A. Smales and B. D. Pate[11] have detected 10^{-9} gm of arsenic in germanium dioxide by this method, and at the moment of the completion of the present investigation there appeared G. Szekely's communication[12] report-

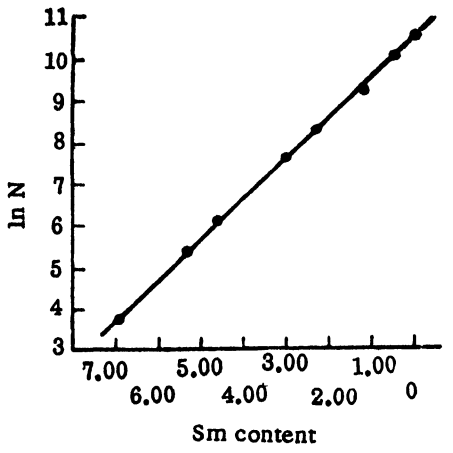

Figure 5. Activity of standard in relation to content of samarium

ing the determination of a 10^{-7}% admixture of copper in germanium.

To determine the possibility of detecting impurities of the above-listed elements during the irradiation of germanium samples in a nuclear reactor, radioisotopes convenient for analysis and obtained as a result of (n, γ) reactions were selected; the sensitivity of the method was also evaluated. The maximum sensitivity can be achieved in conducting the analysis on the basis of the following radioisotopes: Sb^{122} (T = 2.8 days, σ_{ac} = 3.87 barns), Mo^{99} (T = 2.8 days, σ_{ac} = 0.031 (0.1) barns), Cu^{64} (T = 12.88 hours, σ_{ac} = 2.69 barns), Zn^{69m} (T = 13.8 hours, σ_{ac} = 0.0186 (0.054) barns), Eu^{152} (T = 9.3 hours, σ_{ac} = 669 barns).

These calculations, carried out on the basis of published data,[8, 9, 13] show that by irradiating samples with a neutron flux of 2–3 $\times$ 10^{11} n/cm^2/sec for 48 hours, the activities of the Eu, Cu, Zn samples (measured 15–16 hours after the end of irradiation) and the Sb and Mo samples(measured 32–36 hours after the end of irradiation) being of the order of 100 counts per minute, it is possible to determine $\sim 10^{-10}$ gm of Eu, $\sim 10^{-8}$ gm of Cu, $\sim 5 \times 10^{-7}$ gm of Zn, $\sim 3 \times 10^{-8}$ gm of Sb, and $\sim 3 \times 10^{-7}$ gm of Mo.

To determine the above-mentioned impurities a sample of germanium dioxide or a piece of germanium weighing approximately 1 g was placed in a quartz container and subjected to irradiation, together with standards, under the conditions described above. After irradiation the germanium was treated 2 or 3 times with dilute (1:1) nitric acid to remove possible impurities from the metal surface. The sample was then washed with distilled water, dried and powdered in an agate mortar. The germanium sample after these procedures (and the germanium dioxide sample at once) was transferred to a distilling flask to which were added isotopic carriers of the elements being determined and arsenic (10–20 mg each); the samples were then dissolved in aqua regia or 8N HCl on heating.

The arsenic was introduced in order to ensure the subsequent complete separation of the radioactive arsenic isotope As^{77} (T = 40 hours), which is formed as a result of the nuclear reaction $Ge^{76}(n, \gamma)Ge^{77} \xrightarrow{\beta^-} As^{77}$.

After complete dissolution the halides of germanium and arsenic were distilled off by triple evaporation of the solution with concentrated HCl in analyzing GeO_2 and subsequent triple evaporation with HBr in analyzing the metal. This was followed by the separation and purification of the elements being determined. The basic operations of antimony purification consisted in precipitating the sulphide, meta-antimonic acid and extracting the antimony (V) chloride with ethyl ether. The rare-earth elements were precipitated as fluorides, hydroxides and oxalates; zinc, in the form of sulphide and rhodanomercuriate. Copper was removed by electrolysis, hydrogen sulphide precipitation, by rubeanic acid and potassium rhodanide after reduction with sulphur dioxide. Molybdenum was precipitated with α-benzoinoxime and then with fuming nitric acid.

Preliminary experiments with radioactive tracers, as well as the identification of the obtained samples, confirmed that the procedure adopted makes it possible to achieve radioactivation purity of the elements being determined.

For a quantitative determination the precipitate of meta-antimonic acid was ignited at 800–900°C to Sb_2O_4, the oxalates of the rare-earth elements were ignited to oxides and the zinc rhodanomercuriate, copper rhodanide and molybdenum trioxide were thrice washed with alcohol and ether, and dried at 105–110°C for 20–25 minutes. The samples thus prepared were mounted on a target, weighed, and their activity was measured in the same conditions as in analyzing graphite.

The standards were purified according to the following procedure. After irradiation, the contents of the container were eluted up with 1N nitric or hydrochloric acid, 5–10 mg of an appropriate carrier were added, and 2 or 3 of the above-mentioned chemical operations were carried out eliminating radioactive traces, especially due to the Na^{24} eluted from the walls of the quartz weighing bottle. Therefore 5–10 mg of NaCl were introduced at every stage as a holdback carrier. Preparations obtained were mounted and weighed in the same form as the preparations isolated from the samples.

The values of the sample and standard activity were referred to the same time and corrections made for carrier losses during chemical processing. The amount of the element being determined was found from the ratio $M_{sample} = M_{standard}\ (A_{sample}/A_{standard})$, where A is the activity of the sample and the standard. The results of the determination of the impurities of the above-named elements in samples of germanium dioxide and germanium are shown in Table 4.

In order to establish the limit of the applicability of the radioactivation method to determining trace impurities, the sensitivity of the method, which was established from the activity of the standards and the results of experiments carried out by the addition

Table 4. Results of the Determination of Impurities in Germanium Dioxide and Germanium

Sample	*Element being determined*	*Amount found (in % to Ge)*
GeO_2 no. 1	Cu	1.5×10^{-6}
	Zn	10.2×10^{-4}
	Sb	2.15×10^{-5}
	Total content of rare-earth elements (on the basis of europium)	$<10^{-7}$
	Mo	$< 3 \times 10^{-6}$
GeO_2 no. 2	Cu	3.5×10^{-7}
Ge no. 1	Cu	4×10^{-7}
	Zn	5×10^{-4}
	Sb	$< 3 \times 10^{-6}$
Ge no. 2	Cu	$\leq 1 \times 10^{-7}$

Table 5. Sensitivity of the Determination of Impurities in Germanium

Element	*Sensitivity of determination (in % to Ge) for 1 gm sample*
Sum of rare-earth elements (on the basis of Eu)	1×10^{-6}
Copper	1×10^{-6}
Antimony	3×10^{-6}
Molybdenum	3×10^{-5}
Zinc	5×10^{-5}

method, were evaluated. The sensitivity given in Table 5 corresponds to an activity of 100 counts per minute. The precision of the method (average square error of the series of determinations) is of the order of 5–10 per cent.

It should be pointed out that it is also possible to determine amounts of elements which correspond to a sample activity equal to the counter background, i.e., 10–15 counts per minute, which increases the sensitivity of the determination approximately 10-fold. However, the relative error of the determination in this case becomes of the order of 50 per cent.

IV. CONCLUSION

The investigations carried out established the possibility of determining rare-earth trace impurities in various metals and graphite of high purity by the radioactivation method on the basis of the activity of the radioisotopes Eu^{152} and Sm^{153} without recourse to chromatographic separation. A method has been evolved for the simultaneous determination of the content of a number of impurities in germanium dioxide and germanium.

The experimentally established sensitivity of determining impurities in these materials coincides with the theoretically calculated sensitivity in determining these elements in pure form, which indicates that the major sample constituent exerts no influence on the results of the analysis.

Radioactivation analysis has the advantage of high sensitivity and precision over other possible methods of determining trace impurities in pure substances, especially when the chemical properties of the elements being determined are similar to those of the major sample constituent, such as in analyzing a mixture of rare-earth elements, in determining tantalum in titanium and niobium, hafnium in zirconium, tungsten in molybdenum, rare-earth elements in beryllium, zirconium, etc.

At the present time only bombardment with thermal neutrons is used extensively for analytical purposes. A highly interesting possibility, however, is afforded by the use of monochromatic neutrons of various energy levels for the selective determination of elements having high cross sections of neutron resonance absorption, such as In, Ir, Ag, Re, Ta, W, Co and others. The more intense utilization of various charged particles, especially for the determination of impurities of Nb, Ti, V, Cr, etc., which is difficult to accomplish by neutron activation analysis, also broadens the scope of this method.

Consequently, radioactivation analysis may become one of the most widespread methods of determining trace quantities of all the chemical elements.

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Application of Radioactive Isotopes in Chemical Analysis

By I. P. Alimarin, USSR

I. INTRODUCTION

Radioactive elements were first used as indicators in various chemical investigations by G. Hevesy and F. Paneth[1] in 1913 in Germany and by V. I. Spitsin[2] in 1917 in Russia.

After the discovery of artificial radioactivity by Irene Curie and Frederic Joliot and especially since the appearance of nuclear reactors, the method of labelled atoms has become widely used in chemistry, particularly in solving various theoretical and applied problems of analytical chemistry.

At present there are many works of such a kind carried out in various countries.[3-20]

The extremely high sensitivity of the methods of radioactive radiation measurement by modern devices makes it possible to carry on investigations with very small quantities of substance. For example, there is no difficulty in determining 10^{-16} gm of radioactive I^{131} with a half-life of 8 days and still smaller amounts of short-lived α isotopes.

At present in the USSR and other countries, use is made of radioactive isotopes of most of the elements of the Mendeleyev periodic system with a half-life from several hours to several years.

Various radioactive isotopes were used for the study of the analytical reactions mechanism by the method of physicochemical analysis of systems, when studying instability constants of complex compounds by means of isotopic exchange, to determine the solubility of various precipitates and so on. Radioactive isotopes acquired special importance in the study of the behaviour of substances present in solutions in very small concentration where other methods of analysis give no chance for qualitative or quantitative determination of the elements in the solutions.

Methods were elaborated for the isolation and identification of ultra-small quantities of radioisotopes resulting from various nuclear transformations.

The well-known numerous investigations on coprecipitation indicated as far back as the thirties by V. G. Khlopin and his school provided for new data on the mechanism of this process and made it possible to improve the methods of isolation of impurities when analysing substances of high purity.

Radioactive isotopes gave a chance to work out new, more effective methods of separation of elements, especially of those which have similar chemical properties (rare earths, niobium-tantalum, zirconium-hafnium, etc.). In connection with this tendency, first of all should be noted the wide development of extraction methods by organic solvents, ion-exchange chromatography, electroosmosis and isotopic dilution[3, 6] and other techniques.

The high sensitivity of the radioactive tracer indicators method combined with modern techniques of ultra-microanalysis made it possible[21, 22] to carry on investigations with quantities of substance less than 10^{-6} gm, and made work with high activity substances less dangerous.

Application of radioactive isotopes contributed to the improvement of chemical-analytical control in factory laboratories and aided the study of the distribution of element impurities at various stages of a technological process.

That the development of a very sensitive method of activation analysis made it possible to detect very small quantities of impurities is also to be noted.

In this paper results are briefly given of some theoretical and applied research on the uses of radioactive isotopes in analytical chemistry and for production control which were recently obtained in scientific-research and factory laboratories of the Soviet Union.

II. APPLICATION OF RADIOACTIVE ISOTOPES IN SOLVING GENERAL AND THEORETICAL PROBLEMS OF ANALYTICAL CHEMISTRY

Study of the Behaviour of Ultra-Small Quantities of Elements

At present, due to the developments of nuclear physics, a number of new problems of analytical chemistry arise that require further development. This is, first of all, the elaboration of express methods for the isolation of short-lived isotopes in radioactive pure form in the presence of a great number of other radioactive isotopes and a great amount of macroelements.

In solving these problems with the aid of radioisotopes Bi^{210}, I^{131}, Zr^{95}, Y^{91}, Ce^{141}, Ce^{143}, Fe^{59}, P^{32}, Co^{60}, Sb^{124} and Zn^{65} A. K. Lavrukhina[23] has examined the behaviour of many elements in ultra-small concentrations of precipitation, extraction, electrolysis and distillation. As a result of this examination and on the basis of data in the literature concerning this problem[4, 5, 6, 13, 16, 24, 25, 26, 31] the following was established:

As is known, ultra-small quantities of elements

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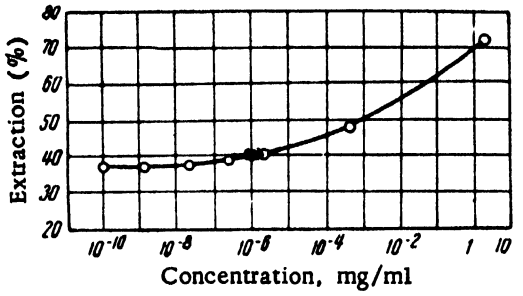

Figure 1

(radioactive isotopes) to a greater or lesser extent are carried away by the precipitates. This capture is complete when radioactive isotopes form either isomorphically or isodimorphically crystallizing compounds with corresponding compounds of macrocomponents or may form almost insoluble compounds with a precipitate ion of the opposite sign. In the other cases precipitation is incomplete; in most cases it is due to the precipitate adsorption and may be eliminated by reprecipitation affording a sufficiently acid medium.

In the case of element extraction the constancy of the distribution coefficients at very low concentrations is generally maintained. This was, in particular, shown on the example of $H(BiI_4)$ and $H_2(Ce(NO_3)_6)$ extraction with diethyl ether. On Fig. 1 the curve showing the dependence of the bismuth extraction degree on its concentration in the solution is given. In not very diluted electrolyte solutions the distribution coefficient is often increased with concentration increase of the substance, for instance in the case of iron, gallium and gold extraction from hydrochloric acid solutions and $H(BiI_4)$ from sulphuric acid solutions by diethyl ether.

In other cases, on the contrary, with concentration increase the distribution coefficient decreases, for instance, for the cerium extraction as $H_2[Ce(NO_3)_6]$ from 1.5*N* solution of nitric acid saturated with ammonium nitrate.

In the case of ultra-small concentrations an increase of the normal potentials is observed, often leading to an isolation of foreign elements together with the element being separated on the electrode. For instance, isolation of Bi^{210} on the reticular platinum cathode together with copper (up to 10 per cent) was observed while macroamounts of bismuth (1 mg/ml) under the same conditions are not isolated.

The change of normal potentials of ultra-small amounts of elements may also be due to the presence in the solution of substances able to form complex compounds in given conditions. The question concerning completeness of the isolation of ultra-small quantities of Bi, Fe, Co, Zn, Ce on a mercury cathode was studied. The results of these experiments showed that the concentration does not act upon the completeness of the separation, except iron, whose separation completeness is decreased with the concentration decrease in the solution (from 97 per cent at a concentration of 5 mg/ml to 85 per cent at a concentration of 0.005 mg/ml).

The behaviour of elements during distillation from solutions does not depend on concentration, but is determined only by the volatilization capacity of these elements.

This study of the behaviour of elements in ultra-small concentrations also enabled the author to conclude that the behaviour of elements in ultra-small concentrations differs from their behaviour in macroconcentrations in those cases when they are in the solution in a radiocolloid state or in the form of complex compounds.

These conclusions are very important for the solution of the problem of concentrating the traces of elements.

Study of the Coprecipitation Phenomenon

In analytical chemistry, of very great scientific and practical importance is the fact of foreign ion capture from the solution by the precipitate resulting from the cocrystallization or adsorption of ions by the precipitates.

Coprecipitation leads to incomplete separation of the elements, but, on the other hand, in recent years, it is widely used in analytical practice for isolation from the solution of various ions being in very small concentrations.

Using radioactive isotopes made it possible to solve many problems of coprecipitation which had not previously been ascertained.

O. Hahn and disciples[18] and V. G. Khlopin and coworkers[30, 31] have in their numerous investigations fixed the chief laws regulating the separation of microcomponent with macrocomponent.

As an example may be cited some new data obtained by V. G. Khlopin and M. S. Merkulova[31] in studying the distribution of radium between the crystals and the solution of lanthanum trifluoride in 3 per cent nitric acid (Table 1).

A number of works[3, 12] must also be noted, containing the results of investigation carried out on the adsorption of various substances by precipitation using radioactive isotopes.

B. P. Shvedov[32] investigated the completeness of

Table 1. Isotherm of Radium Distribution between the Crystals and the Solution of Lanthanum Trifluoride at 100°C*

Lanthanum in a solid phase (in %)	*Radium in a solid phase (in %)*	*Enrichment coefficient*	*Impoverishment coefficient*	*Crystallisation coefficient* $K_f(D)$
9.31	65.24	7.01	0.38	18.4
18.37	79.96	4.35	0.25	17.4
27.56	86.30	3.13	0.19	16.5
27.56	87.80	3.18	0.17	18.7
32.13	89.96	2.80	0.15	18.6
				Average 17.9

* The equilibrium was reached by means of recrystallization of lanthanum trifluoride from a saturated solution containing radium. The barium concentration in a liquid phase was equal to 7.3×10^{-1} mM/l.

Table 2. Coprecipitation of Zn, Co and Fe with Various Sulphides

Metal sulphide	Percentage found in precipitate					
	Zn		Co		Fe	
	Small amounts (1 mg)	Equimolecular amounts	Small amounts (10^{-2} mg)	Equimolecular amounts	Small amounts (1 mg)	Equimolecular amounts
HgS	0.8	40.2	3.2	5.5	0.14	0.3
CuS	0 7	11.2	0.11	0.5	0.10	2.4
CdS	7	9.5	0.10	3.4	0.19	3.2
Bi_2S_3	0.4	3.7	0.10	2.5	0.15	0.5
SnS_2	10	3.0	17.20	8.1	1.81	8.9
SnS	—	1.9	2.20	1.5	0.50	2.0
Sb_2S_3	0.3	1 5	0.12	2.1	0.15	6.5
As_2S_3	0 4	1 1	0.10	1.0	0.16	2.8
PbS	0 3	0.5	0.10	1.1	0.15	1.6
Ag_2S	0.2	0.3	0.10	0.3	0.10	0.3

separating calcium from magnesium by the oxalate method. With the aid of Ca^{49} ($T/2 = 2.5$ hours) it was found that the amount of magnesium captured by the precipitate of $CaC_2O_4 \cdot H_2O$ and the calcium amount being coprecipitated with $MgNH_4PO_4 \cdot 6H_2O$ are very small at an equal content of calcium and magnesium. Coprecipitation in the mentioned conditions may reach several per cent if magnesium is considerably prevailing over calcium. The same author[33] studied coprecipitation of sodium with $CaC_2O_4 \cdot H_2O$ and showed that the precipitate may capture 0.5 to 5 mg of sodium after washing it five times. The precipitate of $MgNH_4PO_4 \cdot 6H_2O$ captures 0.6 to 2.8 mg of sodium. In these experiments Na^{24} with a half-life of 14.3 hr was used.

A. K. Lavrukhina studied the coprecipitation of radioactive isotopes Zr^{95}, Bi^{210}, $Ce^{141, 143}$, I^{131} with hydroxides and sulphides of various metals.[34] The results of these experiments were as follows:

(*a*) The coprecipitation of radioactive isotopes with hydroxides and sulphides of various elements does not depend on the solubility of the latter; thus, coprecipitation of Bi^{210} equals 98–100 per cent with hydroxides—$Fe(OH)_2$[S (molar solubility) $= 3.4 \times 10^{-10}$ M/1] and with $Fe(OH)_2$ ($S = 1.3 \times 10^{-5}$ M/1); with sulphides—HgS ($S = 6 \times 10^{-27}$ M/1) and with CdS ($S = 3 \times 10^{-14}$ M/1).

(*b*) As could be expected, the value of coprecipitation of radioactive isotopes with hydroxides and sulphides is determined by the solubility of these compounds of a given isotope; thus, the coprecipitation approximates 100 per cent if the corresponding hydroxide or sulphide is almost insoluble ($S = 10^{-4}$ M/1) and is very small (several per cent) in the case of good solubility of these compounds.

(*c*) When reprecipitating hydroxides and sulphides, coprecipitation of radioactive asotopes forming almost insoluble compounds is little changed; reprecipitation, as could be expected, considerably decreases the coprecipitation of radioactive isotopes which form soluble hydroxides and sulphides.

Capturing the third cation group by sulphide precipitates in a hydrochloric acid (0.3N) solution was studied by a number of chemists (Kolthoff, Flagg *et al.*). Recently I. P. Alimarin, N. A. Rudnev and L. I. Guseva[35, 36] obtained new data on coprecipitation, utilizing the isotopes Zn^{65}, Co^{60} and Fe^{59}.

As is seen from Table 2, the greatest tendency to capture the indicated ions is to be observed in tin, cadmium, mercury and copper sulphides; in a very small degree this property is observed in silver sulphide.

It is interesting to note that the amount of the coprecipitating cation depends on its concentration and the time the precipitate is present in the solution.

Zinc capture by CuS and HgS precipitation increases in the course of time; as to CdS, the zinc content in it in the course of time does not change. These facts may be explained by alteration of the structure and dispersity of the precipitates.

Addition of surface-active substances, for example, metyl red to the solution, makes it possible, as is seen from Fig. 2, to considerably decrease the coprecipitation degree.

V. G. Khlopin and M. S. Merkulova[31] showed that the surface-active substances present in the solution affect the cocrystallization of isomorphic compounds; as a result, the process of ion exchange between the solution and the surface of the crystals is retarded. Therefore, in the presence of surface-active substances, equilibrium requires more time than in their absence. In cases when surface-active substances during their adsorption on the crystal surface are almost insoluble in the given solvent chem-

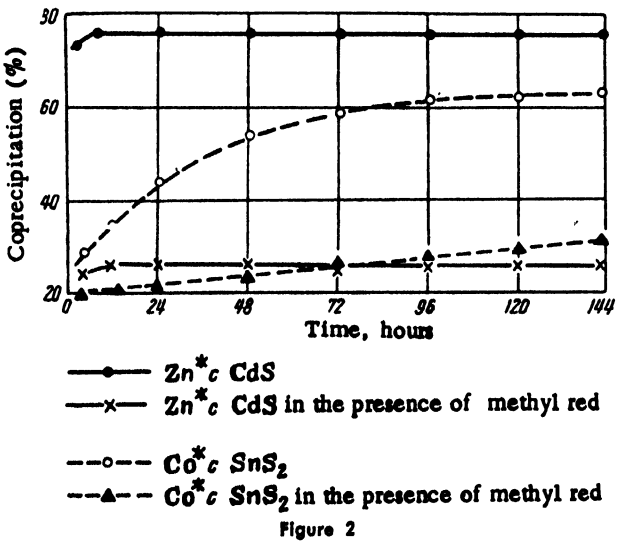

Figure 2

ical compounds with crystal ions, the presence of surface-active substances may not only retard the exchange between the crystal surface and the solution, but entirely stop it as well. As an example of the influence of surface-active substances on coprecipitation we may take the change of the amount of radium captured by lead sulphate in the presence of humic acid (Table 3).

Table 3. Coprecipitation of Radium with Lead Sulphate in the Presence of Humic Acid

Content of humic acid in the solution (mg/l)	*Coprecipitation of radium in percentage*
0	38.3
12.5	14.2
50.0	10.9
100.0	8.6
200.0	2.3

V. I. Kuznetsov[37] made an interesting study of coprecipitation under the action of organic reagents. Using radioisotope W^{185}, the author has shown that the recommended organic precipitating agents—nitron, cinchonine, quinine, and others—do not provide complete isolation of tungsten being diluted to $1:2 \times 10^5$, but, however, mixtures of precipitating agents, as, for instance, methyl violet and tannin, make it possible to completely isolate tungsten from the solution by diluting to $1:10^{10}$ with simultaneous separation from Ca, Mg, Al and a number of other elements.

To study the mechanism of coprecipitation M. B. Neiman and coworkers[38] proposed a new method of physicochemical analysis of systems, using radioisotopes. On one axis of the physicochemical diagram the coprecipitation value is plotted, on the other, the factor influencing coprecipitation, for instance, pH. Plotting of such diagrams by the aid of usual classical methods is very time-consuming; the use of radioactive tracers makes very rapid work possible. Examining the system $SrCrO_4 - BaCrO_4$ (where the isotope Sr^{89} was used) showed that a gradual neutralization of the solution with ammonia reduces the values of strontium capture to 12 per cent, and the addition of 0.01 per cent gelatin decreases the coprecipitation to 6 per cent. Meanwhile, in the case of using the classical Frezenius method of separation, the coprecipitation of strontium, at a pH = 5 reaches 30 per cent.

A. K. Babko and M. L. Shtokalo with the aid of a physicochemical method of analysis investigated the mechanism of isolating antimony traces on manganese dioxide. Sb^{124} used in this case allowed them to prove that during coprecipitation a mutual coagulation of two colloids takes place without forming any compounds.

Study of the Stability of Complex Compounds

The constants of the stability of complex compounds are of great importance in analytical chemistry.

The method of radioactive tracers was successfully used for the investigation of the complex stability. Thus, as far back as 1939, A. A. Grinberg and his coworkers[39] worked out a method for evaluating the stability of complex ions according to the rate of isotope exchange of peripheral atoms and radicals with ions of the complexing agent. Solutions containing bromic potassium were mixed with $K_2[PtBr_4]$ or $K_2[PtBr_6]$ and likewise solutions containing two complexes, for example, $K_2[PtBr_4]$ and $K_2[PtBr_6]$ or $K_2[PtBr_4]$ and $[Pt(NH_3)_2Br_2]$.

For the mentioned systems the author established a rapid exchange between ions in the solution and the addenda incomplex compounds. In the same experiments they succeeded in showing equivalency of all the bonds of the addenda. Besides, it was ascertained that central ions of the complexes are strongly retained at their places and do not exchange within the solution with the corresponding ions.

S. Y. Elovich and N. N. Matorina[40] studied with the aid of radioactive isotopes Fe^{59} and Co^{60}, iron and cobalt citrate and oxalate complex compounds and the distribution of corresponding elements between the cationite and the solution.

I. V. Tananayev and coworkers used the radioisotope Ag^{110} for ascertaining the strength of the bond between alkaline and heavy metals in a molecule of mixed ferrocyanide taking as an example the corresponding compounds of Co and Ni. It was ascertained that strength of the bond of alkaline metal in the mentioned compounds is comparable to the strength of the heavy metal bond; this proved the complex nature of mixed ferrocyanides.

Determination of the Precipitate Solubility

The use of radioisotopes opened new perspectives for the study of solubility of almost insoluble compounds used in analytical chemistry.

As far back as 1913, G. Hevesy and F. Paneth[1, 41] studied the solubility of lead chromate and sulphide using the isotope Pb^{212} (ThB); then in 1917, Vl. I. Spitsin[2] used the method of labelled atoms to determine the solubility of thorium salts. Later on, a number of works were done by B. A. Nikitin, A. E. Polesitsky, V. I. Spitsin, An. N. Nesmeyanov[42] and others (see Table 4).

It should be noted that in determining the solubility special attention must be paid to the formation of supersaturated solutions and to the possibility of finding the substance under examination in the form of a colloid which may pass through the pores of paper and glass filters. A more reliable method for separating the solid phase from the solution is ultracentrifugation.

Table 4 contains a list of some precipitates whose solubility was studied using radioactive isotopes.

Of great interest in analytical practice is the determination of the solubility of hydroxides, fluorides and oxalates of cerium, praseodymium, samarium, accomplished by Y. Skliarenko. The solubility of these compounds was determined with the aid of

Table 4. Determination of Solubility of Some Almost Insoluble Compounds

Compound	Indicator	Authors	References
$CaMoO_4$	Mo^{99} (2.8 d)	V. I. Spitsin I. A. Savich An. N. Nesmeyanov	43
$PbMoO_4$	Pb^{212} (10.7 hr)	V. V. Fomin K. B. Zaborenko M. G. Kolesnikov	44
PbI_2	Pb^{212} (10.7 hr)	V. V. Fomin P. Y. Matyazh K. B. Zaborenko	45
$RaSO_4$	Ra^{226} (1590 yr)	B. Nikitin O. Erbakher	46, 47
$Ra(IO_3)_2$	Ra^{226} (1590 yr)	A. E. Polesitsky P. Tolmachev	48
$BeNH_4PO_4 \cdot H_2O$	P^{32} (14.3 d)	B. V. Volkov An. N. Nesmeyanov	49
$Be_3(PO_4)_2 \cdot 6H_2O$			

radioactive preparations with high specific activity. It was shown that for all the examined elements the most soluble are oxalates, then fluorides and, at last, hydroxides; the product of solubility of hydroxides of these elements is of the order of 10^{-28}.

V. I. Spitsin and his coworkers,[43] with the aid of radioactive molybdenum, studied the solubility of calcium molybdate. The results of measurements are given in Table 5.

The solubility of calcium molybdate in water increases with the increase of temperature from 0 to 80°. Within the interval of temperatures 20–50° the change is small, but at temperatures exceeding 80° the solubility of calcium molybdate begins to decrease. A similar phenomenon is known to be true also for other calcium salts, for instance, sulphate (the solubility maximum of the latter is 38°). There is a reason to suppose that in the case of calcium molybdate the bend on the solubility curve corresponds to the change in salt hydratation.

The results of radiometric measurements of calcium molybdate solubility coincided with the results obtained by the gravimetric method.

In analytical practice it is recommended to precipitate calcium molybdate from hot solutions in order to obtain a more coarse-grained precipitate. On the basis of measurements of calcium molybdate solubility it should be concluded that standing the liquid with the precipitate at room temperature must render the separation of molybdenum from the solution more complete.

As it is known, in analytical practice the molybdate-ion is usually precipitated by lead. In this connection attention should be given to the work by V. V. Fomin, K. B. Zaborenko and M. G. Kolesnikova[44] in which with the aid of ThB was made a study of the solubility of lead molybdate.

Analogous research work[45] was made on the determination of the solubility of lead iodide using radioactive iodine (Table 6).

Recently M. B. Neiman, V. B. Miller and A. I. Fedoseeva[50] worked out a method for the determination of the solubility of almost insoluble compounds consisting in the following. To the solution of the element being determined a precipitating agent is added and the activity of I_1 precipitated is determined. Then a carrier is brought into the filtrate, the precipitation is repeated, and the activity of I_2 is

Table 5. Solubility of Calcium Molybdate in Water

Number of the experiment	Temperature (°C)	Quantity of the solution (gm)	log I_0	Activity of I_0 (imp/min): Found for the taken quantity of the solution	Activity of I_0 (imp/min): Calculated for 100 gm of the solution	Activity of the standard of I_0 imp/min per 1 gm of Mo	Solubility (in gm of Mo) per 100 gm of the solution: Found	Solubility (in gm of Mo) per 100 gm of the solution: Average
1	0	24.80	2.08	120	484	230	0.0021	0 0021
2		16.90	1.90	80	473	230	0.0021	0·0021
3	20	18.17	2.05	113	624	223	0.0028	0.0028
4	50	9.94	2.56	364	3662	1357	0.0027	0.0028
5		10.18	2.60	394	3870	1357	0.0029	
6		8.96	2.71	514	2468	223	0.0111	
7	80	7.33	2.26	186	2537	223	0.0114	0.0113
8		11.74	2.47	298	2538	223	0.0114	
9	100	10.07	2.53	338	3356	377	0.0089	0.0096
10		8.80	2.54	346	3932	377	0.0104	

Table 6. Determination of the Solubility of Lead Iodide in Water with the Aid of Radioactive Iodine

Number of experiment	Time of agitation (hr)	Quantity of PbI_2 in standard (mg)	Activity of standard (cpm)	Activity of 10 ml of saturated solution (cpm)	Solubility of PbI_2 in 100 ml of the solution (mg)
1	6	11.4	336	226	70.4
2	6	11.4	336	229	71.3
3	6	3.3	316	680	71.0
4	6	3.3	316	665	69.5
5	6	3.3	316	662	69.1
					Average 70 ± 1

Table 7. Solubility of $Cu_2(SCN)_2$ in the Solution of $ZnSo_4$ under 20°C

Number of the experiment	I_1	I_2	β	$x \times 10^4$ *mole/l*
1	4460	1950	2.3	5.2
2	7420	2640	2.8	5.0
3	15,490	3550	4.35	3.8
4	645	225	2.8	5.0
5	860	272	3.16	4.1
6	817	295	2.78	4.7

measured. On the basis of the determined ratio of activities the solubility X of the precipitate is found according to the following equation:

$$X = \frac{a(\sqrt{\beta^2 + 4} - \beta)}{2V} \quad (1)$$

where V is volume of the solution, a is mM/l of inactive ions of the carrier. By this method solubility of $Cu_2(SCN)_2$ under 20°C in the solution of $ZnSO_4$ (Table 7) was determined which proved to equal 0.46 mM/l as well as solubility of $Mg(NH_4)PO_4 \cdot 6H_2O$ at a different amount of $MgCl_2$ and NH_4Cl.

III. APPLICATION OF RADIOACTIVE ISOTOPES FOR QUANTITATIVE DETERMINATION OF ELEMENTS

Radioactive isotopes can be successfully used for quantitative determination of elements. For this purpose the following methods are applied.

Method of Isotopic Dilution

In those cases when quantitative separation of components is very difficult, but a part of each component may be easily isolated in pure form with relative ease, quantitative analysis is done by the method of isotopic dilution.

This method was proposed simultaneously by Hevesy and coworkers[51] and by I. E. Starik;[52] it is based on changes in the initial specific activity of the tracer introduced into the mixture being analyzed.

The main advantage of this method in comparison with other analytical methods is the fact that a quantitative isolation of the element being determined is not necessary to determine elements possessing similar properties with sufficient precision.

This method was used widely in the investigation of various mixtures of organic compounds and, particularly of biological preparations, for instance, in the determination of arsenic, sodium, potassium in biological substances as well as in analysis of a mixture of amino acids.[53]

A comparatively small number of works deals with the method of isotopic dilution in inorganic chemistry. I. E. Starik,[52] using the method of isotopic dilution, determined small amounts of lead in granites. As a tracer ThB was used, incomplete precipitation was effected and the quantity of radioelement remaining in the solution was used to determine the inactive content.

I. V. Tananaev and coworkers worked out a method of determining small quantities of rubidium in natural salts particularly, in carnallites and in products of their treatment.

The method is based on the coprecipitation of rubidium with Berlin blue which is obtained as a result of consecutively introducing $FeCl_3$ and $K_4[Fe(CN)_6]$ in the salt solution containing Rb^{86} as a tracer. Berlin blue is filtrated and ignited, the residue is leached and the rubidium is reprecipitated with the aid of $Mg_2[Fe(CN)_6]$ from which, after igniting, practically pure Rb salt is extracted. Then the activity of weighed Rb_2SO_4 is determined.

Radiometric Titration

One of the methods of radioisotope application in analytical chemistry is the radiometric titration.

In 1941 A. Langer[54] published a paper on radiometric titration of magnesium with $Na_2HP^{32}O_4$ in solution.

In a later paper A. Langer[55] recommends radiometric titration of chlorine and bromine using silver radioisotope as a tracer.

By the same method I. P. Alimarin determined cobalt by titration with $K_4[Fe(CN)_6]$ solution. In this case the radioisotope Co^{60} is used as a tracer (Fig 3).

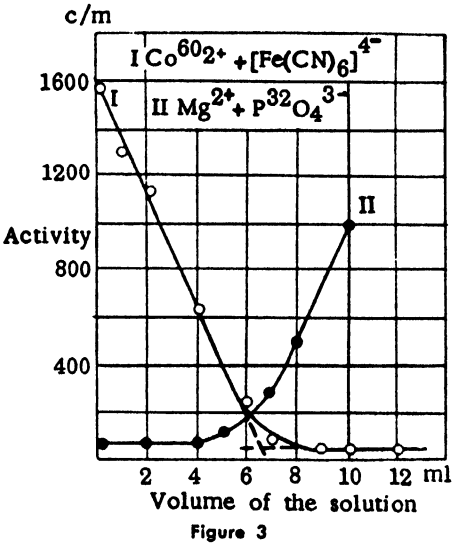

Figure 3

Application of Radioactive Reagents

In the practice of inorganic and organic quantitative analysis wider use is made of reagents containing radioactive, mainly long-lived, isotopes.

I. V. Tananayev and coworkers[56] used $Na_2HP^{32}O_4$ for the determination of a number of metals (Al, Ga, In, Ce, La, Zr, Bi, Fe and U). In most cases the phosphate is precipitated in acetate medium (for Bi and Zr—in a sulphuric acid medium). By selecting suitable conditions these metals may be determined when present together. Methods of aluminium determination in alloys, of indium in concentrates, etc., were elaborated. C. Barcia-Goyanes and E. Serrano[57] determined Al, Zn, Mn, Mg. P Süe[58] worked

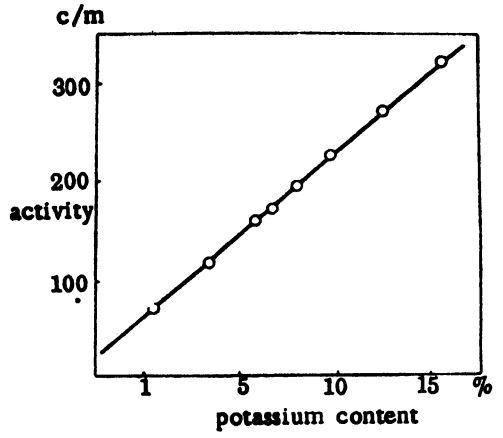

Figure 4

out a micromethod for magnesium determination. $Na_3[Co^{60}(NO_2)_6]$ was used for the determination of small potassium amounts in water as well as in andesite and diabase.[59]

Radioactive reagents were used for the determination of aminoacid mixtures.[60]

There is no doubt that in the nearest future wider use will be given to organic precipitating agents with labelled atoms.

Utilization of the Activity of Natural Elements

Owing to the radioactive properties of a number of natural elements it is possible to determine the content of these elements.

V. A. Shpak and P. I. Novikow[61] determined potassium in salts and rocks by the activity of K^{40}. This isotope, present in a natural mixture in amounts of about 0.012 per cent, has β-radiation with E_{max} = 1.36 Mev. The determination accuracy was within ±1–1.5 abs. per cent.

A. Gaudin and I. Pannel,[62] using an end-window counter, determined the potassium content in various salts with the aid of a standard curve (Fig. 4).

Analysis of salts and solutions by K^{40} was also carried out in another research.[63]

By an analogous method rubidium was determined by Rb^{87}.

To determine thorium impurities in a tungsten wire T. Mikhaleva[64] used the activity of natural Th^{232}. She constructed a special counter with a hollow nickel anode and walls less than 0.1 mm thick. Introducing the tungsten wire into the hollow anode and counting the number of impulses, she succeeded in showing that the thorium concentration (Fig. 5) in various parts of the wire (containing, on the average, 1.1 per cent of Th) varies over wide ranges.

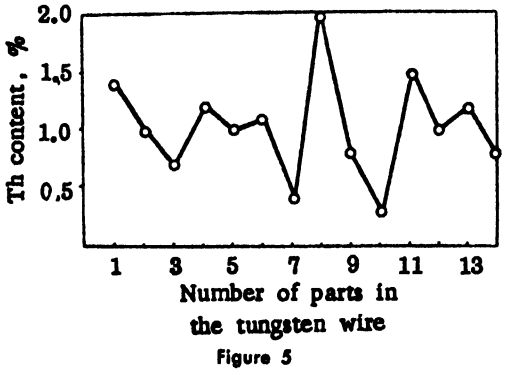

Figure 5

Radiometric Correlation of Analytical Results

Radiometric control allows increased determination accuracy by introducing corrections for the solubility, the incompleteness of separation (coprecipitation) and so forth.

Thus, in determining cerium(IV) by the calorimetric method, Ce^{144} was used without carrier in order to correct the results of cerium separation by the iodate and the bromate method.[65]

I. E. Starik[52] as well as G. Hevesy and R. Hobbi[51] determined, with the aid of the radioactive lead isotope (RaD), very small lead amounts in granites (10^{-5} gm of Pb per 1 gm of rock). The weighed granite sample was dissolved, a definite RaD amount was added and $BaSO_4$ (by Starik) and As_2S_3 (by Hevesy) were precipitated from the solution. The precipitate was dissolved, and colorimetric determination of the lead and radiometric determination of RaD were made. By the RaD loss during the analysis a corresponding correction was made.

Method of Analysis by the Aid of the Reflected Beta-Radiation Intensity

It is known that β-particles may be reflected from various substances, the degree of the reflection depending on the atomic number of the element and not on the density of the electrons (Fig. 6).

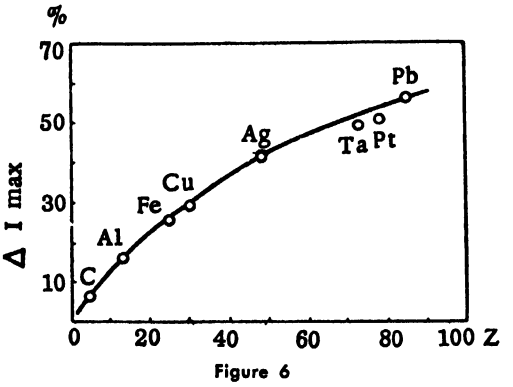

Figure 6

The maximum energy of the reflected electrons (for instance, P^{32}) is a function of the atomic number of reflecting element and is expressed by the equation:

$$E_{refl}^{P^{32}} = 0.243\, Z^{1/3} \qquad (2)$$

with a density of the reflector about 120 mg/cm².

For every reflector, in dependance on the nucleus charge, an energy limit of the scattered electrons exists. The electrons with high energies are practically not reflected.

This property was recently utilized by N. A. Bogdanow and V. F. Funke[67] for express-analysis of chromium-niobium or of iron-tungsten alloys. As a

Table 8. Results of the Purification of Manganese Sulphate Solutions from Zinc Impurity

Initial concentration Zn (in %)	Precipitate	cpm in 100 ml: of the initial solution	cpm in 100 ml: of the purified solution	Purification coefficient	Content Zn in $MnSO_4 \cdot 5H_2O$ after purification (in %)
0.02	$Mn(OH)_2$	2000	18	1100	1.8×10^{-5}
0.12	$Mn(OH)_2$	18,200	6	3000	4.0×10^{-5}
0.02	$MnCO_3$	45,470	3730	12	1.6×10^{-2}
0.02	MnS	47,760	0	great	1.0×10^{-5}
0.12	MnS	46,050	40	1150	1.0×10^{-4}

source of β-radiation Tl^{204} was used. The scheme of the device for analysis is very simple. It is shown in Fig. 7.

The investigated sample of the alloy or pressed powder (1) is placed on the plexiglass diaphragm (2) under which an end-window Geiger-Müller counter (3) is placed. Between the end-window counter and the diaphragm the radioactive isotope (5) is placed on a lead disc (4). Thus the counter is protected from a direct (initial) radiation. Near the window of the counter an aluminium filter-absorber (6) 90 mg/cm^2 thick is placed. The effect of the filter is based on the fact that the radiation reflected by niobium atoms has a greater penetrating capacity than the radiation reflected by chromium atoms.

When analyzing powdered substances it is necessary to press them first because the intensity of reflected radiation depends on the sample density.

It was found that there exists a linear dependence (Fig. 8) between the niobium content and the intensity of reflected radiation. The method makes it possible to determine very rapidly over 3 per cent of niobium with an accuracy $\pm$ 2 per cent. It is also possible to analyze other binary alloys with elements differing sharply in atomic number, for instance, iron-tungsten and others.

IV. APPLICATION OF RADIOACTIVE ISOTOPES FOR ELABORATING NEW METHODS OF CHEMICAL-ANALYTICAL CONTROL

In the modern chemical and metallurgical industry, especially great importance is acquired by the methods for investigating small amounts of impurities and by the increasing rate of the analyses. These tasks are successfully solved not only by physical-chemical methods, but also with the aid of radioactive isotopes. This will be demonstrated by some examples.

1. Using the method of radioactive tracers for study and control of the processes of purification of high purity reagents allowed considerable improvement of the technological schemes and increased accuracy and reliability of the determination of impurities of the order of 10^{-3}–10^{-5} per cent. G. I. Gorshtein[68] showed that in a number of cases it was possible to control the process of reagent purification when the application of usual analytical methods became impossible due to their insufficient sensitivity. For instance, to purify manganese sulphate from zinc impurity, the radioactive isotope Zn^{65} was added to the solution of $MnSO_4$ and then a freshly precipitated manganese protoxide hydrate, carbonate or sulphide was introduced. By measuring the γ-radiation activity of the filtrate the degree of zinc separation was established. The results given in Table 8 showed the effectiveness of Zn impurity isolation on various precipitates.

Analogous experiments showed that successful control over the iron sulphate purification from zinc impurity is possible with the aid of freshly precipitated iron sulphide. Using as a collector manganese dioxide and the radioactive isotope Co^{60}, G. I. Gorshtein established that if 10^{-5} per cent of cobalt is present in zinc sulphate, the cobalt is coprecipitated with the collector to 99.5 per cent and can be then determined in the precipitate.

As is known, obtaining very pure copper is of great importance for electrotechnics. Traces of foreign metals reduce electric conductivity and alter the mechanical properties of the conductors. With the aid of radioactive isotopes of antimony and arsenic, A. K.

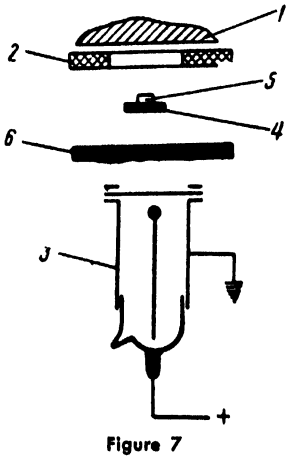

Figure 7

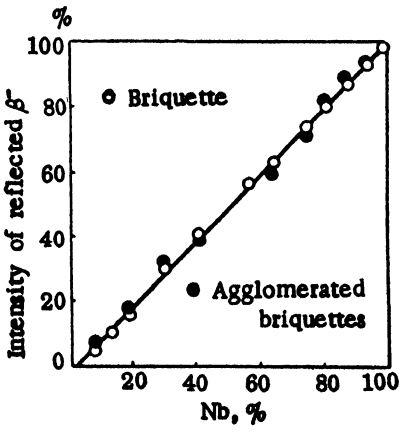

Figure 8. Standard curve for the alloy Cr-Nb

Babko and M. I. Shtokalo verified standard methods of determination of these elements and elaborated methods for separating their traces by coprecipitation.

V. P. Shvedov, E. O. Goldshtein and N. I. Seletkova[69] utilized the radioactive lead isotope, ThB, in studying the conditions of complete lead separation from big quantities of barium, strontium, calcium and magnesium by precipitating it as oxyiodide and oxybromide. A method of quantitative lead determination (after separation of oxybromide or oxyiodide) in an ammonium acetate solution by precipitating it as $PbCrO_4$ was proposed.

2. Analytical determination of a number of rare elements by reason of their similar chemical properties often requires a preliminary separation of the mixture. This may be accomplished effectively by the methods of ion-exchange or distributive chromatography which have been developed on the base of Tsvet's classical method.

D. D. Ivanenko and E. N. Gapon and coworkers,[70] in verifying their theory of ion-exchange dynamics, examined the distribution of radioactive substances over the column and in the corresponding eluants.

Radioactive tracers allow a rapid determination of optimum conditions for chromatographic separation of mixtures and to control this process.

In recent years the ion-exchange method of separation has been widely used both in foreign and Soviet laboratories for investigations of nuclear reaction products and for the separation and isolation of elements with similar chemical properties, for instance, niobium-tantalum, zirconium-hafnium, rare-earth and transuranium elements.[25, 27, 28, 71, 72]

In this connection investigations made by Ryabchikov and coworkers dealing with chromatographic separation on the cationite "РФ" of mixtures of alkaline metals must be mentioned. These investigations in which use was made of the isotopes Na^{24}, K^{42} and Rb^{86} were applied both for obtaining rubidium (free from potassium) used as a standard for spectral analysis and for silicate analysis.

N. S. Poluectov and coworkers examined the methods of chromatographic separation of zirconium and hafnium chlorides in methanol solution of silica gel. When 20 per cent solution of the mixture of tetrachloride zirconium with 0.1–2 per cent hafnium was passed once through the column, the content of the latter decreased to 0.08 per cent.

However, for preparative purposes the separation of zirconium-hafnium mixture by the method of ion-exchange chromatography is more promising. Improvement of the method proposed by B. Lister[73] already allows obtaining on the cationite KY-2 a considerable amount of pure hafnium which serves as an initial material for obtaining the radioisotope Hf^{181}.

Radioactive tracers proved to be very convenient for a rapid determination of exchange capacity of cationites even in rather concentrated solutions of sulphuric acid. D. I. Ryabchikov and coworkers carried out a work on the determination of the exchange capacity of sulphocationites in acid media (up to $2N$). As tracers radioactive isotopes Na^{24} and Co^{60} were used. It was established that of the three examined native sulphocationites (KY' 1, KY-2, CDC) KY-2 has a comparatively high capacity (in $2N$ acid its capacity equals 50 per cent by NaCl and 70 per cent by $CoCl_2$ of the whole exchange capacity).

Utilization of the radioactive isotope Nb^{95} made it possible for M. M. Senyavin and E. P. Zhirov to elaborate a chromatographic method of titanium and niobium separation. These experiments were carried out on cationite KY-2. It was shown that for the separation of mixtures containing a great amount of titanium it is advisable to wash the column with $1N$ sulphuric acid and for the separation mixtures containing a great amount of niobium it is advisable to wash it with $0.1N$ $H_2C_2O_4$.

As to the chromatographic separation of mixtures containing various amounts of components, it should be noted that A. K. Lavrukhina[23] observed a noticeable rate increase in the shift of Y^{91} component over the chromatographic column with a strong decrease of its content (Fig. 9). This probably accounts for the fact that the equilibrium settled in the eluant $Me^{3+} + mR^{n-} \rightleftharpoons [MeRm]^{3-}$ (where Me^{3+} is the ion of a rare earth and R^{n-} the anion of citric or acetic acid)

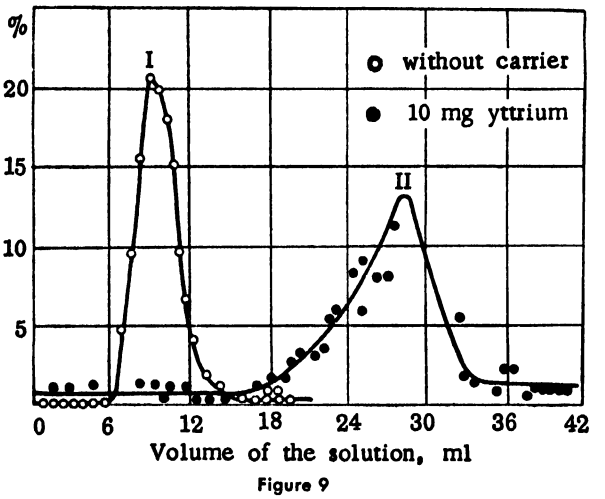

Figure 9

is strongly shifted to the right because of a very high concentration of the complexing agent in regard to the ultra-small concentration of the element. Since the revealed phenomenon may result in a superposition of two or more element bands if their quantities differ strongly, it should be taken into account in the chromatographic separation of mixtures in the presence or absence of a carrier.

The chromatographic method proved a success in separating the radioactive isotopes of various elements. For instance, N. P. Rudenko[29] showed that it is possible to separate Zr^{95} and Nb^{95} within 70 hours on native anionites espatite-TM and AH-2E, the column height being 92 cm, diameter 0.5 cm, and the

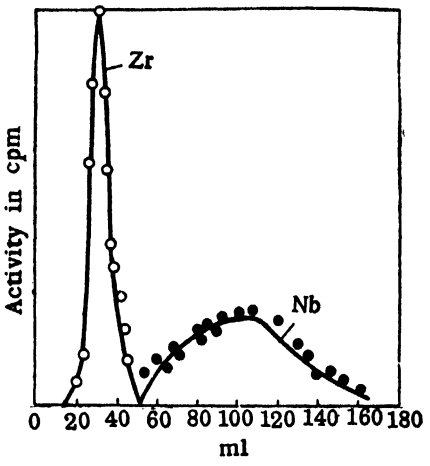

Figure 10

flowing rate of the solution (9*N* by HCL and 0.5*N* by HF) 0.3 ml/min-cm^2. The eluating curve is given on Fig. 10.

On a 25 cm long anionite espatite-TM column F. P. Rudenko succeeded also in separating niobium and tantalum. When the mixture was eluated with a solution of hydrochloric and hydrofluoric acids of the mentioned concentrations, the niobium was eluated within 26 hours and the tantalum within 115 hours.

The importance of the radioactive tracer method is obviously demonstrated in the separation of rare earths mixture. Systematic investigations by D. I. Ryabchikov and M. M. Senyavin[76] showed a rather effective method for separating natural mixtures of rare-earth elements for analytical and preparative purposes; it does not use ion-exchange chromatography directly (as done by F. Spedding[74]) but combines it with extraction of Ce and electrochemical isolation of Sm, Eu and Yb on a mercury cathode.

In an examination of cerium extraction,[76] the distribution coefficients and isolation degrees by organic solvents were determined using radioactive cerium; selectiveness of the process was estimated by using radioactive isotopes of ytterbium, samarium and yttrium. After 24 organic solvents were tested, it was shown that rare earths are not practically extracted from hydrochloric acid solutions into the organic phase. This result was the basis for proposal of an effective method for the separation of iron from the sum of rare-earth elements. Radioactive tracers were also used to confirm that cerium (in a tetravalent state) may selectively and almost quantitatively be extracted with diethyl ether from nitric acid solutions containing not less than 4 gram-equivalents of free nitric acid. As a result of studying a number of regularities the above-mentioned authors in 1950, independently of R. Bock and E. Bock[75] and simultaneously with them, suggested that cerium may be extracted in the form of a complex acid of the following composition: $H_2[Ce(NO_3)_6]$.

In D. I. Ryabchikov's and his coworkers'[76] work on electrochemical isolation of Sm, Eu and Yb, radioactive isotopes of these elements were used for a rapid and accurate determination of the separation completeness. After cerium, samarium and europium were isolated from the cerium group and ytterbium from the yttrium group, the remaining mixtures were separated by the method of ion-exchange chromatography. The application of radioactive tracers made it possible to find optimum conditions for chromatographic separation of mixtures. As a result of this work, preparations of rare earths were obtained.

Paper chromatography combined with the method of radioactive tracers[77, 78] opened new perspectives for the investigation of the composition of mixtures of inorganic and chiefly organic substances.

The two-dimensional chromatogram, after drying, is placed on a plate on which, after it is exposed for some time and developed, a photographic print is obtained showing the distribution of organic substances labeled by C^{14} or S^{35}.

Using radioactive Hf^{181}, E. S. Burkser and G. D. Eliseeva succeeded in working out a microchromatographic method of separation of hafnium and zirconium on paper with the aid of rhodanic acid dissolved in diethyl ether. This method was applied to the analysis of hafnium concentrates. The results obtained coincide with the data of spectral analysis.

3. Because of the intensification of the steel fusion processes, great importance is attached to the development of quick methods of metal and slag analysis that allow operational regulation of the technological process.[81] Using radioactive isotopes made it possible for A. I. Osipov and coworkers[79] to increase the rate of technological control considerably. In open-hearth furnace smelting of high-phosphorus cast irons the use of P^{32} made it possible to control dephosphorization of the metal and, at any moment of the fusing process, to know the content of phosphorus in the slag and, consequently, to determine correctly the moment of its skimming. The control over the fusion conditions regime by phosphorus allowed a precise and rapid marking of the slag in using it as an agricultural fertilizer.

In experimental fusion a mixture of radiophosphorus and iron powder was introduced into the open-hearth furnace. It was placed into a metal tube which was fused during the metal producing process, and its content was distributed over the iron and slag bulk. In these experiments 0.5 mc of radiophosphorus was used per 1 ton of cast iron. The time required for the phosphorus determination in the slag was 5–7 min, and the error did not exceed 6 per cent. In Fig. 11 an example of phosphorus determination in the slag at various periods is given. The results of the radiometric determination of phosphorus were compared with the data of photocolorimetric determination, which took much more time. As is seen from Fig. 11, the results of determination by both methods are in good agreement.

4. Radioactive tracers aided successful solution of problems concerning phase composition of alloys, the nature and conditions of formation and distribution

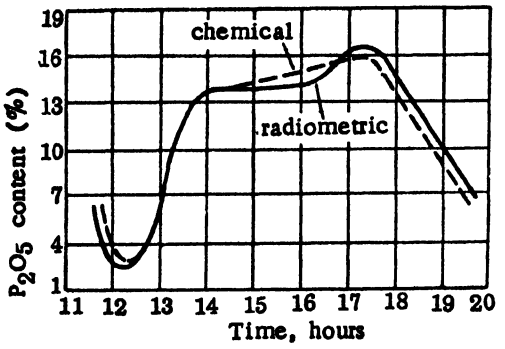

Figure 11

of non-metal inclusions, and the segregation of admixtures in alloys. For instance, the content of chromium in chromous steel carbides was studied.[80] As a tracer radioactive Cr^{51} was introduced into the molten metal in the amount of 10 mc per 1 kg of steel. After taking a metal sample the carbide phase was isolated by electrolytic methods and its chromium content determined by the radiometric method. With this method it was possible to obtain valuable data concerning the kinetics of carbide-forming in the process of tempering hardened chromous steel. At the initial stage of austenite disintegration the chromium content in the carbides corresponds to its average content in steel. The increase of chromium concentration in the carbide changes linearly depending on the logarithm of the tempering time (Fig 12). It was also shown that the rate of chromium conversion into carbide differs considerably from the rate of chromium conversion into cementite.

By irradiating rocks and alloys with neutrons small quantities of various inclusions may be revealed by radioautography.[82]

The radiometric methods of control were widely used in investigations and analyses of various fertilizers, insectofungicides and soils.[83, 84]

CONCLUSION

The use of stable and chiefly radioactive isotopes as tracers becomes more widely used in solving theoretical and practical problems of analytical chemistry.

The examples cited in this paper give only a general idea of the prospects of this method in scientific research. Already a great number of radioisotopes are used in analytical chemistry in studies of the behaviour of substances present in solutions in very small amounts. Especially, much attention is paid to the problems of coprecipitation, adsorption, electrochemical isolation of metal traces, etc., because of the increased significance attached to impurities in pure metals, semi-conductors, alloys, luminous compounds, reagents, etc.

In view of the developing problems of nuclear chemistry and, first of all, the necessity of ascertaining the mechanism of interaction of various particles of high energy with nuclei, elaboration of rapid methods for isolating radioisotopes in a radioactive pure state is urgently needed.

Radiometric methods of analysis are widely used for the study of chemical-analytical properties of new elements.

With the aid of radioactive isotopes various constants are varified—solubility of precipitates, stability of complex compounds, distribution coefficients of elements between phases, boiling and evaporating, temperatures of substance, etc.—which plays a very important role in analytical chemistry.

Labelled atoms undoubtedly will be given wide use in the investigation and elaboration of kinetic methods of analysis as well as in physico-chemical analysis of systems of various kinds.

In recent years the development of methods of analysis by isotopic dilution is increasing, especially in their application to organic and biological substances.

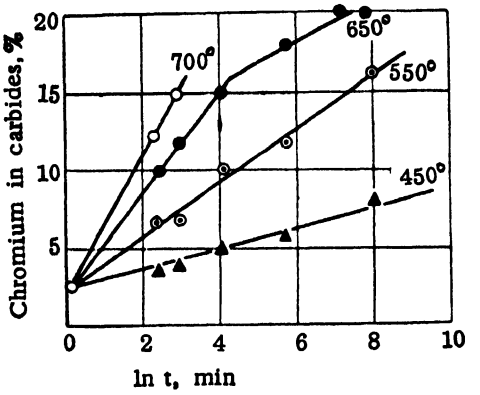

Figure 12

The use of nuclear reactors makes it possible to apply successfully the method of activation to determination of impurities and to phase analysis of heterogeneous systems. This method will become more widely used when not only slow neutrons will be used for activation, but also other particles of various range of energies, obtained with the aid of various accelerators.

The radiochemical methods made it possible to verify and improve the standard methods of analysis of reagents, metals, alloys and mineral raw materials.

Applications of radioisotopes led to increased rate and accuracy of analyses, because in a number of cases the necessity of a complete isolation of the element being determined no longer arose.

The radiometric correlation of the results of determination made it possible to increase the accuracy of determination of small concentrations of elements in minerals and rocks; this is very important for solution of geochemical problems—for instance, for the determination of the age of rocks and minerals and the determination of the Clark number.

Along with the development and improvement of radiochemical methods of analysis, the methods of isotope identification are increasingly improved as the sensitivity and accuracy of the measuring devices for various radiations become higher. In analytical

laboratories scintillation counters are used along with usual Geiger-Müller counters. The elaboration of the investigation methods of spectral composition of α-, β- and γ-radiations of radioisotopes considerably facilitates the work of the analyst who investigates mixtures of radioisotopes obtained as a result of nuclear reaction.

The method of thick-layer emulsions introduced by L. V. Mysovsky and A. P. Zhdanov is now applied in analytical chemistry too—for instance, for the determination of small amounts of uranium and thorium by α-tracks in photoemulsion. This method, which was described more than 20 years ago by M. Deisenroth-Mysovskaya,[85] probably will be used for other α-emitting isotopes too.

In analytical control of technological processes, as with the improvement of the mass-spectroscopy technics, greater use will also be made of stable isotopes, owing to the fact that they do not emit rays of destructive action on living organisms.

The greatest discoveries of our times in the field of nuclear physics allow us to approach in a new manner the solution of many problems of analytical chemistry and technological control. Application of labelled atoms in analytical practice is becoming as usual as the utilization of any other method of qualitative and quantitative analysis.

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Recent Advances in Radioactivation Analysis

By A. A. Smales,* UK

GENERAL PRINCIPLES

"The development of sufficiently accurate methods of chemical analysis of the materials used has been a problem of the first magnitude throughout the history of the (Manhattan) project . . ." Thus briefly, Smyth in his now classic report, recognizes the important contribution made by analytical chemistry. It seems right therefore that the latter subject should reap some of the benefits from the atomic energy programme, and one of these is undoubtedly the availability of piles and particle accelerators associated with the development of atomic energy. Several workers have seized the opportunity to develop radioactivation analysis into one of the most sensitive and specific techniques available to analytical chemists.

The essential basis of the method is that the element to be determined is made radioactive and that this radioactivity, usually but not always after suitable chemical separations, is then a measure of the mass of the element originally present. Because of the great sensitivity of the methods of measuring radioactivity, and because of the almost specific characteristics of individual radioisotopes, e.g., decay period and energy of emitted radiation, the radioactivation method offers very great attractions.

Let us consider what happens when an element is made radioactive by placing it in a homogeneous flux of energetic charged particles or neutrons. The rate of growth of the number of radioactive atoms N^*, with time, is given by

$$dN^*/dt = f\sigma N - \lambda N^* \qquad (1)$$

This, on integration over the period of irradiation, becomes

$$N^* = f\sigma N(1 - e^{-\lambda t})/\lambda \qquad (2)$$

where f is the flux of bombarding particles in units of particles/cm^2/sec, σ is the isotopic cross-section for the nuclear reaction in units of cm^2 per target atom (and might therefore be considered as the "effective area" of the atom for the nuclear reaction), N is the number of target atoms and λ is the radioactive decay constant for the radio-nuclide formed, being connected with the half-life T by the relation $\lambda = 0.693/T$.

The amount of radioactivity A_t, in disintegrations/sec, exhibited by the atoms N^* produced up to a time t is given by the expression

$$A_t = N^* = f\sigma N(1 - e^{-\lambda t}) \qquad (3)$$

$$= f\sigma N(1 - e^{-0.693t/T}) \qquad (4)$$

where t and T are expressed in the same units.

So far it has been assumed that the element is mono-isotopic; however, considering a weight W gm of an element of atomic weight M, and if θ is the abundance of the particular isotope (of the element under consideration) giving rise to the activity, then we have

$$A_t = 6 \times 10^{23} f\sigma\theta W(1 - e^{-0.693t/T})/M \qquad (5)$$

After the irradiation is stopped, the activity formed will of course decay with its characteristic half-life, so that at a time d (in the same units as t and T) after the cessation of the irradiation the activity becomes

$$A = 6 \times 10^{23} f\sigma\theta W(1 - e^{-0.693t/T})\,(e^{-0.693d/T})/M \qquad (6)$$

From this relationship, then, it can be seen that high activity (and therefore high sensitivity) is obtained for a given mass if the flux and the activation cross-section are high. In addition, other things being equal, sensitivity is greater for lower atomic weight elements and for those with high relative abundance of the isotope concerned. The half-life of the radionuclide does not control the inherent sensitivity of the method, except in so far as it becomes a practical limitation, either for long-lived emitters on the time of irradiation, or for short-lived emitters on the time between the irradiation and the actual measurement of radioactivity.

The character of the radiations emitted by the radionuclide formed also affects the sensitivity of the methods, and must be considered in any assessment of its potentialities.

From what has been said so far, it can be seen, provided that the magnitude of the flux, the activation cross-section for the nuclear reaction and the half-life of the radionuclide formed are known, that a determination of the absolute disintegration rate should then enable the calculation to be made of the absolute mass of the constituent being determined. However, accurate knowledge of the flux and cross section and accurate determination of the absolute disintegration rate are not usually possible, but in practice these difficulties are avoided by using a comparative procedure, i.e., simultaneous irradiation

* Atomic Energy Research Establishment, Harwell, Berks.

of samples with standards containing a known proportion of the element being determined.

PRACTICAL STEPS

The practical steps in an analysis by radioactivation are, then, as follows:

(*a*) Irradiate weighed quantities of the sample and standard in suitable containers for a sufficient time to give adequate radioactivity in the element to be determined.

(*b*) After irradiation, dissolve the samples and standards and add a known weight of the element being determined as carrier for the small quantity which has been irradiated.

(*c*) Treat the solution in such a way that the carrier and the element in the sample are in the same chemical form.

(*d*) Carry out chemical separations to isolate the element (or a suitable compound) free from all other radionuclides, i.e., until it is radiochemically pure.

(*e*) Determine the chemical "yield" by any conventional method. The fact that this step is included makes it unnecessary for the chemical separation in step (*d*) to be quantitative, since the final measured activity will be corrected for losses, using the chemical yield figure.

(*f*) Compare the radioactivity of sample and standard under identical counting conditions, making correction if necessary for self-absorption, dead-time losses, decay, etc.

(*g*) Check the radiochemical purity of the isolated active compound by measuring (1) the rate of decay, from which the half-life may be obtained, and (2) the activity through different thicknesses of aluminium, from which an estimate of the energy of the β particles emitted may be made, and (3) the gamma energy using, for example, a scintillation spectrometer.

In certain favourable cases, steps (*b*) to (*e*) may be omitted.

Then the mass of X, the constituent to be determined, is obtained as follows:

$$\frac{\text{Mass of } X \text{ in unknown}}{\text{Mass of } X \text{ in standard}} = \frac{\text{Total activity from element } X \text{ in unknown}}{\text{Total activity from element } X \text{ in standard}}$$

ACTIVATION SOURCE

Although other ways of activating the sample are possible, the most generally useful and available activating source in England is the Harwell pile with its flux of more than 10^{12} neutrons/cm^2/sec. It is possible to calculate the sensitivity of the method under ideal conditions with the Harwell pile for a range of elements as shown in Table 1.

RECENT APPLICATIONS

To illustrate the use of the radioactivation method a number of actual applications recently developed at Harwell will be mentioned. They will be dealt with under two broad headings, the determination of trace elements in materials of (*a*) geochemical interest and (*b*) industrial interest.

Geochemical Applications

Radioactivation methods have been developed for determining nickel, cobalt and copper down to the 10^{-7}, 10^{-8} and 10^{-10} gm levels respectively in a wide range of geological samples. In this case the three elements were determined on the same irradiated sample by using a composite radio-chemical separation scheme. The fact that the half-lives are respectively 2½ hours, 5.3 years and 12.8 hours made it possible to deal adequately with the successive radiochemical separations in the order nickel, copper and cobalt. In addition only one set of counting equipment was needed for checking radiochemical purity of the isolated activities, and the availability of automatic counting equipment designed by Electronics Division, A.E.R.E., for measuring decay curves and maximum β energies made this checking quite simple.

The determinations were carried out on specimens of marine sediments, oceanic rocks and meteorites in an attempt to shed some light on the possible meteoritic origin of the nickel in the marine sediments.[1] A summary of the results for the three ratios involving nickel, cobalt and copper are given in Table 2, from which it was concluded that there was little significant contribution of meteoritic material to these sediments. The particular advantage of the radioactivation method in this case was its sensitivity, which made it possible to determine all three elements

Table 1. Elements Determined in Trace Quantities by Neutron Radioactive Analysis

Elements	*Sensitivity under ideal conditions (using Harwell Pile) (Grammes)*
Europium, dysprosium	10^{-12}
Holmium, indium, iridium, lutetium, manganese, rhenium, samarium	10^{-11}–10^{-10}
Antimony, arsenic, bromine, copper, gallium, gold, iodine, lanthanum, palladium, scandium, sodium, praseodymium, tantalum, terbium, thulium, tungsten, ytterbium	10^{-10}–10^{-9}
Barium, cadmium, caesium, chlorine, cobalt, erbium, gadolinium, germanium, hafnium, nickel, osmium, phosphorus, potassium, rubidium, selenium, yttrium, zinc	10^{-9}–10^{-8}
Cerium, chromium, mercury, molybdenum, strontium, tellurium, thallium, neodymium, platinum, ruthenium, silver, tin, zirconium	10^{-8}–10^{-7}
Bismuth, calcium, iron, sulphur, silicon	10^{-7}–10^{-6}

Table 2. Ratios Involving Nickel, Cobalt and Copper

Material	Number of samples examined	Ni:Co Average ratio	Ni:Co Range	Ni:Cu Average ratio	Ni:Cu Range	Cu:Co Average ratio	Cu:Co Range
Red clay	11	3 1	1.6–7.1	0.85	0.4–1.3	3.7	1.3–5.7
Globigerina ooze	33	4.1	1.8–7.0	0.77	0.4–1.6	5.4	2.0–11.0
Manganese nodules	7	4 3	1 4–6.5	1.2	0.4–2.4	4.3	0.6–7.0
Oceanic rocks	9	2.3	1.4–4.3	1.6	0.2–3.1	2.7	0.7–6.9
Average for igneous rocks		3.5		1.1		3.0	
Meteorites (stones and stony-irons)	9	22.7	12–52	100	75–119*	0.24	0 2–0.4*
Average for meteorites		13 1		92		0.14	

* Omitting Khor Tomiki which gave Ni:Cu 11.7 and Cu:Co 2.0.

at the level of a few parts per million and upwards with adequate precision on no more than a few milligrams of sample—the sample being particularly limited in the case of the marine sediments.

Still another use has been made of the method for nickel, cobalt and copper, this time in fixing the levels for these three elements in two rock samples, a granite and a diabase.[2] These two particular rock samples have been analysed spectrographically and absorptiometrically by a range of laboratories with the idea of setting them up as standards which could be used by other workers. The precision and accuracy of these two conventional techniques are not good however, particularly at very low levels, and the combination of high sensitivity with reasonable precision possessed by radioactivation has enabled the level of the three elements to be fixed with greater certainty. The values obtained by the spectographic and absorptiometric methods by nine different analysts are taken from "Quantitative Spectrographic Analysis of Silicates," by L. H. Ahrens, and are shown in Table 3 together with the results by radioactivation. The latter method is clearly going to be of value in providing standards, on which particularly the spectographic method is so dependent.

Other recent applications of radioactivation methods to materials of geochemical interest have been (*a*) the determination of rubidium and caesium in sea water, the levels being 0.12 and 0.0005 ppm respectively,[3] and (*b*) the determination of microgram and submicrogram amounts of thorium in minerals.[4] One of the aims of this method, like that of the earlier one on uranium[5] was to make possible age determinations on isolated individual minerals from rocks.

Applications to Pure Metals Including Semi-Conductors

The radioactivation method is particularly suitable for determining extremely minute quantities of trace impurities in pure metals and there are a number of recent examples worth quoting.

The determination of calcium at the part per million level in fairly pure iron is almost impossible by any conventional chemical method, while the spectrographic method runs into difficulty because of the ubiquitous nature of calcium in dust, etc.—thus giving rise to high "blanks." Although the sensitivity by radioactivation is low for calcium compared with many other elements, it is still adequate for the parts per million level, and has been applied[6] after irradiation of samples of about 1 gm for periods of between two and ten weeks. The radiochemical separation of the 152 day half-life calcium-45 involved ether extraction of the bulk of the iron, precipitation of the remaining iron, together with manganese, using ammonium hydroxide, then alkaline sulphide "scavenging" and finally precipitation of calcium oxalate. Because of the weak energy of the Ca^{45} beta particles, correction was necessary for self absorption losses. Values obtained on duplicate portions of two iron samples were 7.0 and 7.5 ppm for the first sample and 5.4 and 5.8 ppm for the second sample. At this level there was adequate Ca^{45} activity for verification of radiochemical purity by half-life and beta energy measurement.

Table 3. Results for Nickel, Cobalt and Copper on Standard Rock Samples

Method	Analyst	G1 Ni	G1 Co	G1 Cu	W1 Ni	W1 Co	W1 Cu
		parts per million			parts per million		
Spectrographic	1	5	n.d.	<8	47	35	130
Spectrographic	2	n.d.	3	15	80	25	90
Spectrographic	3	—	n.d.	5	—	30	44
Spectrographic	4	n.d.	—	—	80	50	—
Spectrographic	5	<2.5	<2	6	140	55	140
Spectrographic	6	<10	<5	—	60	26	—
Absorptiometric	7	—	—	trace	70	—	100
Absorptiometric	8	60	10	10	150	20	80
Absorptiometric	9	—	3	20	80	40	130
Recommended value (Ahrens)		(5)	(4)	11	90	36	110
Radiaoctivation		1.0, 1 4	2.1, 2.5, 2 2	9.4, 9.5	73.5, 75.1, 70.5	53, 45.4, 48.1	112, 109.8

There is much current interest in the trace impurity level in alkali metals. Recently sodium has been determined in pure lithium metal[7] down to 0.02 ppm using a "streamlined" radiochemical separation involving a semimicro ion exchange column separation in addition to conventional precipitation steps. The total time required for the whole radiochemical procedure is four hours for four samples and two standards.

An example of the detection and determination of some trace impurities in sodium-potassium alloy, in this case without using any radio-chemical separations, is shown in Fig. 1. In this case the alloy was irradiated in the Harwell Pile, allowed to "cool" for a period of about two weeks and then examined on a single channel gamma spectrometer fitted (curve *A*) with the usual single sodium iodide crystal, and (curve *B*) with sodium iodide and anthracene crystals in the Compton compensating device described by D. H. Peirson.[8] The advantages of the latter can be seen, particularly in picking out the caesium-134 photopeaks at 0.59 and 0.80 Mev and the silver-110 at 0.88 Mev. The two gamma emitting impurities rubidium and silver were determined by comparison with irradiated standards and found to be 100 ppm and 5 ppm respectively. Caesium, although detectable by gamma spectrometry, was determined by radiochemical separation to be 0.11 ppm.

One of the fields in which radioactivation methods have been almost indispensable is that of semiconductors. Here purity requirements are much

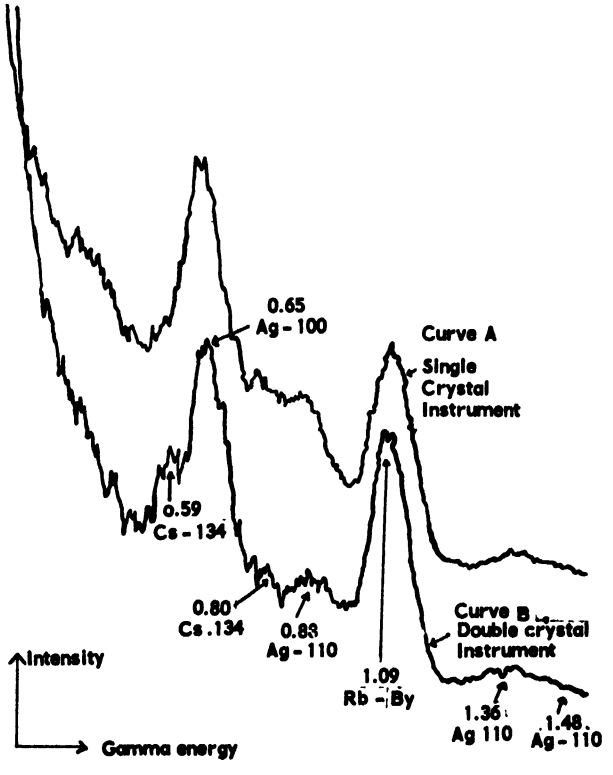

Figure 1. Gamma spectra of irradiated sodium potassium alloy using single and double crystal instruments

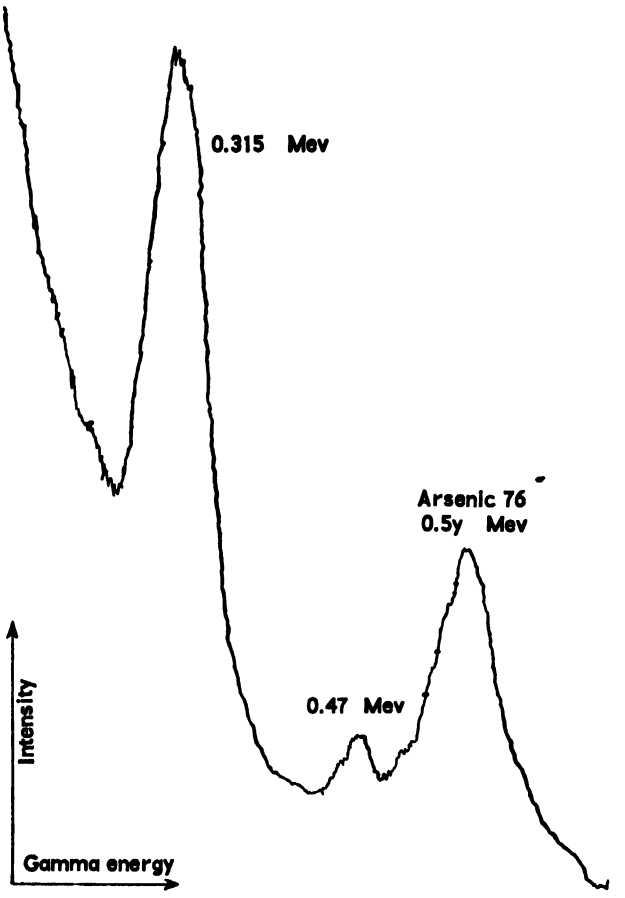

Figure 2. Gamma spectrum of neutron irradiated silicon

greater even than in most atomic energy materials and the great sensitivity and freedom from "reagent blank" difficulties of the radioactivation method have made it very attractive and widely used since the original work on the determination of arsenic in germanium by A. A. Smales and B. D. Pate.[9] Recently the determination of nickel was required in experiments to measure the segregation constant of that element in germanium. Although such properties are most conveniently measured by incorporating a radioactive tracer of the element in the material under examination and then after "pulling" the crystal, cutting the latter into slices and measuring the radioactivity of each slice, this was not possible for nickel where the half-life of nickel-65, 2.6 hours, is too short for convenience in comparison with the time for the experiment. (Other radionuclides of nickel also had disadvantages.) The problem was solved by performing the experiment with inactive nickel and then analysing the slices of nickel-doped germanium by radioactivation.[10] It was possible to determine as little as 0.1 ppm of nickel, although the radioactivation method is not particularly sensitive for that element.

Silicon is coming into prominence now as a semiconductor material and radioactivation methods have been used even more readily on this material than on germanium, because on slow neutron irradiation silicon gives only the 170 minute half-life, pure beta

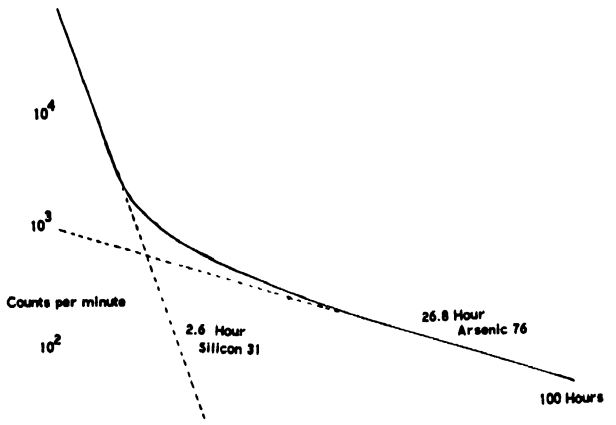

Figure 3. Decay of neutron irradiated silicon

emitter, silicon-31, which is easily handled, whereas germanium gives rise to a longer lived gamma emitter. Irradiated silicon is, therefore, ideally suited for the application of gamma spectrometry for the detection and determination of impurities, and an example of this is shown in Fig. 2 where the arsenic-76 gamma at 0.57 Mev can be seen, arising from an arsenic impurity level at about 1 ppm.[11] The gamma energy combined with the over-all beta decay curve shown in Fig. 3 provides ample evidence for identification of arsenic. It is of course possible to measure the decay of the 0.57-Mev gamma peak directly to get even more specific evidence. Other gamma energies can also be seen in Fig. 2 and have tentatively been identified as due to iridium. By the standard required for ultimate use in semi-conductor work, this particular sample is relatively impure and in the highly purified material it is generally necessary to use radiochemical separations after irradiation. In this manner such impurities as arsenic and copper (to 1 part in 10^{10}) have readily been determined.

CONCLUSION

It is clear that the technique of radioactivation analysis is well established now as one of the weapons in the armoury of the analytical chemist. Industrial and university laboratories in Great Britain are beginning regularly to use the method for their own analytical problems, having set up the quite modest radiochemical facilities necessary, and sending their samples for irradiation in the Harwell Pile. There is no doubt that this technique is proving a very good example of one of the peaceful uses of atomic energy.

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Examples of Activation Analysis

By M. P. Lévêque,* France

Various nuclear reactions have been used in order to make certain activation analyses possible. Following activation, we have endeavored, when carrying out the analyses, to concentrate on strictly physical methods, minimizing chemical treatments.

I. IRRADIATION SOURCES

Source of Neutrons

We used "Zöe," the first French reactor, with fluxes varying from 2.8×10^9 to 2.8×10^{11} n/cm²/sec. By means of a suitable rabbit, we were able to work on short half-life elements (order of magnitude about ten seconds). The other type sources (RaBe), which are easier to handle, are attractive to a great many laboratories outside the French Atomic Energy Commission. These, however, only give small fluxes of thermal neutrons.† Nevertheless, we endeavored to use them for the determination of short-lived radio-elements (55-sec rhodium). The activities obtained in this manner (30 counts per second from 5 mg of rhodium) are small. In view of this, the statistical errors made in taking the counts are large. The SbBe sources are less costly, but their flux decreases rapidly with time (half-life 60 days).

Sources of High Energy X-rays

With a 24 Mev Allis-Chalmers betatron, the concentration in light elements by the (γ, n) or (γ, p) reaction has been measured. However, the sensitivity of these determinations is not very great; for oxygen, it is 0.1% at best under the conditions which were imposed on us for our work.‡

II. ACTIVATION

Choice of the Mode of Activation

The activity produced in each gram of the element to be determined is proportional to the cross-section of the reaction and the radiation flux. Irradiations by protons and deuterons, affect only the superficial part of the samples (a few mg/cm²). In general, they take place with a change in the atomic number Z, and are of interest if a chemical separation is to follow the irradiation. For sizable samples, only neutron or energetic X-ray irradiation can create relatively uniform activation in the mass of the substance. With samples of this type, two observations are in order:

Neutron Irradiation, Shadow Effect

If the cross section of the element is large, the neutron flux is weaker toward the center of the sample than it is on the surface.[3] This may call for an important correction. We encountered this phenomenon on the occasion of the dosage of rhodium in rhodium-bearing platinum.[4] In that case, the error this brings about may vary between 5 and 10%.

X-ray Irradiation

In voluminous samples, the neutrons from the (γ, n) reactions may in turn bring about a disturbing (n, γ) reaction. Let us take, for instance the dosage for oxygen-15, having a half-life of 2.1 minutes, as given by the (γ, n) reaction. Aluminum-26, produced by the same reaction, has a half-life of only 7 seconds, but the (n, γ) reaction also forms Al^{28} with a half-life of 2.4 minutes, which cannot be distinguished from oxygen.[5] For a 100-gm aluminum sample, this effect generates an activity comparable to that which would be caused by an oxygen content of 0.01%.

Choice of the Irradiation Time

The activity produced also varies, according to irradiation time t, as

$$1 - e^{-0.693 \frac{t}{T_{1/2}}}$$

$T_{1/2}$ being the half-life of the radio-element produced. With t between 0 and $T_{1/2}$, this expression is properly represented, within 10 per cent, by the first term of its development: $0.693\ t/T_{1/2}$.

We are endeavoring to obtain the most favorable activity without any chemical separation of the element to be determined. Let us take, for instance, a radioactive isotope X_1, having a half-life of T_1. Among the other elements formed at the same time, those which have half-lives markedly smaller than T_1 are not disturbing. It is enough to allow them to decay before the measurements are taken. If there appear radio-elements having a half-life longer than T_1, it is clear that the most favorable irradiation time is close to T_1. Indeed, the ratio of the activity of the product of interest to that of others is practically constant up to $t = T_1$. Thereafter, it decreases.

Original language: French.

* Chief of Radioelement Application Section, Physical Chemistry Department, Atomic Energy Commission.

† At a distance 4 cm from a source (RaBe) located at the center of a paraffin cube having a side of 20 cm, the thermal neutron flux is only 8.5×10^4 n/cm²/sec.[1]

‡ Sources of protons and deuterons: the College of France cyclotron was used by Mr. Süe and his colleagues, in particular for the dosage of carbon in steels.[2]

III. MEASUREMENTS

In order to characterize the radioactive isotopes formed, we shall determine their half-lives, beta emission and gamma radiation energy.

The beta detector used is a bell-type counter with a thin window (1.5 mg per cm^2), fed by stabilized high voltage and coupled to a counting scale through a preamplifier.

The gamma radiation detector§ is a hollow crystal of NaI(Tl)¶ coupled to an EMI 6260 photomultiplier. The amplifier is inserted in the circuit at the beginning of detection. The counting device is the same as that used for the bell-type counter.

Measurements of gamma radiation are used more and more. As compared with the detection of beta emission the method has a lower counting efficiency (counts per second per curie) despite better geometry (in the vicinity of 4π), but the self-absorption corrections can more often than not be left aside. There are those who even advocate the use of this device for pure beta emitters by using the bremsstrahlung.[6]

Half-Lives

The decay curves plotted in semi-logarithmic coordinates are interpreted by the conventional method. Analysis is by comparing the sample with known standards.

Beta Energies

The absorption curves obtained by the interposition of aluminum screens between the source and the detector, are analyzed according to the Feather method.[7] Each time the radiation energy measured allowed this to be done, it was assumed that the self-absorption effect was equivalent to that of an aluminum screen having a thickness (in mg/cm^2) equal to half that of the source (in general, 100 mg/cm^2).

By a combination of the absorption and decay curves, it was possible to carry out some interesting simultaneous determinations. Thus, activation by slow neutrons of dysprosium and manganese gives two isotopes which have practically the same half-life (Dy^{165}, 2.5 hr; Mn^{56}, 2.6 hr), but different beta energies (Dy^{165}, several beta, maximum energy 1.25 Mev; Mn, 50% of beta of 2.81 Mev). The decay curves of the samples are plotted without a screen and with a 500 mg/cm^2 screen. Such a screen, allowing for the thickness of the source, stops the beta particles emitted by dysprosium, but lets through 15% of those from manganese. Let A_1 be the activity without a screen, A_2 the activity with a screen, f the ratio of the activities of manganese without and with a screen respectively, determined from a known standard.

Then fA_2 is the activity due to the manganese,** and $A_1 - fA_2$ is that of dysprosium. By this method, we have been able to measure, in a non-activated substrate of 500 mg, 0.02 γ of dysprosium in the presence of 5 γ of manganese with an accuracy of 10% for the manganese and 20% for the dysprosium.

Gamma Energy

Gamma energies are determined by gamma spectrometry. The spectrometer consists of: (*a*) a detecting unit, which consists of one NaI(Tl) crystal 1½ in. × 1 in., an EMI 6260 photomultiplier, and a tube which acts as a "cathode follower"; (*b*) a linear amplifier, broad band (gain: 1000, attenuator from 1 to 1/64, maximum output: 100 volts); (*c*) a single channel selector with a threshold voltage which is a linear function of time—the width of the channel may be: 0–0.5–1–1.5 volts, and a broader channel can be created by the addition of external batteries (this selector can operate as a discriminator); (*d*) a scaler, in which the sensitivities and time constants can be varied; and (*e*) a recording millivoltmeter. A complete spectrum takes about 45 minutes.

This device has been used mostly qualitatively; we can mention, for example, the detection of cerium (gamma of 0.140 Mev) in strontium sources (pure beta emitter); and that of sodium (gamma of 1.4 and 2.8 Mev) in zinc dithiocarbonate (gamma of 0.439 Mev).

Quantitative interpretation of these spectra is more difficult.[8] On the other hand, if the gamma energy differences are large enough, the decay curves can be plotted with the help of the discriminator. It has thus been possible simultaneously to measure 10 γ of sodium (2.8 Mevmax.) and 0.01 γ of europium (1 Mevmax.) in 500 mg of a nonactivable substrate.

IV. SOME ANALYSES

Rare Earths: Dy, Eu, Sm

The average values, for the distribution of the rare earths (Dy 7%, Eu 0.3%, Sm 7%),[9] their activation cross sections (n, γ), and the half-lives obtained (Dy 2.5 hr; Eu 9.2 hr; Sm 47 hr) give reason to hope that the simultaneous dosage of the three elements is possible. This has been confirmed by experience (Fig. 1) on samples containing approximately 0.1 to 0.01γ of these elements. The accuracy is low (20 to 30%) but adequate for the specific cases envisioned. In our analyses, two radioelements were disturbing: sodium (half-life 14.8 hr), which falsifies the determination for europium, and manganese (half-life 2.6 hr) the activity of which is superimposed on that of dysprosium, but which can easily be distinguished from the latter. In order to obtain more accurate results, we were thus led to separate chemically the rare earths by precipitation on cerium hydroxide and, following dissolution of the precipitate and oxidation of the cerium, on lanthanum fluoride. In addition the amounts of dysprosium and yttrium in a xenotime were measured. By comparison with appropriate standards, we determine the two elements simultaneously (0.43% Dy; 20.5% Y; within ± 3%), ensuring a very substantial time gain over current methods.

§ DCS—manufactured by C.E.A.

¶ Diameter and height, 50 mm; central well: diameter 15 mm, depth 35 mm.

** Values corrected for the end of activation period. This is not entirely accurated, for the γ from dysprosium are also counted, but with low efficiency, on the order of 1%.

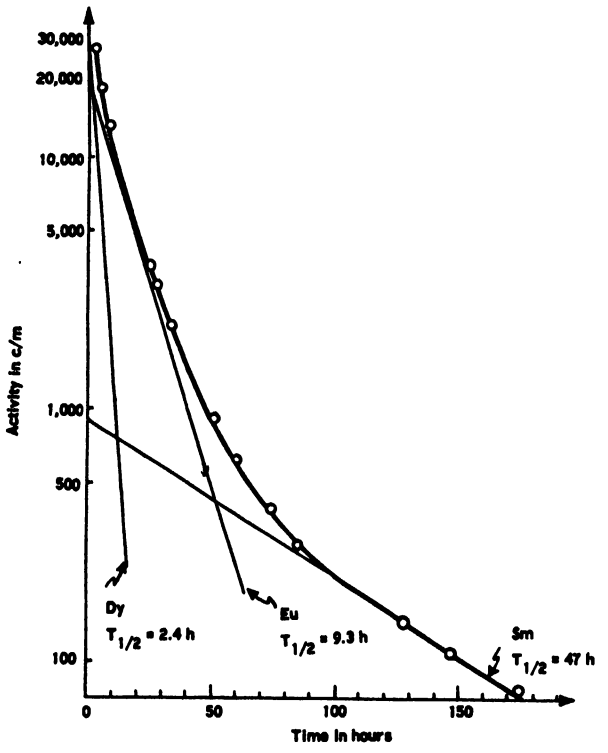

Figure 1. Decay curve for a natural mixture of rare-earths elements

Oxygen

By a (γ, n) reaction, we obtain oxygen-15, having a half-life of 2.1 min. We used the method for the dosage of oxygen in organic matter and in aluminum.[10] With a betatron, as we vary the energy of X-radiation the activation may be selective. In organic compounds, irradiation to 15.6 Mev makes it possible to activate nitrogen alone, at 19 Mev nitrogen and oxygen, and at 24 Mev and over, nitrogen, oxygen and carbon. In general, we have determined only oxygen, the chemical dosage of which is not so frequent as that of carbon or nitrogen (in stearol, stearic acid).

Hafnium

Hafnium, by the (n, γ) reaction, generates hafnium-165, which has a half-life of 19 seconds. By means of a "rabbit," the measurements can be started 30 seconds after the end of the irradiation. A rotary multicontact switch driven by a synchronous motor affords synchronization between the irradiation and the counting. The customary cycle is 10 seconds of counting, with 5 seconds of stoppage.[11] Counting is carried out with a scintillation counter (γ energy of hafnium is 220 kev). Energy discrimination is such that only the 220 kev radiation is counted, excluding the X line due to the excitation of hafnium (60 kev); this is done in order to avoid variations of the counting rate as a function of the density of the samples. The sensitivity of the determination depends on the sodium content of the sample. In our case (about 1% Na) the lower limit of detection is 10 ppm. The precision of the measurements is on the order of $\pm$ 3%.

Fluorine

Fluorine-20, given by the (n, γ) reaction, with a half-life of 12 seconds, is activated and counted under conditions comparable to those we have just described for hafnium. We have thus measured its concentration in various natural and industrial products, and particularly, simultaneously with chlorine, in polymers of chlorotrifluorethylene. The half-lives involved (12 seconds and 35.5 minutes) are different enough to make it possible simultaneously to determine the contents of both halogens, the doses of which (about 49% for fluorine and 31% for chlorine) can be determined within 1%.

V. CONCLUSIONS

The accuracy of the analyses carried out by this method depends, on the one hand, on the activities obtained (statistical counting error), and on the other hand, on possible interferences. Only the statistical errors can be evaluated beforehand. In some series of measurements we had occasion to observe that our errors might run from 1% (a single element present in a 30% concentration), to 20 and 30% (three elements for one and the same decay curve with concentrations of about 10^{-2} ppm). To the extent that this can be done, all samples must be checked by spectrography, in order to check purity of the radio-element detected. Despite these margins for error, the techniques described above revealed themselves to be of quick application and particularly useful in the determination of traces. The fact that in most instances they do not require any chemical processing is particularly to be appreciated when the samples are sparingly soluble (fluorinated plastics, minerals, refractory oxides, etc.).

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Investigations of Diffusion and Atomic Interaction in Alloys with the Aid of Radioactive Isotopes

By G. V. Kurdiumov, USSR

In recent years the investigation of diffusion with the aid of radioactive tracers has been developed in the USSR along two main lines: determination of atomic mobilities in solid solutions and study of the influence of alloying elements on the different properties of alloys. The mobility of the solvent atoms is one of the main factors determining the kinetics of structural changes occurring in solid solutions and their behaviour under stress and at high temperatures. Adding alloying elements leads to changes in atomic interactions and hence in the properties of the alloys. The study of the influence of alloying elements on the temperature dependence of the diffusion and self-diffusion coefficients makes it possible to elucidate the changes in the interatomic binding in solid solutions. At the same time the diffusion and self-diffusion coefficients are direct quantitative characteristics of atomic mobilities in alloys of various compositions.

The use of artificial radioactive isotopes in physical metallurgy permitted direct determination of the diffusion coefficient of the elements, constituting the alloy base. The speed of the diffusion measurements has been greatly increased.

A. M. Zagrubsky in a pioneer work used artificial radioactive isotopes for the investigation of the self-diffusion of gold. His paper was published as early as 1937.[1]

The use of radioisotopes has also played a significant role in the extension of the study of atomic interactions in solid solutions by means of vapour pressure measurements over solid and liquid solutions.

The present report summarizes a number of investigations carried out in the USSR with the aid of radioactive tracers on the above mentioned lines.

METHODS

As the measurement of the diffusion coefficient usually requires measurement of the concentration change with the depth of the diffusion layer, the use of radioisotopes has the advantage that it permits determination of very minute concentrations of the diffusing substance.

In the work on self-diffusion and diffusion summarized below wide use has been made of the integral radioactivity method.[2-5] The substance to be investigated is mixed with the radioactive isotope and is deposited on the surface of the specimen from which it penetrates into the layers below. Thin layers are consecutively taken off the specimen (by mechanical means in most cases). Then the intensity of radioactive radiation of the specimen is measured. This method is quite appropriate for various materials, particularly firebrick.[3]

The use of electropolishing for the removal of thin layers about 5 μ thick and determination of the radioactivity of the dissolved substance makes it possible to measure the diffusion coefficients with a higher degree of accuracy.[6]

The advantages of the use of radioactive isotopes are most fully realized in non-destructive methods, involving determination of the change of activity of the specimen as a whole;[7] these methods may be termed absorption methods. Of particular interest are those absorption methods which utilize β-activity and do not require knowledge of the β-radiation absorption coefficient.

One of the methods that fulfill this requirement is described elsewhere.[8] It consists of measuring the change of intensity of the β-radiation from the two sides of a thin plate (about 0.1 mm thick). The experimental data may be used to determine the coefficient of diffusion by the following formula, which does not include the absorption coefficient:

$$\ln \frac{I_1 - I_2}{I_1 + I_2} = k - \frac{\pi^2 \cdot D}{l^2} t \qquad (1)$$

where I_1 and I_2 are the radiation from sides of the specimen at the moment t, l is the thickness of the specimen, and D is the diffusion coefficient.

The method suggested in reference 9 does not require knowledge of the absorption coefficient either; it permits determination of small values of D and does not require long annealing.

This method is based on the fact that diffusion goes on much faster in the deposited layer than within the specimen. The activity change in the deposited layer in the course of annealing is measured. Fick's differential equation is solved, according to the conditions of experiment.

The third method[10] is based on the fact that the β-activity of the surface of the specimen after the radioactive layer has been deposited and the diffusion has penetrated deep enough, i.e. after a long annealing, obeys the following relation:

$$l = \frac{K}{\sqrt{Dt}} \qquad (2)$$

Original language: Russian.

where K is determined from the activity (I^{∞}) on the surface of a thick layer, containing an uniformly distributed radioactive isotope. The method consists of the measuring of I^{∞} and of the β-activity as a function of time.

The fourth method which may be termed "the imprint method,"[11] makes use of a relation analogous to Equation 2:

$$c = \frac{q}{\sqrt{\pi Dt}} \tag{3}$$

which determines the concentration of substance on the surface of the specimen as a result of diffusion into the specimen, when the amount of the substance initially deposited on the surface is q. In this method the concentration c is measured by counting the number of β-pulses from "imprints" on filter paper obtained by contact electrolytic solution of a very thin layer of the specimen.

Equipment has been developed for the measurement of vapour pressures at high temperatures by the method of outflow of metal vapours through a narrow orifice, with the use of radioactive isotopes.[12, 13, 16]

The method of evaporation from a free surface and measurement of the amount of evaporated substance has been employed[14] for the determination of the vapor pressure of melted solutions up to 2000°C.

Methods made possible only by the use of radioactive isotopes have also been suggested for the determination of thermodynamical characteristics.[15, 40] The experimental procedure implies the measurement of the atom exchange between two samples of the alloy; both samples, the donor and the acceptor, are kept at the same temperature.

RESULTS OF EXPERIMENTS

1. Influence of the Alloying Elements on the Self-Diffusion of Iron

The temperature dependence of the coefficient of diffusion of iron in iron-base solid solutions has been studied by a number of investigators. The temperature dependence of the diffusion coefficient is expressed by the formula $D = D_0 e^{-Q/RT}$; therefore, to characterize the effect of the alloying elements on self-diffusion, it is necessary to ascertain their influence on the energy of activation Q and the pre-exponential factor D_0.

The influence of carbon on the self-diffusion of iron in austenite has been studied.[17] It was shown that the presence of carbon in the solid solution increases the mobility of the iron atoms at temperatures that are of particular interest for practical purposes; at the same time the energy of activation for the diffusion decreases markedly.

The dependence of the diffusion coefficient on the temperature and the carbon content can be represented by the formula

$$D = 10^{-c} \cdot e^{-\frac{69000-7000c}{RT}} \tag{4}$$

where c is the carbon concentration in atomic per cent. The dependence of D_0 and Q on c is shown in Fig. 1.

From the decrease of Q with increase in the carbon content it may be concluded that in the presence of carbon the interatomic bonds in the γ-iron crystals grow weaker. This conclusion conforms with the results of an X-ray study of atomic oscillations in the martensite crystal-lattice; this investigation has shown that the interatomic forces in the α-crystals decrease as the carbon content in the solid solution increases.[18, 19]

The fact that the activation energy for the diffusion of iron is reduced when the carbon concentration in the γ-solid solution increases, has also been established in an investigation on the diffusion of iron in ternary iron-nickel-carbon alloys containing 20% and 25% Ni but different amounts of carbon.[20]

The influence of different amounts of chromium, nickel and manganese on the self-diffusion of iron in austenite was also investigated. It was shown that chromium considerably increases the activation energy.[21] As the Ni content in the solid solution increases the value of Q rises at first, reaching 79 kcal/gram-atom with 25% Ni and then falls again.[20] Manganese acts in a similar way;[22] it reaches its highest value of 98 kcal/gram-atom with 4% Mn.

There are data concerning the influence of a third substance on the diffusion of iron in an iron-nickel alloy containing 24% Ni.[41] It has been found that the introduction of as little as 2–3% titanium, niobium and molybdenum greatly increases the activation energy, whereas 2.5 and 5% vanadium cause a considerable decrease. Chromium causes a marked increase of Q in an alloy with 25% Ni if its content exceeds 5%.

In the course of an investigation of the self-diffusion of iron in the α-phase it was found that chromium increases the activation energy.[9] This result conforms with the evidence obtained from an analysis of the thermal factor in X-ray scat-

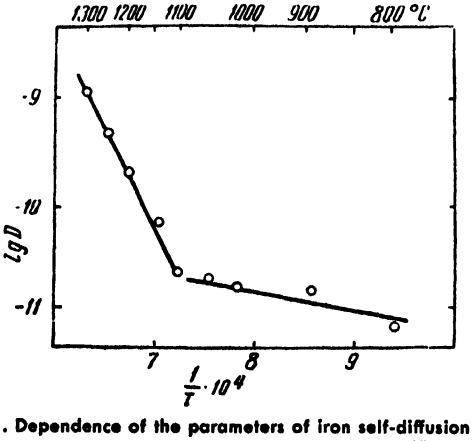

Figure 1. Dependence of the parameters of iron self-diffusion on the carbon content (in at %) in austenite[17]

tering. These data show an increase in the binding forces in α-iron when the latter is alloyed with chromium.[24]

2. The Influence of the Grain Substructure of Metals on Diffusion

In the course of an investigation of the diffusion of iron in iron-nickel-carbon and iron-manganese alloys it was found[20, 22] that within the temperature range 1050–1150°C a break occurs in the linearity of the ln D versus $1/T$ curve (Fig. 2).

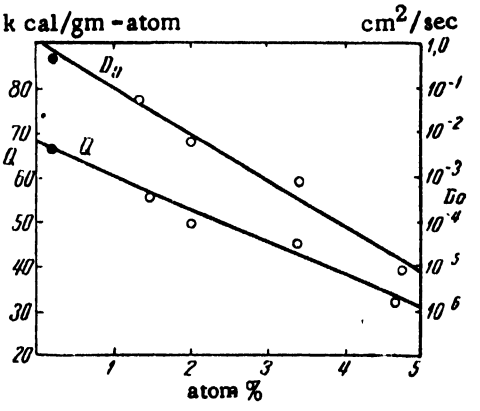

Figure 2. Temperature dependence of iron in the alloy iron-nickel (20%)—carbon (0.2%)[20]

Direct experiments have shown this break to be connected with the $\gamma \rightleftharpoons \alpha$ transformation occurring in these alloys.[25] To this end an alloy was chosen whose martensite transformation takes place below room temperatures. The break in the linearity of the curve occurred only when the alloy was preliminarily cooled in liquid nitrogen, i.e., when the $\gamma \rightarrow \alpha$ transformation took place (Fig. 3). As a result of the martensite transformation on cooling and of the reverse $\alpha \rightarrow \gamma$ transformation which occurs during the subsequent heating to the temperature of diffusion annealing, new boundaries appear inside the austenite grain; these new boundaries disturb the regularity of the austenite crystal structure which causes an increase in the diffusion coefficient in comparison with specimens not subjected to cooling in nitrogen.

Only at temperatures exceeding 1000°C are the structural disturbances provoked by the phase transformations removed. These changes in grain substructure, as established elsewhere,[26] also cause changes in the other properties of austenite.

In reference 22 the variation in the dependence of the logarithm of the activity on the depth of the layer at high ($> 1150°$) and low ($< 1150°$) temperatures was found: log I is proportional to the square of the penetration depth x. The relation $\log I = k.x$ is fulfilled only at temperatures below the break-point of the plot $\log D = f(1/T)$, where the contribution of the surface diffusion reaches its maximum. This fact made it possible to calculate with the aid of the formula derived in reference 27 the diffusion coefficient for the grain substructure boundaries.

Thus, at temperatures below the break-point on the plot $\log D = f(1/T)$ the main contribution to the over-all diffusion current is made by the grain boundary diffusion, and above this point by the volume diffusions. The break in the linear plot should occur both when the boundary length remains constant at all temperatures and when it reduces upon annealing. As shown elsewhere[28] long annealing of the austenite in the case of iron-nickel-carbon alloys at 800–1000° after a $\gamma \rightleftharpoons \alpha$ transformation, results in the recovery of the grain substructure, i.e. the gradual disappearance of substructure boundaries. This follows from the fact that the diffusion coefficients after long annealing gradually approach the initial values characteristic of austenite prior to the transformation. Determination of the time needed to reach an equal degree of recovery made it possible to find the activation energy for the recovery of the grain substructure. For an iron-nickel-carbon alloy with 24% Ni and 0.9% C this energy is 45.6 kcal/gram-atom, as compared with 58 kcal/gram-atom for the activation energy of volume diffusion in the same alloy.

These investigations have shown that alloys possessing a martensitic transformation below room temperature are appropriate for the study of grain boundary diffusion as well as of the influence of different factors thereon.

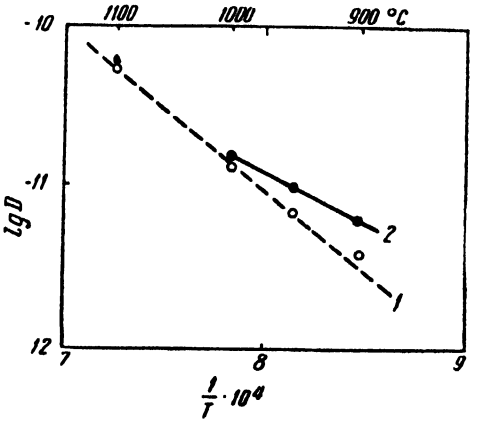

Figure 3. Temperature dependence of the diffusion coefficient of iron in the alloy iron-nickel (20%)—carbon (0.45%): (1) without cooling in liquid nitrogen, (2) after cooling in liquid nitrogen[25]

In the course of an investigation of the diffusion of some substances in γ-iron and in plain carbon steel with the aid of radioactive tracers,[38] it was established that anomalous temperature dependence is caused not only by martensitic transformations. The same effect is observed in the case of $\gamma \rightleftharpoons \alpha$ transformations in pure iron and with the eutectoid transformation in austenite. Figure 4 represents the results of the determinations of the chromium, cobalt and tungsten diffusion coefficients in an eutectoid steel. At temperatures below 1000°C the experimental values of the diffusion coefficients are much higher than the values obtained by extrapolating the straight line representing the temperature dependence of the diffusion coefficient above 1100°.

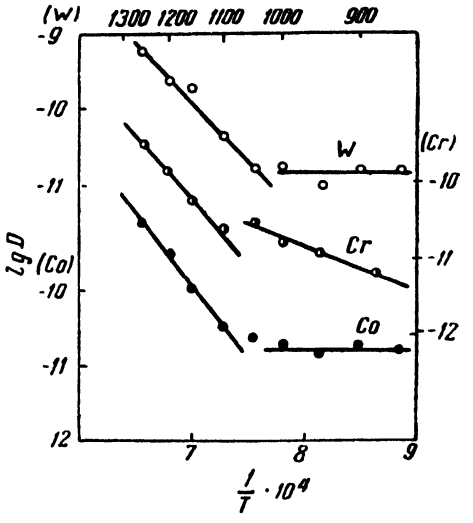

Figure 4. Temperature dependence of the diffusion coefficients of tungsten, chromium and cobalt in plain carbon steel with 0.8% C[38]; each element has its own scale log D

Notwithstanding the growth of the atomic mobilities with increasing temperature, a simultaneous change of the austenite subgrain structure results in the effective diffusion coefficient remaining constant within the temperature range 800–1000°.

It may be assumed that this is due to the large boundary surface produced by transformations and disappearing only at temperatures exceeding 1000°. A study of chromium, cobalt and tungsten diffusion in pure iron[38] showed a picture similar to that presented in Fig. 4.

The data thus obtained show that in measuring diffusion coefficients the possibility of inconsistent values as a result of structural changes caused by phase transformations must be taken into consideration.

3. Diffusion in Non-Ferrous Alloys

Radioactive isotopes have been used also for the study of the diffusion of various substances in nonferrous alloys.

Investigation of the diffusion of silver in solid solutions of aluminum in silver and silver in aluminum is reported elsewhere.[29] It has been established that the activation energy for the self-diffusion of silver is reduced when alloyed with aluminum from 45.4 kcal/gram-atom for pure silver to 31.2 kcal/gram-atom for an alloy containing 7.6 atomic per cent Al. The data obtained permit the assumption that the addition of aluminum to silver reduces the interatomic binding in the lattice of the silver. The authors attribute this effect of aluminum to the increase of the number of conductivity electrons in the solid solution as the concentration of aluminum rises. Examination of the temperature dependence of the shear modulus for the same alloys shows that the modulus decreases as the aluminum concentration in the solid solution grows. These data corroborate the suggestion as to the decrease of the interatomic binding.

Investigation of the diffusion of silver in gold-silver alloys[39] containing 25 and 50 at.%, showed that the temperature dependence of the diffusion coefficient differs above and below 800°. At higher temperatures the activation energy for silver diffusion in an alloy containing 25% Ag is 49.7 kcal/gram-atom at lower temperatures $Q = 43.3$ kcal/gram-atom. Any alloy containing 50% Ag behaves in a similar way. Theoretical analysis of the diffusion process and examination of experimental data led the authors to the conclusion that the break on the plot log D versus $1/T$ can be explained in this case by assuming the existence of two mechanisms: self-diffusion of silver in pure silver and inter-diffusion, i.e., site interchange between silver and gold. The first mechanism has a higher activation energy and therefore prevails at higher temperatures, the second prevails at lower temperatures. Similar results were obtained in the investigation of the self-diffusion of silver in silver-tin alloys.[39]

Data on the influence of the alloying elements on the self-diffusion of cobalt are given elsewhere.[30] The additional of nickel to cobalt raises the activation energy of self-diffusion of cobalt from 62 kcal/gram-atom (pure Co) to 88 kcal/gram atom (alloy containing 4.5% Ni). Further increase of the nickel concentration in the solid solution leads to a decrease in the activation energy. The activation energy of self diffusion of cobalt increases considerably if it is alloyed with chromium[30] or aluminum.[42]

In cobalt-base alloys a break was also discovered on the straight lines representing the plot log D versus $1/T$; in this case it appears at a temperature in the vicinity of 1150°C. A certain increase in the diffusion coefficient below the break-point temperature is probably also due to diffusion along the grain substructure boundaries; these arise as a result of phase transformations occurring when the alloys are cooled down to room temperature and then heated to the temperature of diffusion annealing. In this case the disturbance of the grain substructure provoked by the transformation disappears completely only when heated above 1150°.

The diffusion of chromium in pure nickel and in nickel-base alloys was also studied.[31] The addition of 20% Cr to the nickel raises the activation energy for chromium diffusion from 48 to 58 kcal/gram-atom; subsequent alloying with 2.5% Ti and 0.5% Al leads to a further increase of the activation energy for chromium diffusion up to 66 kcal/gram-atom. These data show that the interatomic binding in a nickel-base solid solution is strengthened when alloyed with chromium, titanium and aluminum; they corroborate the evidence obtained in an X-ray study of the influence exerted by these elements on the interatomic binding in the lattice of nickel.[32] In this latter investigation it was established that adding chromium, aluminum and titanium to nickel decreases the mean square thermal displacements of the atoms and increases the Debye characteristic temperature of the alloy.

SOME REGULARITIES OF SELF-DIFFUSION AND DIFFUSION IN SOLID SOLUTIONS

Study of the self-diffusion of iron in austenitic iron-carbon and iron-nickel-carbon alloys leads to the conclusion that the activation energy Q for iron depends linearly on the iron concentration, whereas the factor D_0 depends on the concentration exponentially.[17, 20] From this it follows that both diffusion characteristics are linked together by the relation

$$D_0 = D_0' e^{\alpha Q} \qquad (5)$$

An examination of the relationship between D_0 and Q for many iron-cobalt- or nickel-base alloys shows that as a rule the experimental points fall on the straight-line plot log D_0 versus Q. Figure 5 presents data for iron- and cobalt-base alloys respectively.[23] The D_0' and α values remain approximately constant for all the investigated solid solutions with face-centered cubic lattices. This is an indication of the similarity of the mechanisms of self-diffusion and diffusion in these alloys. Examination of the dependence of the self-diffusion activation energy on the concentration of alloying elements makes it possible to judge of their influence on the interatomic binding of solid solution lattices and intermetallic compounds.

For a number of pure metals with fcc lattices the activation energy equals approximately 0.67 E where E is the heat of sublimation. If this is taken into consideration it may be concluded from the activation energy values for the diffusion of iron in austenite that the binding energies in austenite decrease with increase of the carbon content.[17] This conclusion seemed doubtful in the absence of direct experimental evidence on the relationship between Q and E for solid solutions; but investigation of the iron vapour pressure over austenite with the aid of radioactive Fe^{59} confirmed this suggestion. The heat of sublimation of iron falls from 103.5 kcal/gram atom for pure iron to 55 kcal/gram atom for steel containing 1% C and to 43.5 kcal/gram atom for steel containing 1.3% C, and in this case the ratio Q/E is again approximately equal to 0.67.[13] Experimental data on the temperature dependence of the vapour pressure for iron and steel with 1.3 weight per cent of carbon or 5.8 atomic per cent, are presented in Fig. 6. Measurements by the same method of cobalt sublimation heat gave the value 95 kcal/gram atom, and the relation Q/E was again found to equal about 0.67.[13]

The data on the relationship between Q and E for austenite show that the diffusion activation energy can be considered as a measure of the interatomic binding of solid solutions as well.

The dependence of D_0 on E makes it clear that both quantities determining the diffusion coefficient temperature dependence are in their turn functions of the binding energy. From a theoretical analysis it follows that D_0 is also related not only to the binding energy but to its derivatives with respect to the interatomic distance. Thus, parameters of self-diffusion and diffusion can indeed characterize the interatomic binding of solid metallic phases.

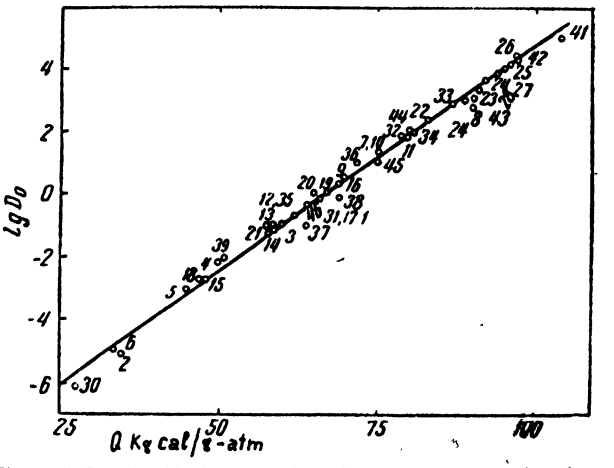

Figure 5. Relationship between the diffusion parameters of various elements in iron- or cobalt-base alloys[23]; D_0 is given in cm^2-sec

From the dependence of the activation energy of self-diffusion and diffusion on the content of alloying elements in binary, ternary and more complicated systems, conclusions can be drawn as to the influence of these elements on the binding in solid solutions and intermetallic compounds. The above mentioned experiments show that adding alloying elements can either increase or decrease the interatomic binding. In a number of systems Q does not change monotonously with the composition of the solid solution: it first grows with concentration and then falls. Thus, it is reasonable to increase the alloying element content only to a definite limit in order to raise the interatomic binding strength. Diffusion parameter data can serve as the basis for the selection of the optimum content of alloying elements in solid solutions.

Data on the influence exerted by aluminum on the self-diffusion of silver led the authors of reference 29 to the conclusion that increase of the concentration of valence electrons with atoms having filled electron d-shells causes a decrease in interatomic binding. This conclusion conforms with the experi-

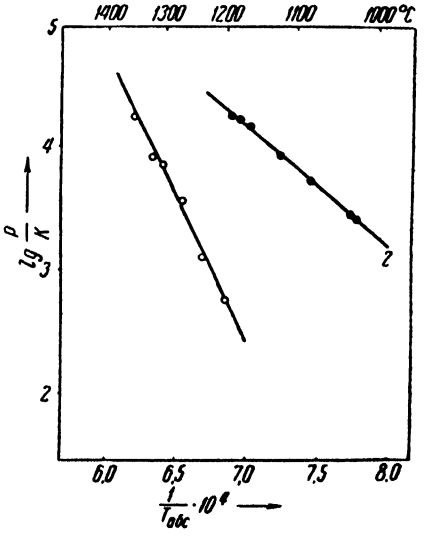

Figure 6. Temperature dependence of the vapour pressure P for iron (1), and steel with 1.3% C (2); the constant K depends on the conditions of experiment and is different for curves 1 and 2[12]

mental results on the dependence of elastic moduli on the concentration of valence electrons in silver- or copper-base alloys.[29, 35]

The majority of iron-, cobalt- or nickel-base solid solutions show an increase in the self-diffusion activation energy and consequently an increase in the interatomic binding. Such behaviour is apparently due to a more intimate electron interaction, unfilled third states being existent in this case. There are reasons to assume the formation of an additional ionic bond and of a definite short-range order in the lattice.[34] However, in order to find an unambiguous answer as to the causes of binding changes, it is necessary to have direct experimental evidence concerning the electron density distribution in alloys.

The data on changes in atomic binding obtained by diffusion studies are in conformity with estimations of the interatomic binding in solid solution lattices based on the investigation of atomic thermal oscillations with the aid of X-rays[19, 24, 32, 36] where the mean-square displacements from equilibrium positions are determined.

Investigations of diffusion in solid solutions undergoing phase transformations reveal the great role of subgrain structure in the diffusional displacement of atoms. The resulting effects of phase transformations occurring at relatively low temperatures are not removed immediately upon transition to the high-temperature phase. In order to abolish these effects it is necessary to heat the alloy to a sufficiently high temperature (e.g., for iron-, nickel- or cobalt-base alloys to 1100–1150°C). Failure to take the influence of the subgrain structure into consideration may lead to wrong results in the determination of the diffusion parameters of an alloy.

To obtain unambiguous data on the temperature dependence of the diffusion rate for a given alloy, it is necessary to measure the diffusion coefficients at sufficiently high temperatures, where boundary diffusion does not exert any marked influence.

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Distribution and Diffusion of Components in Metal Alloys Studied by the Autoradiographic Method

By S. T. Kishkin and S. Z. Bokstein, USSR

I. INTRODUCTION

To characterize the structure of alloys and the processes taking place in them, metallophysics at the present time uses extensively the results of average statistical measurements: the mean composition of the alloy, the mean value of the crystal lattice parameter, the mean value of the interatomic bond, the mean diffusion coefficient, etc.

A real solid solution unlike a liquid one is not an equilibrium system. This is reflected primarily in the inhomogeneity of its structure. Therefore the local distribution of the elements within the phase is the most important characteristic of the alloy.

This characteristic determines most of the thermodynamic properties of a real solid body and especially the course of the processes depending upon the mobility of atoms.

Naturally, the theory of alloying, the theory of the kinetics of various phase transformations are based on data on the distribution of the elements in the alloy. The strength and plasticity of real solid bodies likewise depend substantially upon the mode of distribution. The destruction of metals and alloys, especially at high temperatures, occurs either through plastic flow or through the formation and development of crevices (brittle fracture in microvolumes of the alloy). In both cases the diffusion mobility of the components, which is a structurally sensitive property, and the local structure of the alloy, are of great importance.

The method of autoradiography opens up broad possibilities of obtaining information about local distribution and local mobility. Autoradiography is being widely applied to the study of metal structure both in the Soviet Union and abroad.[1-8] The present paper summarizes some of the results obtained in developing and applying this method to the study of the local distribution and mobility of a number of elements in alloys.

II. METHODS OF INVESTIGATION

Quantitative and Qualitative Radiographic Techniques

The idea of the method is simple and is based on the effect of radioactive radiation upon a photographic emulsion. To study the distribution of elements, a small quantity of a radioactive substance is introduced into the alloy being investigated. A thin section of the alloy specimen is prepared. Upon contact with the emulsion on the photographic plate, the thin section, after exposure and development, produces a mirror image of the distribution of the radioactive element in the alloy. Necessary conditions for obtaining satisfactory results are: close and uniform contact between specimen and the photographic emulsion; use of thin specimens (20–25 microns) of the metal; use of special photographic emulsions sensitive to nuclear radiation, thin, fine-grained, and containing a high percentage of silver halide; due consideration for the character and energy of the radiation (for determining the amount of the radioactive tracers introduced into the alloy and the exposure time).

The procedure of melting alloys is usual. The radioactive tracers introduced into the molten metal or the charge must be in a condition in which it is easily assimilated by the metal. If the isotope, for example, is in the form of an oxide, it must primarily, or in the course of the melting, be reduced to the metallic state. Radioactive carbon in the form of $BaCO_3$ is introduced into an iron alloy by first cementing iron specimens in the above compound.

The required specific activity of the alloy depends on the purpose of the investigation and the character of the radiation. For β-emitters a sufficient activity in many cases is 1–5 mc per 1 kg of the alloy; for the radiation, say, of Cr^{51}, the activity should be considerably higher.

The thin sections are prepared by cutting from the ingot plates, which are 3–4 mm thick; they are planed to a thickness of 2 mm and further ground (in the case of non-magnetic materials, with the aid of a special fixture) to 0.1–0.07 mm. Finishing to the desired thickness of 20–25 microns is accomplished by grinding between two parallel glass plates using very fine abrasive powders and paste.

In using low-energy radioisotopes it is often unnecessary to prepare thin specimens, since the soft radiation is absorbed in the specimen and it is practically the outer surface layers only that emit. For instance, radioactive carbon C^{14} yields β-particles with an energy of 0.155 Mev, which are completely absorbed by a layer of iron 38 microns thick.

Original language: Russian.

NIKFI photographic plates for radiography were employed. An amidol developer was used. Exposures were taken in a dessicator at 3–5°C, which decreases regression and prevents corrosion of the metal specimens. If the metal being investigated exerts a chemical action upon the emulsion, the specimens should be covered with a very thin protective film before exposure. For this purpose the authors employed nitrovarnish dissolved in a special solvent; the thickness of the film thus obtained was below 1 micron.

In definite experimental conditions it is possible to obtain sufficiently clear autoradiographs. The use of a common metallographic microscope with an illuminator for transmitted light provides magnification of 100 diameters and higher (up to 300).

The development of autoradiographic techniques is essential for a quantitative assessment of the chemical inhomogeneity of alloys.

For the purpose of quantitative autoradiography we developed the contact method, which entails a densitometric study of the autoradiograph to evaluate the content of an element. In this case it is necessary to establish the relation between the density of the photographic emulsion after exposure to radiation and the amount of the radioactive substance in the alloy.

The sensitivity of the photographic emulsion to radioactive emission, just as to visible light, may be characterized by densitometric curves (characteristic curves), which define the dependence of the density S upon the exposure It, where I is the emission intensity and t is the time. It is convenient to study the rectilinear section of the curve.

Characteristic curves for a given isotope and photographic emulsion may be obtained by using standard specimens differing in the content of the element being studied and, accordingly, in its activity. The standards must satisfy certain requirements, specifically their composition must correspond to the composition of the alloy being studied, the thickness, to the thickness of the sample (to exclude the effects of self-absorption and reflection); moreover, the element being studied must be distributed in the standard sufficiently homogeneously. It is very important to keep the constant conditions of the photographic process.

It was in accordance with these conditions that characteristic curves were plotted for the NIKFI special photographic emulsion and the radioisotope W^{185} ($E_\beta = 0.43$ Mev; half-life, 73 days). The alloy chosen for investigation was a solid solution of tungsten in nickel with a maximum tungsten content of 3.2 per cent. To obtain a series of alloys of varying tungsten content (0.01–0.05–1.2 and 3.2%), part of the alloy, after the melting of the metal (nickel + radioactive tungsten with a carrier), was poured into the mold and the rest was diluted with the nickel introduced. In these conditions every consecutive alloy differed from the preceding one by a lower concentration and, consequently, a lower

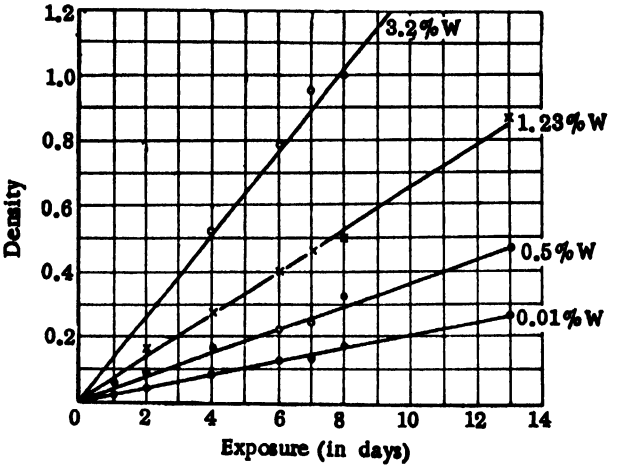

Figure 1. Characteristic curves

activity of the tungsten. To obtain greater homogeneity, part of the liquid metal of each alloy was cooled in water.

Autoradiographs of specimens 50 microns thick were taken simultaneously on one photographic plate with exposures ranging from 1 to 13 days.

The autoradiographic contact prints exhibit a distinct decrease in density corresponding to a decrease of the tungsten concentration in the alloy. The densitometric study of the prints was carried out with a recording microphotometer at a magnification of 30 diameters.

The precision of the density readings within the range of 0–1.2 equals 0.1 per cent. No density fluctuations connected with the grain size of the emulsion were in our case observed, since the surface area being investigated considerably exceeds the grain size of the emulsion used. To lower the effect of regression, the exposures were taken in desiccators at a temperature of 3–5°C.

An approximate calculation showed the experimental error to be 12%. An experimental check of reproducibility yielded a precision of 10%.

An analysis of the characteristic curves obtained showed that within the studied density intervals the experimentally found points, irrespective of the tungsten concentration, conform satisfactorily with straight lines (Fig. 1).

A more rigorous application of the method of quantitative radiography requires an experimental verification of the validity of the interchangeability law, under which the effect of darkening is determined by the product of the intensity and exposure time (It), with due consideration given to the effects of absorption and reflection.

Procedure for Investigating Grain Boundary and Volume Diffusion

An analysis of the state of affairs as far as the structure of the grain boundaries and the diffusion mechanism are concerned prompts the conclusion that the atoms at the interface of two crystals enjoy an increased mobility. The vacuum evaporation

method has indeed demonstrated an increase in mobility with a decrease in grain size.[9]

This method, however, is indirect and yields average statistical results. The preferential movement of elements in many cases along the grain boundaries has been qualitatively demonstrated by means of metallographic analysis and by means of autoradiography in the case of the self-diffusion of tin.[12] G. V. Kurdiumov and co-workers[13] have shown the effect of intragranular structure on the self-diffusion of iron. Interesting data have been obtained by R. Smoluchowski and co-workers[14, 15] in studying the rate of diffusion along grain boundaries as a function of the relative orientation of two neighbouring grains. They established that at definite angles of orientation there takes place anisotropy of diffusion.

At the same time there has been no experimental technique up to now for the separate determination of the parameters of volume diffusion and grain boundary diffusion. The original calculation of J. Fischer[16] suggested for this involves an experimentally undetermined quantity (the effective grain-boundary area) and the boundary itself is treated as a homogeneous plate, which, evidently, corresponds to the real physical state only at considerable angles of the relative orientation of two neighbouring grains.

Since autoradiography provides a direct method of determining the mode of distribution of the element, the use of this method makes it possible to trace the real paths of travel of elements in the alloy. Unlike conventional techniques, this method permits the determination not of the mean diffusion parameter, but of the actual coefficients of diffusion in microvolumes of the alloy.

The following method was developed for the separate determination of mobility in the volume and along the grain boundaries. A thin film of the radioactive substance, the diffusion of which was the object of study, was deposited electrolytically on the alloy specimen being investigated.

The specimen was diffusion-annealed at an appropriate temperature and sectioned at a small angle across the active surface. A densitometric study of the autoradiograph of the sectioned surface makes it possible to find the dependence of the density upon the depth of penetration. If the photometric determinations are taken on the linear section of a characteristic curve, there is always a direct dependence between the photographic density S and the radiation intensity I and, hence, between the density and the concentration of active substance C.

In this way the photometric curve makes it possible to establish the dependence of concentration upon the diffusion distance, i.e., the initial experimental data necessary for computing the diffusion parameters.

The solution of the diffusion equation for the given boundary conditions used by G. Gatos and others, will be expressed by the relationship

$$C = \frac{C_0}{2\sqrt{\pi Dt}} \cdot e^{-X^2/4Dt}$$

where C is the concentration of the diffusing element, X is the diffusion distance, t is the diffusion time, D is the diffusion coefficient, and C_0 is a constant.

There is a linear dependence between the quantity log C, or in our case the logarithm of the photographic density log S, and the square of the diffusion distance X^2. The tangent of the angle of inclination is rectangular:

$$\tan \alpha = \frac{-0.1086}{Dt}, \text{ from which}$$

$$D = \frac{-0.1086}{\tan \alpha t}$$

The method proposed herein for calculating the boundary and volume diffusion coefficients is only a rough approximation, since these processes are regarded as being independent. The authors did not perform a calculation on the basis of Fischer's theory, since a more strict method of calculation is at present being evolved in collaboration with the Institute of Steel.*

The experimental procedure for studying volume and boundary diffusion is shown in Fig. 2.

II. RESULTS AND DISCUSSION

Distribution of Elements in Alloys

A substantial factor in employing the new method is the checking of results by means of some other reliable method. Accordingly, autoradiographic data were compared, wherever possible, with data of metallographic analysis.

Figure 3 gives a comparison of the microstructure of cast steel (0.33% C) and an autoradiograph of the same specimen area under the same magnification (×100). The autoradiograph and the metallographic structure can be matched completely. (The radioisotope C^{14} was used).

Good agreement was also observed in other cases.

The method makes it possible to detect the concentration of this or that element in various phases of multi-component systems.

Phase and Structural Inhomogeneity

The use of autoradiographic techniques to study the distribution of elements and impurities in iron and nickel alloys has pointed to a marked chemical inhomogeneity within a single phase and separate structural elements. The non-uniform distribution of an impurity can be detected at concentrations as low as thousandths of a per cent.

If the content of the element is far from saturation, a preferential concentration of the element is

* This method is being evolved by A. A. Zhukhovitsky, Y. A. Shreider, B. S. Bokstein, I. A. Magidson and I. L. Svetlov.

observed in the grain volume or along grain boundaries, in axes of dendrites or in interdendritic regions. In nickel, for example, alloying elements such as molybdenum, niobium, zirconium and titanium, as well as tin, sulphur, phosphorus, antimony and cerium impurities are present on the grain boundaries and in interdendritic regions. Iron and tungsten are found within grains (Fig. 4).

The distribution of alloying elements in a solid solution may be represented in some instance by a curve (Fig. 5).

For instance, for an average 3.2% content of tungsten in nickel (maximum solubility ~ 30%) there are regions impoverished to 2.3% and others enriched to 4.8% tungsten. The degree of inhomogeneity obviously increases with the decrease in the size of the region being investigated. Non-uniform distribution of alloying elements is observed within a single grain and a separate dendrite. Thus, for a solid solution of tungsten in nickel, radiometric analysis of the chemical composition yielded the following data: in the first order axis, 4.8% tungsten, in the second order, 4.1%, and in the interdendritic regions, 2.5%.

An increased content of elements is observed in the sites of joint of several grains.

It is noteworthy that non-uniformity of a composition may occur at very low impurity concentration. The solubility of niobium in nickel at room temperature is below 6%, but the presence of niobium in the

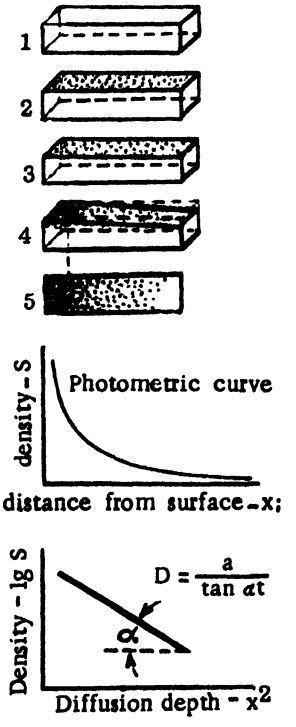

Figure 2. Experimental procedure for determining diffusion parameters by contact autoradiography: (1) initial specimen; (2) coating of diffusing substance; (3) diffusion annealing; (4) slanted section; (5) contact autoradiograph; (6) photometric curve (distance from surface, x; density–s); and (7) concentration dependence, $D = a/\tan \alpha t$; diffusion depth, x^2; density, log S

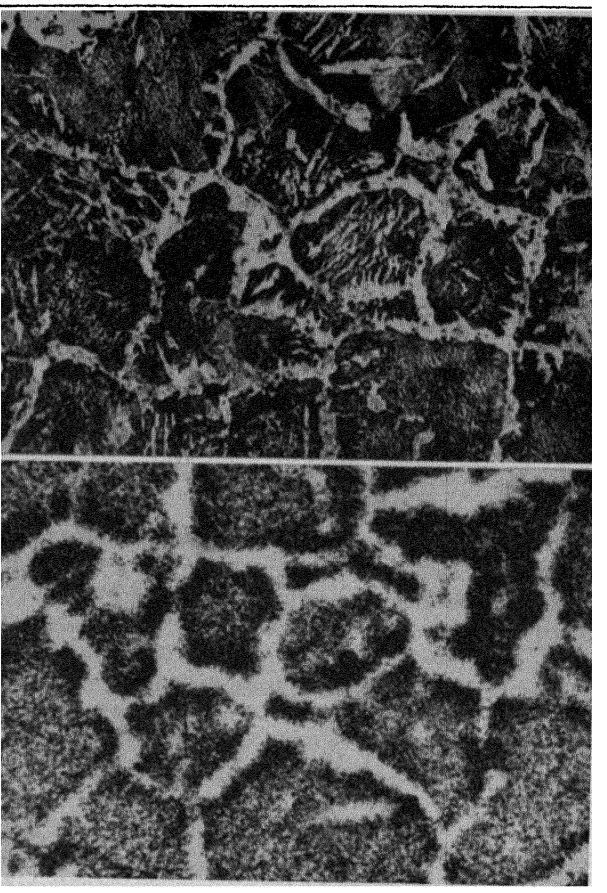

Figure 3. Cast steel, 0.33% C: (a) microstructure, × 100; and (b) autoradiograph, × 100

alloy in the amount of only 0.007% produces a marked enrichment of grain boundaries, where the content is 32% higher than within the grain (Fig. 6). Micro-densitometric analysis of a solid solution of iron in nickel revealed a minimum density and, accordingly, a 20% impoverishment of grain boundaries in the alloying element as compared to the intracrystalline composition (Fig. 7). The non-uniform distribution of elements in an alloy is associated with the peculiarities of the structure of polycrystalline bodies. The variation in chemical composition is particularly pronounced when the grain body and the boundary are compared. This difference cannot be explained solely on the ground of the general theory of crystallization. An analysis of equilibrium diagrams and melting points of nickel and all the investigated metals (tungsten, molybdenum, niobium, zirconium, titanium and tin) offers no explanation of the observed difference. Nor can the observed mode of distribution apparently be explained solely on the basis of surface-active properties of elements. Unfortunately, there are no data pertaining to the influence of elements on surface tension on the crystal boundary. If surface tension at the melting point of the pure metals be taken in the first approximation as a criterion, then in accordance with the values derived from physical characteristics[17] the surface tension of the above metals (with the exception of tin) exceeds that of nickel. Evidently, apart from

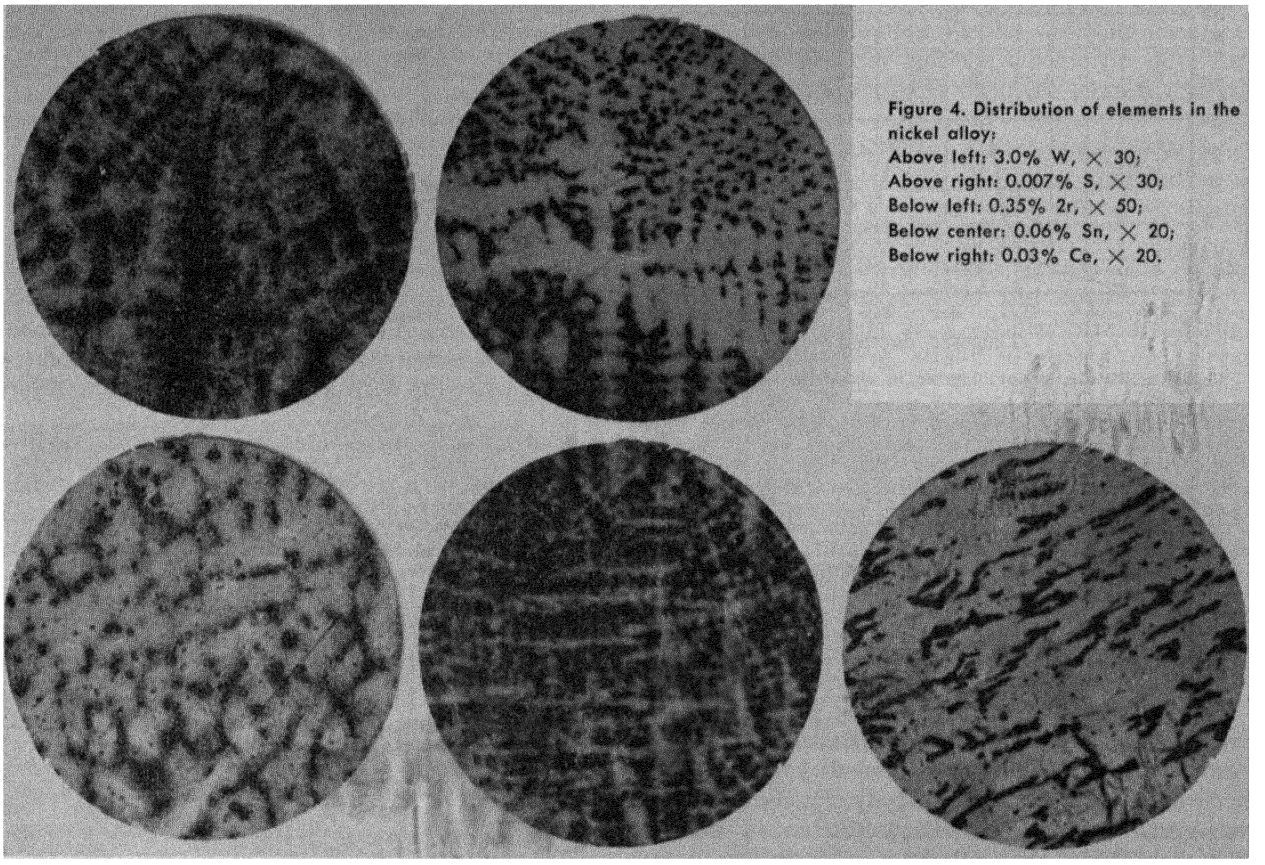

Figure 4. Distribution of elements in the nickel alloy:
Above left: 3.0% W, × 30;
Above right: 0.007% S, × 30;
Below left: 0.35% Zr, × 50;
Below center: 0.06% Sn, × 20;
Below right: 0.03% Ce, × 20.

thermodynamical factors, a substantial influence is also exerted by the peculiarities of grain boundary structure and kinetic conditions due to the diffusivity of the alloy components. Differing conditions of dissolution within the grain and along the grain boundaries, as well as a low mobility of the components, can occasion a distribution of elements which deviates substantially from the equilibrium distribution.

Influence of Heat Treatment

An important practical point is the influence of heat treatment, especially prolonged heating, upon the redistribution of elements and alteration in alloy homogeneity.

The process of redistribution in some alloys proceeds very slowly, with distinct features of its own, and depends on the initial state and composition of the alloy. In the case of lengthy diffusion-annealing we observe generally an increase in alloy homogeneity. However, in some cases, instead of the normal process of homogeneization, there takes place heterogeneization of the alloy, associated, for example, with the formation of tungsten-containing carbides.

A simple alloy of the binary solid solution type (0.5% tungsten in nickel), upon heating to 1200°C for over 150 hours, exhibits no homogeneization of chemical composition in the crystal volume, but only enlargement of the dendritic structure (Fig. 8). This phenomenon should be attributed to the low mobility of the tungsten atoms, provided the nickel atoms are sufficiently mobile, since there occurs dendritic growth, while the tungsten in the axes of the dendrites is retained. Only annealing to 1250°C for 150–200 hours yields a homogeneization of the alloy composition.

Autoradiographic analysis of complex alloys reveals a normal heterogeneization process connected with a diffusion redistribution of alloying elements and coagulation of the separation phase (Fig. 9).

There is also a possibility of heterogeneization within a single phase, connected with the specific properties of the dissolved element and structural peculiarities of the polycrystal. Thus, on heating a solid solution of iron and nickel or a solid solution of tin in nickel, we observe the dislocation of atoms of the dissolved element from the boundary to the centre in the first case and in the opposite direction in the second. Here the prolonged action of high temperature upon the alloy provides kinetic conditions which favour the diffusion processes necessary for the attainment of an equilibrium distribution of elements.

In the case of a nickel-phosphorus (0.017%) alloy prolonged annealing resulted in an increase of inhomogeneity owing to the accumulation of the impurity along the grain boundaries and its coalescence into bigger segregations. A decrease of the total boundary surface upon annealing, due to an increase of the grain size, in some cases produces a continuous impurity pattern (Fig. 10). In iron alloys diffusion annealing produces a more uniform distribu-

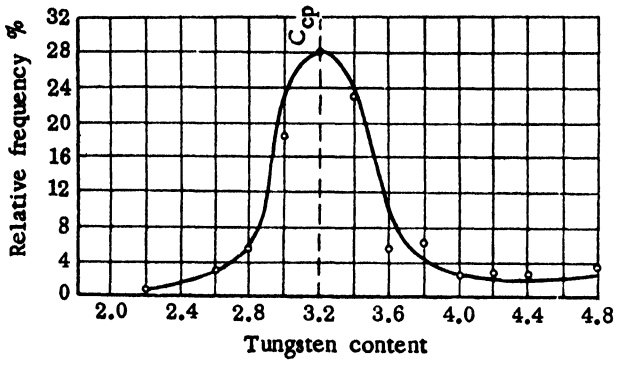

Figure 5. Distribution of tungsten in nickel (in concentration)

tion of sulphur, phosphorus, and carbon in the volume. This problem has been studied in detail by autoradiographic methods at the Central Laboratory of the Ministry of Transport Machine Building. The redistribution of elements (sulphur, carbon and others) in the welding of iron alloys has been studied at the Central Research Institute of the Ministry of the Shipbuilding Industry.

Effect of Plastic Flow

Hot working, particularly in the early stages of deformation, is conducive to a decrease of non-uniformity in the distribution of the alloying elements. For example a densitometric study of a contact autoradiograph of a specimen of a tungsten solid solution in nickel (0.51% W) after various amounts of reduction shows that the distribution curve becomes less diffuse and the value of the root mean square deviation decreases substantially from 0.09 to 0.04 (Fig. 11).

It is important to note that although the dendritic character of the cast structure becomes less pronounced, it is not completely eliminated even after considerable hot plastic flow. For example, after 10, 20 and 50% reduction of a cast alloy (a solution of tungsten in nickel), we observe the gradual disappearance of the dendritic structure, but traces of the latter remain even after 50% reduction (Fig. 12).

A comparative study of the process of the redistribution of elements shows that in a wrought alloy, as compared with a cast one, the homogeneization process proceeds much faster. Whereas, for example, in a cast nickel alloy containing 0.007% niobium prolonged heat treatment for 60 hours at 1200°C does not result in a levelling of the chemical composition, in the case of a wrought alloy it is sufficient to subject it to heat treatment at 1200°C for 1 hour to obtain a marked levelling of the chemical composition (Fig. 13).

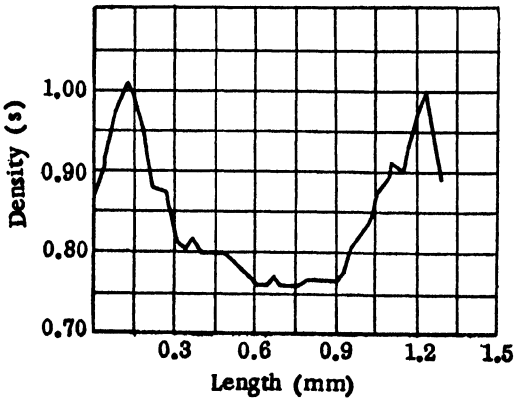

Figure 6. Distribution of niobium in nickel (in grain)

An increased rate of homogeneization in wrought alloys as compared with cast ones may be attributed to the formation of vacancies in the lattice in the process of plastic flow, to the refining of the structure (resulting in shorter diffusion distances and greater boundaries, i.e., regions of higher mobility), as well as to the destruction of boundary interlayers, which prevent diffusion.

The degree of alloy homogeneity also depends on the composition of the alloy. For example, an increase in the content to tungsten in nickel from 0.5 to 3.2% increases the inhomogeneity of the binary alloy.

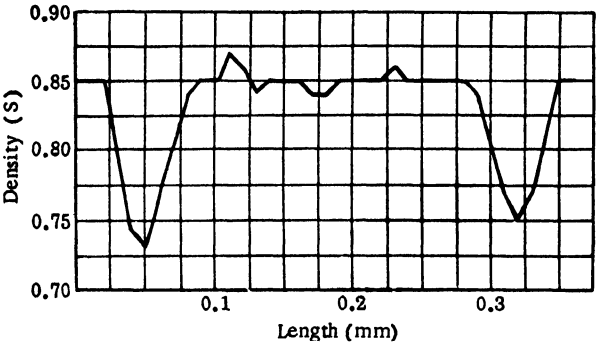

Figure 7. Distribution of iron in alloy (in grain)

Effect of Crystallization Conditions

The mode of distribution of elements is substantially dependent upon the conditions of alloy crystallization.

In studying the distribution of tungsten in a nickel alloy, it was established that the greater rate of crystallization in the case of the liquid metal being cooled in water ensure a greater uniformity of the distribution of the alloying element than in the case of slow crystallization (cooling of the liquid metal in a heated furnace) (Fig. 14).

VOLUME DIFFUSION AND DIFFUSION ALONG GRAIN BOUNDARIES

Local Character of Diffusion

The methods of calculating diffusion parameters existing at present do not, as a rule, take into consideration the realities of a solid body; therefore the quantitative evaluation of the phenomenon of diffusion is not sufficiently strict. The use of autoradiographic techniques in studying diffusion has shown that the process is non-uniform and bears a sharply pronounced local character in a polycrystalline body.

The investigations carried out to establish the qualitative picture of diffusion have shown that the dislocation of tin in various metals proceeds prefer-

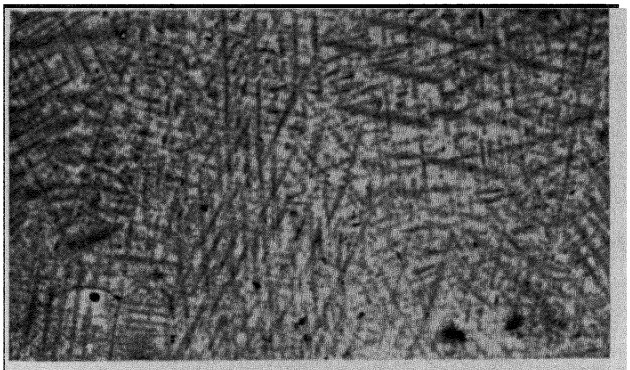

Figure 8. Effect of annealing on redistribution of tungsten in the nickel alloy: annealed at 1200°C for 60 hours, × 20

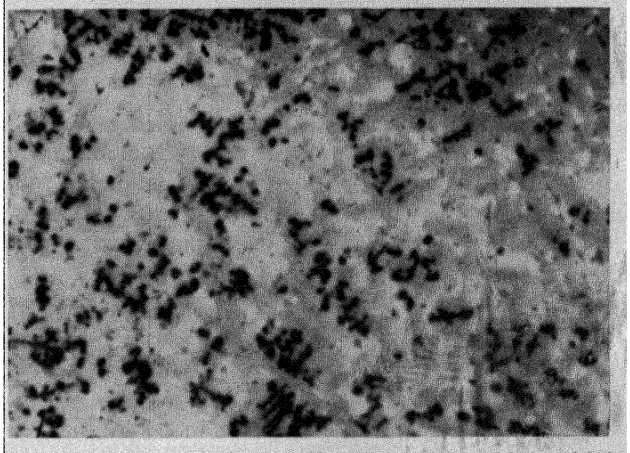

Figure 9. Distribution of tungsten in different phases of the nickel alloy (7, 8% W), × 10

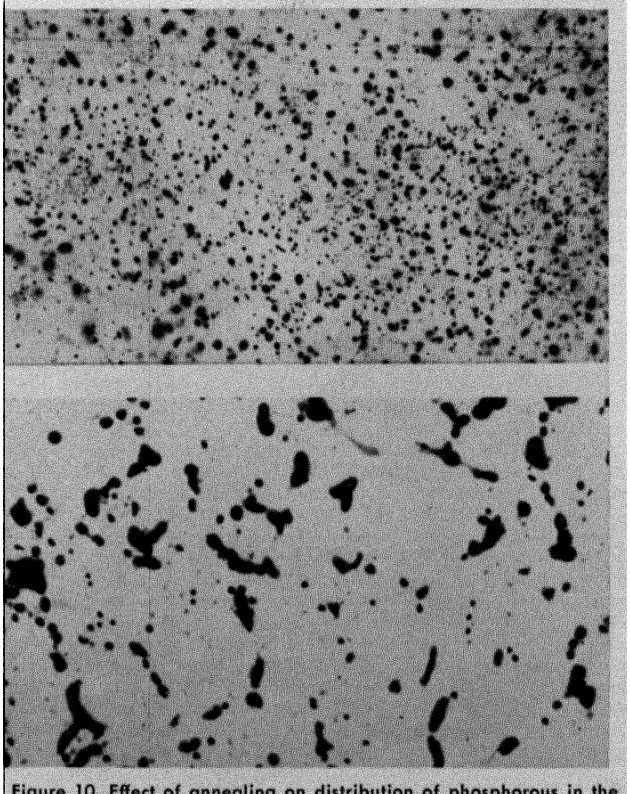

Figure 10. Effect of annealing on distribution of phosphorous in the nickel alloy (0.017% P): (a) cast alloy, × 20; and (b) annealed at 1100°C for 150 hours, × 20

entially along grain boundaries. However, the coefficient of the distribution of the diffusing element between the boundary and the volume for different metals differs and depends upon the temperature of the process.

The self-diffusion of tin (the isotope Sn^{113} was deposited on common tin, which was annealed at a temperature of 100°C) proceeds at a maximum rate along the grain boundaries (Fig. 15).

The diffusion of tin in copper, as well as in cobalt (annealing temperatures 700 and 1000°C respectively) also proceeds at a greater rate along the grain boundaries (Fig. 16).

In nickel, tin diffuses very intensely along the grain boundaries and at a much slower rate inside the grain. The boundary character of diffusion gradually disappears with an increase in temperature (Figs. 17 and 18). However, a study of the kinetics of the process, i.e., a study of the character of diffusion in time, showed that up to 1200°C the rate of tin displacement along the boundaries is greater than inside the crystal.

It is noteworthy that the contact autoradiograph of the active surface after diffusion annealing, but before sectioning (at an angle), exhibits bright areas along the boundaries and dark areas inside. This impoverishment in active tin concentration along the boundaries points to significant diffusion of tin atoms from the surface to the inside at the earliest time preferentially along the nickel grain boundaries.

The diffusion of tin in iron (900°C), unlike the case of nickel, is of the volume type, and it is only at greater depths that an increased tin concentration may be observed on the boundaries (Fig. 24).

To study the diffusion of carbon in iron, the iron specimens were cemented in active $BaCO_3$. The cemented specimen, together with an uncemented one, was annealed at a temperature 500–700°C.

The autoradiographs pointed to distinct boundary diffusion of carbon in the α-phase, which was the more pronounced the lower the temperature of the process (Fig. 19).

The local character of the diffusion mobility of atoms and the necessity for the separate determination of diffusion in the volume and along the grain boundaries are thus experimentally established.

Determination of Diffusion Parameters in the Volume and Along the Grain Boundaries

For a quantitative study of the diffusion of tin in iron and nickel in accordance with the above-described techniques, carefully prepared specimens (ground on a glass plate) were electrolytically plated with a thin layer (fractions of a micron) of active tin (Sn^{113}). The active surface of the specimen was brought into close contact with a similar specimen. Diffusion couples were annealed in a vacuum at an appropriate temperature.

After annealing, the specimen was sectioned in a special fixture across the active surface at an angle

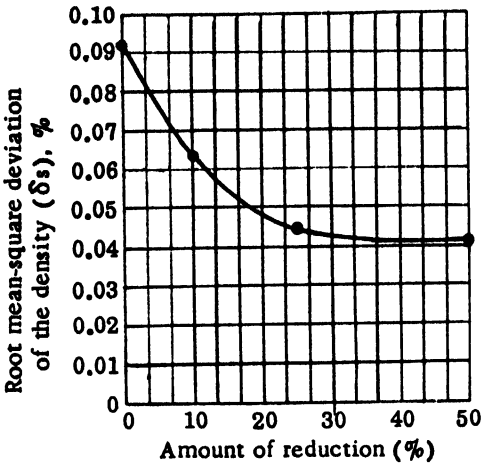

Figure 11. Effect of the amount of reduction on homogeneity of alloy (Ni + 0.5% W)

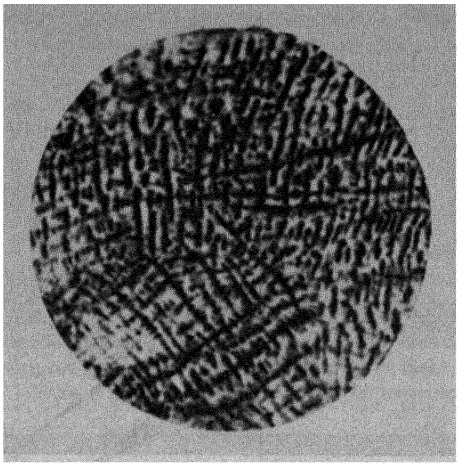

Figure 12. Change in dendritic structure under plastic deformation (nickel alloy); 20% reduction by forging, × 30

of 10′–1° and subjected to contact autoradiography. The densitometric study of the autoradiographs thus obtained was performed along a line in the plane of sectioning; measurements were made both of boundary and intragranular density. Readings of the photographic density were taken at 0.05 mm intervals, this corresponding to the penetration distance of one micron.

The diffusion of tin in iron was studied at a temperature of 900°C. The total penetration distance equalled 124 microns (densitometric data) or 148 microns (counting data). Use was made of photometric curve data to plot the logarithm of the density versus the square of the penetration distance (Fig. 20). The experimental points fall satisfactorily on a straight line. However, at a certain dis-

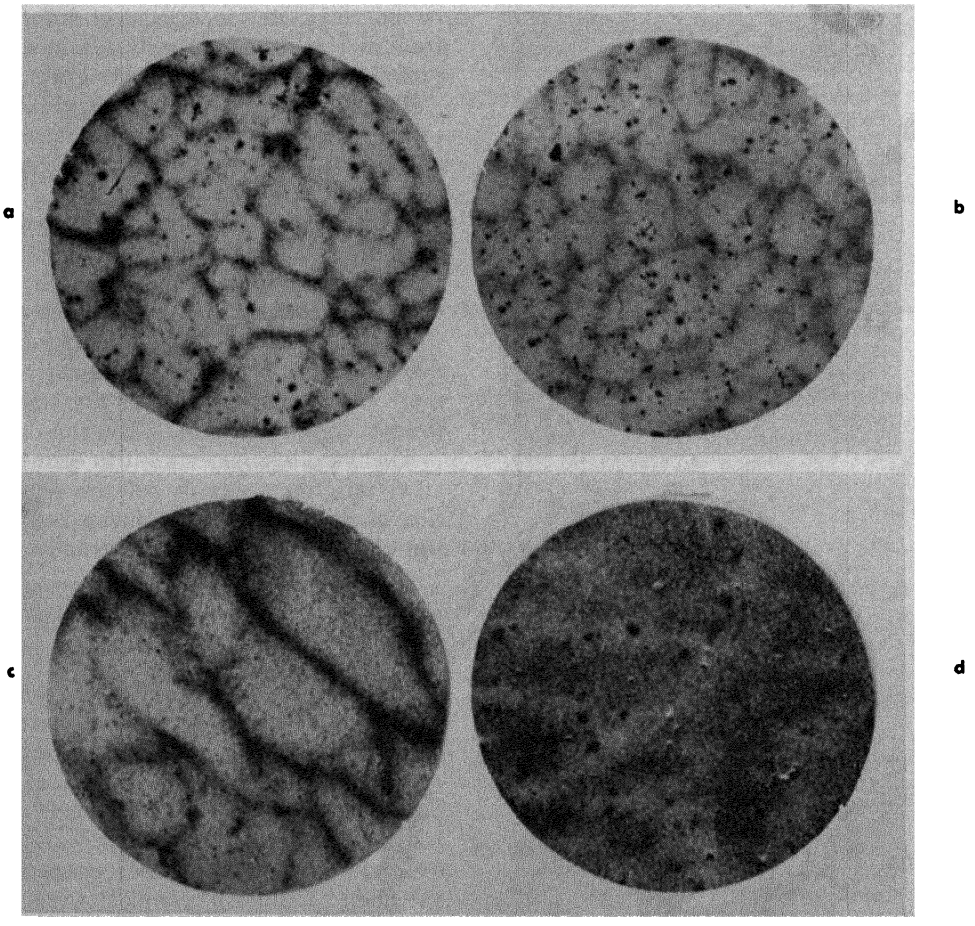

Figure 13. Effect of annealing on redistribution of niobium in cast and wrought alloy (0.007% Nb), × 30; (a) cast alloy × 30, (b) annealed at 1200°C for 60 hours × 30, (c) forged alloy × 30, and (d) annealed at 1200°C for 1 hour × 30

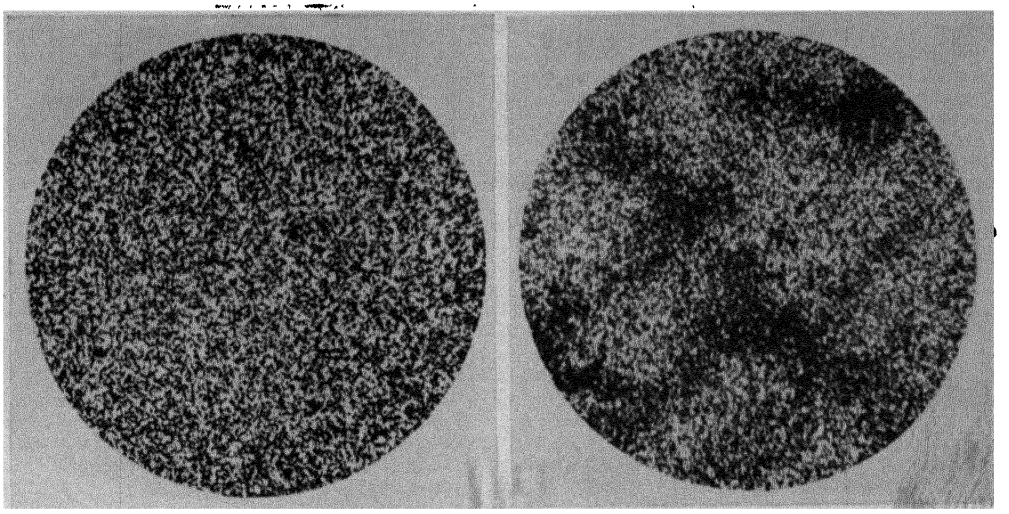

Figure 14. Effect of rate of crystallization on distribution of tungsten in the nickel alloy: (a) quick cooling, × 400; and (b) slow cooling, × 400

tance from the initial surface of diffusion, we observe a bend of the curve, which is evidently associated with a transition from preferentially volume diffusion to preferentially boundary diffusion. A comparison with the autoradiograph does indeed show that the appearance of boundary diffusion corresponds approximately to the position of the bend.

Accordingly, as computation showed, the diffusion coefficients of tin in iron for the grain body (D_g) and the boundary (D_b) at 900° are:

$D_g = 3.1 \times 10^{-11}$ and $D_b = 8.3 \times 10^{-11}$ cm²/sec. i.e., in the latter case it is nearly three times more.

In determining the diffusion coefficient of tin in nickel, photographic density changes were determined separately along the grain boundaries and in the grain volume. At 900°C the penetration distance was 460 microns and the average grain size ~ 500 microns. In this case diffusion was therefore measured within a single grain.

The photometric measurements carried out separately for the grain and the grain boundaries are charted in Fig. 21, which distinctly reveals the increase in tin mobility along the boundaries. For example, at a depth of 180 microns the photographic density on the boundary is very considerable, whereas in the grain centre it equals the emulsion background. Corresponding calculations have shown that the coefficient of diffusion along the boundaries at 900°C is roughly seven times more than inside the grain.

The determination of the temperature dependence of diffusion (700–1000°C) showed that the activation energy for the case of intragrain diffusion (Q) is equal to 52,000 cal/gram-atom, whereas for boundary diffusion it is 21,000 cal/gram-atom (Fig. 22).

In this way the potential barrier to be overcome by an atom in its movement is considerably lower at the interface of crystals than inside them.

A comparison of tin diffusion in iron and in nickel shows that atomic interaction in tin solid solutions on base of iron and nickel is different. In the former case the bulk of the atoms experience a predominantly frontal displacement, whereas in the latter case the process of diffusion at the initial stage proceeds primarily along the boundaries. The observed difference cannot be explained solely on the basis of variations in surface-active properties of these

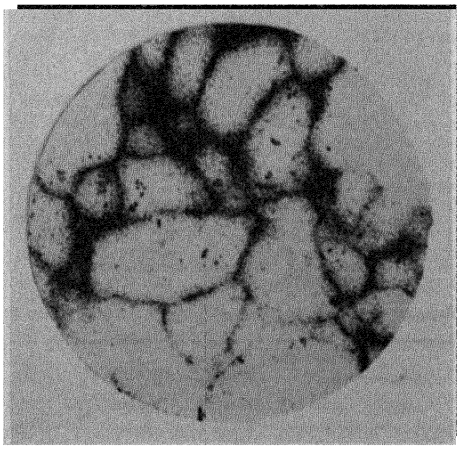

Figure 15. Self-diffusion of tin, × 30

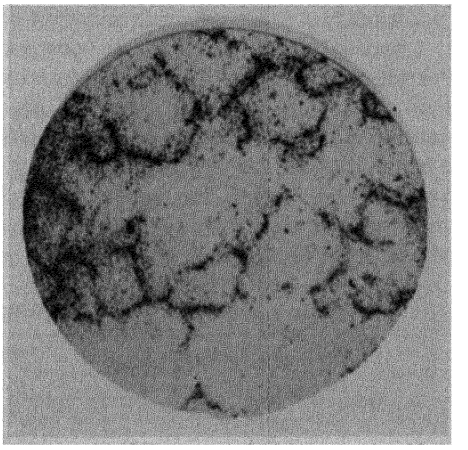

Figure 16. Diffusion of tin in copper, × 30

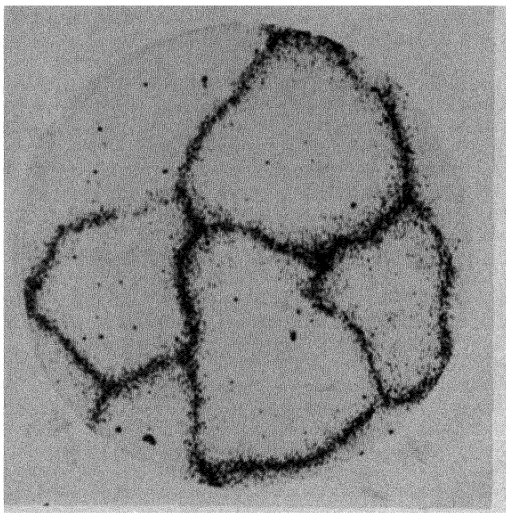

Figure 17. Diffusion of tin in nickel, 800°C, × 50

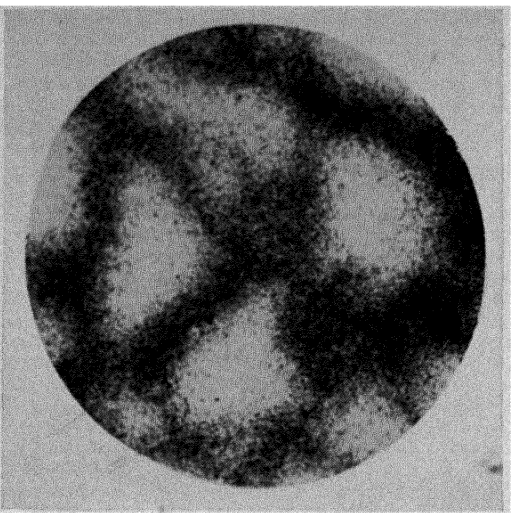

Figure 18. Diffusion of tin nickel, 900°C, × 50

elements. The surface tension at temperatures close to the melting points of nickel, iron and tin is 1350, 1150, and 525 dynes per cm respectively.

Generally speaking, the penetration of tin at high temperatures into iron or nickel, particularly along the grain boundaries, could either be due to capillary forces or could obey the laws of diffusion mobility, the latter taking place not through micro-crevices, but according to the mechanism described in full detail by Y. I. Frenkel.[18] In the latter case, since the grain boundaries have more vacancies and other structural imperfections, the diffusion along the grain boundaries proceeds at a higher rate than the diffusion into the grain. This mechanism, as is known, leaves no room for capillary forces.

In examining the various modes of the penetration of tin into iron and nickel, it is likewise impossible to apply upon the concept of variations in the mutual solubility of elements, since the solubility of tin in nickel is higher than in iron, and from this point of view it is incomprehensible why the diffusion of tin in nickel commences along the boundaries, whereas in the case of iron, tin diffuses into the grains.

Evidently the very structure of the grain boundaries in the case of different metals plays an essential part in this phenomenon.

The addition of a small amount of boron is known to exert a marked influence on the properties of steel and other alloys. However, the mechanism of the influence of minor impurities has by no means been elucidated. A study of the mode of boron distribution by the usual autoradiographic techniques does not appear possible, owing to the fact that the half-life of boron is very short. In this connection interesting results have been obtained in studying the effect of boron (0.01%) on the diffusion of tin in nickel. Comparative data on the volume and boundary diffusion of tin in nickel and in boron-containing nickel at 700–1000°C are tabulated in Table I.

Boron substantially retards the diffusion of tin along the grain boundaries: at 700°C the diffusion coefficient becomes approximately one order of magnitude less from 0.46×10^{-11} to 0.52×10^{-12} cm² per sec. It is notable that boron also retards the diffusion of tin within the grain, but to a much smaller extent than along the boundaries.

An analysis of this effect reveals that the value of the activation energy Q is somewhat higher when boron is added (increasing from 21,000 to 22,800 cal/gram-atom) while the value of the preexponential term D_0 in the diffusion equation $D = D_0 e^{-Q/RT}$ decreases to roughly a third (from 2.1×10^{-7} to 6.7×10^{-8} cm² per sec) (Fig. 22).

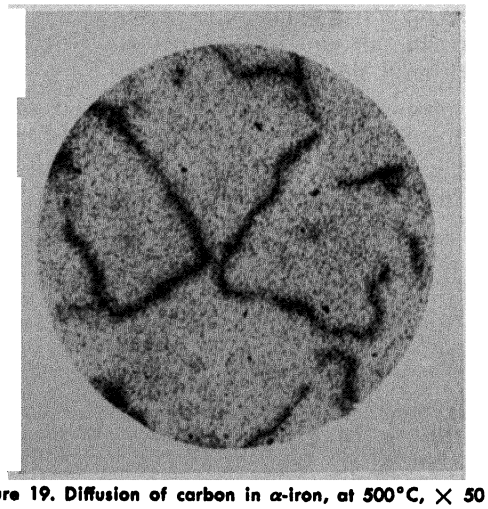

Figure 19. Diffusion of carbon in α-iron, at 500°C, × 50

Table I. Effect of Boron on Diffusion Coefficient of Tin in Nickel

Temperature	Diffusion in grain		Diffusion along boundaries	
	Without boron	With boron (0.01%)	Without boron	With boron (0.01 %)
700°C	0.72×10^{-13}	—	46×10^{-13}	5.2×10^{-13}
800°C	7.1×10^{-13}	4.6×10^{-13}	75×10^{-13}	16.4×10^{-13}
1000°C	400.0×10^{-13}	210.0×10^{-13}	630×10^{-13}	80.0×10^{-13}

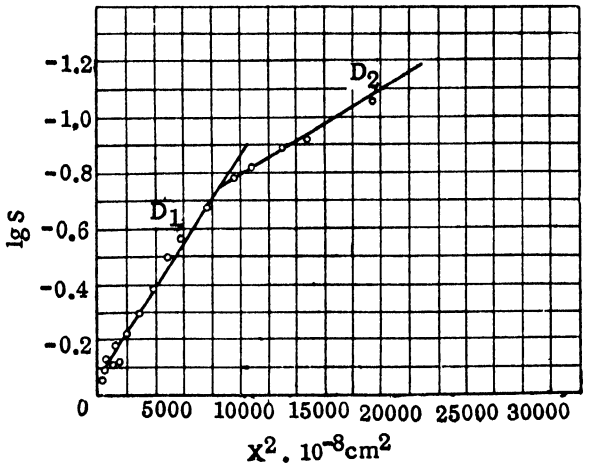

Figure 20. Density as a function of diffusion depth of tin in iron: D_1 (grain), D_2 (boundary)

It may be assumed that boron somewhat increases the strength of interatomic bonds and substantially improves the structure of the grain boundaries. Possibly boron reduces the number of vacancies in the crystalline lattice of the border zone, where it is easiest for them to appear. The retardation of diffusion within the grain is also probably associated with a decrease in the number of "atomic holes" in the metal.

It is a noteworthy fact that at 700°C the diffusion coefficient of tin in nickel along the grain boundaries is approximately two orders of magnitude higher than the coefficient of diffusion within the grain; at 800°C it is one order of magnitude higher; and at 1000°C it is only one and a half times higher. Evidently, an increase in temperature evens out the differences in the conditions for the diffusion mobility of atoms in the crystal lattice of the grains and the boundary regions. Diffusion within the grain is accelerated nearly a thousand-fold when the temperature is increased from 700 to 1000°C, while diffusion along the grain boundaries increases by only a little more than one order of magnitude (fourteen times).

IV. CONCLUSIONS

1. Autoradiographic techniques make it possible to carry out a direct and local study of the structure and properties of real bodies in microvolumes. The use of radioactive tracers provides a means of obtaining, instead of average statistical values, local values characterizing the structure of the substance and the diffusion mobility of atoms.

2. Autoradiography furnishes a qualitative and quantitative picture of the distribution mode of elements in metal alloys, and permits a general theory of alloying to be developed, based upon the selective alloying of both grains and intergranular boundaries. This direction in developing theories of alloying is important in view of the local character of deformation and destruction of alloys.

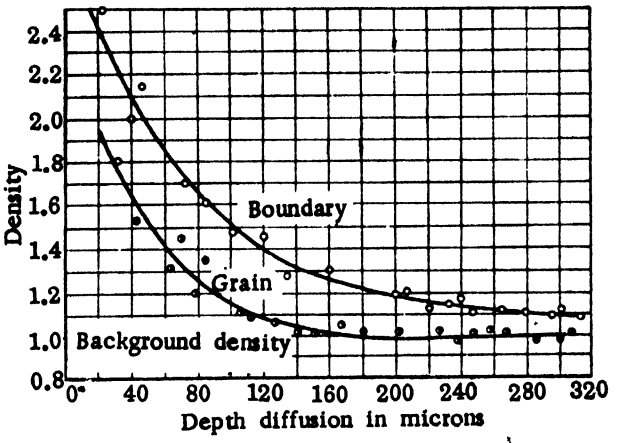

Figure 21. Density for tin diffusion in nickel in grain and along grain boundaries

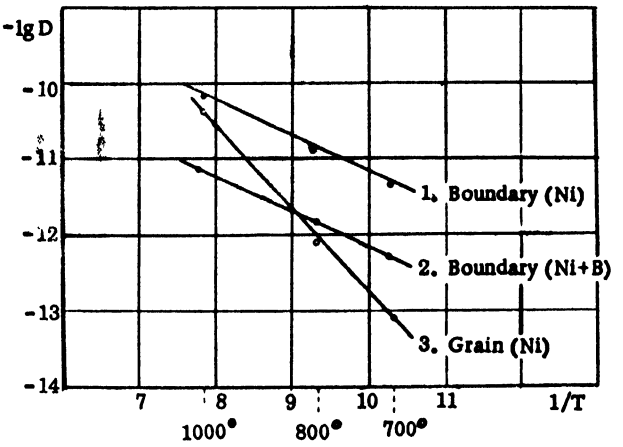

Figure 22. Diffusion of tin in nickel and boron-containing nickel (0.01% boron)

3. The method of autoradiography yields data which offer a quantitative solution of the problem of the diffusion of components in the alloy by treating diffusion along the grain boundaries and diffusion within the crystal separately. The solution of this problem is particularly important for a study of the transformations in metals, which often commence on the grain boundaries. It is also important in the characterization of alloys used in high-temperature conditions and static loads, since these alloys often experience destruction along the grain boundaries.

4. The method of autoradiography, permitting a quantitative evaluation of the diffusion mobility of atoms along the grain boundaries, is instrumental in gaining an insight into the mechanism of the influence of minor amounts of impurities upon the properties of metals.

The present paper has been compiled on the basis of experimental work carried out by the authors in collaboration with L. M. Moroz and T. I. Gudkova.

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An Investigation of Cobalt Diffusion in Cobalt-Aluminium and Cobalt-Nickel-Manganese Alloys with the Aid of the Radioactive Isotope, Cobalt-60

By S. D. Gertsricken and I. Y. Dekhtyar, Ukrainian SSR

The phenomena of diffusion play an essential part in a number of processes occurring in alloys. Radioactive isotopes offer new possibilities for exploring these diffusion processes.

At present there are not enough data in the literature concerning the parameters of the said process in alloys (such as activation energy E, and the so-called thermo-independent factor D_0). Diffusion in alloys is studied not only with the object of accumulating experimental facts, but also of determining the laws that govern this process.

The investigation of alloys composed of the transition elements of the iron group, is interesting from its physical aspect, especially because the atoms of these elements have an incomplete d-electron shell. Owing to the complex interactions between s- and d-electrons during the formation of alloys including these elements as their components, the interaction between their atoms has certain distinctions from metal alloys of the usual type.

This circumstance must be reflected in the values of diffusion parameters.

To reveal the specific features of diffusion in alloys based on transition elements, the authors undertook an experimental evaluation of the parameters of cobalt diffusion in the following alloys: cobalt-aluminium, cobalt-iron, cobalt-chromium, and cobalt-nickel-manganese with a fixed manganese content and varying contents of cobalt and nickel.

THE DIFFUSION OF COBALT IN THE COBALT-ALUMINIUM-ALLOY

The study of diffusion in the cobalt-aluminium alloy is interesting because of the fact that along with the cobalt atoms in the alloy having incomplete d-shells, there are atoms of aluminium capable of "giving away" their electrons.

Alloys containing 10 atom-% of aluminium were prepared in an argon atmosphere out of carbonyl cobalt and 99.9% pure aluminium.

The alloys were homogenized by annealing for 60 hours in vacuum at 1200–1250°C. The diffusion of cobalt was examined by taking off layers of the alloy and measuring their integral γ-activity.[1]

The objects studied were samples of the alloy electroplated with a thin layer of cobalt from a solution of cobalt sulphate holding a definite percentage of Co^{60}. The depth of the cobalt coating was about one micron.

The diffusion coefficient was estimated within the temperature interval between 1040 and 1220°. Each of the experiments included the use of several samples, the temperature during experiments being maintained at the said level with average fluctuations of ± 3°. The diffusion coefficient of this alloy may be expressed by the formula

$$D = 2.65 \exp\left(\frac{-67{,}500}{RT}\right) \text{cm}^2/\text{sec} \qquad (1)$$

The following temperature dependence was found for cobalt self-diffusion:[1]

$$D = 0.2 \exp\left(\frac{-62{,}000}{RT}\right) \text{cm}^2/\text{sec} \qquad (2)$$

Thus an addition of aluminium to cobalt increases the activation energy of cobalt diffusion. Evidently, this may be referred to increase of the energy of interatomic bonds. The said bonds in these alloys have certain distinctions owing to the gaps in their d-shells and the possibility of these gaps being filled with atoms of other metals like aluminium, during alloying. To a certain extent, these interatomic bonds may be characterised by the following coefficient of fullness:[2]

$$q = \frac{d_0 - d_s}{d_0} \qquad (3)$$

where d_0 is the amount of uncoupled d-electrons per atom in the gaseous state of the alloy, and d_s is the number of uncoupled d-electrons in the solid alloy. The value of d_0 is known from spectroscopic data, while d_s is the atomic magnetic moment also ascertained experimentally.

Aluminium when alloyed with cobalt[3] lowers the magnetic moment of cobalt atoms from 1.71 (pure cobalt) to 1.56 and 1.51 μ_B in alloys with 6.52 and 8.1 at.% of aluminium respectively. The number of uncoupled d-electrons per 1 atom of cobalt is $d_0 = 3$. Therefore, according to Equation 3 the coefficient of fullness for pure cobalt is $q = 0.43$. As the addition of aluminium lowers the magnetic atomic moment of cobalt, the coefficient of fullness of an alloy with

Original language: Russian.

10% aluminium will be higher than that of pure cobalt, namely, $q = 0.46$. Thus, the coefficient of fullness grows in proportion to the activation energy of the diffusion process.

COBALT DIFFUSION IN THE COBALT-IRON ALLOY

Cobalt diffusion was studied in a cobalt-iron alloy of equiatomic composition. Unlike the alloy discussed previously, both the components here belong to the transition group. The alloy was prepared out of carbonyl cobalt and iron fused in an argon atmosphere. The alloy was homogenized during 60 hours at 1200–1250°. Diffusion coefficients were determined by the absorption method, and calculated according to the known formula:

$$I_t = I_0 e^{\mu^2 Dt} [1 - \exp(\mu\sqrt{Dt})] \quad (4)$$

where I_0 and I_t respectively present the values of β-activity before and after diffusional annealing, μ is the β-ray absorption coefficient, D is the diffusion coefficient, and t is the time of diffusional annealing. The absorption coefficient μ for this alloy was assumed to be the same as for pure cobalt,[4] — 334 cm^{-1}. Having determined the ratio I_t/I_0 from experiment, we may directly find $\mu^2 Dt$ from special tables, whence knowing μ and t we can find D.

Figure 1 presents a graph of the temperature dependence of the diffusion coefficient, which for temperatures corresponding to the γ-region of this alloy is expressed by the formula:

$$D = 5 \times 10^{-6} \exp\left(\frac{-37{,}000}{RT}\right) \text{ cm}^2/\text{sec} \quad (5)$$

It is interesting to note that during the transition from the γ-region to the α-region the value of the cobalt diffusion coefficient shows an abrupt rise (Fig. 1).

The activation energy of cobalt and iron self-diffusion[1] respectively equal 62 and 68 kcal/mol. The significant decline in the activation energy of diffusion in the CoFe alloy compared to that of pure Co and Fe may apparently be explained by decrease of the energy of interatomic bonds in this alloy. Departing from the known magnetic atom moments for Co, Fe and Co-Fe,[3] the experimenters calculated q

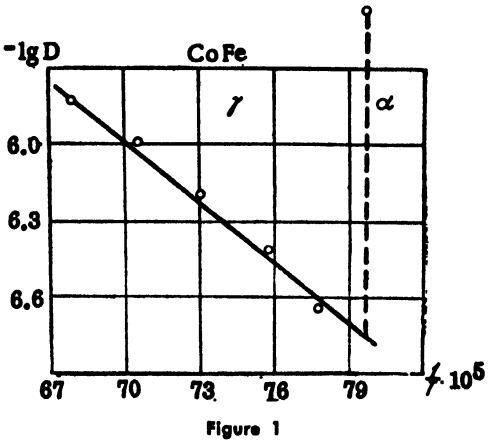

Figure 1

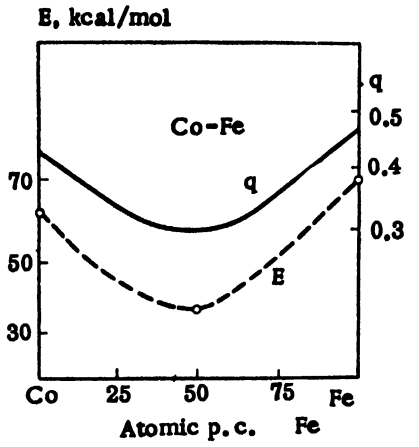

Figure 2

(Fig. 2). The data of Table 1 were employed in the calculation of coefficient q.

The value of d_0 was estimated by the rule of additivity. Figure 2 is a graphic representation of the dependence of q on the composition of the alloy. Thus, a decline in the activation energy of cobalt diffusion in the CoFe alloy is accompanied by a decrease in coefficient q.

COBALT DIFFUSION IN COBALT-CHROMIUM ALLOYS

Cobalt diffusion in cobalt-chromium alloys was assayed as previously, by the method of absorption. The alloys were prepared of carbonyl cobalt and electrolitic chromium smelted in an atmosphere of argon. The alloys were homogenized for 100 hours at a temperature of 1200–1250°C. Cobalt diffusion was gauged in the γ-region when the temperature was between 1020–1240°C.

Table 2 contains the values of the activation energy of cobalt diffusion for a series of tested alloys together with the corresponding values of q.

The values for q here were calculated from the atomic magnetic moments of the system Co-Cr[3] which exhibit a linear decrease following the decline in chromium concentration. The magnetic moment falls to zero at approximately 28 at.% Cr. The values of d_0 for the alloys were found by the rule of additivity. The number of uncoupled d-electrons of cobalt and chromium is respectively 3 and 5.

Figure 3 is a graphic illustration of the dependence of the activation energy of cobalt diffusion on the concentration of chromium. As in the previous

Table 1

	d_0	d_s	q
Cobalt	3	1.71	0 43
Iron	4	2.22	0.45
Cobalt-iron (50:50)	3.5	2.43	0.31

Table 2

Atom—% Cr	*0*	*6.75*	*11.5*	*16.5*	*27.5*
E, kcal/mol	62.0	73.3	86.3	102	110
q	0.43	0.55	0.67	0.78	0.98

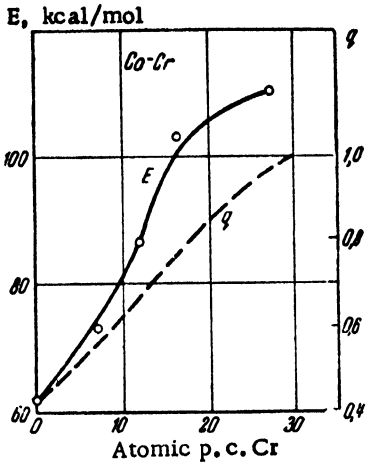

Figure 3

alloys, the activation energy varies in the same way with the concentration of chromium as do the values of q.

Cobalt Diffusion in Ternary Cobalt-Nickel-Manganese Alloys

Cobalt diffusion was investigated in Co-Ni-Mn alloys with a stable manganese content and varying contents of cobalt and nickel, the ratios being 1:3, 1:1 and 3:1 accordingly. The composition of the alloys in weight per cent is given in Table 3.

All these alloys are single-phased.

They were all smelted from pure electrolytic metals in a high-frequency smelting furnace. Two weighed samples were taken from each alloy and resmelted with an addition of radioactive Co^{60}. Stability of composition was ensured by simultaneous smelting. All samples were annealed in sealed quartz ampules at 1200°C for 70 hours. Samples of inactive alloys were formed as small cylinders 3 mm high and 8 mm in diameter, active samples as round plates of the same diameter, 500 microns thick.

Usually, when diffusion is assayed in alloys, the procedure is carried out with the observation of a definite concentration gradient. In the given instance cobalt diffusion was tested by establishing contact between two samples of identical composition, except that one of them contained Co^{60}. Diffusional annealing was effected in the temperature interval between 1020 and 1180°.

Experimental conditions in our case were similar to those of diffusion in an infinite medium. The depth of diffusion did not exceed 100 mm.

The equation for diffusion in such conditions is known to be as follows:

$$c(x, t) = \frac{c_0}{2}\left[1 - \exp\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad (6)$$

Table 3

Alloy No.	Co	Ni	Mn	C	Si
1	19.5	60 0	20.3	0.02	0.19
2	40.6	38.79	20.45	0.03	0.14
3	59.7	19.5	20.6	0.03	0.17

where $c_0/2$ is the concentration of labelled atoms in the place of contact between the two halves of a compound sample, and $c(x,t)$ is their concentration at a distance of x from that place. Knowing the values of $c(x,t)$ and c_0 with the help of tables we may figure out D, the diffusion coefficient. To avoid mistakes which might arise in the estimation of c_0, the experimenters calculated the ratio between concentrations c_1 and c_2 at distances of x_1 and x_2 from the place of contact.

$$F = \frac{c_1}{c_2} = \frac{1 - \exp\left(\frac{x_1}{2\sqrt{Dt}}\right)}{1 - \exp\left(\frac{x_2}{2\sqrt{Dt}}\right)} \qquad (7)$$

Curves were drawn showing the dependence of F on $x_1/2\sqrt{Dt}$ for different values of the $a = x_2/x_1$ parameter. The value of F is estimated from experiment, and for each given a we find on the graph the value of $x_1/2\sqrt{Dt}$. Hence we calculate the diffusion coefficient.

The diffusion coefficient was likewise calculated by assaying the ratio between integral activity at a depth of x and the integral activity in the place of contact. After the removal of a layer with a depth of x_i (counted from the place of contact), the value of the sample's γ-activity is found to be

$$N = \int_{x_i}^{\infty} c(x, t)dx \qquad (8)$$

By applying Equation 6 to Equation 8 we obtain

$$N = \frac{x_i c_0}{2}\left[\Phi(\alpha) + \frac{\Phi_1(\alpha)}{2\alpha} - 1\right] \qquad (9)$$

where

$$\alpha = \frac{x_i}{2\sqrt{Dt}}, \quad \Phi(\alpha) = \exp \alpha, \quad \Phi_1(\alpha) = \frac{2}{\sqrt{\pi}} e^{-\alpha^2} \qquad (10)$$

When $\alpha = 0$, $x_i = 0$, the expression for integral activity in the place of contact assumes the following form:

$$N_0 = c_0\sqrt{\frac{Dt}{\pi}} \qquad (11)$$

Then for N/N_0 we have

$$\frac{N}{\sqrt{\pi}N_0} = \alpha\left[\Phi(\alpha) + \frac{\Phi_1(\alpha)}{2\alpha} - 1\right] \qquad (12)$$

The right part of Equation 12 is tabulated as a function of α. Thus, from the experimentally estimated values of N and N_0 we may find the figure of the diffusion coefficient.

Diffusion coefficients were assayed for several samples and the obtained numbers were reduced to an average.

Table 4 holds the average values of diffusion coefficients and diffusion parameters (Fig. 4).

Analysis of the obtained figures shows that the activation energy of diffusion increases together with

the increase in the concentration of nickel, in accordance with decrease of cobalt content. As pointed out already, the calculation of q requires knowledge of the magnetic moments of the binary alloys of the elements of this ternary system. Such data, however, are not available. For Co-Ni alloys the magnetic moment per atom is subject to the rule of additivity, whereas for the Mn-Co system the magnetic moment falls steadily with the increase of manganese content, while in the case of Ni-Mn alloys the magnetic moment increases until manganese concentrations of about 12 at.%, but with further increase in such concentration it begins to diminish. Therefore, in the case of ternary solid solutions of Co-Ni-Mn, with the manganese concentration being constantly at the level of about 22%, we may roughly assume that the magnetic moment per atom of the alloys will increase from alloy 1 to alloy 3, while q will respectively diminish.

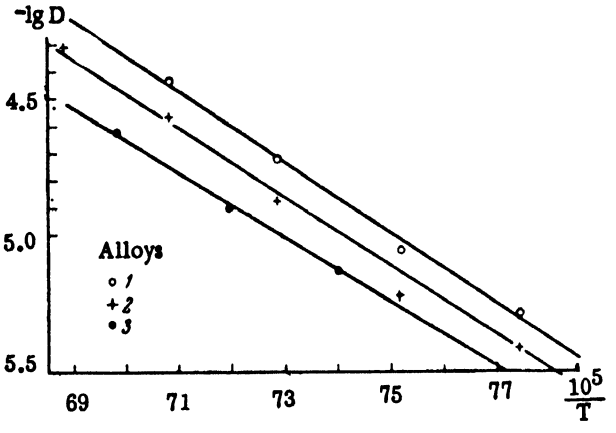

Figure 4

Table 4

T°K	D, cm²/24 hours		
	First alloy	Second alloy	Third alloy
1293	4.25×10^{-6}	3.8×10^{-6}	—
1333	8.8×10^{-6}	5.7×10^{-6}	—
1353	—	—	7.4×10^{-6}
1373	1.9×10^{-5}	1.3×10^{-6}	—
1393	—	—	1.3×10^{-5}
1413	3.8×10^{-5}	2.7×10^{-5}	—
1433	—	—	2.4×10^{-5}
1453	—	5.0×10^{-5}	—
E, kcal/mol	60.5	57.5	54.5
D, cm²/sec	0.86	0.22	0 05

The same picture is to be observed in the alterations of the activation energy of diffusion.

SUMMARY

1. Cobalt diffusion was studied in cobalt-aluminium, cobalt-iron, cobalt-chromium and cobalt-nickel-manganese alloys with the use of the radioactive isotope Co^{60}.

2. It has been demonstrated that diffusion activation energy and q, the degree of filling the vacancies in the d-states of transitional elements, vary with the composition.

Apparently, the value of q may to a certain extent characterize the energy of interatomic bonds in the alloy.

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Record of Proceedings of Session 21C

FRIDAY MORNING, 19 AUGUST 1955

***Chairman:* Mr. A. H. W. Aten (The Netherlands)**
***Vice-Chairman:* Mr. J. M. Otero Navascues (Spain)**
***Scientific Secretaries:* Messrs. I. D. Rojanski and A. Finkelstein**

PROGRAMME

21C.1. Reaction mechanisms

P/708 Application of tracer atoms in the study of the mechanisms of chemical reactions.....V. N. Kondratyev

P/163 Stable and unstable isotopes in heterogeneous catalytic reactions .....J. Turkevich

P/149 Tritium as a tool for industrial and chemical research.....W. G. Brown *et al.*

DISCUSSION

21C.2. Activation analysis

P/632 Quantitative determination of impurities in high purity metals through radioactivation analysis. .....J. V. Jakovlev

P/706 Application of radioactive isotopes in chemical analysis.....I. P. Alimarin

P/770 Recent advances in radioactivation analysis.....A. A. Smales

DISCUSSION

21C.3. Research in metallurgy

P/702 Investigations of diffusion and atomic interaction in alloys with the aid of radioactive isotopes.....G. V. Kurdiumov

DISCUSSION

The CHAIRMAN: This morning, we shall discuss isotopic indicators, one of the oldest fields to be covered by this Conference. As a matter of fact, the subject is much older than the notion of atomic energy itself. I think that it is most fitting that this meeting should be held after the speech which was made by Mr. Hevesy last Monday evening and which many of you heard. Mr. Hevesy was the discoverer of the principle of the use of radioactive isotopes. I am very sorry that he has been called away to another conference and cannot be in Geneva now. I am sure that we shall all think of him quite often during the course of this morning's meeting.

The first lecture this morning will be on the application of tracer atoms in the study of the process of chemical reactions.

Mr. V. N. KONDRATYEV (USSR) presented paper P/708.

The CHAIRMAN: I should like to thank Mr. Kondratyev for his very interesting lecture, which is of a very fundamental nature as the use of indicators offers us a very close approach to the ancient idea of our chemists, which was to see the way in which individual atoms moved in the course of a chemical transformation.

The next communication will be by Mr. Turkevich on "Stable and unstable isotopes in heterogeneous catalytic reactions."

Mr. J. TURKEVICH (USA) presented paper P/163.

The CHAIRMAN: I should like to thank Dr. Turkevich for his interesting talk. I think he has given us a very beautiful example that by using isotopic tracers one can still find out many and interesting facts about very old problems like the reaction between CO_2 and carbon which people have already been studying for more than a century.

I should now like to call on Professor Katz to give his talk on "Tritium as a research tool in chemistry and industry."

Mr. KATZ (USA) presented paper P/149 as follows: The report that I am about to present has been prepared by Messrs. Brown, Kaplan, Van Dyken and Wilzbach who have all been active in the application of tritium to tracer studies. Circumstances

have made it impossible for the authors to be present, and I am therefore presenting this paper in their behalf. Mr Brown was in Zurich early this month but unfortunately was unable to remain in Switzerland for the Conference

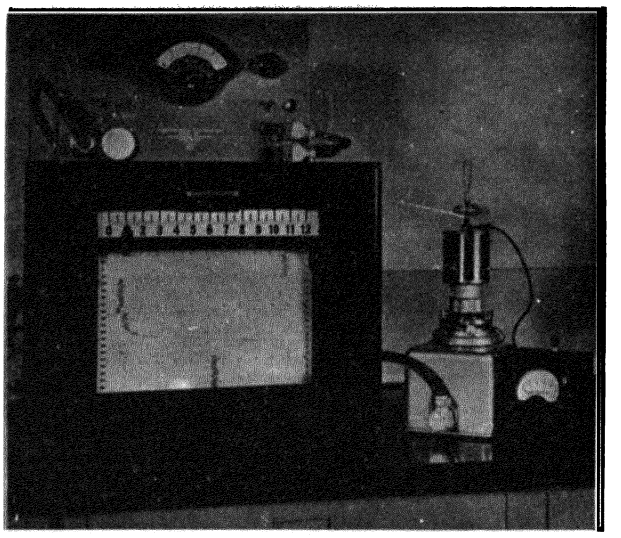
The chemistry of hydrogen constitutes a substantial fraction of presently known chemistry, and it is readily apparent that a large variety of potential research and industrial applications suggest themselves for a tracer for hydrogen. Tritium, produced by the reaction on Li^6 in nuclear reactors, can serve very well in this capacity, although there are of course some problems in which the use of the stable isotope deuterium may be preferable It will be of interest, in the time at our disposal, to consider a few of the chemical and industrial applications which suggest themselves for the radioactive hydrogen isotope tritium.

Table I summarizes the properties of tritium and compares it to the radioactive isotope C^{14}, since for many problems in the fields of organic and biochemistry either of these two isotopes may be employed more or less interchangeably as tracers It can be seen that tritium is especially characterized by the short range of its radiation, which in the past has made analysis for tritium somewhat of a problem. By comparison to C^{14}, then, tritium is economical; because of its much shorter half-life, it can be used with much greater dilution, and the rapid turnover of tritium in the body combined with the low energy of its beta particles makes the hazards of working with tritium less serious than for many other materials.

Table I. Properties of Tritium and Carbon-14

	T	C^{14}
Half life, years	12 4	5700
Energy, average, kev	5 7	50
Range, mg cm^2	0 9	28
Tolerable dilution	10^{11}	10^{11}
Cost 10^{-4} curie	\$0 10	\$36 00
Permissible continuous dose, 10^{-6} curies day	100	10

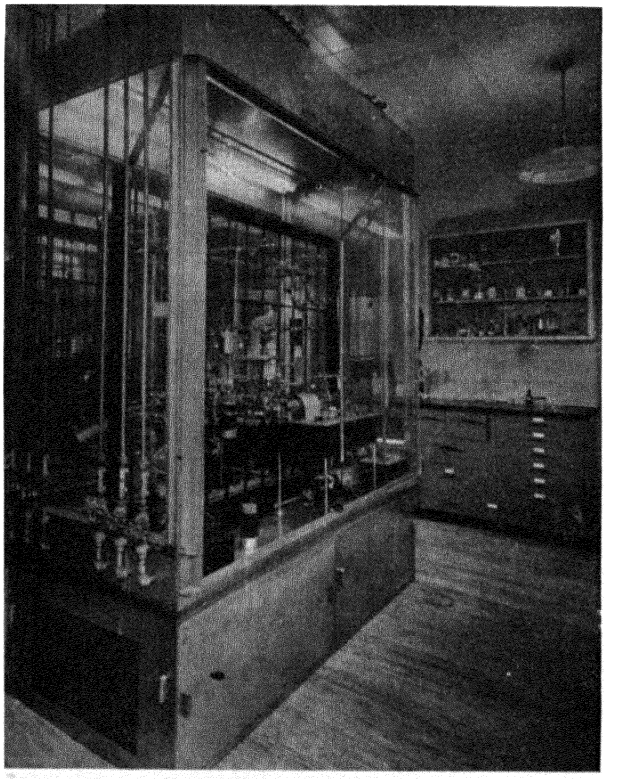
Slide 1 (Fig 1 of P/149) shows the analytical system employed for the assay of tritium Samples of gas suitable for assay are readily obtained from samples of water or of organic compounds by fusion with zinc metal Organic compounds may be heated at 650°C with zinc metal to which small amounts of nickel oxide and water have been added Under these conditions 90 per cent of the tritium in sample appears in the gas phase This one-step procedure is as satisfactory as the older two-step procedures At Argonne, the preferred method of determining tritium activity in gas samples is to transfer the sample to an ionization chamber and to measure the ionization current using the apparatus shown on the slide The reactor tube *A* is opened by rotating tube *B*, and the gas is allowed to expand into the evacuated ion chamber *C*. Currents corresponding to amounts of tritium ranging from 10^{-10} to 10^{-2} curies can be measured with an accuracy and reproducibility of 1 per cent



Slide 2

Slide 2 shows the vibrating reed electrometer used for measuring the ionization currents. We have found this to be a very satisfactory device In the higher concentration ranges, quite satisfactory results can also be obtained with less sensitive and less expensive types of electronic measuring devices

Another piece of apparatus which we find most useful in working with tritium-labelled compounds is shown on Slide 3 This is an enclosed vacuum-frame hood in which a conventional vacuum line is constructed Glass doors on the hood can be closed, and adequate ventilation can be secured by pulling air through the filters located on the sides of the hood.



Slide 3

Table II. Tritium Labelling by Reduction with Complex Hydrides

Compound	Reagent	T elsewhere (%)
CH_3CHTOH	$LiAlH_4$ *l*	0 026
$(CH_3)_2CTOH$	$LiAlH_4$-*t*	0 015
$(C_6H_5)_3SiT$	$LiAlH_4$ *l*	0 0
C_6H_5CHTOH	$LiAlH_4$-*t*	0 03
C_6H_5CHTOH	$LiBH_4$ *l*	--
CH_2TOH	$LiBH_4$ *l*	-

We have found this method of working with tritium highly satisfactory, and the use of such equipment to protect the researcher from both chemical and radiation hazards contributes materially to experimentation with tritium.

For studies in organic chemistry involving tritium, it is of course necessary to secure organic compounds containing tritium at specified positions. This can be achieved in a variety of ways.

Table II illustrates one method of preparing tritium-labelled compounds. In this procedure, the tritiated organic compounds are prepared by reduction of the appropriate organic compound with tritiated lithium aluminium hydride, lithium borohydride, and sodium borohydride. The introduction of tritium into the borohydrides is accomplished by direct exchange with a tritium-hydrogen gas mixture at elevated temperatures. Tritiated lithium aluminum hydride is prepared from tritiated lithium hydride in the usual fashion. Such reductions, as can be seen from the table, succeed very well in introducing tritium into very specific positions of the organic molecules.

Another method of obtaining tritium-labelled organic compounds is illustrated in Table III. Wolfgang, Rowland and Turton at Brookhaven have found that organic compounds can be labelled surprisingly well by utilizing recoil tritons. In this procedure, the organic compound is mixed with a lithium compound such as lithium carbonate, and the mixture irradiated with thermal neutrons in a nuclear reactor. We have examined several simple aromatic compounds in this fashion, as illustrated here. The organic compound was intimately mixed with 3 per cent of its weight of lithium sulfate and irradiated. Specific activities of 100 to 200 microcuries per gram were readily obtained with very little evidence of decomposition; recoveries of product purified to constant specific activity were greater than 50 per cent. The fraction of the total tritons incorporated into non-labelled positions is shown in column two. Partial degradation studies carried out to ascertain whether the position of the tritium label was completely random indicated that in certain cases, such as in benzoic acid, labelling is indeed preferential. In ortho-toluic acid, there is very definite evidence for preferential labelling in the aromatic ring rather than in the aliphatic side-chain.

Table III. Tritium Labelling with Recoil Tritons

Compound	% of tritons incorporated	Activity produced μc/gram	Distribution
C_6H_5COOH	25	106	*o*, *p*>*m*
o-$CH_3C_6H_5COOH$	25	114	Ring>CH_3
$C_6H_5COOCH(CH_3)_2$	–		Ring>chain
Anthracene	37	166	Random
Cholesterol	—	200	?

This method of labelling should have very important applications, particularly where a detailed knowledge of where the label is placed is not vital. The principal limiting factor is of course the radiation damage, and this can be controlled to a certain extent by using particles of lithium compound large enough to absorb some of the energy. This is illustrated by experiments on cholesterol, where irradiation of cholesterol admixed with 60 micron particles of lithium carbonate yields a good recovery of labelled material, whereas irradiation in the presence of lithium myristate gel causes the formation of insoluble material from which no cholesterol can be isolated at all.

We may now turn our attention very briefly to the use of tritium as a tool in research and industry.

Table IV summarizes broadly the uses of tritium in chemical research. For example, tritium labelling can be used to study competitive methylation in carbohydrates, it can be used to study the mechanisms of organic reactions involving hydrogen or proton transfer. In this way, numerous reactions involving nitrobenzyl halides have been so investigated, with results which indicate that some presently held ideas may require modification.

Table IV. Use of Tritium in Chemical Research

(1) To identify a molecule or group.
(2) To investigate hydrogen transfer processes
  (A) fate or source of H atom,
  (B) nature of process.

A particularly valuable application of tritium is in the investigation of rate-processes. In order to interpret isotopic tracer studies it is of course always necessary to guard against exchange reactions and isotopic discrimination in rates. To this end, numerous studies have been carried out on tritium isotope effects. In our work, we have been particularly concerned in isotope effects in the oxidation of 2-propanol by chromic acid, in the oxidation of ethanol by bromine, and in the hydrolysis of silanes. Details of these studies are to be found in our full report submitted to this Conference. These studies help to provide a sound basis for the interpretation of tritium tracer studies as well as having intrinsic interest for students of reaction kinetics.

With respect to industrial application, a general idea of the scope of such application is indicated in Table V. Tritium may be employed for analytical purposes by the isotope dilution method. The low cost of the isotope and the simplicity of preparing labelled compounds should make the routine use of such procedures economically feasible. The use of tritium-labelled compounds should also facilitate

studies of such procedures as laundering, cleaning of dairy equipment, and the removal of insecticides from foods, as well as for the processes involving removal of hydrogen-containing material. Tritium may also be used in measuring such properties as thickness of surface films and the retention of dyes by fabrics. Additional applications are the use of tritiated water for measuring water solubility in hydrocarbons, for studying the diffusion of water through films and similar processes. Although the uses of tritium so far have not been extensive, it is reasonable to expect important applications to many problems in such diverse fields as hydrology (to trace water flow), atmospheric pollution, petroleum exploration, and in process control.

An idea of the scope of industrial application is indicated in Table V.

Table V. Industrial Applications of Tritium

Analytical
(1) product analysis by isotope dilution
(2) material absorbed or removed
Physical
(1) flow patterns
(2) diffusion phenomena
Chemical
(1) combustion processes
(2) catalytic processes

We can conclude this brief survey then by pointing out once again that in tritium we possess a relatively inexpensive tracer for hydrogen. Tritium can be readily manipulated and assayed, and there is every reason to expect an ever-expanding role in science and technology for this versatile isotope.

DISCUSSION OF PAPERS P/708, P/163, P/149

The CHAIRMAN: We now come to the moment where we discuss the first three papers. There is a question from Mr. Farrington Daniels with respect to the first paper by Mr. Kondratyev.

Mr. DANIELS (USA): This method of combining isotopic tracer measurements with other kinetic data is a powerful tool for working out the complicated intermediate steps. Professor Kondratyev and his associates are to be commended for this excellent extension of our understanding of chemical kinetics. Similar methods have been helpful in studying the decomposition of nitrogen oxides. The pyrolysis of organic halides is another field of opportunity for tracer techniques. Does Mr. Kondratyev wish to expand on his last paragraph and suggest other fields of research of particular significance for his techniques?

Mr. KONDRATYEV (USSR): The paper I presented did not include the latest data we have on the oxidation mechanism for various substances.

Nor did it include a considerable body of data on vulcanization processes. I had the opportunity to say only very little about these processes. Then we have a good deal of information on the influence of molecule structure on the mobility of various atoms, particularly in the case of bromides. Some of these data have already been printed and some are in the press.

Mr. KONDRATYEV (USSR): I had an opportunity of asking Professor Turkevich several questions before he submitted his paper, and we have already discussed them privately. Hence I now have only one question, which I submitted to the Chairman. It concerns the following: in what is termed the multiple theory of catalysis which Balandin is working out in the Soviet Union, the geometrical correlation between the substance undergoing transformation and the catalyst is of essential significance. I should like to know what Professor Turkevich thinks of Balandin's theory, and whether he does not feel that Balandin's proposals have much in common with his own ideas on the geometrical distribution of hydrogen-deuterium and hydrogen by the catalyst method.

Mr. TURKEVICH (USA): May I say to Professor Kondratyev that there is not only a similarity between the ideas of Professor Balandin and the point expressed in my papers, but there is a genetic relationship: he inspired very many of them. I do feel, however, that we have extended some of his ideas by these new techniques and shown limitations of his ideas in other works. For instance, according to Professor Balandin's ideas, as we understand them, in the case of hydrogenation of benzene the geometry requires that all the hydrogens jump on the benzene molecule at the same time. Consequently, when using deuterium, one ought to expect a hexadeuterocyclohexane. Unfortunately, we observed this same scramble of deuterium and hydrogen. May I say, then, in conclusion, that we have been inspired by Dr. Balandin and we have also found some limitations on his ideas.

The CHAIRMAN: A question has been put to Dr. Katz, which reads: "Can you always assume that tritium is a true stand-in for hydrogen? Has not some work shown that this is not so?"

Mr. KATZ (USA): This is obviously true, as exemplified by the very considerable amount of work which has been done relating to the differences in the rate of reaction of a carbon hydrogen, carbon deuterium, and carbon tritium bond. In the talk I gave, I referred to work on the oxidation of ethanol by bromine, of isopropyl alcohol by bichromic acid and to hydrolytic reactions on silanes, all of which are directed to pointing out the differences that occur in rates—the differences between the carbon hydrogen bond, the carbon deuterium bond, and the carbon tritium bond. It is well known that there are great pitfalls in the interpretation of experiments involving hydrogen labels particularly because it is here that the maximum amount of isotope effect in the rates is going to be revealed, and therefore it is necessary to get data of the sort I mentioned very briefly in order to interpret intelligently experiments in which tritium is used as a label, particularly in biologically important systems.

Mr. VINOGRADOV (USSR) presented paper P/632 as follows: The radioactivation method is based on the irradiation by nuclear particles (in most cases, by slow neutrons) of the samples to be studied and the formation by nuclear reactions of radioactive isotopes, from the activity of which the amount of various chemical elements in the sample can be determined.

The sensitivity of the radioactivation method of analysis depends essentially on the activation cross-section of the chemical element to be determined, on the density of the flux of bombarding particles and also on the period of irradiation and the half-life of the radioactive isotopes formed. The yield of the various reactions can be calculated.

The author established the necessary conditions and performed systematic determinations of rare-earth elements in graphite, beryllium oxide and beryllium metal, pure bismuth, lead, zirconium, sodium, derivatives of the rare earths, and also a series of elements occurring as impurities in metallic germanium and other materials.

Radioactivation analysis is a comparatively easy method of solving one of the complex problems of analytical chemistry, the determination of minute quantities of rare-earth impurities in various materials. The solution of this problem is of practical importance, since nuclear reactor construction calls for a high degree of purity in the structural materials such as graphite, beryllium, zirconium and sodium, and especially purity from impurities in the form of rare-earth elements, which have a large capture cross section for neutrons. In this brief oral statement, therefore, we shall confine ourselves to the practical process of determining rare-earth elements by radioactivation.

The author has demonstrated the possibility of determining all the rare-earth elements by the activity of europium-152 or samarium-153 without separating the rare earths by chromatography, which would complicate and lengthen the analysis procedure. The isotopes mentioned were selected on the basis of the data on the activation cross-sections and half-lives of radioactive isotopes of the rare-earth elements given in Table 1 of the paper. These data show that for a fairly short period of irradiation, say 48 hours, the rare-earth element activity will be dominated by the contributions of dysprosium-165, europium-152, samarium-153 and lanthanum-140. This situation was confirmed by an analysis of the decay curve for an irradiated mixture of rare-earth elements approximately corresponding to the proportions in which they occur in nature. Figure 2 of the paper illustrates the general character of the decay curves for these elements from the mixture of rare earths.

Quantitative determinations of europium and samarium were arrived at by comparing the activity of isolated specimens with the activity of control samples.

A correction for lanthanum content was introduced in determining samarium. The content of rare-earth elements was estimated on the basis of the proportions of europium or samarium in the natural mixture. In these experiments, the total quantity of rare-earth elements was determined both by europium (in graphite and germanium) and by samarium (in beryllium, bismuth and lead). The rare-earth content proved to vary: I will cite a few figures—6×10^{-7} per cent in graphite, 10^{-7} per cent in germanium, 10^{-5} per cent in beryllium, 3×10^{-6} to 10^{-7} per cent in bismuth and 10^{-7} per cent in lead.

The determination by samarium of the rare-earth content in sodium, potassium and their alloys indicated that this content is too small to be detected by this method.

In these experiments, the samples were irradiated by a flux of $2\text{–}3 \times 10^{11}$ neutrons/cm^2/sec for a period of 48 hours.

The experiments showed that radioactivation analysis could be successfully employed in determining rare-earth elements occurring together.

Radioactivation analysis has a certain advantage over the X-ray spectrum method in the quantitative determination of the main component in the concentrates also obtained in the process of producing the rare-earth elements. Thus, for example, the quantity of lanthanum, gadolinium, dysprosium and lutetium in concentrates containing over 50 per cent of one of these elements may be determined with an accuracy of the order of 2–3 per cent.

Calculations show that by taking advantage of differences in activation cross sections, half-lives and beta- and gamma-radiation energies, it is possible to determine, by beta-radiation, for instance, lanthanum or dysprosium up to 10^{-5} per cent, or by gamma-radiation, lanthanum up to 10^{-5} per cent, and so on. These data are set out in Table 3 of the paper.

By using the more intense neutron fluxes available in nuclear reactors, it is possible to increase appreciably the sensitivity of the determination of rare-earth elements and to shorten the period of irradiation. The sensitivity of the method may be increased by separating the rare earths by chromatography after irradiation. Theoretical calculations show that a determination sensitivity of 10^{-4} to 10^{-7} per cent can be attained for various rare-earth elements by chromatographic separation after irradiation of 100-mg samples in a flux of 5×10^{11} neutrons/cm^2/sec.

It is worth noting that by using the neutron flux from, for instance, a 500-mg radium-beryllium source, europium can sometimes be determined in samarium with a sensitivity of 0.05 per cent, or dysprosium can be determined with the same sensitivity in the yttrium earths, poor or rich in gadolinium, which are obtained in the production of individual rare earths.

In addition to rare-earth elements, the author has determined antimony, molybdenum, copper and zinc in germanium dioxide and metallic germanium. The presence of extraneous admixtures in the crystal structure of germanium greatly affects its electrical

properties. Hence, the determination of minute amounts of impurity in germanium is extremely important. A number of elements in a mixture were determined simultaneously by the radioactivation analysis method, the methods used, after the sample had been irradiated, to isolate and purify the elements being distillation, extraction and precipitation by means of organic and inorganic reagents. The results are set out in the printed paper.

A very promising line for the further development of the radioactivation method is that of using not only thermal neutrons but also other nuclear particles for analytical purposes. Great possibilities are opened up by the use of monochromatic neutrons of different energies for the rapid and selective determination of elements having large resonance-absorption cross sections for neutrons, such as indium, iridium, tantalum, manganese, silver, etc. The field of application of radioactivation analysis can also be extended by the more intensive use of various charged particles to determine heavy as well as light elements, such as niobium, titanium, chromium and others, traces of which are difficult to determine by neutron activation. This method will undoubtedly be applied especially in the inspection of pure materials, such as graphite, germanium, etc., and also in geochemistry for the determination of the rarest and most widely scattered chemical elements.

Mr. VINOGRADOV (USSR) presented paper P/706 as follows: In the USSR, as in other countries, the radioactive isotopes of the majority of the elements in D. I. Mendeleev's periodic system have now found a broad field of application in analytical chemistry. By means of them it has become possible to study more closely the mechanism of a number of analytical reactions by the method of physico-chemical analysis of various systems, the instability constants of complex compounds by the isotope exchange method, the solubility of precipitates, etc. In other words, they have made it possible to solve a number of fundamental problems in analytical chemistry.

Radioactive isotopes have also proved particularly valuable in developing methods of quantitatively determining small amounts of impurities in pure metals, semi-conductors, alloys, luminescent compounds, reagents, etc. The use of radioactive isotopes has considerably speeded up analytic processes by eliminating the need in many cases for complete isolation of the element to be determined.

What I have said applies particularly to groups of elements with very similar chemical properties, such as the rare-earth elements, titanium, niobium, tantalum, zirconium, hafnium, etc.

Radiochemical methods have made it possible to estimate the accuracy and correctness of the conventional methods of separating elements and to improve them, and this in turn has helped to introduce more reliable methods for the analysis of natural raw materials and their derivatives.

In this oral review, of course, I cannot dwell on all the widely different ways in which radioactive isotopes can be applied in analytical chemistry; it was not even possible to do so in the printed paper. I shall merely describe here a few experiments recently carried out in research and industrial laboratories in the Soviet Union.

As you know, in analytical chemistry it is not so much the actual determination of an element that causes the greatest difficulties as its separation by various means from other accompanying elements. For this reason, labelled atoms have been used mainly to study the precipitation of slightly soluble compounds, the process of electrolysis, the extraction, chromatography and distillation processes, etc. I will now give a very brief account of the results of this type of research.

The most usual separation method is that of precipitation. For instance, we have studied the co-precipitation of the radioactive isotopes zirconium-95, bismuth-210 and cerium-141 with the hydroxides and sulphides of various metals. The results of these experiments showed that the co-precipitation of radioactive isotopes with the hydroxides and sulphates of various elements does not depend on the solubility of the latter; thus the co-precipitation of Bi^{210} is 98–100 per cent with ferric hydroxide (molar solubility $S = 3.4 \times 10^{-10} M/1$), with ferrous hydroxide ($S = 1.3 \times 10^{-5} M/1$) and with the sulphides of mercury ($S = 6 \times 10^{-27} M/1$) and cadmium ($S = 3 \times 10^{-14} M/1$).

As might be anticipated, the extent of co-precipitation of radioactive isotopes with hydroxides and sulphides is governed by the solubility of these same compounds of a given isotope; thus, co-precipitation is close to 100 per cent in the case where the corresponding hydroxide or sulphide is almost insoluble ($S = 10^{-4} M/1$), and very insignificant (a few per cent) when these compounds are readily soluble.

The sulphides of tin, cadmium, mercury and copper have the highest propensity for capturing these ions; this property appears in the sulphide of silver to a very small extent (Table 2 of P/706).

It is worth noting that the amount of the co-precipitating cation depends on its concentration and on the time the precipitate remains in solution.

Zinc capture by copper and mercury precipitates increases with time, but in the case of cadmium the zinc content does not vary with time. These facts are explained by changes in the structure and dispersion of the precipitates.

The degree of co-precipitation can be reduced considerably by adding surface-active agents such as methyl red (Fig. 2 of P/706).

A new method of physico-chemical system analysis has been proposed for studying the mechanism of co-precipitation, using radioisotopes. The amount of precipitation is plotted on one axis of a physico-chemical diagram and the factor governing co-precipitation, e.g., pH, along the other.

The preparation of these diagrams by the ordinary

conventional methods is a very laborious task, but with radioactive tracers it can be completed very quickly. It has been shown on the basis of the study of the system of strontium and barium chromates, using the isotope Sr^{89}, that the gradual neutralization of the solution with ammonia reduces the extent of strontium capture to 12 per cent, and the addition of 0.01 per cent gelatin reduces precipitation to 6 per cent, but if the conventional Fresenius method of separation is used, strontium co-precipitation at pH = 5 amounts to 30 per cent.

Labelled atoms have also been used to study the solubility of many slightly soluble compounds (listed in the paper).

I should like to say a few words about the general method we have devised for determining solubilities in which a precipitating agent is added to a solution containing the element to be determined and a radioactive isotope and the activity of the precipitate I_1 is found, after which a carrier is introduced into the filtrate and a fresh precipitation is performed; the activity of the precipitate I_2 is measured. The solutility X of the precipitate is found by determining the ratio between the activities β according to the equation:

$$X = \frac{a\sqrt{\beta^2 + 4} - \beta}{2V}$$

where V is the volume of the solution, and a represents the inactive carrier ions in millimoles. This method is used to determine the solubility of ammonium manganese phosphate and other substances.

I will now deal with the isotopic dilution method.

In those cases in which the quantitative separation of components is very difficult but part of each component can be isolated in pure form fairly easily, the isotopic dilution method is used for quantitative analysis.

The main advantage that this method of analysis has over other methods is that the quantitative separation of the element to be determined is unnecessary, so that elements having closely similar properties can be separated with tolerable accuracy.

This method has made it possible to determine small quantities of rubidium in natural salts, particularly in carnallites and products derived from them. The method is based on precipitation out of a solution of a specimen of salt containing rubidium-86 by means of consecutive additions of ferric chloride and potassium ferrocyanide solutions, the rubidium co-precipitating with Prussian blue. The co-precipitate is filtered out and ignited and the residue is leached; the rubidium is reprecipitated with the aid of the double salt magnesium ferrocyanide. The precipitate is ignited and a practically pure rubidium salt is extracted. After weighing, the activity of this rubidium sulphate is determined.

Another method involving the application of radioisotopes to analytical chemistry is radiometric titration. This method has been used to determine cobalt, for example. In this case the tracer used is the radioisotope Co^{60} (Fig. 3 of P/706).

Ever-widening applications are being found in practical inorganic and organic quantitative analysis for reagents containing radioactive and preferably long-lived isotopes. Labelled sodium phosphate has been used to determine a number of metals (aluminium, bismuth, cerium, lanthanum, zirconium and iron). In most cases the phosphate was precipitated in an acetate medium (sulphuric acid in the case of Bi and Zr). By choosing appropriate conditions, it is possible to determine these metals when they are all present together. A method has been developed to determine aluminium in alloys, indium in concentrates, etc.

There is no doubt that organic precipitating agents with labelled atoms will also be widely used in the very near future.

The value of the radioactive tracer method is illustrated particularly strikingly in the separation of complex mixtures of elements by ion-exchange chromatography methods and also by these methods in conjunction with extraction.

In this connection, I might mention the work done on the chromatographic separation of mixtures of alkali metals using the cation-exchange agent RF. These studies, in which the isotopes Na^{24}, K^{42} and Rb^{86} were employed, have been applied both in producing rubidium (free of potassium) for use as a control in spectrum analysis, and in silicate analysis.

In addition, methods of separating the chlorides of zirconium and hafnium in a methyl alcohol solution by chromatography, using silica gel, have been studied. When a 20 per cent solution of a mixture of zirconium tetrachloride with 0.1-0.2 per cent of hafnium was passed through the column once, the hafnium content fell to 0.08 per cent.

The radioactive isotope niobium-95 has been used to develop a chromatographic method of separating titanium and niobium. The cation-exchanger KU-2 was employed in these experiments. It was shown that for separating mixtures containing a large quantity of titanium it was best to wash the column through with 1N sulphuric acid, but 0.1N acid was best for mixtures containing a large quantity of niobium.

The chromatographic method has been successfully applied to the separation of the radioactive isotopes of various elements. For instance, it has proved possible to separate zirconium-95 and niobium-95 within 70 hours by using the native anion exchangers apatite-TM and AN-2F, the column being 92 cm high and 0.5 cm in diameter and the flow rate of the solution being 0.3 ml/cm²/min.

In conclusion, it may be said that the labelled atoms method, using stable and, more particularly, radioactive isotopes is being employed more widely every day to solve theoretical and practical problems in analytical chemistry.

Side by side with the development and improvement of radiochemical methods of analysis, progress

is constantly being made in perfecting methods of identifying isotopes and increasing the sensitivity and accuracy of the measuring instruments used for various types of radiation. Along with the ordinary Geiger-Müller counters, scintillation counters are establishing themselves in the routine of the analytical laboratory. The work of the analytical chemist is being considerably lightened by the development of methods of investigating the spectrum composition of the α-, β- and γ-radiations of radioactive isotopes.

The CHAIRMAN: I should like to thank you very much, Mr. Vinogradov, for giving us those two lectures one after the other.

Mr. A. A. SMALES (UK) presented paper P/770 as follows: The paper presented earlier in this session by the Russian delegate has outlined the general methods used in analysis by radioactivation. I can therefore devote the time available to me in discussing some of the recent work at Harwell on this subject. I will deal with the work under two broad headings—the determination of some trace elements in materials, firstly of industrial interest and secondly of geochemical interest.

The radioactivation method is particularly suitable for determining extremely minute quantities of trace impurities in pure metals, and I would like to mention one or two examples.

The determination of calcium at the parts per million level in fairly pure iron is almost impossible by any conventional chemical method, while the spectrographic method runs into difficulty because of the ubiquitous nature of calcium in dust, etc.—thus giving rise to high "blanks." Although the sensitivity by radioactivation is low for calcium compared with many other elements, it is still adequate for the parts per million level and has been applied after irradiation of samples of about 1 gm for periods of between two and ten weeks, with results on duplicate portions of two iron samples being 7.0 and 7.5 parts per million for the first sample, and 5.4 and 5.3 parts per million for the second. At this level there was adequate calcium-45 activity for verification of radiochemical purity by half life and beta energy measurements. The advantage of radioactivation in this example was the overcoming of reagent "blank" difficulties.

There is a current interest in the trace impurity level in some alkali metals and alloys. We have recently determined sodium in pure lithium metal down to 0.02 parts per million using a "streamlined" radiochemical separation involving a semi-micro ion exchange column separation in addition to conventional precipitation steps.

I would also like to mention the detection and determination of some trace impurities in sodium-potassium alloy, in certain cases without using radiochemical separations, but instead examining the samples, after irradiation followed by "cooling" for the sodium-24 and potassium-42 to decay, on a single channel gamma spectrometer fitted with a Compton compensating device. This was devised by Mr. D. H. Peirson of the Electronics Division at Harwell. I will digress for a minute from radioactivation analysis to illustrate the advantage of this instrument.

Table VI. Results on Sodium Potassium Alloy Samples

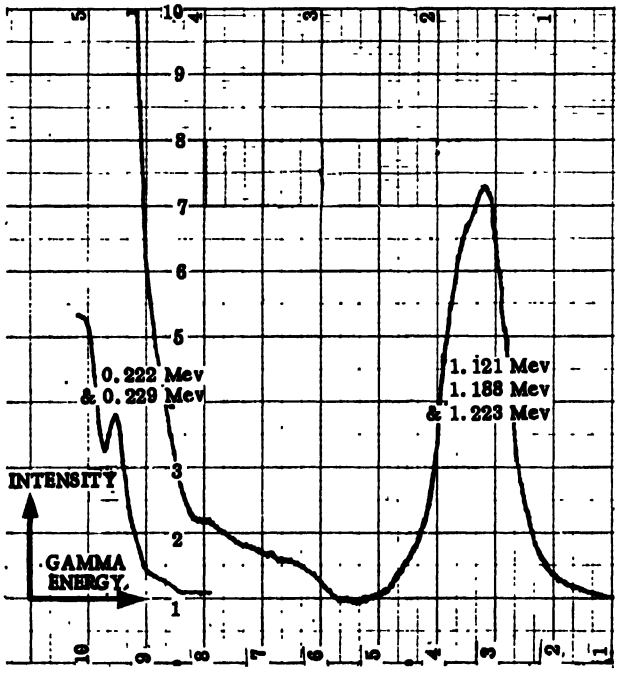
	Sample A	*Sample B*
Mercury	< 0.5 ppm	2 ppm
Chromium	< 0 2	0 2
Rubidium	77	100
Caesium	0.15	0 11
Silver	< 0.02	5
Antimony	< 0 001	0.04
Strontium	< 0.5	< 0 5
Cobalt	0 02	0.002

We can see in Slide 4 the gamma spectrum of tantalum-182 using a normal single crystal spectrometer, showing the photopeak at 1.2 Mev and the associated Compton absorption at lower energy.

The same sample is shown on the Peirson instrument (Slide 5), where the major part of the Compton contribution has been compensated for. Here you have the photopeak, and you can see the decrease in Compton absorption.

To return to radioactivation, Slide 6 shows the gamma spectrum on the Peirson instrument of one sodium potassium sample. Rubidium-86 at 1.1 Mev and caesium-134, with two gammas at 0.6 and 0.8 Mev can be quite clearly identified and measured in this case by comparison with standards. The fuller results on two samples of alloy are shown in Table VI where radiochemical separations have also been used for some of the elements.

You can see that we have determined the mercury, chromium, rubidium, caesium, silver, antimony, and cobalt in those two samples of NaK alloy.



Slide 4. High energy gamma spectrum of tantalum-182 (compensated for Compton continuum)

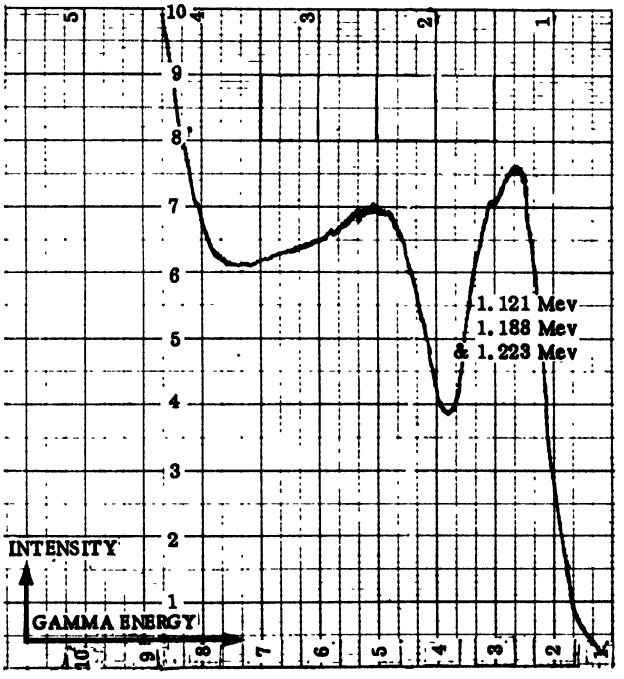
Table VII. Ratios Involving Nickel, Cobalt and Copper

Material	*Number of samples examined*	*Ni·Co average ratio*	*Ni:Cu average ratio*	*Cu Co average ratio*
Red clay	11	3 1	0 85	3.7
Globigerina ooze	33	4.1	0.77	5.4
Manganese nodules	7	4 3	1.2	4 3
Oceanic rocks	9	2.3	1.6	2.7
Average for igneous rocks		3 5	1.1	3.0
Meteorites (stones and stony-irons)	9	22 7	100	0.24
Average for meteorites		13 1	92	0.14

As was pointed out by Mr. Vinogradov, one of the fields in which radioactivation methods have been almost indispensable, is that of semi-conductors. Here purity requirements are much greater even than in most atomic energy materials and the great sensitivity and freedom from "reagent blank" difficulties have made radioactivation very attractive and widely used since our early work on arsenic and germanium.

Silicon is now coming into prominence as a semi-conductor material and radioactivation methods can be applied even more readily to this material than to germanium, because on neutron irradiation, silicon gives only the 170 minute half-life, pure beta emitter silicon-31. Irradiated silicon is therefore ideally suited for the application of gamma spectrometry for determination of certain impurities.

An example of a rather impure silicon sample is shown in Slide 7 where copper-64 and zinc-69 can easily be identified, the levels being 3.1 ppm and 106 ppm respectively. For samples of the purity required for ultimate use in semi-conductor work, radiochemical separations are generally necessary and in this manner such impurities as arsenic and copper down to one part in ten thousand million have been determined.



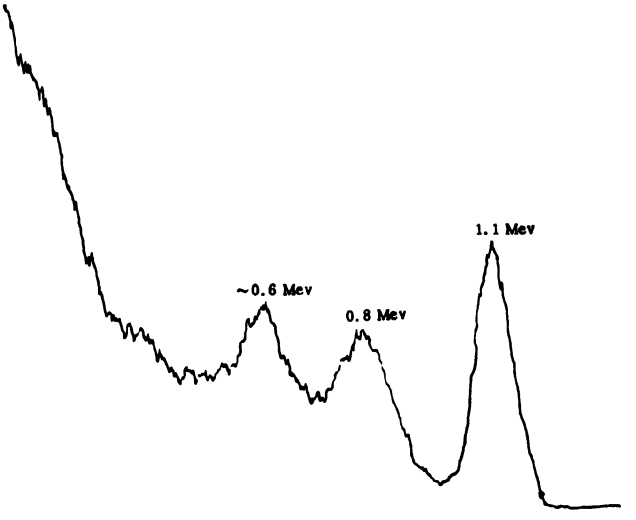
Slide 5. High energy gamma spectrum of tantalum-182

Turning now to the geochemical field, we have developed radioactivation methods for determining nickel, cobalt and copper down to the 10^{-7}, 10^{-8} and 10^{-10} gm levels respectively in a wide range of geological samples. In this case the three elements were determined on the same irradiated sample by using a composite radiochemical separation scheme. The half lives concerned are respectively 2½ hours, 5.3 years and 12.8 hours, and it was possible to deal adequately with the successive radiochemical separations in the order nickel, copper and cobalt. In addition, only one set of counting equipment was needed for checking radiochemical purity and the availability of automatic counting equipment designed by our Electronics Division for measuring decay curves and maximum beta energies made this checking quite simple.

The determinations were carried out on specimens of marine sediments, oceanic rocks and meteorites, in an attempt to shed some light on a suggestion by Professor Hans Petterson that the nickel in deep sea sediments may in part be derived from meteoric materials.

The ratios involving nickel, copper and cobalt are significantly different between average meteoritic and average available terrestrial materials as can be seen in Table VII.

The published value of the average nickel to cobalt ratio in igneous rocks is 3.5; for meteorites 13.1. All the marine sediments average about three to four. For nickel to copper, and copper to cobalt ratios, the results are equally in favour of the conclusion that



Slide 6. Gamma spectrum of Na-K alloy 40 days after irradiation

there is little significant contribution of meteoritic material to deep sea sediments unless some remarkable differential behaviour of the three elements has taken place. The particular advantage of the radioactivation method in this case was its sensitivity, which made it possible to determine all three elements at a level of a few parts per million and upwards, with adequate precision, on no more than a few milligrammes of sample, the sample being particularly limited in the case of the marine sediments and meteorites. The latter seem to be particularly well-guarded by the various museums!

The same methods have been used in attempting to fix the levels for nickel, cobalt and copper in two rock samples, a granite and a diabase. These samples have been analysed spectrographically and absorptiometrically by a range of laboratories all over the world with the idea of setting them up as standards which could be used by other workers. The precision and accuracy of these conventional techniques are not good, however, at low levels and the combination of high sensitivity with reasonable precision possessed by the radioactivation method has enabled the level of the three elements (and ultimately I hope several others) to be fixed with greater certainty.

The spectrographic and absorptiometric results obtained by several workers are quoted by Dr. L. H. Ahrens in his book "Quantitative Spectrographic Analysis of Silicates" and are shown in Table VIII.

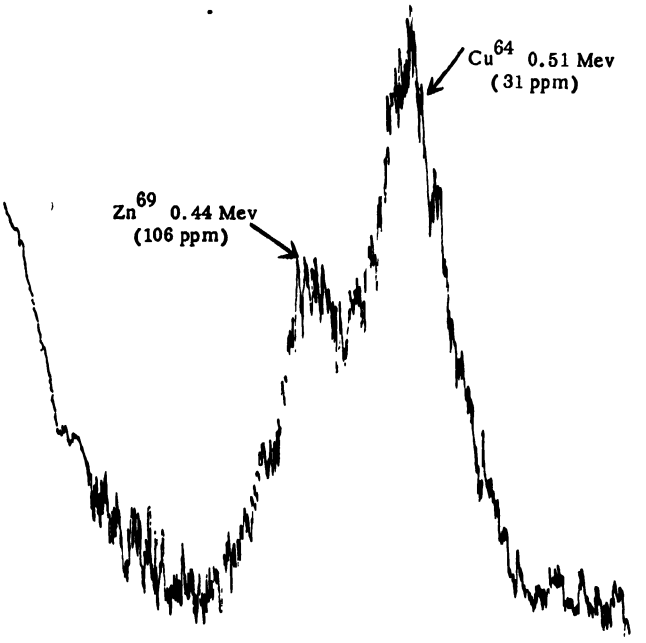
Table VIII

	G1			*W1*		
	Ni	*Co*	*Cu*	*Ni*	*Co*	*Cu*
	parts per million			*parts per million*		
1	5	n d.	< 8	47	35	130
2	n.d.	3	15	80	25	90
3	—	n.d.	5	—	30	44
4	n.d.	—	—	80	50	—
5	<2 5	< 2	6	140	55	140
6	<10	< 5	—	60	26	—
7	—	—	trace	70	—	100
8	60	10	10	150	20	80
9	—	3	20	80	40	130

The first six analysis determinations were done spectrographically, and if you look at the differences in the figures reported you will see—compared, for example, with the absorptiometric determinations 7, 8 and 9, for nickel, for cobalt and for copper (that is, in the granite and then in the diabase)—that we have this variation through here, and you will see that my earlier statement on the lack of precision in this conventional technique was not an exaggeration.

In Table IX I have shown the values "selected" by Dr. Ahrens from those in Table VIII, and also I list the values we obtained by radioactivation. The nickel quoted by Dr. Ahrens is 5 in brackets, which means it is only an order of magnitude. Our results are 1.0 and 1.0. For cobalt he quotes 4 as the order of magnitude. We get 2.1 and 2.1. (All these are of parts per million.) For copper he quotes 11. We get 8.7, 11.1, 8.8, 9.1, 9.5, 9.6—giving an average of 9.5. Similarly in the diabase the precision of the radioactivation method is quite good and the agreement on the copper figure with the selected value is rather remarkable. It would seem that the radioactivation method is clearly going to be of value in providing standards, on which particularly the spectographic method is so dependent.

Other recent applications at Harwell to materials of geochemical interest have included the determination of microgram and submicrogram amounts of thorium in minerals—one of the aims of this work,



Slide 7. Double crystal gamma spectrum of irradiated silicon

Table IX. Some Trace Elements in Standard Rock Samples

	Granite G I.			*Diabase W. I.*		
	Ni ppm	*Co*	*Cu*	*Ni*	*Co*	*Cu*
Spectrographic (quoted by L. H. Ahrens)	(5)	(4)	11	90	36	110
Radioactivation (Harwell)	1.0, 1.0	2.1,2.1	8.7, 11.1, 8.8, 9.1, 9.5, 9.6, Av. 9.5	76, 71, 78, 73, 78, 63 Av. 73	54, 52 45, 46 50, 46 Av. 49	111.5 111.1 111.2 108.0 112.8 118.9 110.4 109.2 Av. 111.6

together with our earlier work on the determination of uranium by radioactivation, was to make possible age determinations on isolated individual minerals from rocks. We have also been able to determine the rubidium and caesium content of sea water, the levels being 0.12 and 0.0005 ppm respectively.

To conclude, it now seems clear that the method of radioactivation is well established now as one of the weapons in the armoury of the analytical chemist, if I am permitted to use such a simile at this Conference. Industrial and university laboratories in Great Britain are beginning regularly to use the method for their own analytical problems, having set up the quite modest radiochemical facilities necessary, and sending their samples for irradiation in the Harwell Pile. There is no doubt that this technique is proving to be a very good example of one of the peaceful uses of atomic energy.

DISCUSSION OF PAPERS P/632, P/706, P/770

Mr. HARRISON BROWN (USA): Dr. V. V. Iakovlev, in the concluding paragraph of his most interesting paper on radioactivation analysis, mentions the possibility of utilizing irradiation with charged particles for the determination of elements which are difficult to detect by neutron activation. I would like to enquire whether such work has been undertaken in the USSR, and, if so, which elements have been studied and what ions and accelerating voltages have been used.

Mr. VINOGRADOV (USSR): We have two aspects of the matter in view. In the first place, we thought it would be very interesting to use monochromatic neutrons for the selective determination of certain elements with large cross sections, such as iridium, silver, etc. As regards Mr. Brown's observation on the possibility of using other charged particles, we are now attempting this and propose, in particular, to use deuterons. The elements with which we are concerned are vanadium, chromium and others.

Mr. LÉVÊQUE (France): We have made determinations of rare earths in graphite in a somewhat similar way, and the general shape of the decay curve was substantially the same. However, our method differs from the one you have described in the following respects:

1. The estimation of the total quantity of rare earths is made from the determination of the dysprosium, in order to reduce the time required for analysis and to increase the sensitivity of the method.

2. The determination is made directly on the graphite powder without chemical separation.

3. To reduce interference from radiomanganese, which has exactly the same period as the radio-dysprosium, two decay curves are traced, the first without an absorptive screen between sample and counter, and the second with a 500 mg/cm² aluminium screen placed between the sample and the detector, to stop all the beta particles emanating from the radio-dysprosium.

Mr. HARRISON BROWN (USA): In Dr. I. P. Alimarin's survey of the application of radioactive isotopes in chemical analysis, mention is made of the determination of small amounts of uranium and thorium by alpha tracks in nuclear emulsions. Could the speaker, Dr. Vinogradov, be kind enough to tell us more about nuclear emulsion techniques in use in the USSR for analytical purposes or recall analyses used? What supplementary techniques are utilized?

Mr. VINOGRADOV (USSR): I can tell you this. The emulsions are prepared in factories. The novel feature of the technique of using emulsions to record alpha particles is that we bring them directly into contact with the polished surface of minerals or rocks. Then the film is removed and viewed in a stereoscopic microscope. At present we intend—and perhaps Mr. Brown will find this interesting—to apply this method to research on rock meteorites, but we do not know ourselves whether we shall be successful.

Mr. LÉVÊQUE (France): I should like to ask Mr. Vinogradov what is the activity of the thallium-204 source used in analysis by beta back-scattering.

Mr. VINOGRADOV (USSR): As far as I recall, this thallium-204 source was used for analysing tungsten alloys. I cannot say how intense the source is. This work is by Bolgdanov and Funke and was published by an industrial laboratory. I will try to get it at our exhibit. This exhibit has a device built on a similar principle for marking tungsten alloys.

Mr. SAELAND (Norway): May I ask Mr. Smales if activation analysis of zinc in technical aluminium or aluminium oxide has been tried in the United Kingdom? If so, what method was used and what was the sensitivity?

Mr. SMALES (UK): We have not in fact tried to determine zinc in aluminium or aluminium oxide so that I am afraid I cannot help Mr. Saeland on that point.

Mr. RODDEN (USA): If a reactor is not available, Mr. Smales, in your opinion what is the best neutron source for the work about which you were talking?

Mr. SMALES (UK): If a reactor is not available, the work in which I am interested would not be done. The neutron flux available in portable neutron sources is of no real value in the trace element work in which I am interested. Mr. Vinogradov pointed out that a radium-beryllium source of 500 millicuries or something of this order could be used to determine fractions of a per cent of one rare earth in the presence of another, and that sort of thing. However, this is not really the level in which I am interested.

Mr. KAUFMANN (USA): I should like to ask Mr. Vinogradov whether he thinks it will be possible to determine small amounts of oxygen in high purity metals by the radioactivation method.

Mr. VINOGRADOV (USSR): I know that method; it has been described in the literature. I think it will

have useful practical applications, along with other more complicated methods of determining oxygen.

Mr. LÉVÊQUE (France): I should like to add a remark on the determination of oxygen in very pure metals. We have already published a method using the (γ, n) reaction on oxygen-16. This reaction is done with a betatron, and yields oxygen-15. The oxygen can be determined by comparison with a control. This method is particularly valuable in determining oxygen in aluminium. Unfortunately, we have confined ourselves so far to a sensitivity of 0.1 per cent.

Mr. SMALES (UK): Perhaps I could also add a little information on the determination of oxygen. We have determined oxygen by neutron irradiation, but using the (n, α, T) reaction on oxygen to give fluorine-18. Here again, even with the pile flux available to us, the sensitivity is only about 0.1 per cent.

Mr. G. V. KURDIUMOV (USSR) presented paper P/702.

DISCUSSION OF PAPER P/702

Mr. WALTON (UK): I should like to ask Mr. Kurdiumov whether he could give any further indication of the experimental methods that have been used for getting these very interesting results on diffusion coefficients.

Mr. KURDIUMOV (USSR): One of the main methods used in these experiments was the study of the distribution of a radioactive isotope by removing layers after annealing. This method was used in a number of experiments. We also used certain other methods, those known as "absorption methods," in which the activity of the specimen was measured before and after annealing without damaging the specimen. Some absorption methods developed in the USSR allow the diffusion coefficient to be determined when the beta-radiation absorption coefficient is unknown, thus making these determinations more reliable. These methods are described in detail in works published in the collections of papers available at our exhibit, more particularly in the collection of papers on the technical uses of radioactive isotopes read at the conference held in July of this year at the Academy of Sciences of the USSR in Moscow. In addition, a number of papers have been published in other collections and in the periodical *Zavodskaya laboratoriya* (The Industrial Laboratory), which are also available here. Anyone wishing to learn more about these methods can study them in detail in these works.

Mr. WALTON (UK): I have some further queries. I wonder whether Mr. Kurdiumov could tell me whether he has looked at the diffusion coefficient of any non-metals in metals—such as sulphur or iodine or phosphorus in metals. Secondly, have you looked at the diffusion coefficients either in the presence of radiation or after irradiation? Has there been any work of that type?

Mr. KURDIUMOV (USSR): We have investigated the diffusion of carbon in steel. Papers in this field have been published in the Proceedings of the Academy of Sciences of the USSR.

Work in the Soviet Union has not been entirely confined to metals. In particular, one investigation was concerned with the diffusion of certain elements in refractories and the influence on diffusion of the chemical composition of refractories. I have no personal knowledge of the work done on the influence of irradiation.

Mr. EPRAMIAN (USA): We are very much indebted to Mr. Kurdiumov for his very fine paper on the use of tracers in diffusion. His report contains a wealth of information. Very often, a single sentence is worthy of a separate paper.

I should like to emphasize one aspect of diffusion studies and then, if time permits, should like briefly to summarize a few of the aspects which are being investigated in the United States.

The main point that I should like to make is that, in the study of diffusion, it is necessary to determine the diffusion coefficients of both constituents in a binary solid solution. Much work in the past has been done on the study of the diffusion coefficient and the activation energy for the diffusion of one component in the binary system. The reason why it is essential to have the two self-diffusion coefficients for both atom type A and atom type B in a solid solution is that, if we are to develop a theory for diffusion, we must have the data for both atoms and their movement in the binary mixture. If, for example, one adds one atomic per cent of lead to silver, the diffusion coefficient and activation energy for self-diffusion of silver is, quite surprisingly, very markedly affected by this small addition of lead.

In the United States, we have quite an intensive program on this subject. Many of our scientists have become interested in the problem. We now have groups which are doing diffusion studies using single crystals of silver as the matrix, to which are added such elements as copper, gold, lead, thallium, germanium, palladium, and so forth. In each case, the self-diffusion coefficient and activation energy for each species are determined.

This problem is also being investigated theoretically. Two theories are being developed, neither of which is wholly acceptable at the present time. In one case, the consideration is the strain energy when one puts a large atom in a matrix composed of smaller atoms. In the other case, the scientist has considered the electronic effects, the perturbations introduced in the lattice when one puts in something which has a different valence from the matrix. In some cases, one theory will explain the experimental data; in other cases, the other theory will do that. This is, however, under continued development.

I should now like to mention just a few of the other aspects of the problem of diffusion which are being investigated in the United States.

One problem which has been quite interesting is that of diffusion along grain boundaries. The investigators have grown specimens consisting of two crystals, which are separated by a single grain boundary. The relative orientations of the two grains are varied in a series of samples. The tracer is deposited on the surface and allowed to diffuse into the sample. It is quite clear that the diffusion is more rapid along the grain boundary. The investigators have, however, studied the rate of this penetration as a function of the relative disorientation of the two crystals in the sample. This has very nicely been correlated with the density of dislocations, which may be calculated from a grain boundary model. In essence, it varies directly with the concentration of dislocations, as one would expect.

Another problem which is being explored is the effect of the order/disorder reaction in metals on the rates of diffusion. This is being currently investigated using β brass, and it is found that the activation energy for diffusion is changed by a factor of 2 upon going through the critical temperature of order. In this case, the investigator is again measuring the diffusion coefficient and activation energy for both the copper atoms and the zinc atoms in the β brass. This should be published in the near future, and I think it is a very interesting investigation.

Another problem which I should like to mention briefly is that of lattices which are anisotropic, that is, crystals which have different properties in different directions—for example, thallium, antimony, zinc and bismuth. These have non-cubic lattices, and have properties which vary in different crystallographic directions. We have, by the use of tracers, investigated the anisotropy of the diffusion coefficient and activation energy for these anisotropic lattices. We are now beginning to investigate the anisotropy of diffusion in single crystals of uranium. We do not yet have the results to report, but if Mr. Kurdiumov or his colleagues have any data on this we should be interested to hear anything they can report on this subject.

These are but few of many investigations, but I feel that I have taken enough time in this session.

The CHAIRMAN: Thank you, Mr. Epramian, for that important contribution. Do you want to say anything in this connexion, Mr. Kurdiumov?

Mr. KURDIUMOV (USSR): Perhaps there will be some more questions; if so, I will answer them all together.

Mr. SMITH (USA): Mr. Kurdiumov's work on transformations in metals and alloys is world famous, and it is gratifying to see the new results obtained with the use of tracers. The effect of the transformation and subsequent diffusion in the gamma alloys of the iron, nickel, carbon alloys is particularly interesting. I should like to ask if Mr. Kurdiumov can state the grain size and the sub-grain size of the gamma alloys in which the enhanced diffusion rate was observed, and also if he has determined the orientation difference between the sub-grains by X-ray means.

Mr. KURDIUMOV (USSR): I will answer your question first, Mr. Smith. The grain size was fairly large and consistent, so that the grain of the austenite itself should not have had any effect. The alloy specimens were pre-heated at 1200–1300°, but the higher diffusion rate was observed at a lower temperature, below 1100°. As regards the size of the coherent bodies within the grains, it was possible to establish, by measuring the width of the interference lines, that the size of these bodies was of the order of 10^{-5}–10^{-6} cm. They begin to increase somewhat at a temperature of 700°–800°. As the temperature approaches 1000°, however, there is still further widening of the lines and it is not until the heating has reached 1100°–1200° that we get a structure corresponding to the original state.

I should also like to say something in connexion with Mr. Epramian's statement. I am well acquainted with the extremely interesting papers by American authors published in a number of periodicals, such as the *Journal of Metals*, on diffusion in metals and the study of the diffusion mechanism, representing both theoretical and experimental work. We used the formulae of Mr. Fisher and his associates to calculate the boundary diffusion along the internal surfaces caused by the martensite transformation. These formulae enable the value of the activation energy to be inferred quite definitely. To obtain the boundary diffusion coefficient itself, however, one would have to know the size of the boundary layer, which can only be estimated.

Work has also been done in the Soviet Union on the determination of diffusion at the boundaries of grains which are visible under the microscope, using the autoradiography method. There is a work on this subject by Bockstein and Kishkin, which is available here among the conference documents.

I have no data on the question of the influence of anisotropy on diffusion in single crystals of uranium.

The CHAIRMAN: Thank you very much, Mr. Kurdiumov. This paper is still open for discussion, if anybody else wishes to raise a point.

Mr. DIENES (USA): I was very interested in Mr. Kurdiumov's work on the carbon and iron system, and I should like to ask what techniques one uses to prevent any change in the carbon concentration during the high temperature diffusion, that is to prevent any decarbonization.

Mr. KURDIUMOV (USSR): We ground the surface of two samples, coated them with a radioactive isotope, placed the two samples together and kept them in a vacuum at a high temperature. X-ray examination showed that the decarbonization had not been at all substantial.

The CHAIRMAN: If nobody else wishes to say anything, I should like to thank our speakers once more, and I also wish to express our gratitude to those who have contributed to this morning's success by putting questions or by making remarks. The session is closed.

Session 22C

RADIOACTIVE ISOTOPES IN CONTROL AND TECHNOLOGY

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Development in Thickness Gauges and Allied Instruments

By J. L. Putman,* UK

Measurements of the absorption or scattering of radiations by a medium are already well established as means of assessing its thickness or bulk density. It is proposed in this article to outline the present state of British commercial production and use of instruments employing these principles, and to describe research which is likely to lead to new instruments in the near future.

BETA AND GAMMA RAY ABSORPTION

The most widely used instruments at present are those which measure the transmission of beta particles or gamma rays from a source through a material to a detector on the opposite side. When such an equipment is calibrated for use with a particular material, it can be used as a non-contacting thickness gauge to give a continuous indication of thickness in production.

The absorption of beta particles between source and detector is mainly due to energy losses on collision with electrons. Thus the absorption depends chiefly on the number of electrons per unit area in the material traversed. Since the number of electrons per atom is nearly proportional to its mass, for all the lighter elements except hydrogen, the absorption is nearly a function of mass per unit area, and it has become customary to express thicknesses to be measured in mg/cm^2. Using these units, the absorption by different materials becomes nearly independent of their density or atomic weight. Calibrations for elements of neighbouring atomic numbers are almost identical, but discrepancies do occur between heavy and light elements, owing to differences in the electron/mass ratio of the atoms, and to the effects of nuclear scattering. These can affect comparative measurements, for example, when light materials such as paper are loaded with heavy elements. In practice, instruments are generally calibrated separately for each type of material to be measured.

Beta particle transmission gauges are used routinely for measurements from 1 to 1200 mg/cm^2. Several different sources are needed to cover this range adequately. For measuring a particular thickness of material with the best possible accuracy it is desirable to choose a source of beta particles which are at least 50% absorbed in the thickness to be measured. When this is done, since the emergent radiation falls off nearly exponentially with thickness, relatively small changes in thickness result in easily measurable changes in the number of emergent beta particles. The apparent advantages in sensitivity of using beta particles which are heavily absorbed are offset by statistical fluctuations when only a few particles emerge to the detector. It is found generally that beta particles from a given source can be used successfully for measurements from 0.2 to 4 times the "half-thickness" for absorption of the particles, and that best results (thickness to about 1%) are obtained at the equivalent of 0.5 to 2 half-thicknesses. For low energy beta particles, the range is further limited by absorption in air between the source and detector, and in the detector window.

Syke[1] has shown that by collimation of the emergent radiations, scattered beta particles can be prevented from entering the detector, thus increasing the apparent absorption in small thicknesses and improving the accuracy of their measurement. Some commercial gauges use this technique to extend the range of measurements with a particular source. Collimation also reduces errors due to movements of the measured material in the source-detector gap.

Pure beta-emitters are preferred as sources, especially for the smaller thicknesses, since the more penetrating gamma rays are very little absorbed and reduce the sensitivity of the system to changes in thickness. Long half-life is desirable to avoid the need for frequent recalibration. High specific activity is required, especially when the beta particle energy is low, otherwise self-absorption limits the effective strength of the source. For example, early attempts to employ Ca^{45} (maximum beta particle energy 0.25 Mev) have been superseded by the use of Pm^{147}, which is more easily produced in high specific activity (as a fission product) and has a longer half-life. Table I shows a series of beta emitters in popular use for thickness gauges.

Most of these sources are now available as foils containing the radioactive material sealed between thin sheets of silver.[2] Tl^{204} is supplied as an electroplated deposit, covered with a thin protective plating of cadmium.[3] Activities from 5 to 20 mc are commonly used in conjunction with ionization chambers as detectors.

Much greater thicknesses up to several inches of steel can be measured by using gamma ray sources. A typical application is to the gauging of hot-rolled metal strips.[4] A useful series of gamma emitters is given in Table II.

* Atomic Energy Research Establishment, Harwell, England.

Table I. Sources of Beta Particles Used in Thickness Gauges

Isotope	*Half-life*	*Maximum energy (Mev)*	*Approximate half-thickness mg/cm² (Al)*	*Approximate useful range of operation mg/cm²*
S^{35}	87 d	0.167	2.0	0.5–5
Pm^{147}	2.6 yr	0.23	4.5	1–12
Tl^{204}	4 yr	0.77	35	10–150
Sr^{90}	20 yr	0.53	17	
$+Y^{90}$	(in equilibrium)	2.2	160	50–650
Ce^{144}	280 d	0.30	7.5	
$+Pr^{144}$	(in equilibrium)	3.0 (+γ-rays)	220	100–1000
Ru^{106}	1 0 yr	0.03		
$+Ru^{106}$	(in equilibrium)	3.5 (+γ-rays)	270	130–1200

In gamma ray thickness gauges, scintillation counters compete for favour with ionization chambers as detectors, because of their higher sensitivity for gamma rays. Tests at A.E.R.E. have shown that a scintillation counter, employing only a few stages of electron multiplication and used in conjunction with a vibrating reed electrometer, has stability comparable with that of a good ionization chamber and is much more sensitive.

Both beta and gamma ray transmission type thickness gauges are available commercially. At least three British manufacturers produce standard instruments and several firms have developed their own gauges for specific purposes. An alpha particle transmission gauge has also been designed[5] for the measurement of very small thicknesses up to 2 mg/cm².

Ionization chambers are by far the most widely used detectors and these operate fed-back valve electrometers or vibrating reed electrometers. Generally the gauges are used as null instruments, indicating the deviation of thickness from a standard value. This is achieved by balancing the response of the detector against that from a second detector and source separated by a standard thickness of material, or alternatively by applying a balancing potential electronically. Commercial gauges using either method are made. The first method, though it uses two sources, has the advantage of automatic compensation for source decay in the balanced condition. It also compensates for changes in air absorption with temperature, pressure and humidity in the measuring gaps, provided that conditions can be kept identical in the two gaps.

Various types of display are available. The most commonly used employs either a centre-zero meter or a system of coloured lights to indicate deviations from a standard thickness, and relies on manual control of the thickness. Some commercial instruments record actual thickness in addition to deviations from a standard. Gauges are also made which operate servo controls to keep the thickness within specified limits automatically.

Table II. Gamma Emitters Used in Thickness Gauges

Isotope	*Half-life*	*Gamma ray energy (Mev)*
Tm^{170}	127 d	0.085
Se^{75}	127 d	0.40–0.067 many γ-rays
Ir^{192}	74 d	0.61–0.14 many γ-rays (mean about 0.5 Mev)
$Cs^{137} + Ba^{137m}$	33 yr	0.66
Co^{60}	5.23 yr	1.33, 1.17

Routine applications of beta transmission gauges include the continuous monitoring in production of paper, plastic films and wrapping materials, linoleum, synthetic hardboard and thin metal strip. Beta and gamma ray transmission gauges are also used in the inspection of hollow extruded aircraft components.

In conditions which define the actual thickness, both beta and gamma ray transmission gauges are used to measure the density of products. A beta particle transmission gauge made commercially is used in conjunction with servo-mechanisms to control and standardise the packing of tobacco in cigarettes. An alpha particle gauge is being developed for measuring gas pressures from 1 to 500 microns.[6] In experiments at A.E.R.E., a gamma ray transmission gauge has been used externally to distinguish between different densities of fuel in a pipe-line. In this last application, the hydrogen content of the fuel plays an important part in determining the absorption of gamma rays, since the electron/mass ratio in hydrogen is twice as high as in other light elements. Fuels differing in density by as little as 0.3% have been distinguished under experimental conditions and the method is considered as an alternative to existing techniques for interface detection in long distance pipe-lines.

LEVEL DETECTORS AND PACKAGE MONITORS

A simplified form of transmission gauge is used as a level detector for liquids or solids in enclosed systems. An application to the monitoring of packages is in use in several factories.[7] In this device, a radioactive source is fixed at a critical level on one side of a conveyor belt carrying filled packages, and a collimated detector is mounted at the same level on the opposite side. The source is chosen so that its radiations can easily penetrate the walls of an empty container to operate the detector, but are absorbed when the package is filled above the critical level. A location system is required, to ensure that packages are properly situated between the source and detector at the time of measurement. A beam of light and a photo-electric cell are often used for this purpose. Facilities are provided for ejecting empty or underfilled packages automatically.

Although the electronic control of a package monitor of this type is quite complex, especially when it is required to operate at high speeds, the detector itself is of simple design, since only gross changes in radiation level are significant. An extremely simple and cheap device has been designed by Pulsford. In this a halogen-quenched counter is used to trigger a cold cathode discharge tube, the mean current from which operates a relay. The cold cathode tube is quenched at mains frequency because its anode is supplied with an unsmoothed half-wave rectified alternating potential. A similar fluctuating anode potential has been used successfully with an unself-quenched counter filled with pure argon.

SCATTERING OF BETA PARTICLES

Beta particle back-scatter gauges are used to measure the thickness of coating such as paint or metal plating on a base material. A beta particle source is arranged near a detector (often in an annular ring around it), so that particles from the source cannot directly enter the detector, but so that both source and detector are exposed to the surface to be measured. The proportion of beta particles scattered back by the surface into the detector is nearly proportional to $\sqrt{Z}$, where Z is the atomic number of the surface layers and reaches a steady "saturation" value when the layer thickness is increased to about 3 half-thicknesses for the beta particles. For intermediate thicknesses of coating, a response is obtained which is intermediate between those appropriate to the base material and to the coating, and from this the coating thickness is assessed. In practice, the detector response is offset against one which corresponds to zero thickness of coating, and the unbalance current obtained is nearly proportional to coating thickness over a limited range.

For coatings greatly differing from the base material in atomic number, high sensitivity can be obtained. Thicknesses down to 0.75 microns of tin or cadmium on iron have been measured within 0.05 microns using Tl^{204} as a source. When the atomic number of the coating is near to that of the base material (as in nickel on iron), the sensitivity is reduced and very high electronic and mechanical stability is essential.

Commercial units are now available, operating with standard electronic equipment which can alternatively be used as a transmission thickness gauge. Unfortunately the position of the scattering surface affects the response, and these gauges are not easily applied to the measurement of coatings on curved surfaces. In an attempt to overcome this difficulty, an instrument has been made at A.E.R.E. to inspect small areas of surface. A scintillation counter is used as detector, and the source, which is a capsule of Kr^{85}, is mounted in a 6 mm diameter collimating tube inside a tapered light guide. The phosphor is a thin flat ring of NaI(Tl) which is connected by the light guide to a standard photomultiplier. An area of surface only 9 mm in diameter is inspected. This instrument is still in an experimental stage.

SCATTERING OF GAMMA RAYS

The back-scattering of high energy gamma rays (about 1 Mev) has been in use for some time as a measure of thickness when only one side of the material is accessible. In particular gamma ray back-scattering gauges have proved valuable for measuring the wall thickness of tubes and enclosed tanks up to a practical limit of about 2 cm of steel.

Originally the gauge consisted of a gamma ray source separated from a Geiger counter with a shaped screen of heavy material thick enough to reduce direct radiations to a low level. Radiations falling on the surface to be measured were scattered (generally through angles from 50 to 90 degrees) into the detector and their number was a measure of the thickness of scattering material. Gauges of this pattern suffered from some disadvantages. First the distance between source and detector necessitated by the screening of direct radiations, coupled with the low gamma ray sensitivity of Geiger counters, made the use of relatively large sources (1 mc or more) essential: additional screening, for the protection of users, added to the considerable weight of the unit. Secondly, quite a large area of surface contributed to the scattering and the thickness measured was a mean thickness over this area.

In a new type of gamma ray thickness gauge, developed at Harwell[8, 9] and now in commercial production, gamma rays scattered through a large angle (near to 180 degrees) are distinguished from direct radiations by virtue of the decreased energy resulting from Compton scattering. The need for screening between source and detector is thus avoided. A 20 μc Co^{60} source is used and its container is held in contact with the surface to be measured. It is mounted on the housing of a scintillation counter at a distance of 2.5 cm from the sodium iodide phosphor. This arrangement constitutes the portable measuring head of the instrument. It is connected through up to 70 metres of concentric cable to the ground equipment, which incorporates the power supply, amplifier and a simple kicksorter to select the pulse amplitudes corresponding to the 0.209 and 0.214 Mev back-scattered radiation. The resulting pulse rate is recorded with a built-in ratemeter. Correction for source decay is incorporated in an adjustment which uses the Compton recoil electrons produced in the phosphor.

The measuring head weighs 2 kg, including a shock-mounted frame for convenient carrying. Measurements of wall thickness to $\pm$ 4% can be made up to 2 cm of steel, and the calibration is almost independent of tube diameter. Local irregularities, such as pitted corrosion inside a tube, are readily detected.

Whereas gamma rays of energies around 1 Mev lose most of their energy in a medium by the Compton process of electron recoil, low energy gamma rays

are mainly absorbed by the photo-electric process. The probability of photo-electric absorption per atom of a medium[10] is proportional to $Z^{4.5}/E^{3.5}$, where Z is the atomic number of the medium and E the energy of the gamma rays. By comparison, the probability per atom of a Compton recoil is proportional to Z. It is evident, therefore, that if the energy of the gamma rays is suitably chosen, photo-electric absorption will compete with Compton recoil in determining the number of gamma rays scattered back by a thick medium. Also the relative effect of photo-electric absorption is strongly dependent upon atomic number, with the result that materials of high atomic number scatter back less gamma rays than those of low atomic number.

This principle has been applied experimentally to the sorting of coal and shale, using the 0.085 Mev gamma ray from Tm^{170} and has shown promising results.[11] The shale, which has a mean atomic number Z of about 13, scatters back less gamma rays than pure coal, whose atomic number is very nearly 6. In a test with 50 samples of arbitrary shapes and varying qualities, the counting rate of back-scattered radiations was compared with the ash content of the separate samples. Samples with ash content greater than 30% could be reliably sorted from those with ash content below 20% purely on a basis of the observed counting rates. An instrument is being developed for the automatic sorting of coals into different qualities at the pithead and is expected to be more economic in use than orthodox methods relying on density.

NEUTRON SCATTERING AND ABSORPTION

Now that portable neutron sources are readily available, increasing use is being made of the properties of neutrons in scattering and absorbing media. One of the most popular sources is a mixture of polonium and beryllium in a sealed capsule. Neutrons are produced by the (α, n) reaction in beryllium: a source containing 1 curie of Po^{210} yields about 2.5×10^6 neutrons/second, accompanied by an equal number of 4.45 Mev gamma rays. Although the half-life of the source is rather short (140 days), the relatively high neutron yield and the practical absence of gamma rays from the polonium make it convenient to handle.

A soil moisture gauge has been built[12] which relies on the moderation and scattering of neutrons by hydrogen atoms in the soil. The gauge consists of a Po-Be source of fast neutrons attached to a BF_3 slow neutron counter and ratemeter. The unit is simply laid on the surface of the soil and the ratemeter response is a measure of the total hydrogen content per unit volume of soil. Experiments show that depths of 6 to 7 inches of soil contribute to the reading but that most of the response is attributable to the first 4 inches of soil. Tests with pure water, sand, topsoil and sawdust, with corrections for the combustible hydrogen content of the last two, have shown that the response of the instrument is practically independent of the presence of other elements with atomic numbers greater than 5 (except, of course, the strong neutron absorbers), and that the results are virtually unaffected by packing or bulk density. Calibration curves of counting rate against hydrogen content obtained with the test substances were identical within an experimental error of about $\pm$ ½% in hydrogen content.

It is expected that instruments of this type will not be restricted to soil measurements. Their use for measurements of moisture in grain, timber and stone is being considered. A portable battery-operated gauge will be developed.

Nuclear reactions produced by neutrons in absorbing media have been studied, particularly for the logging of boreholes.

When a neutron is absorbed by a nucleus, prompt gamma rays are emitted whose energies are characteristic of the absorbing nucleus and hence give information about the chemical nature of the absorber. In an instrument designed at A.E.R.E.[13] a Po-Be source of neutrons is attached at a small distance from a gamma ray scintillation counter. The counter, which uses a sodium iodide crystal as phosphor, is fed to a single channel kicksorter, which selects pulses of amplitudes corresponding to a particular range of gamma-ray energies. The neutron source and counter are attached to a long cable and can be lowered down a borehole, to operate the kicksorter and a ratemeter at ground level.

In field experiments it has been found possible to distinguish between crude oil and brine in sandy strata through a 1 cm steel pipe encased in concrete, even when the borehole itself is full of oil. The instrument, which is being developed for oilwell control, is expected to be of considerable value in oilfields where the oil is displaced by brine in the underlying strata.

More complicated instruments are envisaged in which the gamma rays are analysed into several energy channels, with continuous recording of the separate counting rates. These are expected to supplement the information obtainable by other borehole-logging techniques.

ACKNOWLEDGEMENTS

The developments described above are mainly due to research by A.E.R.E. workers and instrument manufacturing firms. The author wishes to acknowledge the advice of his A.E.R.E. colleagues, particularly Messrs. S. Jefferson, D. B. Smith and J. F. Cameron, and to thank Mr. G. Syke (Baldwin Instrument Co., Ltd.), Mr. R. Y. Parry (Ekco Electronics Ltd.), and Mr. E. N. Shaw (Isotope Developments Ltd.), for their helpful comments upon the manuscript.

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The Versatility of Radiation Applications Involving Penetration or Reflection

By C. E. Crompton,* USA

Nations constructing or operating either research or power reactors will soon encounter a demand for byproduct material radiation sources. Each year many hundreds of sources of varying design and utility are finding application in virtually all phases of academic research, applied industrial research and industrial production. The types of radioactive sources are multiplying rapidly as the unique radiation characteristics of each isotope are being exploited. It is hoped that a discussion of the great versatility of radiation applications will prove helpful to other nations and groups planning to utilize byproduct materials to improve their technology. This paper will deal only with those applications where the *amount of radiation* reaching the detector by penetration or reflection is important. The beta and gamma emitters shown in Table I are typical and include radioisotopes which have had great economic and technical import in their use. These isotopes will be featured as radiation sources in the subsequent discussion.

The quantitative evaluation of the amount of radiation reaching a sensitive film has long been a useful technique in both the industrial and medical professions. The ready availability of low cost reactor-produced radiation sources has led to an enormous growth in industrial non-destructive testing of metal castings and welds. Similarly these radiation sources have been used for diagnostic and therapeutic benefit in medicine. Well designed portable "gamma cameras" employing thulium-170 are now available for diagnostic medical use as well as for industrial radiography. Such uses, together with autoradiography, involve film as the detector and will not be discussed here.

APPLICATIONS OF GAMMA RADIATION

The basic principles of the attenuation of gamma radiation have been successfully applied to quantitatively measure mass, density or thickness. The quantity of radiation absorbed is proportional to the intensity of the incident radiation (I_0) and to the thickness (t) of the absorbing material. This relationship is expressed in equation 1 where μ is the linear absorption coefficient in reciprocal centimeters and I is the emergent intensity.

$$I = I_0 e^{-\mu t} \qquad (1)$$

By dividing the linear absorption coefficient, μ, by the density one obtains the mass absorption coefficient in terms of $(mg/cm^2)^{-1}$. If gamma absorption were purely a function of wave length and density, the mass absorption coefficient should be constant for all materials for a given gamma energy. Since this

* US Atomic Energy Commission

Table I. Radiation Sources

Isotope	*Radiation type*	*Maximum energy in Mev*	*Half-life in years*
Strontium-90 (Yttrium-90)*	Beta	2.18	25
Thallium-204	Beta	0.775	2.7
Promethium-147	Beta	0.223	2.26
Sulfur-35	Beta	0.167	87 days
Carbon-14	Beta	0.154	5740
Nickel-63	Beta	0.063	85
Ruthenium-106	Beta	0.041	1
Hydrogen-3	Beta	0.019	12.5
Cobalt-60	Beta	0.3	5.3
	Gamma	1.33	
Europium-152,-154	Beta	1.9	5.3
	Gamma	1.2	
Cesium-134	Beta	0.66	2.3
	Gamma	0.79	
Cesium-137 (Barium-137)*	Beta	1.2	37
	Gamma	0.66	
Thulium-170	Beta	0.97	127 days
	Gamma	0.84	

* Daughter activities.

is not precisely the case, a calibration measurement is usually made for each particular material being measured. Figure 1 reveals the relationship between absorber thickness and per cent transmission of gamma radiation for various materials.

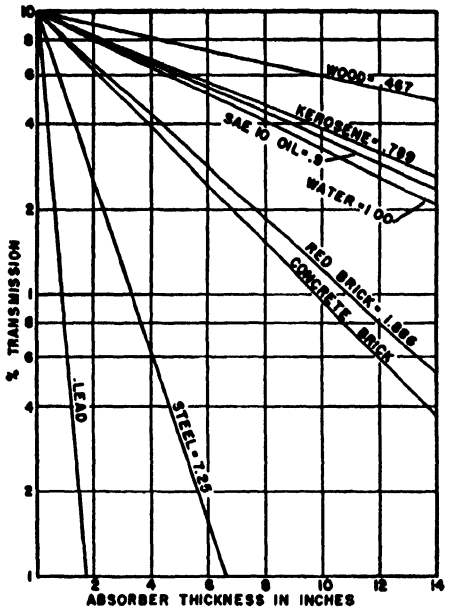


Figure 1. Relationship between absorber thickness in inches and per cent of gamma radiation transmitted for various materials

A gamma gage is being successfully used in the Hawaiian sugar industry[1] to continuously measure the weight of "bagasse" (crushed and pressed sugar cane) moving in a free falling stream from a conveyor belt. Figure 2 reveals that a gamma ray source of cesium-137 passes edgewise through the sheet of material. The free falling stream eliminates uncertainty of rate of movement of the conveyor belt and a true blank reading is obtained every time the stream is interrupted. This technique gives a continuous and permanent record of milling performance which is of considerable value. The same detector signal which actuates the recorder can be used to actuate automatic controls regulating the cane fed into the crushers.

Cesium-137 was chosen rather than cobalt-60 since the crushed cane attenuates 18% of the cesium radiation and only 11% of the cobalt radiation. This increased attenuation improves the precision of the measurement. By selecting a source size that results in 10,000 counts per minute, the over-all error in estimating mill loads is ± 5%.

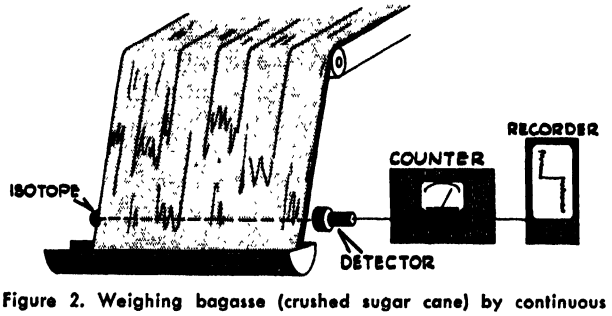


Figure 2. Weighing bagasse (crushed sugar cane) by continuous gamma-ray attenuation

A similar type of gage is also used by this same industry to weigh raw sugar as it falls in a thin stream. The sugar absorbs about 25% of the radiation from a cesium source whose radiation also passes edgewise through the thin stream. The weight of sugar is measured to ± 1%.

The need for remotely measuring the amount of water stored in a distant snow pack has been met by a cobalt-60 gamma gage.[2] Commitments for both hydroelectric and irrigation water supplies are usually made on the basis of such snow measurements. Snow survey and precipitation data from mountainous areas have, in the past, given only limited information because of the inaccessibility of many important water sheds during the winter months.

Forty millicuries (mc) of cobalt-60 were mounted at the lower end of a heavy lead tube as shown by Fig. 3. This serves to collimate the radiation. At the position of the Geiger-Mueller detector, a distance of 15 feet above the ground, the principal energy is contained within a circle of 1½ feet in diameter. For continuous calibration of the instrument a small strontium-90 source is included in the housing of the G-M tube. Over a range of up to 45 inches of water equivalent, the error is less than 5%.

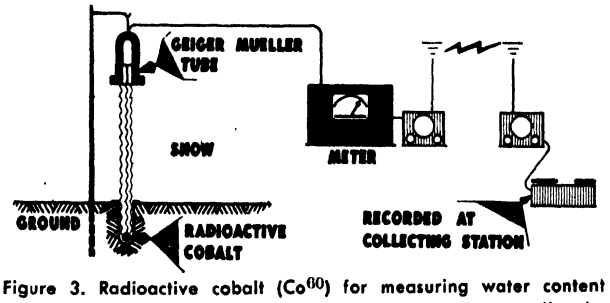


Figure 3. Radioactive cobalt (Co^{60}) for measuring water content of snowfall. Advantages: (1) measures amount of water directly; (2) measurements taken remotely; and (3) higher degree of accuracy

The output signal of this gage is in the form of pulses whose rate is directly proportional to the intensity of radiation. The pulse signal is cabled to a telecoding device which produces an audio tone which is then frequency modulated at a rate equal to the coded signal from the G-M tube. This modulated audio tone is then transmitted to a central collection center by RF transmitter once daily for a ten minute period.

Gamma gages are presently being used industrially to routinely measure metal sheet thicknesses such as 2 inches of steel and 3 inches of aluminum. One such gage, designed to routinely gage 2 inches of steel, employs a sealed 500 mc source of cesium-137.

A unique and extremely versatile instrument illustrates the manner of using gamma radiation in numerous industrial situations to precisely measure density of liquids, solids, and slurries. This device is also able to discern the interface between materials of slightly different density. The radiation source involved is usually cesium-137 or cobalt-60. The "sens-

ing" element and the source are most commonly mounted on the outside of the pipe or tank that contains the material to be measured. Thus, conditions of temperature, pressure or corrosion do not affect the operation of the gage.

The unique sensing element or detector is a cell which directly converts radioactive energy into electrical energy.[3] The cell consists of two electrochemically dissimilar electrodes separated by a filling gas. The electric field which exists between the dissimilar electrodes collects the ions formed by ionizing radiation and results in a flow of electrical current. The magnitude of the current is a function of the incident radiation intensity. No high voltage power supply is required to operate this detector. The ion collection efficiency is only about 50% which improves the signal to noise ratio by about a factor of 10 over conventional ion chambers.

The ease of expansion of its scale is one further factor contributing to the versatility of this radiation device. Referring to Fig. 1 it can be seen that a sample of kerosene 10 inches thick transmits 38% of cesium radiation whereas the same thickness of water would transmit 32%. Ordinarily this results in only 15% of the recording meter span being utilized. Introduction of a balancing current in the circuit to cancel the unwanted portion of the signal and expand the scale usually increases the complexity of the equipment and, more important, makes the value of the load resistor extremely critical (1% change in resistance shifts the density scale by about 6.5%). By using a negative compensating "cell" connected in parallel with the positive measuring cell, this drawback is avoided. The compensating cell has a source of radioactivity mounted on a screw that projects into a recess in the cell. By adjusting the position of this source the compensating current can be accurately adjusted to expand the scale without losing accuracy.

Figure 4 reveals a settling vessel into which a heterogeneous fluid is pumped and later separates into two layers. A valve is opened and the lower layer allowed to drain. A new quantity of the heavier liquid is then added to the remaining lighter phase

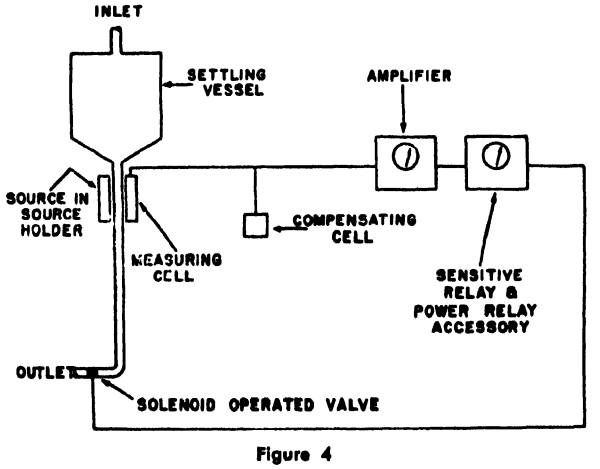


Figure 4

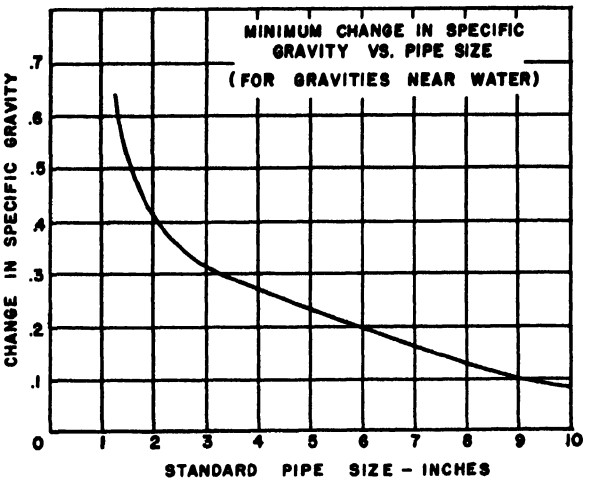


Figure 5. Minimum change in specific gravity vs. pipe size: (for gravities near water)

and another separation takes place. In all, three individual separations take place with the heavier phase remaining constant in density and the lighter phase increasing in density. The density difference in successive separations is 0.284, 0.148 and 0.073 respectively. In each case, when the valve is opened, the interface is detected when it passes the cells and control action is initiated. The signal current from the detector goes to an amplifier and thence to a relay system with power to operate a solenoid valve. The automatic valve is located down stream at a distance which compensates exactly for the time constant of the instrument.

This type instrument measures successive densities with a precision of 2% of the density difference. Figure 5 reveals that a minimum density change is required depending upon the size pipe used. Thus a 6 inch pipe requires a minimum density difference between phases of 0.2 specific gravity units. This technique is now used for detecting the passing interface between dissimilar petroleum products being pumped through the same pipeline.

These same measurement "cells" may be stacked to any desired height since each cell has a "male" and a "female" end. When stacked the cells are electrically in parallel. Thus stacked, these sensing elements are used to measure liquid level when an equally long *strip* radioactive source is employed. As the liquid level rises the current output decreases with a linearity which varies only about 1%.

Although one would not ordinarily expect to find radioisotope applications involving X-ray attenuation, there is a very interesting example of how the X-rays which follow *K*-capture can be utilized. About 5 millicuries of the radioisotope Fe^{55} was used as a source of manganese X-rays. The device was designed to quantitatively analyze for sulfur in liquid or solid petroleum products.[4] This use is based upon the fact that X-rays are absorbed resonantly, thus permitting discrimination. Sulfur selectively absorbs manganese X-rays to an extent 20 times greater than carbon and 450 times greater than hydrogen. Thus

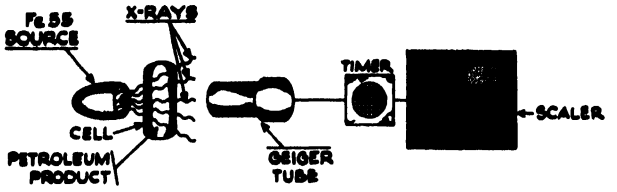


Figure 6. Sulfur analysis with X-rays from radioactive iron: sulfur analysis in 5 minutes (± 0.05%); saves ½ hour per sample over bomb or lamp methods; non-technical operators can be used. Note: absorption of manganese X-rays from Fe^{55}; (a) sulfur absorbs 20 times more than carbon; and (b) carbon absorbs 450 times more than hydrogen

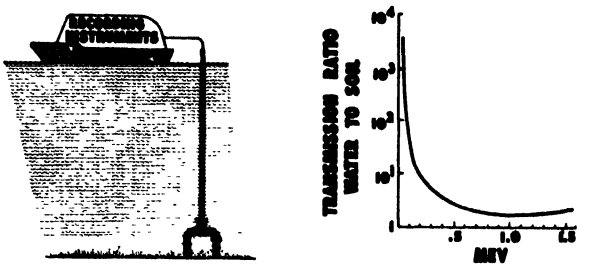


Figure 7. Bremsstrahlung gage for measuring silt density. Advantages: (1) more accurate; (2) measurements easily and quickly made; and (3) eliminates collecting samples

minute amounts of sulfur can be analyzed to ± 0.05% in 5 minutes time by the device schematically illustrated in Fig. 6.

It is appropriate to briefly discuss the usefulness of bremsstrahlung associated with beta sources. These are also referred to as beta ray excited X-ray sources.

The primary absorption processes of gamma rays vary both with the energy of radiation and the atomic number, Z, of the absorber. It is also recognized that the photoelectric effect is a significant absorption process only for gamma rays of low energy. Since the photoelectric effect is inversely proportional to the fifth power of the atomic number, the attenuation by means of this process should yield a sufficient difference between materials of *low* atomic number.

Figure 7 is related to the development of a device to continuously measure and record the density of silt at the bottom of large bodies of water (lakes) and the silt content of moving streams.[5] The chart in this figure clearly illustrates that the *ratio* of transmission through water to the transmission through wet soil varies considerably over the energy spectrum of electromagnetic radiation.

When gamma radiation of moderate energies proved unsatisfactory, it was necessary to select a radiation source of long half-life, ready availability and of low energy. It was found that beta rays from a 20 millicurie strontium-90 source incident upon a lead disc produced the desired bremsstrahlung radiation. Figure 8 depicts the probe containing the source and detector spaced about 12 inches apart. It was demonstrated that a wide difference in counting rate may be obtained for small differences in silt density.

At the present time bremsstrahlung radiation from a tightly sealed 300 mc strontium-90 source is being utilized in an industrial gage to routinely measure and record the thickness of steel sheet.[6] Due to its greater range of penetration, the energy of radiation from this source offers considerable advantage over conventional beta radiation.

APPLICATIONS OF NEUTRON RADIATION

The use of neutron sources for routine industrial purposes has not yet become commonplace. There are, however, several examples which illustrate the versatility of neutrons in providing useful information. Perhaps the most striking use is that connected with the routine measurement of both soil moisture and soil density to an accuracy of ± 5% within six minutes time.[7]

Other devices used for the "in place" determination of soil moisture content or density have had several inherent disadvantages such as long equilibration time, frequent need for calibration curves and difficulty of physical placement.

The elements necessary for construction of a nuclear moisture and density measuring system are depicted in Fig. 9. An access tube slightly more than 1 inch in diameter is placed in the soil. The probe containing the neutron source and detector (Fig. 10) is lowered into the access tube. Fast neutrons emanating from the source are slowed by collisions with atoms of the surrounding medium.

In a mass of soil a fast neutron is slowed or moderated primarily by a series of elastic scattering collisions. Hydrogen is more effective in slowing fast neutrons than any other element. Hydrogen is a good moderator because its cross section for elastic scattering is large and because in a collision with a hydrogen atom a neutron may lose a large fraction of its kinetic energy. Neutron moderation by other elements in the soil is small and in normal soils most of the hydrogen present is contained in the soil moisture. The detector is designed to detect slow neutrons and can be calibrated in terms of moisture content.

Since this method also involves gamma detection in the measure of soil density, the detectors of choice are apt to be a BF_3 proportional counter or a scintil-

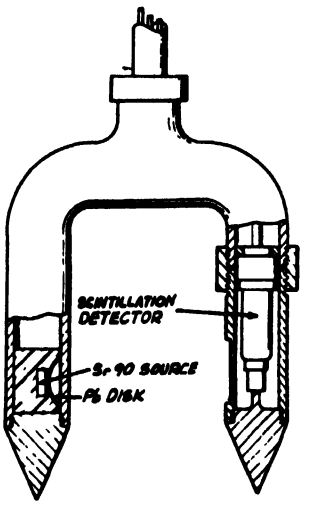


Figure 8

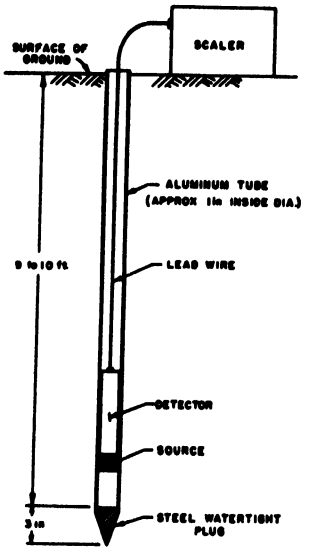


Figure 9. Sketch of moisture and density measuring device

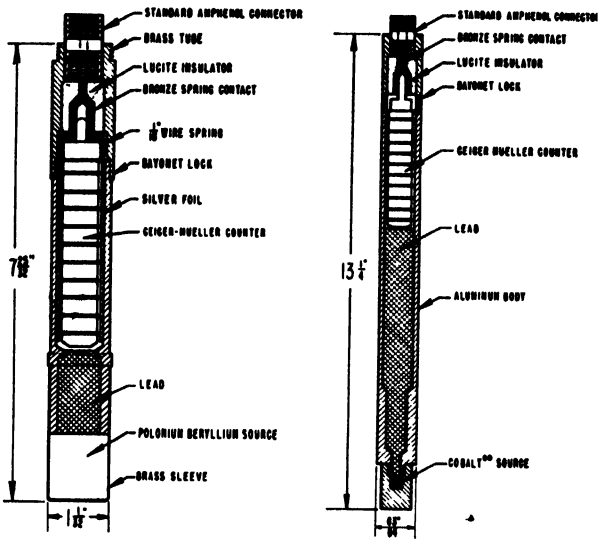


Figure 10. (1) moisture probe, details of construction; and (2) density probe; details of construction

lation counter probe. During actual use the number of slow neutrons which return to the detector are counted during a preset time interval. However, a Geiger counter is also successfully used when wrapped with a 3 mil silver foil to detect thermal neutrons. A three minute equilibration time is required before counting the radioactive Ag^{110} (24 second half-life). A 5 millicurie polonium-beryllium neutron source proved satisfactory.

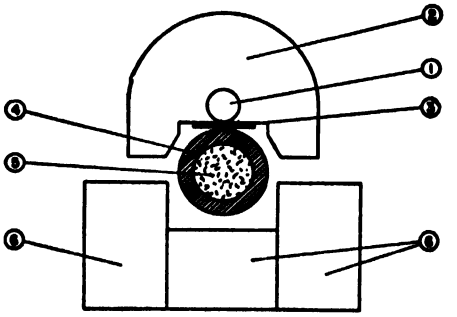
For the subsequent determination of soil density the unit housing the gamma source and detector is lowered into the access hole. The gamma radiation which is backscattered by the surrounding medium is detected and the count recorded. The scattering of gamma rays is somewhat analogous to the scattering of neutrons in that gamma photons suffer a change of direction and loss of energy in a collision. Unlike neutrons, which interact with nuclei, gamma rays are scattered primarily by electrons of the intervening atoms in their path. As the numerical density increases the probability of scattering by *single* collisions increases and the count rate increases. Since an increase in numerical density interposes a greater number of atoms between the point of first collision and the detector, there is an increased probability of scatter away from the detector by secondary collisions. Thus the count rate first increases with density, reaches a maximum, and then decreases. This scattering phenomenon can and does, however, serve as a measure of mass density.

Cobalt-60 radiation is used successfully as the gamma source since the absence of low energy components is an advantage. A source containing less than two millicuries provides sufficient counts to achieve the statistical accuracy needed. The uncertainty of the measurements, expressed in pounds per cubic foot, amounts to 0.13 to 0.15 for moisture determination and 1.60 for density measurement. At present there is a wide demand for such an instrument as has been described. Rapid, accurate and inexpensive, it will contribute to future engineering work.

Neutron scattering will undoubtedly become more widely used in the process industries where control of moisture content is important. Figure 11 illustrates an early use of neutron scattering to measure oil saturations in cores or sand packs.[8] This method permits local saturations to be measured in a core enclosed in a steel pressure vessel without interrupting the flow. In this use the detector plate used was rhodium whose induced radioactivities decay with half-lives of 44 seconds and 4.2 minutes.

APPLICATIONS OF BETA RADIATION

The beta source is probably the most versatile of all radiation sources now in use. Beta radiation is being used to gage mass, density, or thickness in an unbelievably large number of situations. To mention a few: metal foil and sheet, artificial leather, tire fabric, boxboard, plastic sheet, paper, floor tile, ad-



ARRANGEMENT OF NEUTRON SOURCE, DETECTOR PLATE, AND SAND PACK.
1. Neutron source.
2. Neutron source holder (lead).
3. Detector plate.
4. Steel-walled pressure vessel.
5. Sand pack.
6. Lead shielding.

Figure 11. Arrangement of neutron source, detector plate, and sand pack: (1) neutron source; (2) neutron source holder (lead); (3) detector plate; (4) steel-walled pressure vessel; (5) sand pack; and (6) lead shielding

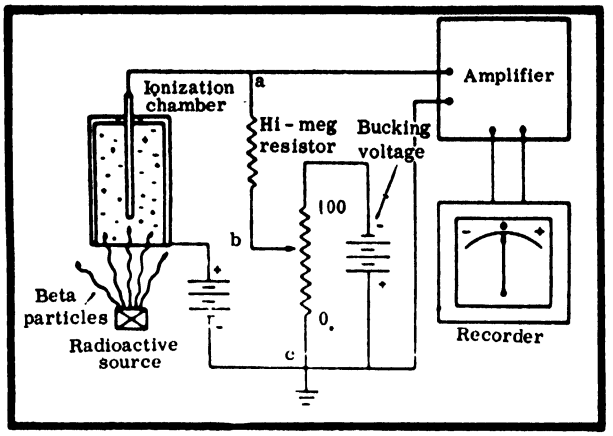


Figure 12. Basic elements of a beta radiation gage. Material being measured is interposed between the radioactive source and the radiation detector

hesive tapes, ink films and cigarettes. Beta radiation may be used in three different circumstances. It will prove advantageous to consider each separately—thickness by penetration, thickness by reflection and concentration by reflection.

Thickness by Penetration

This technique requires that the material to be measured be placed between the radiation source and the detecting device. Figure 12 depicts the basic elements of a beta ray gage. Instruments are now in use which include automatic periodic standardization against a reference source and which maintain an accuracy of 1%. Other pertinent features will be mentioned in connection with specific illustrations.

The most important process by which beta particles may be absorbed is that of electron scatter through interaction of the incident betas with the orbital electrons of the absorber.

With this fact in mind, consider the number of electrons per gram of the common light elements. $_1H^1$ is the principal isotope of hydrogen whose atomic weight is very close to one. Thus hydrogen contrasts sharply with other elements for which the atomic weight is roughly twice the atomic number. Due to this fact hydrogen has twice as many electrons per gram (6×10^{23}) as do the other light elements such as carbon, oxygen, and sulfur (3×10^{23}).

There is sufficient difference between the attenuation of beta particles by hydrogen and carbon to suggest a practical measuring device to determine the hydrogen carbon ratio (H/C) in hydrocarbons. It is not surprising, therefore, to find a commercial instrument already in use in petroleum laboratories which rapidly and conveniently measures the hydrogen carbon ratio of liquid samples.[9] This is done as a result of two measurements: (1) a beta absorption measurement and (2) a specific gravity measurement. As shown in Fig. 13 the strontium-90 beta ray source is designed to radiate with equal intensity in *both* directions. The beam to the left traverses a fixed absorber, then proceeds to an ionization chamber detector. The equal and opposite beam traverses a sample cell and a wedge-shaped absorber before entering the other detector. A galvanometer indicates the difference in the magnitude of the electric currents produced in the two ionization chambers. Since the identical chambers are connected to two equal and opposite voltages derived from a resistor divider network and have a common gas supply, the instrument calibration is free from these variables.

The wedge-shaped absorber is adjusted so that the stopping power of the sample *plus* the wedge is equal to the stopping power of the standard invar absorber. A balance simultaneously measures the density of the liquid sample by the usual weight displacement method. The position of the wedge may be adjusted to better than 0.001 in. by an interpolation method and to 0.003 in. by a very much faster nulling procedure. This latter accuracy corresponds to about 0.05% hydrogen. For 15 minutes analysis time (including changing of samples, etc.) the results obtained have a probable error of 0.02 weight per cent. The principle employed in this device should be of value in other industries such as those dealing with resins and plastics.

Low energy beta emitters such as carbon-14 and nickel-63 can be used to measure very thin films of low atomic number while more energetic beta emitters are used for thicker sections of higher Z. Gaging has been of singular value to industry because virtually all of the raw materials entering into the manufacturing process are purchased on a *weight* basis, but the majority of finished goods are sold on a *unit* basis. Thus control of weight per unit becomes a vitally important factor. A beta gage offers noncontact automatic measurement to a high degree of accuracy and supplants slower destructive type testing. Figure 14 illustrates the resultant improvement in process control with beta gaging.

An interesting application of carbon-14 as a gaging source is its use to measure the mass per unit area of thin films used as samples for infrared spectrophotometry.[10] The sample is placed between the aluminum foil window of a quartz fiber electroscope and a 1.5 cm diameter source of radioactive barium carbonate which is mounted at a distance of 1.5 cm from the electroscope window. The relation of the logarithm of the discharge time in seconds to the weight in milligrams per square centimeter of the film is almost linear for such materials as aluminum

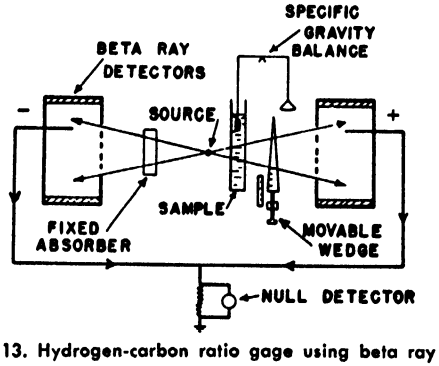


Figure 13. Hydrogen-carbon ratio gage using beta ray source

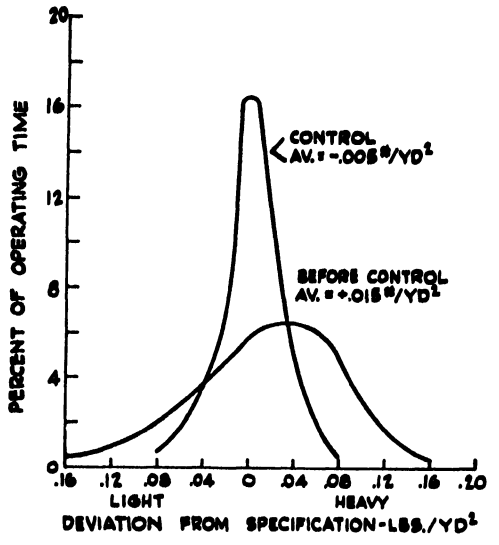


Figure 14. Frequency distribution curves

foil and "cellophane." The mass per unit area, as determined by beta particle absorption, is directly applicable to spectrographic measurements since it is essentially the concentration-thickness product which appears in the absorption law. The advantage of this technique is that it eliminates contact measurement and is simple.

Carbon-14 sources are also being utilized for continuous and automatic industrial gaging of moving sheet materials. Such gages greatly decrease the time required to control sheet thickness to small prescribed tolerances.

Another unique application of a weak beta emitter involves the routine measurement of ink films on the rollers of a lithographic press.[11] Making such measurements during press operation presents a difficult access problem. The problem of ink distribution not only involves the properties of the ink but also the characteristics of the rollers in the ink distribution system. The rollers transfer 4 to 6 micron thicknesses at high speed. Thicknesses over 7 microns produce smudges and those below 3 microns lead to faulty printing.

By the novel approach of electroplating a 2 inch wide band of radioactive nickel-63 on the rollers in question, a "built-in" thickness gage was obtained. A simple thin end window G-M tube was positioned to record the amount of beta radiation penetrating the ink. Assuming the "opacity" of the ink to be constant, calibration curves were drawn up after relating counts per minute to milligrams per square inch of ink as measured by a wet film thickness gage. Figure 15 reveals the ink roller arrangement involved in this study. The rollers were "flashed" with a thin electroplate of copper after the nickel-63 band was deposited. This insured constant surface tension characteristics across the roller. An excellent linear calibration curve was obtained plotting logarithm of counting rate versus absorber thickness. Table II lists the measured ink film thicknesses while the press was in operation. The first set was obtained while ink was being fed to the rollers but with no printing being done; the second set of values was obtained during actual printing. At present it is contemplated that the output of this gage be fed to an automatic control to adjust the ink supply to the intermediate rollers.

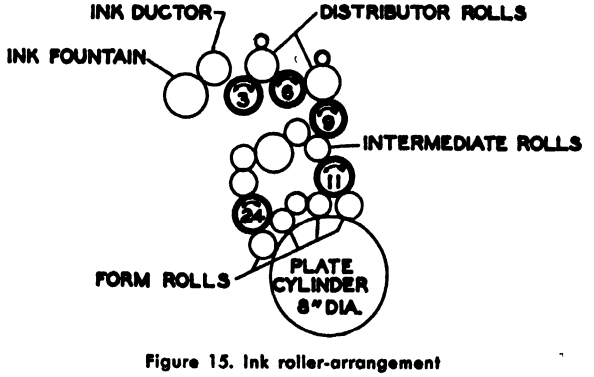


Figure 15. Ink roller-arrangement

Table II

	Roller No.	Thickness of ink in microns Center	Feeder side
Ink, no print	3	9	8
	6	7	7
	9	6	6
	11	6	6
	24	6	7
Ink, print	3	18	16
	6	10	8
	9	9	7
	11	6	5
	24	5	4

It is appropriate to consider briefly some of the factors involved in automatic control using the output signal of beta gages. Virtually all processes are subject to sporadic, short-term variations and cyclic variations for which it is not desirable to make correction. It is necessary, therefore, to incorporate certain time delays in the design of the control circuit. Otherwise the system would constantly oscillate. The time delays must be based upon the speed of the material measured and on attainable correction speeds of the related equipment. Experience supports the contention that automatic control is the means whereby the fullest benefits may be derived from the use of radioactive gages.

Strontium-90 beta gages have been those most commonly used in the past few years and therefore demonstrate most clearly the amazing versatility of

Table III. Approximate Range of Thickness Measured by Strontium-90 Beta Gage

Material	Density in gm/cm³	Thickness in inches
Aluminum	2.7	.0002–0 075
Asbestos	2.5	.002 –0.075
Copper and brass	8.9	.0006–0.020
Glass	2.7	.002 –0.075
Paper	1.0	.005 –0.200
Plastics (Celluloid)	1.4	.004 –0.145
Rubber	1.0	.005 –0.200
Steel	7.8	.0006–0.020
Textiles	—	5 to 150 oz/yd²

Table IV. Comparison of Process Control

Industry	*Application*	*Process control (2 sigma limits, i.e., 95% correlation)*		
		Conventional control (normally sampling method)	*Radiation gage with manual control*	*Radiation gage with automatic control*
Paper	Fourdrinier paper machine	±12%	±10%	±3%
Metals	Tandem cold roll mill	±10%	±7%	±1.5%
Rubber	Sheeting calender	±10%	±6%	±3.2%
Rubber	Tire Fabric calender	±6.5%	±5.5%	±3.5%
Plastics	Calender	±7%	±3.5%	±2.5%
Impregnation	Saturator dip coater	Automatic control provided an improvement factor of 2.5 over conventional.		
Abrasive	Abrasive maker	Automatic control provided an improvement factor of 2 over conventional.		

penetration and reflection applications. Table III gives approximate values for the range of thickness of materials measured by strontium-90. Table IV reveals what can be accomplished in various industrial situations in achieving better process control through the use of beta gaging with either manual or automatic control.

Cold rolling of steel sheet whose initial thickness is less than 0.002 inches requires very fine tolerances. Electrical alloy steels which can be rolled to minute thicknesses are of considerable interest because they can be made into tape cores. Such tape cores show electrical properties so unusual that they can often replace vacuum tubes in complex electronic equipment. Beta gages solved the problem of how to accurately measure strip rolled ultra thin (to thicknesses of between 0.0005 and 0.0001 inches). These gages automatically compensate every half hour for changes in temperature, humidity, dust collection on the radiation window and other external conditions.

Beta gaging has also greatly improved the control of extrusion laminated polyethylene coatings.[12] In this process, a conventional thermoplastic extruder melts polyethylene and forces it continuously through a sheeting die to form a film at 450–550° F. This hot film is pressed between a sheet of paper and a water cooled metal roll thus laminating the plastic and paper. The thickness must be uniform to provide consistent protection, smoothness, and dielectric properties. A 16 per cent error is caused by a change in plastic thickness of less than 0.0001 inches. Since both paper and plastic coating variations were troublesome, two beta gages are now used; one measures the weight of the raw paper and the other the weight of the coated paper.

Five strontium-90 beta gages are employed in each production line making abrasive paper in various plants in this country. Figure 16 schematically outlines the production process and the location of each of the gages. With this arrangement non-uniformity at *any* stage of the production process is immediately revealed and corrected.[13] The savings experienced

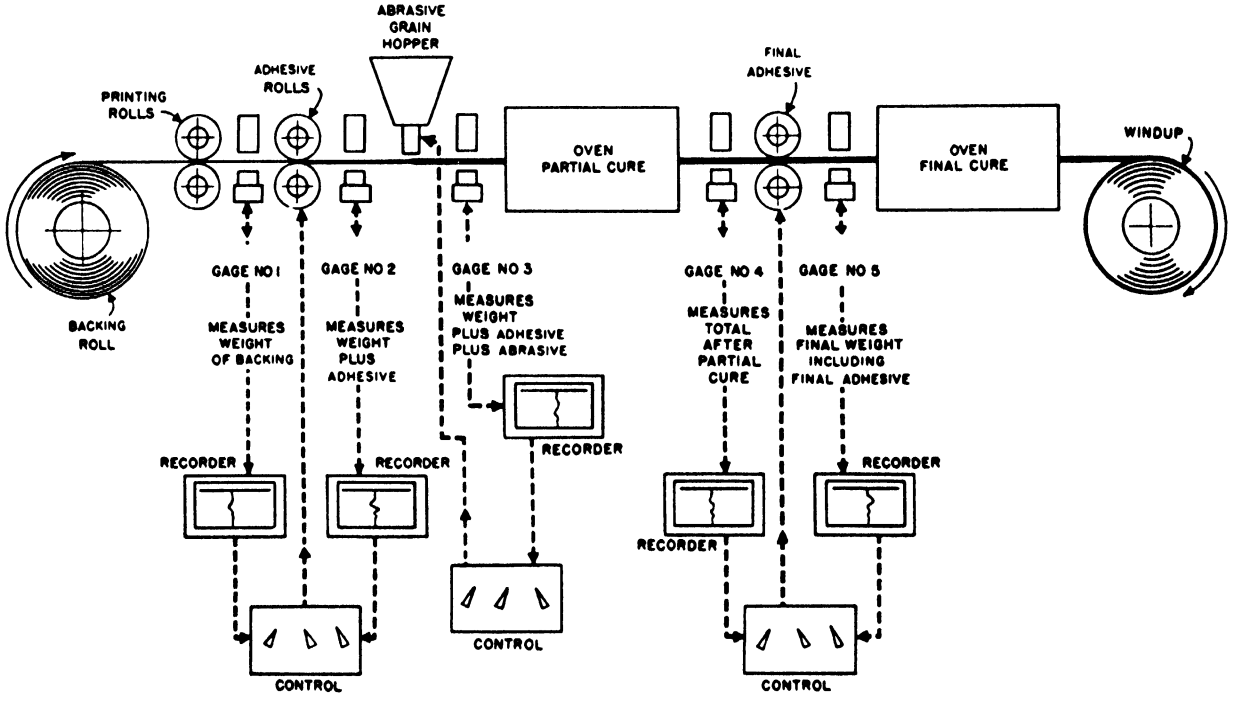


Figure 16. Schematic sketch indicates how precise gaging is combined with close production control in coated abrasive manufacture at the Carborundum Company

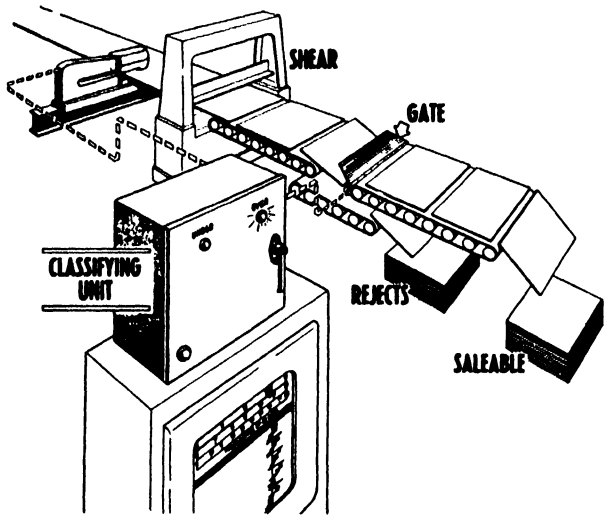


Figure 17. Automatic classification of tinplate

here are typical of most gaging benefits: (1) saving of material previously used in destructive testing, (2) reduction in machine "down time," (3) improved efficiency of raw material utilization, (4) reduction of inspection personnel, (5) increased operating speeds, (6) reduction in rejected or off-specification products.

Industries producing products made from tinplate recognize that even slightly off-specification plate means excessive wear of the dies used to form the final products and often results in some cracked products. Figure 17 depicts a gaging unit employed in the manufacture of tinplate. This device classifies and sorts tinplate according to a specified percentage deviation from the standard.

At the present time the cigarette industry is using beta gages to solve the long standing problem of more accurately controlling the amount of tobacco used in cigarette production.[14] The amount of tobacco represents about 90% of the cost of producing cigarettes. Cigarette machines feed a measured amount of "carded" tobacco to a narrow belt upon which the tobacco is compressed. It is then transferred to a tube belt upon which the cigarette paper has been superimposed. Emerging at the rate of 270 feet per minute a continuous cylinder or "cigarette rod" is later cut into cigarette lengths by a rotating chopper.

The dielectric or capacitance gage used to measure the weight of *individual* cigarettes required two improvements. The first was a means of improving the stability of the dielectric gage which is very sensitive to variations in moisture. The second was a means of measuring the average rate of flow of tobacco *and* adjusting the tobacco feed accurately. It was found that a Sr^{90} beta gage offered a solution to both problems.

Due to the beta gage's inherent stability its output signal was used as a zero or reference point for the dielectric gage thereby stabilizing the latter. It further permitted the automatic measurement of cigarette density variations. Such variations were automatically remedied by adjusting the tobacco feed at a rate proportional to the weight error *and* to the duration of that error. This insures that the uncut cigarette rod is unusually uniform.

The beta gage makes use of a chamber system wherein the absorption by the cigarette rod is compared against a standard. As shown schematically in Fig. 18 the two ionization chambers are located close together to minimize the effects of changes in ambient conditions. Zero stability was the primary technical specification which had not been achieved with other types of gages but which was solved using radiation gages. The effective density of a cigarette rod is approximately 200 milligrams per cubic centimeter. The minimum acceptable output drift of less than 5/10 of one per cent over any 24 hour period is equivalent to a one milligram per cubic centimeter change in cigarette density. The nuclear gage measures density variations of approximately 10 per cent on each side of the desired mean. The density measurement is averaged over about one second's time which corresponds to a four foot length of the rod.

The brass industry has long faced a very difficult gaging problem. Various types of contact gages are not satisfactory, particularly at high rolling speeds, because inaccuracy and marking of the product are undesirable. The successful use of beta gages has increased production speeds and reduced scrap losses and off-specification products.

Thickness by Reflection

One of the interesting features of beta radiation is that quantitative information can be derived from the backscattered radiation.[15] The essential components of a device to exploit this principle are shown in Fig. 19. The source of radiation is shielded from the detector and both are located in the *same* housing.

The ability of a material to backscatter beta rays is a function of the density of interacting electrons per unit volume, i.e., the atomic number. The backscattering coefficient, μ_b, equals a constant, f, times the mass absorption coefficient, μ_a. The coefficients are expressed in terms of reciprocal milligrams per square centimeter and the constant, f, ranges between 2.5 and 3.0. Figure 20 reveals the change in detector response, I, with increasing thickness of backing material and the subsequent change upon addition of increasing layers of a coating material of *higher*

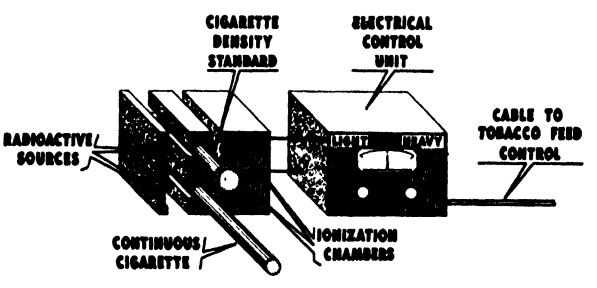


Figure 18. Gaging cigarette firmness with radioisotopes. Advantages: (1) more uniform firmness; (2) saves tobacco; and (3) eliminates manual control

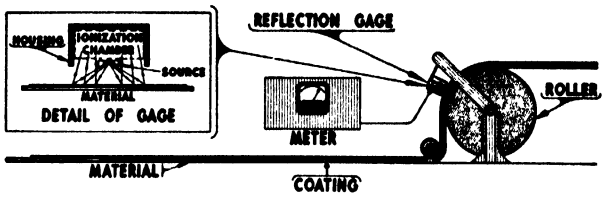


Figure 19. Radioactive source for reflection (backscattering) thickness gage. Advantages: (1) can measure thickness of coating and/or material; (2) measurement made from one accessible side; and (3) can measure a variety of materials with one calibration

atomic number. Had the coating material been of lower Z than the backing material, the detector response would have decreased.

Through the use of strontium-90, cobalt-60, cesium-137, ruthenium-106, and sulfur-35 virtually the whole range of measurable thicknesses have been covered. The inherent accuracy of such a gage is $\pm$ 0.05% of sample thickness or $\pm$ 0.01 mg/cm^2 whichever is larger. The sensitivity of this type of gage involves the factor $[(Z_b/Z_c)^n - 1]$ thus emphasizing that the atomic numbers of the backing (Z_b) and coating material (Z_c) must be sufficiently different to result in different "infinite thickness" detector currents.

Typical uses of beta backscatter type gages include measurement of metal platings such as nickel or chromium superimposed on other metallic surfaces, plastic coating on wire, porcelain coatings and paint or lacquer coatings on metallic surfaces.

An interesting example of backscatter gaging occurs in the continuous measurement of zinc coating applied in a continuous coating process.[16] Destructive testing procedures used previously were quite unsatisfactory. Two "heads" containing radioactive sources and detectors are located in the conveyor line and monitor *both* surfaces of the strip. This automatic measuring instrument correlated very well with data obtained by weighing the chemical coating. Approximately 95% of the values agree with the chemical determination within 0.06 ounces. This application required that the steel base metal be thicker than 0.015 inches for the particular device employed and that the distance from the measuring head to the strip be constant within 0.060 inches at a distance of approximately ½ inch. Irregularities are spotted immediately and corrected by machine adjustment thus insuring closer quality control of the coating.

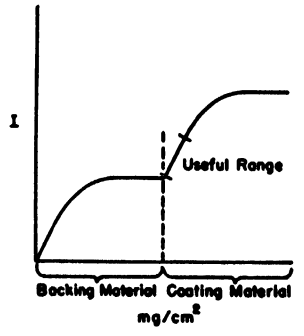


Figure 20. Detector response, I, vs. backscatter thickness

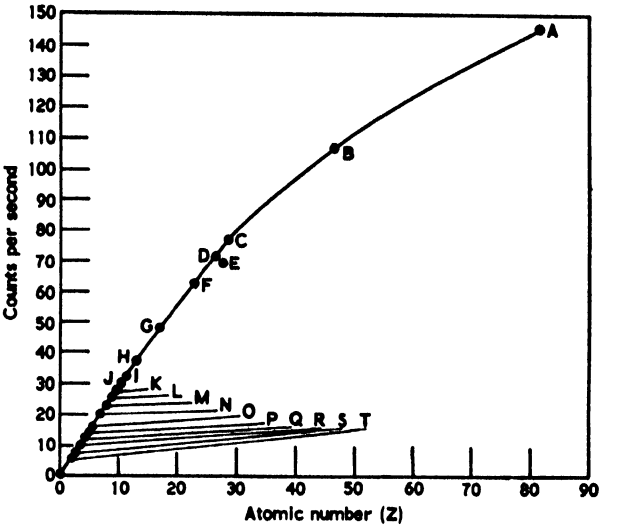


Figure 21. Curve established using pure Ag, Cu, Al, Pb with Sr^{90} source: other materials plotted by counting rate only. Basis: 40,000 counts in all cases. A: Pb; B: Ag; C: Cu; D: galvanized steel; E: H; F: cast iron; G: yellow paint; H: Al; I: white paint; J: transite; K: glass; L: mortar; M: concrete; N: bituminous concrete; O: linoleum; P: phenol-formaldehyde plastic; Q: mesonite, bakelite, oak; R: celotex; S: cork expansion joint; and T: paraffin.

Although the protective coating industry reflects one of the oldest manufacturing technologies in the world, the development of unusually durable traffic paint for highways has been a difficult task. Past efforts to quantitatively evaluate the performance of such traffic paints under a variety of conditions of wear have not been satisfactory. A portable beta ray backscatter gage employing a Geiger tube detector has been developed which will measure changes in paint film thicknesses with great precision. The backscatter rate from various common materials is plotted versus atomic number in Fig. 21. Undoubtedly this same type of gage, which employs only 10 microcuries of strontium-90, will prove useful for other similar problems.

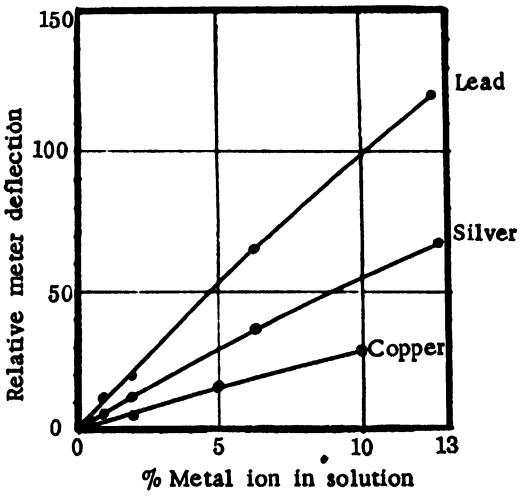


Figure 22. Relative meter deflection vs. per cent of metal ion in solution-construction gage

Concentration by Reflection

One of the most intriguing applications of beta ray backscatter is that of measuring the chemical composition of solutions. High atomic number ions in a solution of low average atomic number can be detected and measured quantitatively by backscatter. A backscatter "head" can be modified to provide for the passage of the solution to be measured.[17] Figure 22 depicts the ease of detecting a small percentage of copper, silver or lead in solution. Although concentration gages are not in routine industrial use at the present time, they hold considerable promise.

It is difficult to include in a brief paper many interesting aspects and details encountered in the enormous variety of radiation reflection and penetration applications. In addition, many of the gages and devices mentioned here involve features not yet patented and thus complete information is lacking. It is hoped that despite such inherent limitations this has served to emphasize the versatility and future utility of these radioactive byproduct materials which have become so widely available.

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Application of Radioisotopes to Control Technological Processes

By G. G. Jordan, V. B. Brodsky and B. S. Sotskov, USSR

Various specific phenomena which take place during the interaction between radioactive radiation and a substance make it possible to use radioactive isotopes for the elaboration of new highly effective methods of control of technological processes. Working in the direction of using atomic energy for peaceful purposes, Soviet scientists and engineers have solved a number of problems, viz.: non-contact measuring of the thickness of moving ribbons; measuring the thickness of coatings; measuring the density of liquid and gaseous media; measuring the level of a liquid or the interface of two media, etc.

The instruments constructed for these purposes are based on the absorption and dispersion of radioactive radiation and on the ionization of gases by alpha-particles.

The present paper contains a brief description of some examples from the experience gained in the USSR in applying radioactive isotopes to control technological processes.

1. INSTRUMENTS FOR THICKNESS AND DENSITY MEASUREMENTS BY ABSORPTION

The methods elaborated by A. M. Bogachev, B. I. Verkhovsky and A. I. Makarov and the instruments constructed by them are designed for continuous automatic measurement of the thickness of a ribbon in the process of its production. These methods are based on the absorption of beta- and gamma-radiations. The results of this work were used by the authors to control the production of rolled steel.[1, 2]

The considerations we may be guided by in choosing radiation sources for the devices based on absorption are as follows:

The average quadratic error Δd in thickness measurements by the method of absorption can be found from the expression:

$$\Delta d = \pm \frac{\sqrt{(\Delta nd)^2_{instr} + (\Delta nd^2_{fl}}}{n_0 \mu e^{-\mu l}} \qquad (1)$$

where $(\Delta nd)_{instr}$ is the average quadratic error due to the inadequacy of measuring instruments; $(\Delta nd)_{fl}$ is the average quadratic error connected with the statistical fluctuations of the number of radioactive nuclear disintegrations; μ is the linear coefficient of radiation absorption in the controlled material; n_0 is the value of the radiation flow falling on the absorber; and d is thickness of the material.

In those cases when it is possible to neglect the error due to the instrument, i.e., when $(\Delta nd)_{instr} \leqslant 0.5\ (\Delta nd)_{fl}$, the absolute and relative errors in thickness measurements can be found from the formulas:

$$\Delta d = \frac{e^{\mu \frac{d}{2}}}{\mu \sqrt{n_0 \tau A}}; \quad \frac{\Delta d}{d} = \frac{e^{\mu \frac{d}{2}}}{\mu d \sqrt{n_0 \tau A}} \qquad (2)$$

where τ is the time of measuring and A is the radiation record efficiency.

These expressions have the minimum when $\mu = 2/d$. If, consequently, the error due to the instrument is small it is advisable to use isotopes for which radiation $\mu = 2/d$. It should be noted that the most usable thicknesses of rolled stock can be measured through the radiation of a small number of radioactive isotopes chosen by the above method.

The minimum activity (in mc) of a source suitable for thickness measurements with a prescribed average quadratic absolute error can be evaluated with the aid of the expression:

$$I_1 = 0.27 \times 10^{-7} \frac{e^{\mu l}}{\mu^2 (\Delta d)^2 \tau A q \Omega} \qquad (3)$$

where Ω is the solid angle in steradians at which the radiation receiver divided by 4π is seen from the source; and q is the quantity of gamma-quants or beta-particles per one act of disintegration.

If, due to industrial conditions, an average quadratic relative error is prescribed, the minimum source activity can be found from the expression:

$$I_2 = 0.27 \times 10^{-7} \frac{e^{\mu d}}{(\mu d)^2 \left(\frac{\Delta d}{d}\right)^2 \tau A q \Omega} \qquad (4)$$

Since precise measurements in shop conditions can meet with difficulty, it is advisable to consider the case when predominant errors are those due to instruments.

Errors due to instruments can be divided into two groups: errors proportionate to the value of the flow falling on the absorber, and those which do not depend on the flow value.

Original language: Russian.

The first group comprises, in particular, the errors connected with the change in the ionization chamber voltage and in the geometrical conditions of measuring. The second group comprises, in particular, the errors connected with the faults of measuring devices.

The errors of the first group cannot be reduced by increasing the source intensity. Those of the second group can be reduced by increasing the radiation flow and by a reasonable choice of an isotope.

Supposing $(\Delta nd)_{instr} \geqslant (\Delta nd)_{fl}$, we obtain from Equation 1 the expressions:

$$(\Delta d)_{instr} = \pm \frac{(\Delta nd)_{instr}}{\mu n_0 e^{\mu l}}; \left(\frac{\Delta d}{d}\right)_{instr} = \pm \frac{(\Delta nd)_{instr}}{\mu d n e^{\mu d}} \quad (5)$$

which are minimum when $\mu d = 1$.

The formulas for the minimum radiation source activity are:

$$I_3 = \frac{0.27 \times 10^{-7}(\Delta nd)_{instr} e^{\mu l}}{\mu q \Omega \frac{\Delta d}{d}} \quad (6)$$

$$I_4 = \frac{0.27 \times 10^{-7}(\Delta nd)_{instr} e^{\mu l}}{\mu q d \Omega \frac{\Delta d}{d}} \quad (7)$$

In cases where it is necessary to take into account both mistakes, i.e., $(\Delta nd)_{fl}$ and $(\Delta nd)_{instr}$, for evaluation of source activity we must apply the more general relations given in Equation 1.

For the working principle of the instruments to control the thickness of a ribbon see Fig. 1. The differential ionization chamber equalizes the two flows of radioactive radiation. One flow passes through the controlled material. The other one, which is compensatory, after passing through the diaphragming blind, penetrates into the chamber. The device employs the transformation, with the aid of a vibrotransformer, of the ionization current into a signal of alternative voltage. After being amplified, the signal sets into motion the servomotor whose axle is rigidly linked with the blind. Thus the automatic equalization of the ionization currents is effected, and the angle to which the blind turns indicates the thickness of the absorber. The compensatory method of measuring reduces essentially the influence of the external conditions (temperature, atmospheric pressure), the change in the amplification factor of the amplifier and the radiation source disintegration on the results of thickness measurements. In this respect the above method has an advantage over those described before, for instance in references 4 and 5.

Three types of instruments have been designed for measuring the thickness of steel sheets in the process of their rolling. With the aid of these devices it is possible to measure rolled steel 5μ–150μ, 50μ–1 mm and 2 mm–10 mm thick respectively.

In the instruments of the first type Tl^{204} with an activity of 10 mc is employed as a radiation source, in those of the second type Ce^{141} with an activity of 5 mc is used for this purpose, and in those of the third type it is Ir^{192} with an activity of 5 c that is used for the same purpose.

Considerable industrial exploitation of these appliances has shown that the error in thickness measurements made by instruments of the first two types does not exceed ± 1.5 per cent of the thickness measured. The maximum error in gauging thickness with the aid of an instrument of the third type is equal to ± 50 μ, the material measured being in a fixed position. In industrial conditions, because of the vertical vibrations of a ribbon gauged, the maximum error reaches ± 0.18 mm.

For a general view of the instrument for measuring the thickness of rolled steel from 0.05 mm to 1.0 mm see Fig. 2.

Beta-ray absorption was also used to control production in the cotton industry. Pismannik and Slatinsky together with their collaborators designed a number of devices for measuring the unevenness of cotton tape, the squeezing of textile fabrics, etc.

In the device for measuring the unevenness of fabrics Tl^{204} with an activity of 30 mc was applied.

The differential ionization chamber was employed as a radiation detector.

The indications of the instrument, with the aid of a special electronic appliance, give the starting data

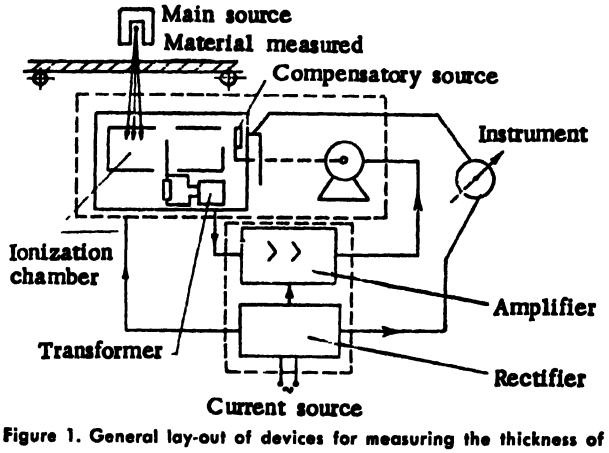

Figure 1. General lay-out of devices for measuring the thickness of a ribbon

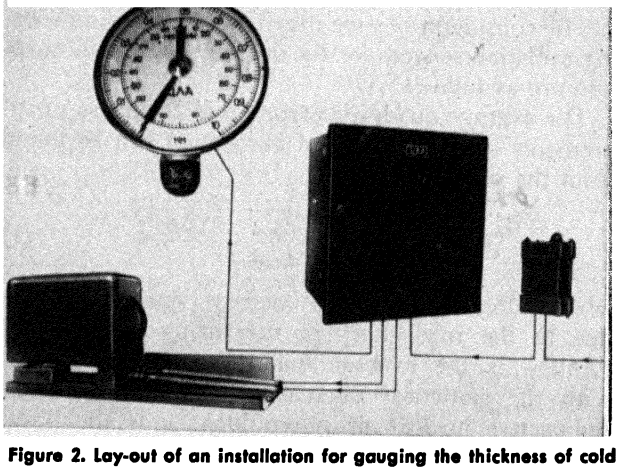

Figure 2. Lay-out of an installation for gauging the thickness of cold rolled steel

for computing the variation factor with 1 per cent tolerance.

This group of instruments includes devices for measuring the thickness of tube walls and the density of various materials. Essential methodological results of the use of radioactive radiation to control the thickness of walls were described by O. N. Vavilov and I. M. Frank in one of their early works.[3] In the devices for measuring the difference in tube wall thickness, recently designed by Kardash and his collaborators, a scintillation counter is employed as a detector of gamma-radiation penetrating through metal.

B. G. Mendelev and S. O. Bogin constructed an appliance which makes it possible to control the filling of iron tubes for gas-absorbers with barium. This device is based on beta-rays absorption. Sr^{90} with an activity of 5 mc is employed as a radiation source. A Geiger-Müller counter plays the role of radiation-recorder.

G. G. Jordan, C. S. Furman and a group of their collaborators constructed an automatic recorder for the remote measuring of the density of a liquid in pipes over 50 mm in diameter. Co^{60} and Cs^{137} with an activity of 10 mc are used as gamma-radiation sources. They applied the compensatory method of measuring. This device is suitable for measuring the density of a liquid from 0.5 gm/cm³ to 2.5 gm/cm³. Its scale is calculated to gauge density within the limits of 1.0–1.5 gm/cm³, with an absolute error + 0.01 gm/cm³.

Figures 3 and 4 reproduce a general view of the device designed by E. G. Kardash and his collaborators[6] for continuous remote measurement of the concentration of soil in dredge pulp. This device is based on recording the change in gamma-rays absorption according to the composition of pulp. Measurements are taken with the aid of an ionization chamber.

Graduation graphs for various pulp-pipe diameters are given in Fig. 5.

The author's investigations have shown that pulp weakens gamma-radiation according to the exponential law:

$$\frac{I_{mix}}{I_{wat}} = e^{-\frac{Q_{soil}}{Q_{mix}} d_0 (\mu_{soil} - \mu_b)} \qquad (8)$$

where I_{mix} is radiation flow that has passed through the tube filled with a mixture; I_{wat} is radiation flow that has passed through the tube filled with water; Q_{soil}/Q_{mix} is the ratio of the volume of soil to that of mixture; d_0 is the inner diameter of the pulp-pipe; and μ_{soil} and μ_b are the linear coefficients of soil and water absorption.

The scale of the device has been graduated in percentages of soil content in the pulp and in pulp density units. Measurements are taken with a ± 2 per cent tolerance (in density units ± 0.01 gm/cm³).

For tubes 500 mm in diameter, Co^{60} and Cs^{137} with an activity of 100 mc are used as radiation sources.

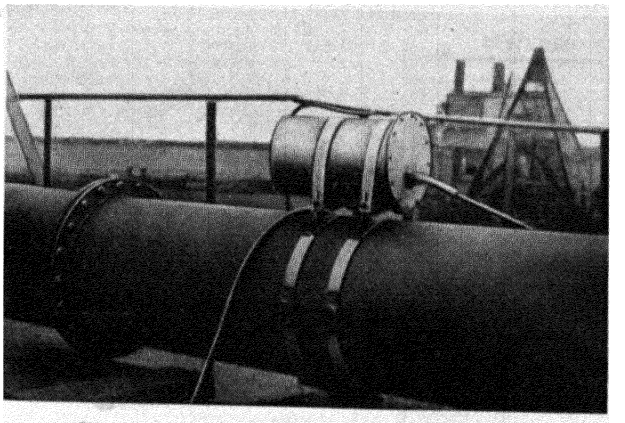

Figure 3. Device mounted on the tube of a dredge

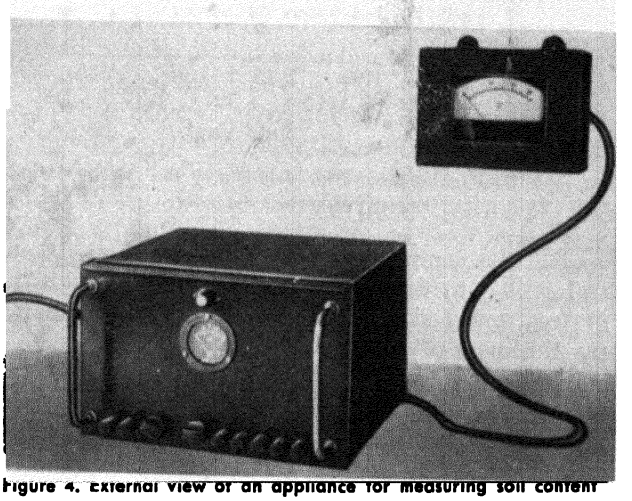

Figure 4. External view of an appliance for measuring soil content in dredge pulp

Such devices are employed in dredge pumps engaged in building the Kuibyshev, Stalingrad, Kakhovka and other big power stations; they are also employed in dredge pumps utilized by the river transport. The use of these devices raises the productivity of dredge pumps by 15 20 per cent. Automatic recorders attached to these devices make it possible to obtain curves characterizing the work of the dredge pump.

Similar devices designed by S. I. Remiel and R. B. Popov are used to control the density of aluminia pulp for aluminium production. S. V. Starodubtsev and B. S. Skobkin designed appliances for the same purposes but with a slightly different structure. They also created a portable device for gauging soil plugs in pulp-pipes.

2. DEVICES FOR GAUGING THE THICKNESS OF COATINGS, BASED ON REVERSE BETA-RAYS DISPERSION

A number of works have been published on the use of beta-rays dispersion for measuring the thickness of coatings.[7, 8] Among the appliances recently constructed we shall mention the devices created by A. M. Bogachev, B. I. Verkhovsky and A. I. Makarov[9] for the continuous non-contact measuring of the thickness of a steel ribbon tin coating. They

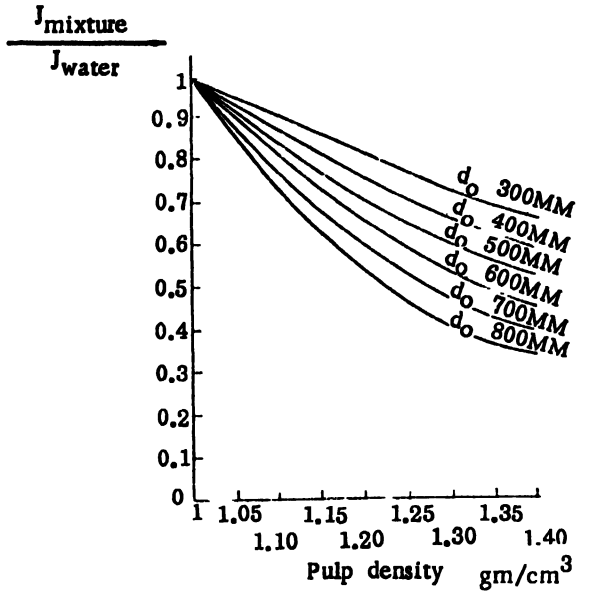

Figure 5. Graduation graphs for determining the density of pulp in pipes of various diameter

applied the compensatory method of radiation control similar to that described when dealing with the devices designed by the same authors for gauging the thickness of rolled steel.

Tl^{204} with an activity of 40 mc was used as a radiation source. The scale of the device covers the range of thicknesses from 0 to 0.005 mm. The maximum error in measuring does not exceed ± 0.0001 mm. For a general view of the device see Fig. 6.

3. DEVICES FOR RECORDING THE LEVEL OF A LIQUID IN SEALED VESSELS BY THE METHOD OF GAMMA-RAYS ABSORPTION

Below we shall briefly describe a number of appliances designed in the USSR for automatic control of the level of liquids in sealed vessels. All these devices are based on using the difference in absorbing gamma-rays by the media on both sides of the interface. The source and the detector are placed on the opposite sides of the vessel. In appliances of this type it proved advisable to employ Geiger-Müller counters as radiation detectors, and Co^{60} as a source. G. G. Jordan elaborated a method, and together with his collaborators he constructed a number of devices for remote measurement and control of levels or positions of the interfaces of two media. These instruments can be used to control such systems as gas-liquid, liquid-liquid, gas-solid or gas-dry substance, liquid-solid or liquid-dry substance; they also can be used to determine the level of boiling or bubbling liquids.[10]

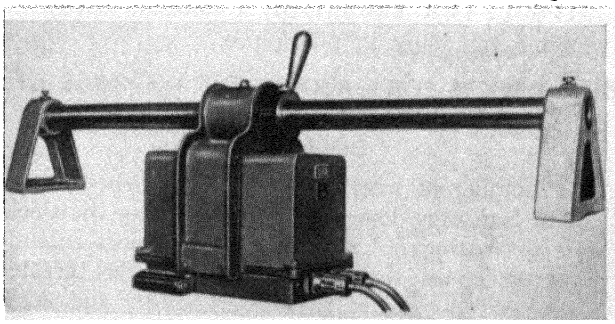

Figure 6. External view of a device for gauging the thickness of steel sheet tin coating

The receiver and the source of radiation are fixed to the ends of a tubular bracket which can slide along a tank. The average speed of counting the impulses is measured with the aid of an electronic structure. When the middle of the counter is in the position of the interface, the system is in equilibrium. In this position of the counter the voltage of the speed-counting recorder is equal to some supporting voltage supplied by an external source.

When the level of the liquid shifts the equilibrium upsets, an electric signal is generated which sets in motion the servomotor linked with the bracket. The counter and the receiver cease to shift when the middle of the counter again returns to the level of the liquid.

A shift of the bracket is attended by a turn of the pointer of an indicating instrument. The whole structure makes it possible to record indications and insert an automatic system of level regulation.

To control the level of a liquid in reservoirs of large diameter the radiation source and the counter are placed in special columns on both sides of the tank. In this case the source and the counter are shifted together by means of selsyns controlled by the servomotor.

The whole apparatus is designed to gauge shifts in the level within the range of 1000–1300 mm with an absolute error of about 5 mm. This method can be used to measure a considerably greater shift with the same absolute error. The device is designed for objects from 2–5 cm up to 5–7 m in diameter. The thickness of tank walls up to 100 mm (steel) does not hamper the normal operation of the device.

As it has already been pointed out, this device employs gamma-radiation of Co^{60}. The activity of the radiation source is selected so that the average quadratic fluctuations of the recorded radiation should be less than the value of the signal generated during a shift in the level by a magnitude equal to the admissible error in measuring. The method of computing the source activity is described in detail in a work by G. G. Jordan.[10]

For the example of a level-gauge recording in case of an object with the periodically variable level see Fig. 7.

Industrial exploitation has shown that such devices are reliable in work. They are advisable for the automation of various technological processes, especially when one deals with aggressive, explosive and toxic media and also with dry substances.

Other devices for similar purposes were designed by L. K. Tatochenko and S. V. Medvedev. These devices are used to control and measure the level of chlorine in sealed containers.

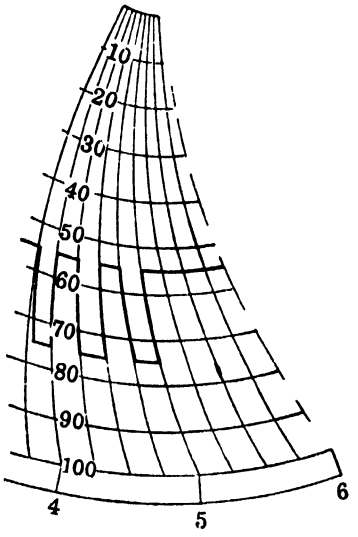

Figure 7. Position of liquid level

In all such instruments designed by them Co^{60} is used as a radiation source. The role of detector is played by Geiger-Müller counters working under the current regimes. This ensures the simplicity of electronic appliances and the convenience of servicing the installation.

Level-Indicators for Metal

These devices are used when it is necessary to maintain a liquid metal at an unchanged level, with a tolerance of 20–50 mm.

They employ preparations with an activity of about 10 mc. The radiation flow is gauged by means of

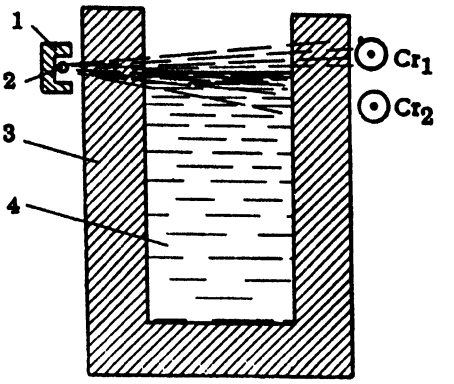

Figure 8. Lay-out of a level-indicator. (1) setting; (2) radiation source; (3) vessel wall; (4) liquid

two counters. For the disposition of the source and the counters see Fig. 8.

For a general lay-out of the device see Fig. 9.

The counters Cr_1 and Cr_2 control the work of two thyratrons in whose anode circuits the relays R_1 and R_2 are inserted. Signal lamps "normal," "high" or "low" light up according to the level of the metal, and the signal bell rings or not. The device may also be used in an automatic system of level regulation as a transmitter. For an external view of the apparatus see Fig. 10.

The eleven-position level-regulator for liquid metal is based on the same principle; it has ten similar relay channels working from ten separate radiation sources.

Level-Gauge for Liquid Metal

The device is designed to measure the level of a

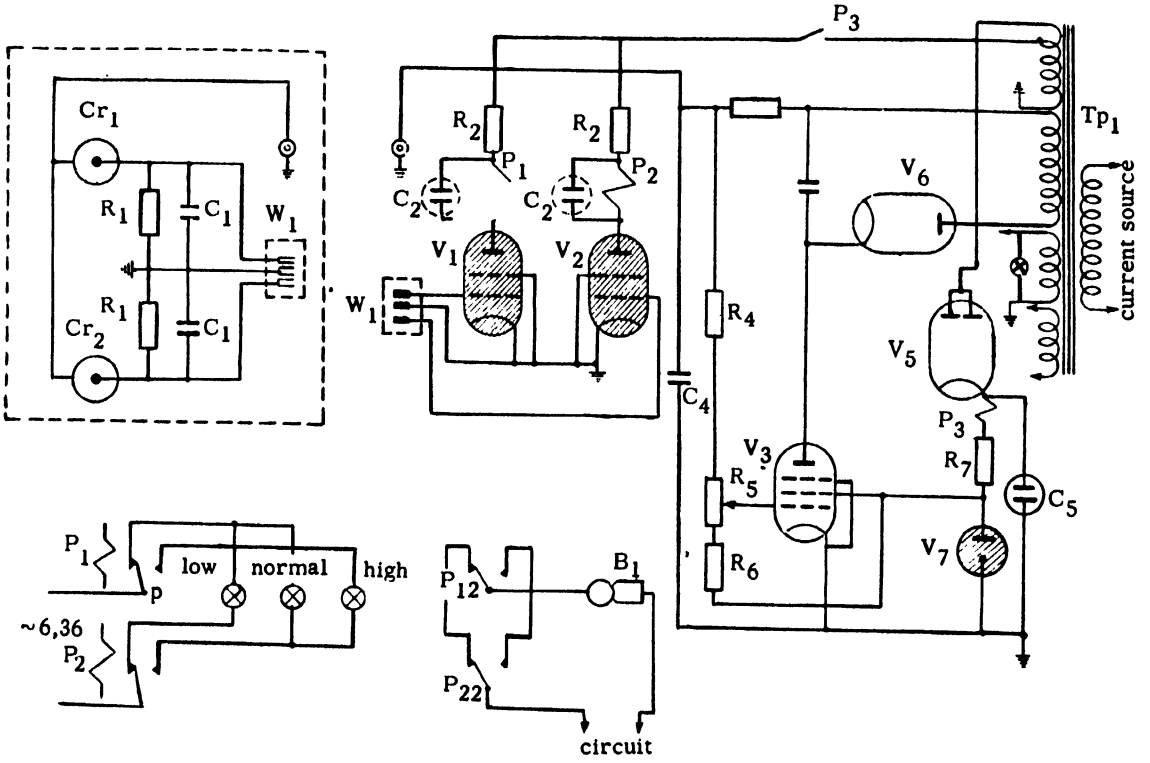

Figure 9. General lay-out of a level-indicator for liquid

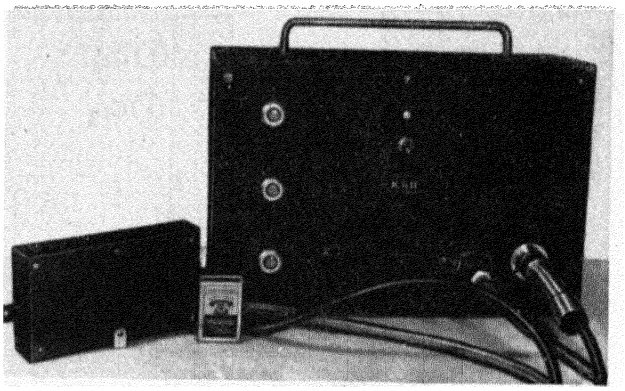

Figure 10. Level-gauge for liquid metal

liquid metal; it is equipped with an automatic recorder of indications and can also be used in an automatic system of level regulation as a linear transmitter. An automatic potentiometer is used to record indications. A radiation source in the shape of a wire about 150 mm long and a halogen counter are vertically disposed on the opposite sides of a vessel with a liquid metal. The dependence of the counter strength of current on the level position of the metal is practically of a linear character. A signal is sent to the automatic recorder or into the automatic system of level regulation.

Level-Gauge for Liquid Chlorine

The device is designed to measure the level (or to control expenditure) of liquid chlorine in a container. The working principle of the device is similar to that of the level-gauge designed by G. G. Jordan. Since the change in the level of liquid chlorine in a container is one-sided, it proved possible to simplify essentially the mechanical part of the device. The general lay-out of this appliance is similar to that of the devices described previously.

For transmission of indications the device is equipped with a rheochord from which the signal is sent to an instrument with a pointer. Errors in level measurements do not exceed 5–10 mm. For a photo of the device see Fig. 11.

4. ALPHA-IONIZATION MANOMETERS

In designing manometers based on the ionization of a gas by alpha-particles V. B. Brodsky,[12] G. G. Jordan and a group of their collaborators made considerable progress.

Appliances were constructed for direct and remote measurement, control and record of the density and pressure of a gas in various technological processes taking place at a reduced pressure.

The authors applied the compensatory method of measuring the ionization of a gas in an ionization chamber.

The lower limit of the pressure measured is determined by the dark current of the secondary electrons struck from the chamber collector by an alpha-particle.

The expression for the ratio of the current of secondary electrons to the ion current, in the case

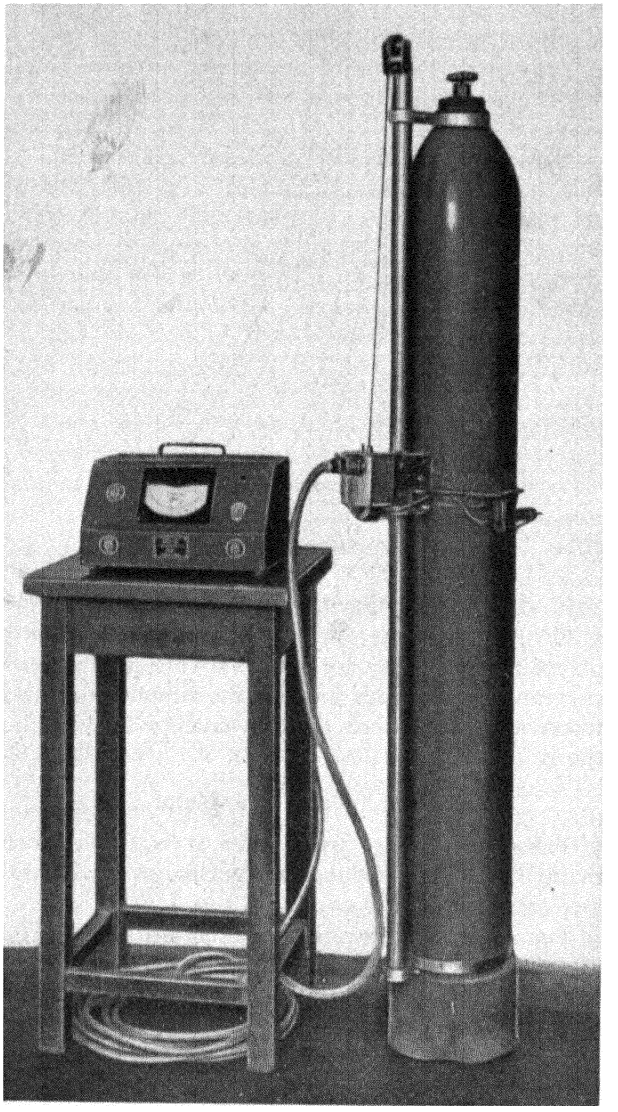

Figure 11. Level-gauge for liquid chlorine in a container

of a point source disposed in the centre of the bottom of a cylindrical ionization chamber with a collector made of thin wires parallel to the cylinder axis, is as follows:

$$\frac{I_e}{I_u} \sim \frac{10b760N}{2\pi R\eta nLp}\left(\frac{l+h}{\sqrt{R^2+(l+h)^2}} - \frac{n}{\sqrt{R^2+h^2}}\right) \qquad (9)$$

where I_e is the current of secondary electrons; I_u is the ion current; P is pressure in mm Hg; b is the diameter of the collector wires; l, h, R is the length of the collector wires, the distance between the chamber bottom and of the collector rod and that between the chamber axis and the centre of the collector rod respectively; N is the number of rods in the collector; n is the number of ion pairs formed by one alpha-particle per 1 cm length for a given gas at the pressure of 760 mm Hg; η is the source of efficiency (it depends on the geometry of the source and the chamber); and L is the average volume of the chamber.

This ratio agrees very well with the experimental data and shows that for lowering the lower limit of

the pressures measured, the alpha-source intensity being prescribed, it is advisable to decrease the square of the collector.

An industrial manometer measuring within the range of 10 μ–10 mm Hg is as an example of such a device. An ionization chamber signal is modulated with a frequency of 50 cycles and amplified by an ordinary amplifier of alternate voltage. The amplifier output end is connected to a servomotor operating a special autopotentiometer fed from a separate stabilized source. The autopotentiometer generates a compensatory signal opposite in sign to the input signal. When the signals coincide the system is at rest, and the angle to which the potentiometer axle turns indicates the gas pressure. A change in the pressure involves an appropriate turn of the potentiometer axle to a new position of signal compensation. The gas pressure can be registered by a remote recorder.

The device has two ranges for pressure measurement: 10 μ–1 mm Hg and 100 μ–10 mm Hg with a tolerance of about $\pm$ 2 per cent of the upper measurement limit of each range.

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Studies and Industrial Applications of Bremsstrahlung from the Beta Rays of Yttrium-90

By P. Lévêque,* P. Martinelli,† and R. Chauvin,‡ France

The inelastic scattering of β-particles by atomic nuclei causes the emission of X-rays (bremsstrahlung), the theory of which was developed, among others, by Bethe and Heitler (1934). Accurate experiments conducted by a number of workers show reasonable agreement with the theory.[1-4]

In view of possible industrial applications, a study was made by these authors of the bremsstrahlung emitted by various materials when excited by Sr^{90}–Y^{90}. This pure β-emitter, which is long lived, is found in the fission products of uranium (fission yield 5.3%). It seemed worth while to resort to these X-rays for low energy radiography, a range in which the only radioactive emitter currently available is thulium-170, with a 129 day half-life, the spectrum of which[5] is a complex one.

Equipment

We used a recording γ-spectrometer (see Fig. 1).

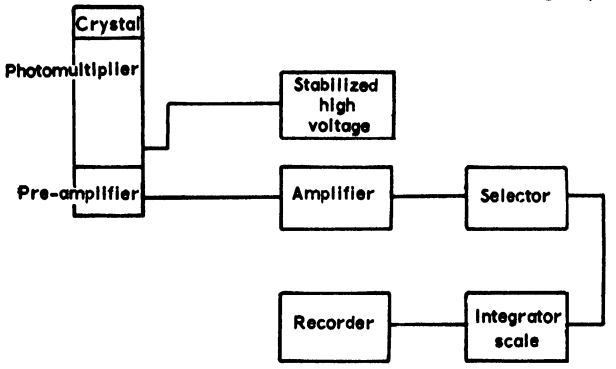

Figure 1. Block diagram of γ-spectrometer

It consists of:

1. A detector head made up of an NaI crystal (Tl), 1½ in. × 1 in., the aluminum cover of which has a thickness of 172 mg/cm², of an EMI 6260 photomultiplier tube, and of a preamplifier playing the rôle of a cathode follower.

2. One broad-band linear amplifier (1.5 megacycle) designed to the following specifications: gain 1000, output voltage 100 volts, attenuator: 1, ¼, ⅛, 1/16, 1/32, 1/64.

3. A one channel selector, the threshold of which may vary as a linear function of time.

4. A scaler, with variable sensitivities and time constants.

5. A recording millivoltmeter.

A plexiglass support is set on the crystal, making it possible to place the sources and targets in well defined positions (see Fig. 2).

EXPERIMENTAL STUDY OF THE BREMSSTRAHLUNG BY THE TRANSMISSION METHOD

According to the respective positions of the source, target and detector, transmission or back scattering may be used at will. Transmission was used for most of our measurements.

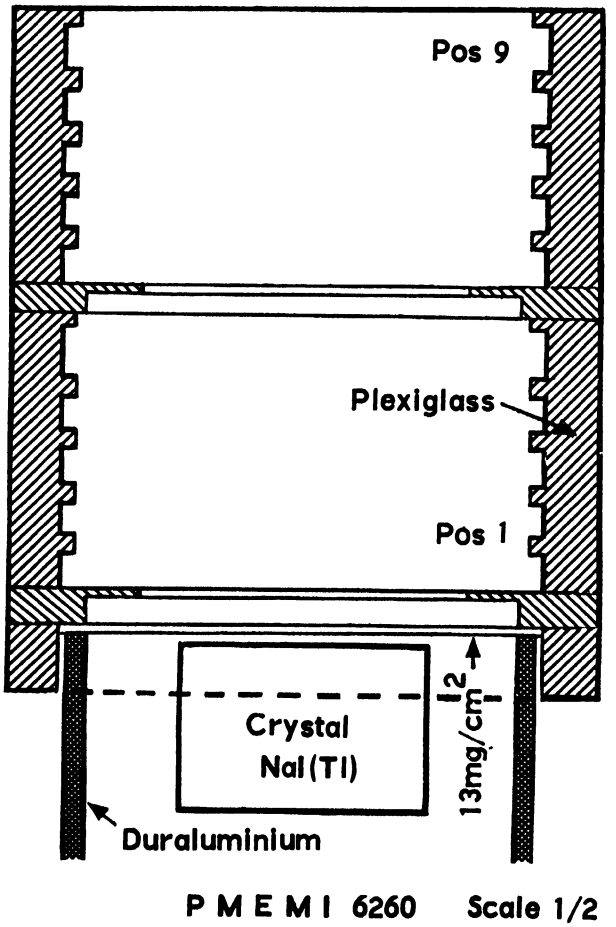

Figure 2. How sources and screens are attached

Original language: French.

* Chief of Radioelement Application Section, Physical Chemistry Department, Atomic Energy Commission.
† Section on radioelement applications, CEA
‡ Assay section, bureau of mining research and extraction at the CEA.

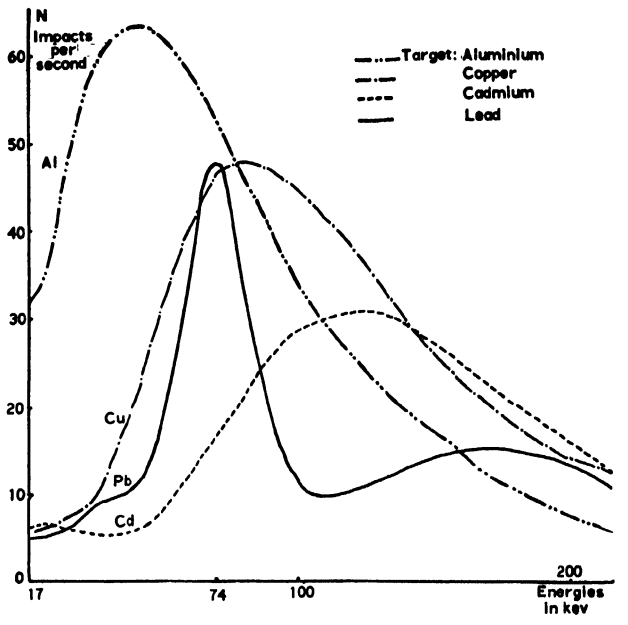

Figure 3. Bremsstrahlung spectra of Sr^{90}-Y^{90} (2.18 Mev β^-) transmitted by 1 gm/cm² targets

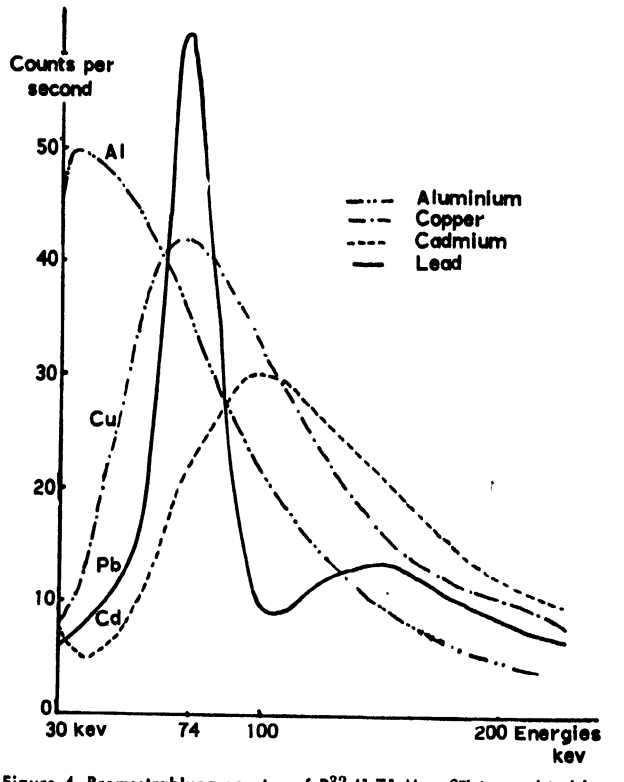

Figure 4. Bremsstrahlung spectra of P^{32} (1.71 Mev β^-) transmitted by 630 mg/cm² targets

For the industrial applications, three important factors have to be determined:

1. The configuration of the spectrum.
2. The X and beta yield.
3. The determination of the over-all absorption coefficients for X-rays in such common materials as iron and aluminum.

EXPERIMENTAL CONDITIONS

The strontium source in use has an over-all activity of 18.4 ± 0.4 μc. It was obtained by the evaporation of a nitric solution of strontium nitrate on a cellulose sponge block (spontex) crushed between two sheets of polystyrolene 0.12 mm thick.§

The source then appears as a disk 8 mm in diameter, 34 mg/cm² thick.

The bremsstrahlung is obtained by interposing, between the source and detector, targets 1 gm/cm² thick, which corresponds approximately to the travel of the β-particles emitted by Y^{90} (2.18 Mev).¶

The source is placed directly on the target, itself located 90 mm away from the upper surface of the crystal. (position 9, see Fig. 2).

The spectra are drawn for Al, Cu, Cd, Pb targets (see Fig. 3). As a comparison, the same spectra are established using a source of P^{32} (see Fig. 4). The origin of the abscissae is at 17 kev for Sr^{90}–Y^{90}.

Shape of the Spectrum

The continuous spectrum of the bremsstrahlung presents a maximum of intensity for energy E_b. As the thickness of the target increases, the maximum is shifted toward the higher energies, due to preferential reabsorption of soft X-ray by the target itself (Fig. 5).**

Under our experimental conditions, an empirical relationship makes it possible to compute, to an accuracy of better than 10%, the kev energy of the maximal intensity as a function of the atomic number Z and the thickness of the targets in gm/cm²:

$$E_b = AM^{0.2}\,Z^{0.7}$$

where $A = 8.6$ for a source made up of Sr^{90}–Y^{90}, and 7.6 for a P^{32} source (see Fig. 6).

X/β Yield

Conditions under which Measurements Are Taken

The measurement of β-activity of the source is taken with a bell counter. The source-counter distance is 30 cm. We have computed that absorption in the source, the air and the counter window reduces the number of the 2.18 Mev and 0.53 Mev β-particles which actually get into the counter to 68% and 9.3% respectively. Once all the corrections have been made, the activity of the source used is 9.2 μc ± 0.2 μc for Y^{90}. Only this activity is of interest, the 0.53 Mev β^-produce practically no bremsstrahlung.[6]

The X activity is measured with the photomultiplier described earlier.

We have taken counts in 20 kev energy bands

§ Preparation made by Artificial Radioelement Division of CEA.

¶ Under our measuring conditions, the 2.18 Mev β-particles are completely stopped by 1050 mg/cm² Al. For the heavier elements (Pb), less matter is needed (810 mg/cm²).

** This continuous spectrum should be completed by the X lines of the elements which make up the target. In fact, a K band of 74 kev is observed for lead. For elements with a low atomic number (practically where $Z < 40$), even the K lines are absorbed by the aluminum cover of the crystal by the target itself, or their energy is under the detection threshold.

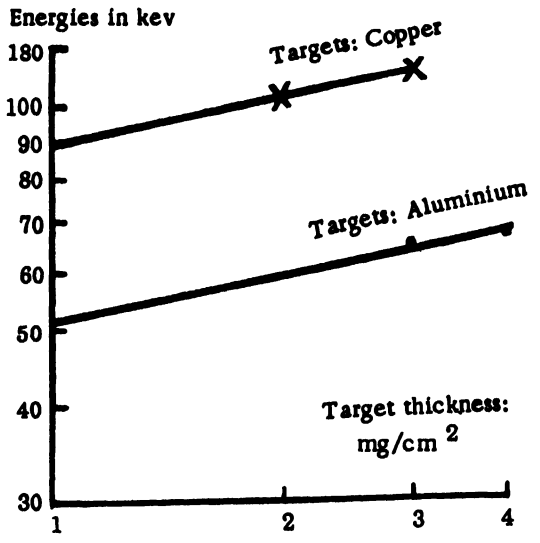

Figure 5. Variation of the maximal bremsstrahlung intensity as a function of target thickness for Sr^{90}-Y^{90}. Ordinates and abscissae shown in logarithmic divisions: one from 1–100, the other from 1–1000; 100 units

(between 17 kev and 200 kev), as well as in 100 kev wide bands (between 200 and 1000 kev). This enabled us to allow for the variations of absorption in the aluminum cover as a function of energy, as well as of the yield of the crystal.††

Since the source was flat, very thin, in contact with the target, and at a fair distance from the crystal, we assume that the bremsstrahlung produced, either by transmission or back-scattering, is isotropic, over a 2π solid angle, as is the beta radiation which excites it.

Results

We have thus determined the number of X photons (having an energy greater than 17 kev) produced by each beta particle, in four cases, for

†† In rigor, step by step corrections would have been needed in order to make a proper deduction, at the low energies, for the Compton effect contribution of the hardest X-rays. We have saved ourselves this painstaking computation since thecorresponding correction, on the order of 2% at the most, is smaller than the errors accumulated in our measurements.

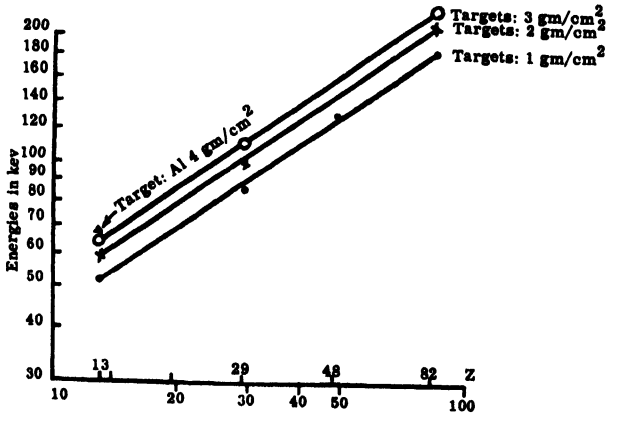

Figure 6. Variation in the maximum bremsstrahlung intensity as a function of Z for Sr^{90}-Y^{90}

Table I. X/β yield (above 17 kev) Sr^{90}–Y^{90} for 1 gm/cm² targets

Yield	*Aluminum*	*Copper*	*Cadmium*	*Lead*
By transmission	2 9%	2.8%	2.3%	2.2%
By back-scattering	1.2%	1.8%	2.8%	5.9%
Total	4.1%	4.6%	5.1%	8.1%
Practical (sandwich)	3.9%	4.2%	3 9%	4 2%

Table II. Yield of the Bremsstrahlung in Energy for a Source of Sr^{90}–Y^{90} and 1 gm/cm² Targets

Aluminum	*Copper*	*Cadmium*	*Lead*
0.42%	.55%	.56%	.57%

1 gm/cm² targets: the X/β yield produced by transmission; the X/β yield produced by back-scattering; the X/β yield taken as a whole; and the X/β yield as practical for a flat source placed between two 1 gm/cm² targets.

This last named ratio will be the practical yield of the sources. The values obtained are shown in Table I. It should be noted that, by reason of the reabsorption of the secondary radiation by the target, thick targets of low atomic number give a practical yield greater than that of the high atomic number targets. This apparent inversion is reduced for targets of lesser thickness and disappears under back-scattering. With a 630 mg/cm² target, the practical X/β yield for lead is close to 7% while, for aluminum, it is but little different from the yield for the 1 gm/cm² target.

Efficiency Measured in Energy

For the β spectrum, an average energy equal to 0.4 of the maximal energy has been taken.[7]‡‡

Table II gives the energy efficiencies which correspond to the bremsstrahlung due to transmission. These yields, as well as the X/β^- efficiency, are considerably better for heavy elements if targets of lesser thickness are used.

Case of Back-Scattering

In order to determine the optimal target, we used the device shown on Fig. 7. An aluminum screen (1 gm/cm²), protects the photomultiplier from the β^- emission of the source. The increase in measured activity when placing targets behind the source is due to the bremsstrahlung which is scattered back by these targets. The curves obtained have not been corrected for absorption of the X-rays in the alumi-

‡‡ By way of comparison, let it be stated that, for monokinetic electrons, the energy yield is given approximatively by the following formula.[5]

$$\frac{\frac{dE}{dn}\ \text{rad}}{\frac{dE}{dn}\ \text{ion}} = \frac{(E + mc^2)Z}{1600\, mc^2}$$

This yield, or efficiency, does not allow for self absorption of the bremsstrahlung, is 5 to 20 times greater than the practical yield, according to the target, by taking, for E, the average energy of the β emitter considered.

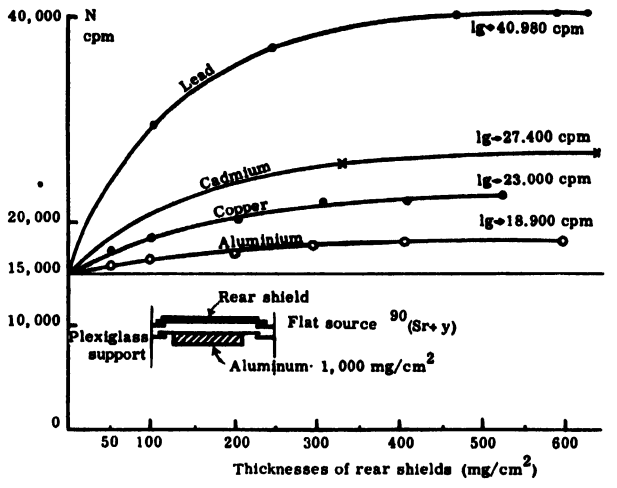

Figure 7. Back-scattering bremsstrahlung; discriminator threshold 17 kev

num screen. However, they are such as to warrant the statement that, with Y^{90}, beyond 500 mg/cm^2, there is no increase in the bremsstrahlung. It will be of interest, therefore, when preparing transmission type radiographic sources, to use but a limited thickness of a heavy target (300 mg/cm^2 at most) and to complete the protection with a light element (aluminum for instance, see Fig. 8).

INDUSTRIAL APPLICATIONS

Radiographic Sources

The sources of bremsstrahlung are sources of low energy X-rays, the practical domain of application of which extends from 20 to 200 kev. Along with the Th^{170} sources, they make radiographs of thin parts possible (welds on sheets, for instance).

We thought, in particular, for that purpose, in terms of the use of Sr^{90}. Preliminary tests carried out with a flat 10 mc source enabled us to see a 0.1 mm deep slit on a 1 cm thick steel penetrometer.

The best results will be given by more compact

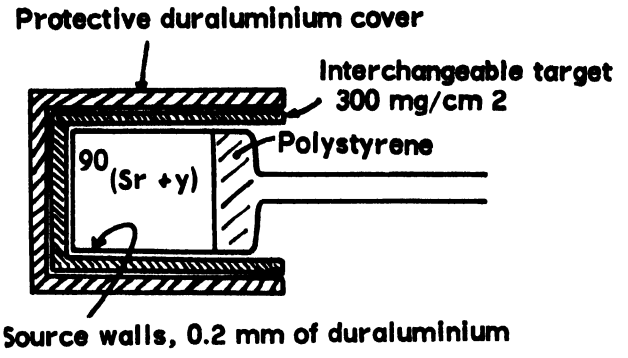

Figure 8. Source for radiographic work

sources. The sources under preparation are of the thin wall type (0.2 mm of duraluminum). They will be used with interchangeable containers in order to modify the quality of the radiation.

For common applications, the activity of the sources will range between 1 and 5 curies (of Y^{90}). The spectrum of the radiation they will emit will probably be altered by reason of the braking of the rays in the source itself and complex reflexion phenomena. For the same reason, the practical X/β yield or efficiency will be less than that of the sources reviewed in this paper.

Figure 8 shows a model of a radiographic source with an interchangeable target. For the more common applications, it will be wiser to attach the target permanently to the source.

Thickness Measurements

Such measurements can take place according to two principles:

The first is by counting, or recording with a discriminator or selector, of the radiation transmitted by the part to be measured. One can use a photomultiplier or single channel selector, a counter scale and an integrator.

The curves on Fig. 9 show absorption, by iron and aluminum, of the radiation obtained with targets

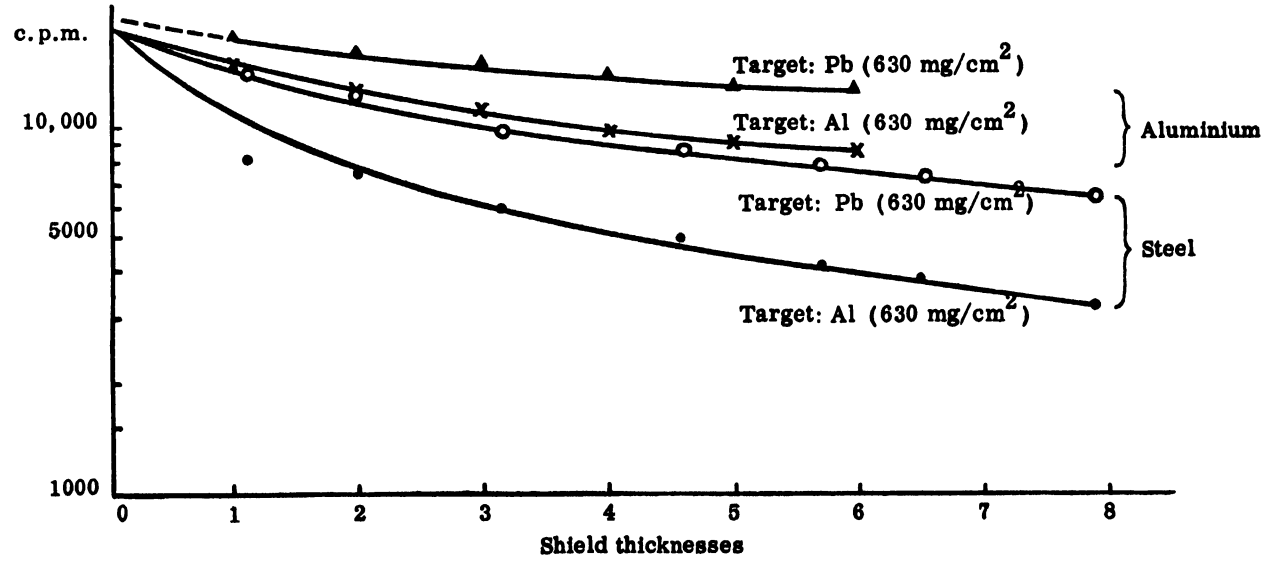

Figure 9. Absorption of Sr^{90}-Y^{90} bremsstrahlung in steel and aluminum

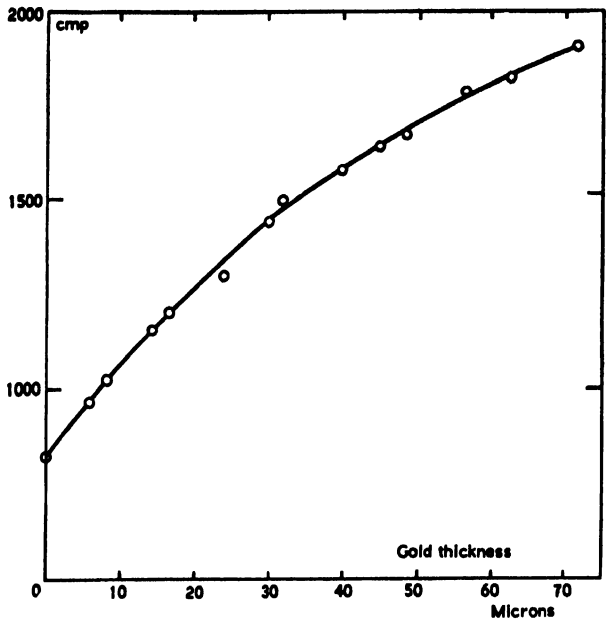

Figure 10. Measurement of thickness of gold deposit on copper. Copper base: 525 mg/cm^2; source Sr^{90}-Y^{90}

of different natures. Maximal sensitivity is reached, in both instances, with a 630 mg/cm^2 aluminum target. These curves are practically exponential where the absorbent thickness exceeds 2 gm/cm^2. Thus, we can talk about half thicknesses equal, respectively, to 5.5 mg/cm^2 for iron and 7.5 mg/cm^2 for aluminum, when the bremsstrahlung is generated in an aluminum source.

The second is by selector counting, by aligning on an X*K-line* produced through a thin screen (cadmium, rare earths, tin, tungsten, lead) and evaluating or estimating the absorption in the part to be measured.

The measurement of small thicknesses of metallic deposits can be made, in some instances, by irradiating the substance to be observed by means of a β^- source and measuring the height of the *X-K* line of deposit fluorescence.

With a Sr^{90}–Y^{90} source, deposits of gold on copper, of a thickness comprised between 0 and 120 μ can be measured very well by back-scattering to a precision of the order of 3%.

The work can also be carried out by using the device as a discriminator in some cases. Contrast is far better than by using β^- back-scattering (see Fig. 10).

Analysis by Fluorescence

The method consists of irradiating the substance to be studied after it has been dissolved or pulverized, and to observe the intensity of the characteristic *K* lines. Calibration and corrections are necessary. The use of a proportional counter should make it possible to improve and extend the method. As for the X-rays, a line can be isolated by Ross's method of the balanced filters.

CONCLUSION

The utilization of bremsstrahlung-induced X-rays makes it possible to extend the range of the portable radiographic sources toward the low energies. One is entitled to the belief that this phenomenon will find many other applications.

NOTE

We had completed much of this work when we received the March 1955 issue of *Nucleonics,* with an article by L. Reiffel, titled "Beta ray excited low-energy X-ray sources" and the April issue of the same publication, with a letter by Kereiakes and Krebs. We are in agreement with L. Reiffel, in particular as regards the efficiencies and concepts of radiographic sources.[8–11]

Our own studies have been the object of an application for a French patent, which was filed on April 12, 1955, and of a letter to the Editor of the *Journal de Physique et le Radium* sent on April 16, 1955, under the same title and signed by P. Lévêque and P. Martinelli.

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Application of Radioisotopes to Leakage and Hydraulic Problems

By J. L. Putman and S. Jefferson,* UK

Measurements of flow and leakage in hydraulic systems involving large volumes of liquid under varying conditions of accessibility have shown the peculiar aptitude of radioactive techniques for measurements of this kind, and especially the usefulness of penetrating gamma rays. Large-scale operations are often involved, in which the actual manipulation of the radioactive material plays a small, though important part. A brief survey of some of these projects is given.

LOCATION OF LEAKS IN BURIED WATER MAINS

It is common practice when laying new water mains to fill the excavated trench as soon as possible after laying a section of the main. This is necessary to avoid the flooding or collapse of a trench in bad weather, to avoid refilling the trench with saturated earth, which is difficult to consolidate, and to minimise inconvenience to the public, especially when the main passes close to a road. In some circumstances it is even desirable to back-fill the trench before the newly laid main has been pressure tested. This procedure in the past was attended by considerable risk, since any leaks which were then found in the main on pressure testing were difficult to locate and often involved the re-excavation of long sections. The development of radioactive techniques has greatly facilitated the detection of leaks in buried mains, so that contractors can confidently take the risk of early back-filling.

Three radioactive methods have been developed[1] for finding leaks in sections of main up to 5 km long. Each involves the introduction of Na^{24} in solution into the main, usually in the chemical form of $NaHCO_3$. Na^{24} has been chosen as a tracer because:

1. It emits penetrating gamma rays (1.4 and 2.8 Mev).
2. It is quickly prepared in high specific activity by the irradiation of ready-made ½ gram pellets.
3. The tolerance level in drinking water is high (8 microcuries/litre).
4. The half-life is conveniently short (15.0 hours), so that radioactive solutions can be allowed to decay before discharge from the main.

In the first method[2] a length of main to be tested is filled uniformly with a radioactive solution. This is achieved by first dissolving a radioactive tablet and mixing the solution uniformly in about 500 litres of water, then pumping this solution at a controlled rate into the main whilst water is flowing along it. The arrival of radioactivity at the end of the required section is detected with a gamma ray counter and the isolating valve at this point is closed. All known outlets from the main being closed, it is then raised to pressure and maintained so for about half an hour, to allow some radioactive solution to pass through any leaks into the surrounding soil.

The radioactive solution is now passed along the main out of the section under test and a search is made for activity in the earth around the main, particularly at pipe junctions. This is done by inserting a gamma ray counter in a hollow probe into bar holes made in the ground. Geiger counters and scintillation counters have been used alternatively as detectors. Samples of ground water are taken as additional evidence at points where leakage is indicated. Leak rates of more than 100 ml/hour are detected as a matter of routine. The smallest leak rate which has been positively identified by these methods was measured and found to be about 2 ml/hour. It is evident, however, that this method would be laborious to apply to long lengths of main.

Longer lengths in which high leak rates occur can be tested by measuring the velocity of water in the main when all other outlets but the leaks have been closed. In this method[3] a small volume of solution of relatively high specific activity is inserted into the closed main, taking care that the total activity is such that when diluted in the total contents of the main it would result in a specific activity well below drinking tolerance. Under the action of the water supply pressure, the water flows along the main, carrying the radioactive solution with it. The activity is detected with gamma ray counters placed at convenient points of access, such as hydrant junctions, and by timing its passage between successive points the velocity of the water is found. When a point of leakage is passed, an abrupt change in velocity occurs, and by comparing the apparent velocity in the section containing the leak with the velocities in the previous and succeeding sections, the position of the leak can be located within a few metres. This method is only applicable when the flow in the main is high enough

* Atomic Energy Research Establishment, Harwell, England

to be turbulent (about 500 litres per hour in a 10 cm main); under turbulent conditions, little spreading of the radioactivity along the main occurs, but if streamline flow occurs, spreading is considerable and velocity measurement becomes difficult. Smaller leaks have been located by this method by superimposing a steady controlled flow rate at the outlet end of the main.

To localise small leaks in a long main, however, a third method is generally used, in which both inlet and outlet stopcocks are closed, and pressure is maintained in the main by supplying water at a ferrule in the middle of the suspect section. When pressure equilibrium is established, a small volume of radioactive solution of total activity about ½ millicurie is injected into this supply. This flows mainly towards the greatest leak, and counters placed on each side of the supply ferrule indicate the direction of the leak. Repeated application of this technique localises the leak to a short section of main.

In all of the above methods of test, every precaution is taken to keep the radioactive solutions under control, and the closest co-operation is maintained with the appropriate health authorities, to avoid any possibility of radioactivity reaching the consumer. In addition, solutions normally have specific activities one tenth of the drinking tolerance based on continuous consumption and on the rare occasions when mains in service are tested, the radioactive solution and any added water are heavily chlorinated. This is done both to prevent bacterial infection and to render the water thoroughly unpalatable for drinking.

It is well known that alternative methods of leak detection exist and the radioactive techniques are only intended to supplement these. Radioactive methods are especially applicable to newly laid mains and to operations in soil which is already waterlogged. During the last 2½ years a large number of such investigations have been made by Harwell personnel and in no case has a significant leak remained undetected. A mobile team has now been formed by a commercial firm to apply these techniques for general use.

Leaks in large bitumen lined storage tanks have been detected by similar methods. The lower part of a tank is filled with a Na^{24} solution. After the removal of the solution a portable scintillation counter is used to examine the inside of the tank for activity which has seeped through the lining.

LEAK DETECTION IN LONG MAINS AND OIL PIPE-LINES

The methods described above are limited by practical considerations to lengths of main not exceeding about 5 km. In some leakage problems, particularly in the operation of oil pipe-lines, much longer lengths may be suspect and the localisation of leaks to short sections by orthodox means is difficult. For such problems, a technique is being developed by which the search for leaked-out pockets of radioactivity is made from inside the pipe-line.[1, 4]

First a quantity of radioactive solution is fed into the pipe-line from the input end. This may be in oil or water solution; we have used Na^{24} in water. This is followed with nonradioactive liquid, pumping speeds being such as to ensure turbulent flow and avoid undue spreading of the product. At a distance of the order of 1 km behind the radioactive solution the detector is released into the pipe-line. This is in the form of a sealed container carrying two halogen-quenched Geiger counters and a slow-speed wire recorder, all battery operated. The container is towed by a flanged unit similar to the impellor of a "go-devil" pipe scraper and is carried along the line by the flowing liquid.

Points of leakage where the radioactive solution has leaked out of the pipe-line are detected by the Geiger counters, whose pulses are fed to the wire recorder. In addition, a series of small gamma ray sources (each about 200 microcuries of Co^{60}) are placed at convenient intervals against the outside of the pipe-line as distance markers.

When the detector unit reaches the delivery end of the pipe-line, the wire record is removed and played back more rapidly into a recording ratemeter, which makes a paper record of the distribution of activity along the pipe-line. By relating areas of high counting rate to the easily recognisable records of the distance markers, the location of leaks can be determined.

The unit has been tested successfully for lengths up to 20 km. It is expected to operate over much greater distances after adjustments to the speed of the wire recorder.

FLOW MEASUREMENTS IN LARGE DIAMETER PIPES

Tests of a more academic nature have been made in collaboration with the British Electricity Authority to determine the nature of flow in 1½ metre diameter pipes.[5] By means of an adjustable injector, small volume injections of radioactive (Na^{24}) solution were made at different points on a pipe radius and their time of flow over different lengths was studied, using a collimated counter with a portable ratemeter. Comparison of radioactive methods of labelling with salinity methods showed the former to be superior in convenience and sensitivity.

It was established that even under turbulent conditions, the mean velocity of discrete small volumes of water is not uniform over distances less than about 5 times the pipe diameter. Once turbulent flow has been established, however, bulk flow can be estimated accurately from radioactive measurements of velocity and the known cross-section of the pipe.

Unfortunately the cross-section is not always accurately known. In such cases the radioactive dilution method is applicable provided that thorough mixing occurs, as it does for example when the water passes through a turbine. A steady stream of high

specific activity solution is released at a known controlled rate into the input pipe and samples are taken of the effluent water. The specific activity of these samples is compared with that of measured dilutions of the original radioactive solution, and from the ratio of counting rates obtained, the dilution of the radioactive solution in the pipe is obtained, and hence the flow rate of the water can be deduced. The accuracy of the method is limited to the accuracy of control of the flow of radioactive solution and perfect mixing is not always easy to ensure.

INTERFACE DETECTION IN OIL PIPE-LINES

Radioactive tracers have been used for nearly three years to label interfaces between successive products in oil pipe-lines, but the method is not yet fully established on a routine basis. Br^{82} was used as ethylene dibromide in experimental tests on pipe-lines up to 60 km in length, but its half-life of 35 hours is too short for routine operation.

The use of Sc^{46} is proposed, as this also emits high energy gamma rays, has a half-life of 85 days and is available as a by-product of the production of carrier-free Ca^{45}.

Several methods of injection have been developed. For fixed locations an adjustable "single-shot" pump is used, which delivers an appropriate volume of solution from an earth-screened reservoir of radioactive solution. For portable use, sealed expendable capsules are used, whose contents are injected either mechanically or by gas pressure from a soda-syphon capsule. In injection devices for the portable capsules the expendable container is flushed out automatically with clean oil or fuel to ensure its safe disposal after use, and a non-return valve prevents the escape of radioactive solution when the pipe-line is operating at high pressure.

As shown above in experiments with water mains, the radioactive labelling of interfaces is limited to conditions of turbulent flow, otherwise spreading of the radioactivity becomes serious. In oil pipe-lines passing more than one product, turbulence is an essential condition in any case, for streamline flow would result in intermixing of successive products over a long length of line, which could not be tolerated.

When soluble tracers are used, they are spread along the pipe-line during flow by exactly the same mechanisms which cause the intermixing of products across the marked interface. It can readily be shown that the activity in a given section is proportional to the differential of the concentration curve with respect to distance along the pipe-line,[6] hence:

$$\text{Ratio (Fuel 2/Fuel 1)} = k\int_{-\infty}^{x} f(x)\,d$$

where $f(x)$ is the instantaneous counting rate measured outside the pipeline as the active solution moves past a counter and k is a constant normalising factor. This relationship has been verified experimentally[6] in tests on a 60 km line, and is used to determine the exact moments to divert intermixed products at the output end of a pipeline and to reconnect to pure supplies of the second product when the requisite purity is obtained.

Some inconveniences in the handling of radioactivity in solution and the safe disposal or use of slightly radioactive fuels are averted by the use of self-contained units, which measure fuel density or hydrogen content from outside the pipeline. These methods also have the advantage that labelling is unnecessary and radioactive operations are confined to the output end of the pipeline. The density measurement can be made by the absorption of gamma rays.[7] When the interface is between two fuels which absorb gamma rays equally, some other property of the fuels must be used. A technique[8] using neutron moderation has been successfully tested in the laboratory and is being developed for field use.

The moderation and scattering of neutrons in hydrocarbons depends almost exclusively on their hydrogen content because hydrogen nuclei have nearly the same mass as neutrons. An arrangement consisting of a polonium-beryllium fast neutron source attached to a BF_3 slow neutron counter, is placed against one side of a section of pipeline. Fast neutrons from the source are slowed down and scattered by collision with hydrogen nuclei in the fuels, though practically unaffected by the steel walls of the pipeline. The BF_3 counter is biased to respond only to the low energy neutrons scattered back by the fuel. The device has been shown capable of distinguishing easily between different grades of fuel.

RADIOACTIVE TRACERS IN SILTATION INVESTIGATIONS

In the applications described above, the fluids involved have been more or less under control. The investigation of mud movements on the bed of a river illustrates the use of radioactive tracers in uncontrolled conditions.

In dredging the estuary of the river Thames for shipping it has been found that five times more mud and silt has to be removed than can be explained by the quantity of silt carried down by the river and its tributaries. It has been suggested that dredged mud dumped out at sea is carried back up the estuary by counter-currents on the bed.

At the request of the Port of London Authority an investigation has been undertaken in collaboration with the Hydraulics Research Establishment, D.S.I.R., Wallingford, to examine the movements of mud masses on the river bed. To this end a preliminary experiment[9] was made in July 1954 to test the feasibility of radioactive techniques and to obtain such quantitative information as the dilution of the tracer material in migrating mud and the levels of activity which can be used without hazard to the public.

Samples of river mud were analysed and found to

consist mainly of sand particles imbedded in light, finely divided organic material. Glass was chosen as a suitable tracer material, having density similar to that of the sand. About 5% by weight of scandium oxide was therefore dissolved in 100 grams of soda glass and the glass was ground to have a size distribution corresponding to that of the inorganic constituents of the mud. A quantity of 85 grams of the ground glass was irradiated to have an activity of about 4 curies of Sc^{46}, which emits high energy gamma rays with a half-life of 85 days.

After a suitable period to allow the unwanted Na^{24} activity to decay, the irradiated glass was mixed on board a boat in a specially constructed steel drum together with about 30 kg of "liquid mud" from the river bed. The whole was then lowered to the bed of the river at slack water following low tide, and the ends of the drum were opened with a spring release mechanism.

From another boat, sealed gamma ray counters were lowered to the river bed and these operated a ratemeter on deck, allowing the activity on the river bed to be explored. The same boat was fitted with echo sounding apparatus which gave information as to the depth and nature of the river bed. The experiment showed conclusively that the injected radioactive material remained always associated with accretions of "liquid mud," a glutinous fluid which is believed to be the chief agent for the movements of silt in the estuary. Where the bed consisted of consolidated mud, no activity was found, except in one freshly dredged area where the liquid mud remained long enough to begin to consolidate; here the radioactive tracer remained with the consolidating mud.

Evidence of radioactivity was found 11 miles upstream on the fifth day after injection, but counting rates obtained were barely twice background. Activity continued to be present in liquid mud areas up to two weeks after injection, when measurements were discontinued. By this time, there were indications that much of the tracer material was consolidating with the mud and was being gradually covered up by fresh inactive mud, which lowered the apparent river bed activity. No activity was found downstream of the injection point, but the conditions of the experiment were such as to favour tidal movement upstream, and this evidence is not regarded as conclusive.

A further experiment on a larger scale is in preparation at the time of writing. This will be designed for the specific purpose of settling the direction of bulk mud flow.

Other experiments of a similar type are planned to examine the littoral drift of beaches in connection with investigations of coastal erosion.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support and assistance of a number of establishments and firms in carrying out the projects described in this article. These include: The Ministry of Supply, The Ministry of Housing and Local Government, The Port of London Authority, The British Electricity Authority, The Hydraulics Research Station (D.S.I.R.), The British Hydromechanics Research Association, United Kingdom Pipelines, British Petroleum and Messrs. Biggs, Wall & Co.

It is also a pleasure to express our grateful appreciation of the help of many colleagues from the above establishments and from A.E.R.E., whose efforts, sometimes in rigorous conditions, made this work possible.

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The Use of Artificially Radioactive Isotopes in the Study of the Processes of the Production of Steel and Iron

By A. M. Samarin, USSR

The use of artificial radioactive isotopes has made it possible to carry out investigations which hitherto were practically impossible. Radioisotopes have secured greater precision and reliability of the results obtained from both laboratory and large-scale investigations, and substantially facilitated studying the processes of pig iron and steel production.

Artificial radioactive isotopes—"tracer" atoms—have been widely used in determining the thermodynamic functions of metallurgical reactions, in studying the kinetics of these reactions and processes of steel making and in disclosing the mechanism of separation of admixtures in the course of solidification of steel and alloys. The influence of various factors on the processes of steel making has been revealed in commercial furnaces (blast, open-hearth and electric), the movement of charge materials and gases in blast furnaces has been studied, and observations made of the melting of ferro-alloys added to liquid metal, and of the distribution of alloying elements in the baths of open hearth furnaces. Important theoretical and practical data have been obtained from investigations of the process of crystallization and the causes of waste and lower quality of the metal. Artificial radioactive isotopes have been used to control the wear of blast furnace lining, to determine rapidly the phosphorus pentoxide content in the open-hearth slag, to measure the thickness of sheets in the process of rolling, etc.

DETERMINATION OF THERMODYNAMIC FUNCTIONS

Measurement of the vapour pressure of alloy components in a solid or liquid state is a direct method of determining the thermodynamic properties of corresponding solutions. The application of "tracer" atoms has afforded the possibility of measuring the vapour pressure of substances noted for low volatility, as for example, of refractory metals with high melting point.

Figure 1 presents a diagram of an apparatus for measuring the vapour pressure of the solution components, based on the determination of the velocity of evaporation from an open surface. The application of high-frequency currents as the source of heat renders it possible to conduct investigations at temperatures as high as 2000°C. The installation reached a high degree of vacuum, preliminarily charged with radioisotopes alloys kept in a liquid state. This helped to determine the vapour pressure of the solution components directly from the activity of the condensate.

Such an appliance was used by the staff of the Stalin Steel Institute in Moscow when studying the binary systems: Fe-P, Fe-S, Fe-Si and Fe-Cr.[1, 2, 3]

Relation of the logarithm of vapour pressure to concentration at temperatures of 1813, 1868 and 1893°K of iron and phosphorus over a liquid binary alloy.

Figure 2 shows the results of determination of the partial pressures of iron and phosphorus vapour at temperatures of 1813, 1868 and 1893°C. It has been ascertained that when the content of phosphorus dissolved in liquid iron is low, the system is a diluted

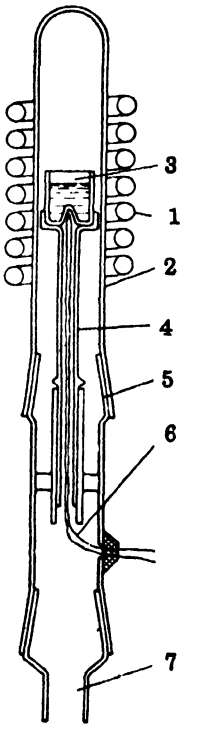

Figure 1. Scheme of the installation for vapour pressure measurement of solution's components: (1) induction coil; (2) pipe of transparent quartz; (3) crucible with molten metal or alloy; (4) support for crucible made of refractory material; (5) quartz-glass seal; (6) thermocouple; and (7) glass-glass seal connected with a vacuum system

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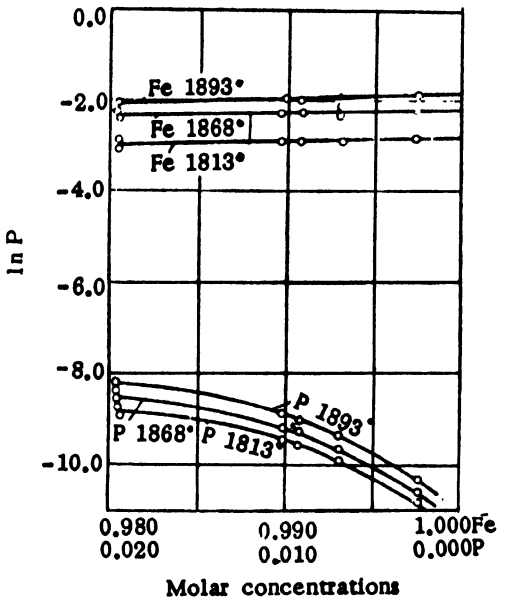

Figure 2. Relation of the logarithm of vapour pressure to concentration at temperatures of 1813, 1868, and 1893°K of iron and phosphorus over a liquid binary alloy

solution; the activity of the components is proportional to their molar concentrations. Experimental data have demonstrated that the partial molar heat content of iron within the range of 1540–1620°C proved to be practically independent of the temperature and amounted to 32,000 cal/gm-atom.

The heat of solution of phosphorus in iron within the same range of temperature and molar concentration from 0.0023 to 0.0200 does not depend either on temperature or concentration. The heat of solution is equal to 31,300 cal/gm-atm, and this value coincides with that of formation of iron phosphide. Consequently, it may be assumed that in liquid iron nearly all of the phosphorus is in the form of iron phosphide, and the system iron-iron phosphide, within the investigated range of concentration, is an ideal solution.

Winkler and Chipman were the first to use the phosphorus isotope P^{32} in studying the equilibrium of the reaction of dephosphoration.[4] When investigating the processes of dephosphoration and desulphurization, Soviet researchers[5-8] studied the distribution of phosphorus and sulphur between iron and slags of the simplest composition. In order to prevent phosphorus and sulphur concentrations from influencing the equilibrium state of the corresponding reactions, investigations have been conducted with infinitely diluted solutions of these elements both in iron and in slag.

The application of radioactive sulphur and phosphorus isotopes has under these conditions, too, helped to achieve a high degree of precision in determining the distribution coefficients.

Equilibrium and distribution coefficients were determined by measuring the activity of metal and slag.

It has been ascertained that the heat effect of the process of transition of phosphorus from iron into slag composed of iron oxides is positive and amounts to some 45,000 cal/gm-atm.

The addition of alkaline-earth metal oxides (except magnesium oxide) to this slag greatly increases the coefficient of phosphorus distribution. And, vice versa, the addition of silica to the slag drastically reduces the value of the coefficient of phosphorus distribution, which is accompanied by a marked increase in the heat effect of the process. This points to the fact that a decrease in the distribution coefficient is to some extent caused by a decrease in the entropy of phosphate-ion in the slag, resulting from a greater content of silica in the latter.

The value of the coefficient of phosphorus distribution between liquid and molten fayalite at different temperatures proved to be of the order of 0.03.

By means of S^{35}, the radioactive sulphur isotope, it was possible to investigate the distribution of this element between iron and slag of various composition. It has been found that the transition of sulphur from iron into slag composed of iron oxide is attended with evolution of some 15,000 cal/gm-atm.

Alkaline earth metal oxides added to iron oxides slag do not considerably affect the coefficient of sulphur distribution. When studying the distribution of sulphur between liquid iron and fayalite, it has been found that the distribution coefficient drops approximately tenfold (down to 0.4) as compared with the distribution coefficient between iron and slag composed of iron oxide, which is accompanied by a rise of the value of the heat effect of the process.

The need for greater precision in determining the equilibrium state of distribution of elements between liquid metal and slag called for a search for new methods of experiments. Thus the method of determining the coefficient of distribution has been suggested and employed which helps in obtaining more precise results.[7] The method is essentially as follows: The equilibrium of distribution is achieved by means of successively charging on the surface of the liquid metal in the protective atmosphere small portions of preliminarily fused slag of a given composition containing a radioactive isotope of the element whose distribution is to be studied. Since slag is added in small quantities, as powder, the temperature of the metal remains constant. The equilibrium thus attained is determined by the absence of changes in the activity of the metal samples taken after the addition of individual portions of slag.

Thus a precision determination of the values of the heat effects is secured. It has been found that the heat of dephosphorization of iron by slag composed of CaO, Al_2O_3, SiO_2 and FeO amounts to 70,000 cal/gm-atm and that desulphurization by slag consisting of CaO and Al_2O_3 is accompanied by an evolution of 40,000 cal/gm-atm.

INVESTIGATIONS OF THE KINETICS OF METALLURGICAL REACTIONS AND PROCESSES

The results of investigations of the kinetics of metallurgical reactions and processes are the theoreti-

cal basis of intensification of metallurgical industry and raising the quality of the iron and steel.

"Tracer" atoms were used in studying the kinetics of dephosphorization and desulphurization of steel and pig-iron with a low concentration of phosphorus and sulphur, i.e., when the change in the content of these elements is within the range of accurate chemical analysis. This is of importance in elaborating methods of obtaining the purest possible steel, free from any impurities.

The kinetics of desulphurization has been investigated, use being made of soda ash and slag consisting of calcium oxide and alumina.[9, 10] The application of the radioactive sulphur isotope S^{35} helped in disclosing the possibility of profound desulphurization with the use of both soda-ash and calcium-alumina slag; the content of sulphur was reduced to several ten-thousandths fractions of a per cent. The equation of the kinetic process of desulphurization so found shows that the speed of this process is proportional to the concentration of sulphur in the metal to a degree which increases, depending upon the temperature, from 1 to 2. This influence of temperature leads to the assumption that the diffusion transfer of sulphur through non-mixing layers in liquid slag is the limiting factor of the speed of the desulphurization process.

When studying the kinetics of the dephosphorization of steel, it was found that chemical analysis did not ensure the required degree of accurate determination of phosphorus content in metal or slag. The use of the phosphorus radioactive isotope[11] has made it possible to investigate the kinetics of transition of phosphorus into slag at very low concentrations of this element in metal, i.e., when the rate of the process is negligibly small. It has been found that the speed of the process of dephosphorization is proportional to the value of the interface between slag and metal, and the concentration of phosphorus in the metal.

In order to find the step that limits the speed of reaction in such heterogeneous systems as metal and slag, the kinetics of isotope exchange of iron between metal and slag has been studied when these phases are in thermodynamic equilibrium.[12] In this investigation the iron radioactive isotope Fe^{59} was used which had been preliminarily added to the slag. It has been found that diffusion in the slag phase, or, in the presence of intermixing, the process of mass-transfer in the slag is the most retarding step in the process of isotope exchange of iron between liquid metal and slag; the passage of iron through the interface slag-metal occurs much faster.

The results obtained from studying the kinetics of isotope exchange were used in computing the coefficient of diffusion of iron in acid slag at temperatures ranging from 1350 to 1550°C and in slag of a fayalite composition at a temperature range of 1250–1400°C.

When determining the influence of stirring on the kinetics of the reaction of the isotope exchange of iron, it has been found that the rate of the process of exchange is increased both through the stirring of the slag only and owing to the stirring of both phases (the stirring was effected by blowing nitrogen through a melt). The dependence of the coefficient of the mass-transfer on the intensity of stirring has been represented as the function $\beta = AU^m$. The value m, approximating 0.4–0.5 corresponds to diffusion kinetics; when both phases are stirred, $m = f(U)$. At some values of U the index m exceeds one.

Radioactive isotopes of calcium and sodium were used to investigate the phenomenon of transfer in slag melts, notably of the transfer of ions in cases of electrolysis. Thus the transference numbers of cations of the said elements in molten calcium phosphate and sodium silicate were measured respectively.[13] It has been found in both cases the transference numbers of cations closely approximate one.

The study of the kinetics of metallurgical reactions and processes in laboratory conditions is necessary to disclose the mechanism of the reaction and processes and to determine the energy of activation of metallurgical reactions. The results of such studies cannot, however, be utilized directly on a commercial scale, since many additional factors influence the speed of steel-making processes in commercial furnaces. Therefore several investigations of the kinetics of the processes of steel making in modern large open hearth furnaces are a prerequisite for the study of the most effective methods of raising productivity. It is only the application of "tracer" atoms that has made possible to investigate the movement of liquid metal in the baths of open hearth furnaces, to determine the speed of melting ferroalloys added to the bath of liquid metal, and the speed of distribution of alloying elements in the volume of the liquid steel bath.

The staffs of the Zaporozhstal, Novo-Tula and Karl Liebknecht iron and steel works investigated the absorption of sulphur by metal charges from the atmosphere of open hearth furnaces at various periods of heating.[14] Sulphur radioactive isotopes were added to the fuel (oil or a mixture of coking and blast furnace gases). Samples of metal, slag and gas were taken at different periods in the course of experimental heatings and the intensity of their radioactive radiation was determined.

The investigations so conducted helped to find that during melting some 10–20 per cent of the sulphur contained in the gas phase pass into the metal; at the same time the sulphur passes from the charge into the gas phase, though to a lesser extent. In the refining period but 1 per cent of the sulphur contained in the atmosphere of the furnace passes into the metal. Enrichment of the air with oxygen increases the speed of melting of the metal charge and helps in obtaining metal with a lower sulphur content.

Major results of importance to the theory and practice of steel making have been obtained in studying the hydrodynamics of the steel bath and the mechanism of the slag formation process. With the help of the recently elaborated method of determin-

ing the radioactivity of metal and slag samples, it became possible to considerably reduce the quantity of radioactive isotopes to be introduced into the bath of the open hearth furnace so as to obtain reliable measurements of the speed of counting radioactive radiation. The introduction of very small additions of radioactive isotopes to liquid metal or slag makes it possible to "tag" the corresponding volumes and observe their movement and distribution in the bath.

It has been established that radioactive cobalt introduced to the bottom through the middle door in a 350-ton open hearth furnace is evenly distributed in the volume of the bath within 10–20 minutes during the period of rapid decarbonization. When this isotope is introduced through the last door, the time required for an even distribution of small additions in 24-ton, 50-ton and 350-ton open hearth furnaces is 10, 45, and 55 minutes respectively.[15]

It has thus been found that the spreading of small additions in liquid metal is effected by means of turbulent diffusion. The effective coefficient of turbulent diffusion or mass-transfer in liquid iron was calculated on the basis of experimental data. It proved to be equal to 100–500 cm^2sec^{-1}, i.e., millions times more than the coefficient of molecular diffusion. The connection between the value of the mass-transfer coefficient and the rate of oxidation of carbon has been found, the latter determining the degree of turbulization of the movement of liquid metal.[15]

In addition, the coefficients of the mass-transfer have been determined in the bath of open hearth and electric arc furnaces of various capacity, use being made of radioactive isotopes of chromium, tungsten and sulphur.

When determining the speed of melting of ferro-alloys added to liquid metal, it has been found that the melting of a piece of ferro-chromium weighing 20 kilograms, placed in a 190-ton open hearth furnace, is completed in 10–20 minutes.[16]

It is only by using radioactive isotopes that it became possible to study the mechanism of slag formation or the speed of melting steel scrap during the melting of steel in open hearth furnaces.

The staff of the Urals Institute of Metals have investigated the open hearth hot-metal process having set before themselves the task of determining the beginning of interaction between slag-forming substances and the speed of melting iron scrap after the pouring of liquid pig iron.

In order to determine the beginning of interaction between iron ore and metal, a radioactive isotope of iron, as oxide of the latter, was introduced into the ore, charged into the furnace, at various horizons of the layer of dry substances (ore and limestone). When the latter are successively added in a 100-ton open hearth furnace—ore-limestone-ore—the upper layer of the ore starts to interact with the liquid pig iron 20–30 minutes after the beginning of melting, and the lower layer of ore in an hour or 90 minutes, i.e., after flushing the primary slag from the furnace. In other words, the iron ore, charged under the limestone, takes little part in the process of interaction between the metal and the slag, and notably in dephosphorization.

When determining the speed of melting steel scrap, radioactive isotopes of iron or cobalt were introduced into the last ladle of liquid pig iron poured into the furnace. The speed of melting scrap was determined by the decrease in intensity of radiation of the metal samples taken from the furnace. Naturally, the speed depends on many factors, among which particularly important are the temperature control, the condition of the bath after the pouring in of liquid pig iron, and the time of the end of interaction between the pig iron and iron ore.

As a result of determining the speed of the passage of radioactive isotopes of iron from the slag of the furnace into the metal[17] it has been suggested that the kinetics of reactions between metal and slag in commercial furnaces, too, is not determined by the energy barrier on the interface slag-metal.

Phosphorus radioactive isotopes have been used to study the kinetics of dephosphorization in open hearth furnaces of various capacity.

Phosphorus radioactive isotopes introduced to the bottom of a 30-ton furnace in the period of intensive boiling are quite rapidly and evenly distributed in the volume of the metal and slag. The kinetic curves, as illustrated by Figs. 3 and 4, testify to the fact that in the above conditions a state approximating the equilibrium of phosphorus distribution is achieved in about 30–40 minutes after the melting of the charge. This is followed by a slow rephosphorization caused by rising temperature. For example, the kinetic curves drawn on Fig. 4 show that the dephosphorization rate is proportionate to the concentration of phosphorus in the metal. This follows from the same Fig. 4 which shows a straight line drawn in the coordinates of the logarithms of the activity (concentration) of phosphorus in metal against the time.

The application of radioactive isotope of phos-

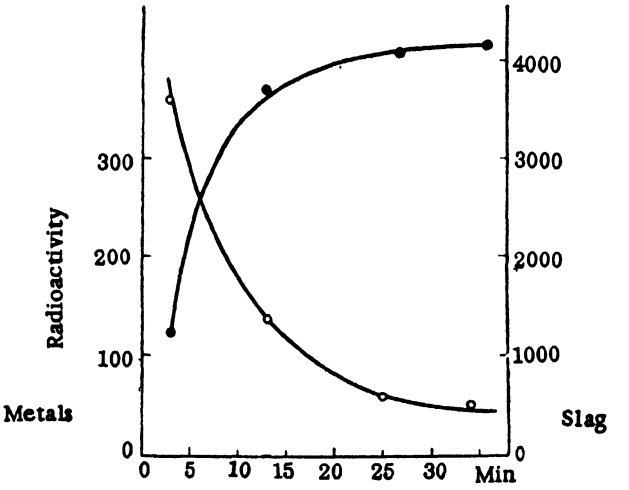

Figure 3. Relation of the radioactivity of the metal samples (open circle), and slag (dot), containing P^{32} and taken from the open hearth furnace in the course of heating

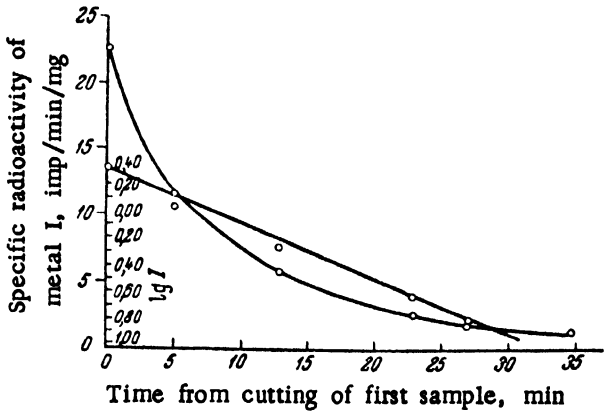

Figure 4. Change in radioactivity of metal samples containing P^{32} and taken from an open hearth in the course of heat. The curve is drawn in co-ordinates: specific radioactivity-time; the straight line in the co-ordinates: the logarithm of specific radioactivity-time

phorus has facilitated research connected with finding a rational technology of obtaining in large-sized open hearth furnaces steel and slag of high phosphorus content, suitable as a fertilizer. The positive role of the slag, remaining in the furnace after the tapping of steel, in the process of slag formation in the subsequent heat has been revealed, as well as in the dephosphorization of the metal in the period of melting.

When studying the kinetics of dephosphorization of high phosphorus pig iron in 350-ton open hearth furnaces,[18] the kinetic equation of the process of dephosphorization has been specified and the connection between the constants of speeds of reaction of phosphorus and carbon oxidation established.

An even distribution of a small addition of phosphorus radioactive isotopes in the baths of 350-ton open hearth furnaces is attained in about an hour.

The sum total of the data obtained in investigating the process of dephosphorization in commercial furnaces supports the concept that the kinetics of the dephosphorization reaction is of a diffusion nature.

The kinetics of desulphurization in an arc furnace has been explored through the application of radioactive isotopes of sulphur at the Chelyabinsk iron and steel works.[19]

The investigations devoted to the study of pig iron and steel production hardly contain any experimental data regarding the processes which occur on the surface dividing the phases—on the surface of the bubbles of carbon monoxide and non-metallic particles suspended in steel. At the same time the speed of decarbonization and purification of liquid metal from phosphorus and sulphur, and the processes of formation of heterogeneous oxide and oxysulphide particles greatly depend on some reactions which take place on the surface of the dividing phases.

The experiments performed in studying hydrometallurgical processes of the non-ferrous metal industry point to the importance of the results obtained from the theoretical and practical viewpoint,

In hydrometallurgical processes the kinetics of solution and effectiveness of recovery of metals are largely due to the formation of skin on the surface of the dissolving metal resulting from the presence of various impurities in the solutions.

Formerly the process of formation of skin could be determined only qualitatively; today the application of the method of radioactive indicators has made it possible to ascertain the quantitative features of the process of formation of surface skin and determine the number of elements sorbed by the metal surface, the thickness and density of coating, and to study the kinetics of their formation under various conditions. The radiography method has been employed to study the distribution of skin-forming elements on the surface of dissolving metals. Thus, when investigating the formation of skin by using the radioactive isotopes Cu^{64}, Zn^{65}, Fe^{59}, Hg^{203}, S^{35}, Sb^{126}, As^{76}, Ag^{110} and Ca^{45}, the influence of the presence of various impurities on the speed of solution of gold and silver has been determined.[20]

This method of investigation will undoubtedly be widely used in studying the processes of producing pig iron and steel as well.

REVEALING THE SOURCES OF STEEL CONTAMINATION BY NON-METALLIC INCLUSIONS

The production of steel with a minimum content of non-metallic inclusions to a considerable degree depends on the availability of reliable data on the origin of these inclusions. It is practically impossible to determine the source of non-metallic inclusions present in steel by chemical analysis methods or by means of metallographic examinations. When using these methods one is unable to assert that, for instance, the presence of aluminium silicate results from steel being contaminated only by particles of reactions of deoxidation by silicon and aluminium, since the appearance of aluminium silicates is equally possible as a result of contamination of steel by particles of slag and refractory materials of the furnace lining and of steel-pouring facilities.

The use of radioactive indicators makes it possible to "tag" the materials contiguous to steel in the process of its production and thus to determine the influence of every source separately on the contamination of the metal by non-metallic inclusions. Methods have been elaborated which provide for a quantitative determination of steel contamination by exogenous non-metallic inclusions in the process of its tapping and pouring.[21] The radioactive isotope of calcium, Ca^{45}, as $CaCO_3$ and CaO, was used in the capacity of an indicator.

When determining the degree of contamination of ball-bearing steel by non-metallic inclusions in the course of melting and pouring, it has been found that the slag of the reduction period of heat in arc furnaces with acid or basic lining is not the source of contamination either in the process of melting or of simultaneous tapping of the steel and slag into the ladle. When bottom pouring is used, the steel may be contaminated by non-metallic inclusions be-

cause of the destruction of the refractory lining; this source accounted for 9 per cent of the total content of non-metallic inclusions in steel, and the erosion of the ladle brick up to 18 per cent. This method was also applied in establishing the effect of destruction of refractory materials of the crucible in case the slag becomes involved through contamination by non-metallic inclusions when melting steel in high-frequency furnaces.

The detection of sources of contamination of ball-bearing steel by non-metallic inclusions is carried on in conditions of large-scale production. It has been found that the degree of contamination by non-metallic inclusions owing to the destruction of the ladle lining depends on the material of the lining. The contamination of steel by inclusions owing to the destruction of the ladle lining made of high alumina brick proved to be 2–2.5 times less than that of steel poured out of a ladle lined with chamotte brick.

A method of contact autoradiography was employed to study the influence of the methods of pouring metal on the distribution of exogenous inclusions in ingots.[22] The method of investigation so elaborated has permitted finding the nature of distribution of radioactive inclusions added to the stream of steel flowing out of the ladle in ingots weighing up to 800 kilograms. Radioactive isotopes of calcium in the shape of calcium silicate or calcium oxide were introduced as indicator. Analysis of autoradiograms made of longitudinal and transverse templets, cut out of ingots, and of the center gate and siphon guards has helped to reveal the character of distribution of inclusions in ingots bottom-pour and top-pour.

The analysis of the radiograms points to the absence of displacement of non-metallic inclusions by growing crystals when the ingot solidifies. The introduction of radioactive isotopes of calcium in the course of pouring makes it possible to trace the distribution of exogenous non-metallic inclusions in the ingot at the moment of its solidification and to ascertain the influence of the method of pouring on the character of their distribution.

Ag^{110}, a radioactive isotope of silver, was used as indicator to detect the causes of waste in finished pipes because of skin and of lamination. In the course of pouring steel an oxidized "crust" was tagged, which appears on the surface of the metal when the mould is filled. Subsequent control of the billets after the first piercing, and of finished pipes by means of a specially adapted Geiger-Müller counter have helped in finding that the lamination and rolling skin waste is due to a turn of the "crust" during the pouring of the metal. A change in the conditions of steel, deoxidation and improvement of pouring helped to considerably lower the percentage of waste.

INVESTIGATIONS OF THE PROCESSES OF STEEL CRYSTALLIZATION

Experimental study of the processes attending the solidification of steel in the moulds are very complicated. In this connection attention has been lately given to the extension of the means of research, and notably to the use of radioactive isotopes in investigating the kinetics of steel solidification, the hydrodynamic state of metal during crystallization, and the mechanism of redistribution of impurities during their transition from one aggregate state into another.

When determining the speed of crystallization of rimming and killed steel under various conditions of cooling, radioactive additions were successively introduced into liquid steel at various stages of cooling with a subsequent detection of the boundary dividing the phases by means of contact radiography of templets cut out of ingots.[23] In this way data were obtained on the speed of advance of crystallization under controlled conditions of cooling. As a result of this investigation an equation was found to determine the thickness of the crust, d, in ingots of rimming steel. It appears as follows:

$$d = K\sqrt{t} = (5.17 - 1.87h)\sqrt{t}$$

where h is the height of the horizon in the ingot (in cm) and t is the time that elapsed after the filling of the mould (in minutes). The introduction of the new variable (h) reflects the real regularity of change in the coefficient of solidification of steel along the height of the ingot.

The application of radioactive indicators has made it possible to specify the concept regarding the nature and intensity of movement of metal in the mould. An approximate value of the speed of the descending streams of liquid near the boundary of solidification has been found and the order of value of the turbulent diffusion coefficient in cooling killed steel determined. It should be noted that it is only with the use of radioactive isotopes that experimental investigation of the hydrodynamic state of liquid steel has really been started.

Radioactive indicators have been used repeatedly to study the distribution of elements along the section of ingots, between the axes and inter-axial space of dendrites, as well as to ascertain the influence of thermal treatment on equalization of the composition of steel.

An investigation of the conditions of the capture of outside inclusions in the melt by branches of growing crystals has shown that the capture is strongly influenced not only by interphase tension, but also by the linear speed of the growth of crystals.

A great part of research dealing with crystallization has been conducted on commercial ingots weighing up to 10 tons.

The speed of solidification of steel ingots weighing 2.65 and 6.2 tons has been determined both by the old method of pouring and the method of "tracer" atoms, by means of introducing radioactive isotopes of iron into liquid steel at various periods after the mould has been filled.

A comparison of the data obtained by the two methods has proved that the formulae hitherto ac-

cepted for determining the solidification speed of steel ingots define not the speed of growth of dendrites, but that of the final solidification of steel, since the tipping of the casting mould is instrumental in removing, together with the liquid steel, the dendrites that break off, and the liquid metal involved.

The use of radioactive indicators has helped to ascertain with a greater degree of accuracy the duration of solidification of steel in the mould, required to obtain an ingot with a proper macrostructure. A study has been made of the effect of warming the upper part of the ingot on the speed of crystallization of chrome-nickel steel along the vertical axis of the ingot.

INVESTIGATIONS OF THE BLAST FURNACE PROCESS

Studying the movement of materials and gases in the blast furnace is closely connected with finding means of further increasing the productivity of the furnace. When investigating the movement of the charge, radioactive isotopes were introduced into the ore, coke, agglomerate and limestone.[24] The movement of materials was determined by measuring the intensity of radioactive radiation in the charge by means of counters of nuclear particles placed along the outer casing of the blast furnace. The speed of movement of materials can also be determined by detecting radioactivity in pig iron and slag. It has been found that the speed of movement of agglomerate and coke can be controlled within a wide range by changing the technological factors of the process. The application of radioactive isotopes has helped to ascertain that the agglomerate moves at a faster rate in the centre of the blast furnace shaft than in the periphery, while hitherto the contrary, i.e., a higher speed of movement of the agglomerate in the periphery, was accepted. The movement of gases in the blast furnace shaft was investigated by introducing through the tuyere a radioactive inert gas and fixing the moment of its detection at various points in the shaft. It has been found that the gas passes with a velocity of 22–24 m/sec through the shaft of a blast furnace with a capacity of 1145 m^3.[25]

INVESTIGATIONS OF THE PROCESSES OF BONIFICATION

The use of "tracer" atoms has opened up great prospects for the study of processes of bonification, particularly of flotation processes, which occur on the surface of mineral particles and within the flotation pulp. The concentration of reagents in flotation processes is frequently rather insignificant, and hence the hitherto employed methods of determining very small quantities of reagents adsorbed by the surface of the mineral have not produced any accurate results.

The staff of the Mining Institute of the USSR Academy of Sciences investigated the interaction between sulphide minerals and reagents into which radioactive isotopes S^{35}, P^{32}, Ca^{45} and Na^{22} were introduced.

Previous investigations of many years have proved that a dosed effect of oxygen ensures positive practical results. It was not, however, possible on the basis of these data alone to gain a comprehensive idea regarding the physical essence of the phenomena accounting for this effect of oxygen.

The application of radioactive isotopes introduced into the composition of the collector has shown that the favourable effect of oxygen on the flotation of sulphides (pyrite, chalcopyrite and sphalerite) in a neutral medium consists in greater adsorption of the collector on the surface of the mineral. When oxygen acts on pyrite in a lime medium, the adsorption of the collector declines, and, quite the reverse, it increases when oxygen acts on chalcopyrite and sphalerite; in other words, this medium exhibits the selectivity of the action of oxygen on sulphide minerals.[26–30]

Contrary to the data in various publications, it has been found that sphalerite does absorb ethyl xantogenate. These results have been obtained both on natural minerals and on artificially prepared zinc sulphide. It follows then that the impurities making part of sphalerite do not influence the adsorption of ethyl xantogenate.

The use of ethyl, butyl and isoamyl xantogenate (S^{35}) under ordinary flotation conditions has helped to establish that there exists no direct relation between the lowered density of xantogenate layer on the mineral and the capacity of the latter for flotation.

An oxygenless medium is characterized by an absence of the selective capacity and greater activity of fixing reagents on the mineral in proportion to the increase in the content of oxygen in water.

Lime influences the lowering of absorption of the collector by sulphides to a greater extent than caustic soda. It has been established that large quantities of pyrite absorb calcium ions, while sodium ions are absorbed very slightly.

CONTROL OF METALLURGICAL PRODUCTION

Artificial radioactive isotopes have been widely applied in constructing various instruments designed to control the processes and finished products of the metal industry. New opportunities have been created for greater reliability and acceleration of control.

Several newly elaborated methods used at present on an industrial scale will serve only as illustration. When refining pig iron with a high phosphorus content, the method of prompt analysis of phosphorus pentoxide in slag has been used. It has been found that sufficient accuracy is achieved and time of analysis considerably reduced when a negligible quantity of radioactive isotopes of phosphorus P^{32} is spent (0.04–0.05 mc per ton of metal). The application of this method allows to institute slag control and to sort slag more accurately as a fertilizer.[31]

A method of prompt analysis of calcium oxide in slag in the course of heating has been elaborated, based on the use of the radioactive isotopes of calci-

um. The application of this method greatly simplifies the control of slag basicity.

Calipers for continuous contactless measurement and appliances to control the thickness of the metal strip are being widely used in the metallurgical industry. The instruments are based on continuous translucence of the moving strip with rays of some energy or other, depending on the material of the strip in question. The instruments, constructed by the Lebedev Institute of Physics, possess a wide range of measurement (from several microns to scores of millimeters), the possible errors amounting to about 2 per cent.

The application of these instruments at rolling mills has made it possible to increase the speed of rolling.

At present it is possible to control the rolling of strips 20–30 microns thick. Had the thickness of such strips been controlled by hand, involving a stoppage of the rolling mill, the operation would not have been possible at all.

The staff of the Institute of Physics of the Latvian Academy of Sciences[32] are successfully introducing into industry the instrument they have constructed for sorting metal strips. At the beginning of the technological process the strips are given radioactive tags according to a certain code. Then, at every successive stage of the technological process (rolling, etching, etc.), where the treatment of various grades differs, instruments are placed which record the radioactive tags and "decipher" the code, determine the grade of the material and indicate the way for some or other cut of strip to be directed.

Since 1951 many metallurgical plants in the USSR have been using radioactive isotopes to control the wear of the hearths and bottoms of the blast furnaces. The gist of the method is as follows: small gamma-radiating sources (Co^{60}) are placed at various points of the refractory lining, as shown on Fig. 5. The wear of any layer of the lining is judged either by the appearance of radioactivity in the pig iron or by measuring outside the furnace the intensity of radiation of the radioactive preparations placed in the lining.[33]

Radioactive indicators have also been employed to control the service of the open hearth bottoms.

The method of radioactive dilution can now be used to determine the weight of liquid steel in the ladle, which makes for reduced waste of metal during pouring.

Artificial radioactive isotopes have come to stay in scientific research work devoted to the production of pig iron and steel.

At the Third Conference on Physical Chemistry Steelmaking, held at the end of last January, 64 papers were read on the recent experimental investigations, ten of which were conducted with the use of radioactive isotopes.

The application of radioactive isotopes at metallurgical plants has contributed to the setting up there of special laboratories of radioactive research methods; it has helped to draw into this work the scientific staff of the Central Scientific Research Institute of Ferrous Metallurgy and summon the services of workers of other research institutions of the country for investigations at plants.

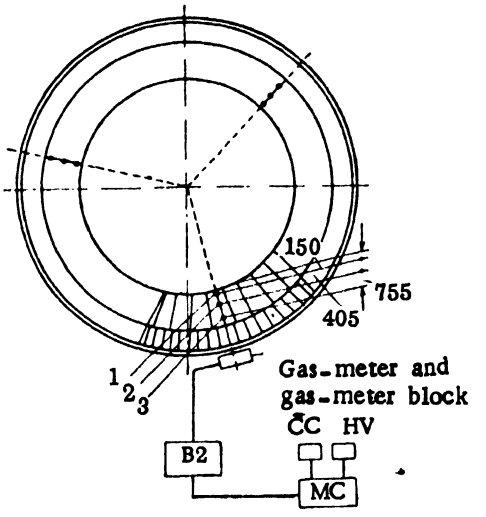

Figure 5. Chart of studies of burn-out of refractory lining of blast furnaces. The lining of the blast furnace is made of carbonaceous blocks (near center) and of refractory bricks: (1, 2, 3) capsules with radioactive Co^{60} isotope inserted in carbonaceous blocks, the radiation is recorded by a gas meter; (B2) transition block; (MC) meter control panel; (CC) calculation chart; (HV) high voltage rectifier

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The Use of Radioactive Isotopes in the Study of Wear of Machine Parts

By B. D. Grozin, USSR

The application of radioactive isotopes considerably broadens the possibilities of experimental investigation of the processes of wear. This method has the following advantages:

1. High sensitivity in establishing the state of wear, reaching 10^{-8} grams and more.

2. Possibility of simultaneous establishment of wear in several details during the process of operation without disassembling the machines and disturbing the conditions of work.

3. Convenience of automatic recording of wear processes.

4. Application of radiography in studying the phenomena of metal-transfer, diffusion and other accompanying processes.

Thanks to the high sensitivity of the method of investigation by applying isotopes, the time necessary for performing the experiment is greatly decreased and the results are much more accurate.

The availability of a great number of radioactive isotopes permits the choice of the most convenient isotope for solving the problem put to us.

In choosing isotopes it is necessary to consider the following conditions.

1. The introduced isotope must not differ very much from the chemical characteristics of one of elements belonging to the metal undergoing examination; it should equally distribute itself along the surface of the detail and to a significant depth and not form undesirable chemical connections with the material of the detail and surrounding environment.

2. The type and energy radiated are of vital importance. When placing the experiment, it is necessary to consider the factors of energy absorption and dispersion.

The choice of the isotope is connected with the method of activating the details.

At the present time the following methods of activating the details are very popular: (1) electrolytically marking rubbing surfaces with radioactive isotopes; (2) introducting isotopes during fusion and casting; (3) method of radioactive inserts—witnesses of wear; and (4) activating irradiation.

The methods of diffusion and electro-spark treatment have been lately applied.

Each of the above-mentioned methods has its own specific field of action. Choice of the method of introducing isotopes depends upon the character of the problem put before the investigator, depends upon the necessary activity of irradiation in order to acquire a reliable estimation of the wear, size, configuration and working conditions of the detail.

Applying the method of galvanic coating is more rational if it is a technical operation in manufacturing process of the detail. In separate cases this method is applied for putting an active layer on the surface of inserts (witnesses of wear). The method of galvanic coating guarantees a high activity in the thin layer. Electrolysis is performed with usual solutions of metal salts in which isotope salt is added or radioactive anodes are used. If the isotope is in such a chemical combination that it is impossible to introduce it into the electrolyte, it must be chemically transferred into a suitable combination.

The quantity of isotopes introduced into the electrolyte depends upon the necessary thickness of coating, depends upon the volume of the electrolyte and also upon the current efficiency of this particular electrolyte and the conditions of electrolysis.

The introduction of isotopes during fusion and casting is applied to small sized details that do not demand complicated mechanical treatment.

The technology of producing alloys and the casting of details for investigation should not differ from the regular production and should answer the usual technical conditions.

Method of inserts is expediently applied in those cases when the investigated detail is large and demands complicated mechanical treatment, and when it is necessary to receive information of the particular place of wear when wear is unevenly distributed along the surface.

As a rule, active inserts should be manufactured from such material that will not cause perverted influence on the results of the examination of the details, for example, stretching the attended detail.

The essence of the insert method is that small openings are drilled in the rubbing-surfaces of the detail (ϕ, 0.6–1 mm; depth, 0.8–1 mm) or small channels are chipped out and filled in with radioactive metal. In this case the wear of the activized detail is judged by the wear of the radioactive inserts.

Irradiation is performed on the fully treated detail in special laboratories. The depth of irradiation of

Original language: Russian.

the detail depends upon the type of radiation and its penetrative ability as to the given substance.

The introduction of isotopes by means of diffusion consists of putting on the friction surface one or several layers of various metals that diffuse when heating the detail. Each layer of metal may be activized differently. This method of introducing isotopes may be applied to details when the technological process includes diffusion treatment.

Electro-spark treatment of details may be applied to introduce necessary isotopes into the electrode; this method may also be applied for placing isotopes on the friction surface of inserts.

After activation of the details some way or other it is necessary to carefully check the even spreading of radioactive isotopes, which is done with the aid of the radiographical method or the method of analyzing samples of each layer and recording their activity.

Activity recording is done in all cases by the Heygar meter, containing a counting mechanism with automatic recording.

According to the radioactivity of the products of wear, a quantitative definition of the speed of wear in the investigated detail is made the following ways:

1. According to the accumulation of products of wear in the oil and measuring the oil activity by taking samples.

2. According to the accumulation of products of wear in the oil and the continuous measurement of its radioactivity.

3. According to the accumulation of radioactive products of wear on special filters through which oil is let at a regular speed.

In order to improve the effectiveness of counting instead of using one meter, a whole block of meters are used inside of which is placed an irradiating medium.

Recording the process of wear in coordinates, "testing-time—amount of impulses per minute," sufficiently characterizes the dynamics of this process.

In separate cases, when it is necessary to ascertain the speed of wear in weight units, recounting the amount of impulses is done according to previously prepared standards.

The radioactivity of products of wear is measured in the same geometric conditions, relative to the counter, as that of the standard.

One of the methods of preparing such standards is dissolving a certain amount of radioactive metal of the investigated detail in a suitable reagent and dilute the received solution up to specific activity close to the average specific activity of oil in the lubricating system of the working mechanism.

Daily measurement of radioactivity of standards allows us to construct a curve of activity decrease in coordinates "the time of the first measurement—specific activity" (expressed through the amount of impulses per minute).

During simultaneous definition of wear of two or three details, isotopes of various penetrating ability are applied for the activation of those details (first case) or isotopes of various energy radiation (second case).

In the first case isotopes are used having various types of γ and β radiation. In the second case isotopes of identical types of rays but different energy radiation are applied.

The simplest and most widely applied method should be considered the first. That method is based on the complete absorption of β rays by a filter (screen) of specific thickness.

In the second case, when both details are activized by isotopes giving γ irradiation, the method of absorption may be used.

The method suggested by I. M. Frank in 1945 is more exact than the absorption method and permits us to apply isotopes having an insignificant energy to radiation.

The essence of the Frank method is as follows.

The effectiveness of registration of the γ radiation by means of a meter having lead walls depends upon the energy and the thickness of the meter walls.

The effectiveness of meters having aluminum walls depends very little on the energy or on the thickness of the walls. This variation of effectiveness of meters with aluminum and lead walls permits the analysis of the contents of radiation.

Work done on the investigation of friction and wear by the aid of radioactive isotopes may be divided into the following groups:

1. Selection of material for details working under friction.

2. Investigation of the wear of details in internal-combustion engines.

3. The influence of the qualities of the lubricating oils on the wear of metals.

4. Various questions on theory.

SELECTION OF MATERIALS FOR DETAILS WORKING UNDER FRICTION

In many works done by applying radioactive isotopes it was shown that an electrolytic layer of iron followed by oxidation has many advantages in regards to other forms of coating (copperizing, tinning, zincification, etc.) (B. Grozin).

The oxidized iron coating of 7–10 microns thickness has enough plasticity capable of retaining the oil-film and thus creates a condition of thin polishment of the surface of the investigated detail.

Especially good influence is effected by ironizing and oxidizing on the improvement of running-in porous-chromium surface. A coat of iron filling in the whole system of pores strengthens and prevents the brittle destruction of the chromium thickness.

The work accomplished is dedicated to the study of the influence of oxidized iron layer on the process of running-in porous-chromium.

Investigating the wear was performed on Amsler friction type machines. Selection of material and system of investigation was chosen so that in time of

friction the best possible conditions should be available (P = 31 kg/cm², n = 100 rpm, bearing bush material-modified cast iron, R_c = 92.95, roller material-annealed steel, 45).

Cast iron bearing was coated with a layer of radioactive iron (Fe^{59}) by galvanic method and then chemically oxidized.

For the sake of comparison investigations were made on samples without coating. Results of these investigations are shown in Fig. 1, where it can be seen that the samples on friction in working without coating for the same length of time gave approximately ten times more wear than samples with coating.

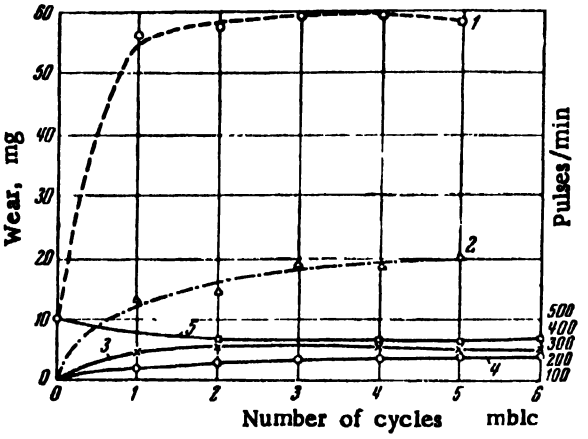

Figure 1. Dependence of wear on number of cycles: (1) bearing bush without covering; (2) roller without covering; (3) bearing bush-iron and oxidized; (4) roller without covering together with covered iron and oxidized bushing; and (5) iron and oxidized bearing bush activity

Microphotography (Figs. 2, 3) illustrates the condition of roller surfaces in work coupled with bearing brass having coating and without coating. In the first case the surface is smooth, without any noticeable traces of deformation. In the second case the surface is very rough and has a severely deformed top layer in which can be noticed accumulations of perlyte and traces of seizure.

Measurement of the activity of samples (bearing bush and rollers) was done after every 100 revolutions of the roller.

Investigations were also made of bimetal sliding bearing which are steel bushes, the inside surface of which are coated with a layer of leaden bronze or silver, 0.5–0.7 mm thick. The inside working surface of the silver bearing is covered with thin layers of soft anti-friction metals.

A study was made of the wear of lead-indium coating and silver layer of bearing and also of the influence of lead-indium coating on the process of running-in.

Investigations were made on an installation, differing from the usual ones in such a way; during investigations the bearing revolves and the shaft remains motionless. This installation permits us to change the sliding speed, the load on the bush, the lubrication and so on.

According to accepted technology anti-friction materials were put on the surface by a galvanic method and so they were activated at the same time.

A radioactive layer of silver (10 μ thick) was additionally put on the usual surface coating of silver.

In order to receive an equal spread of In^{111} after individually coating lead and indium the alloy was annealed for 2 hours in 158° temperature.

Experiments have shown that silver bushes having lead-indium coating quickly run in as seen by the decrease in activity (Fig. 4). The running-in of silver bushes without coating (Fig. 5) is slow. One can observe in Fig. 5 that changing the load (curve 2) more intensively influences the wear than changing the slide speed (curve 1).

Investigating the Wear of Hydroaggregate Details in Kerosene

In order to determine the activity of the liquid current of small tenacity under high pressure and carrying wear products of activated metal details, B. L. Slinko elaborated a method of measuring activity by aid of special filters (see Fig. 6).

The special filter consists of: (1) cylindrical steel body, (2) filter cover in which is installed the body of the filtering element made from thin-walled aluminium pipes, (3) filtering element in form of a tube, made out of felt and placed in the body, (4) thin-walled aluminum pipe (meter body) protecting the Heygar meter from contact with the liquid

The liquid current containing wear products enters the filter through the bottom and leaves through the side branch pipe of the cover.

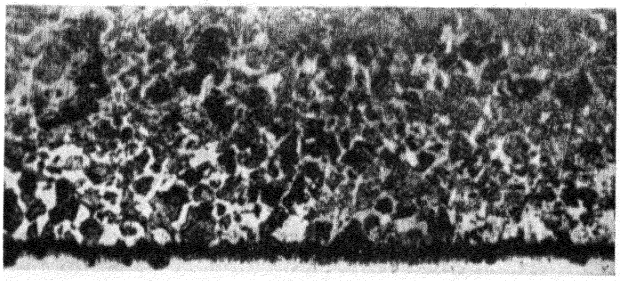

Figure 2. Structure of outer roller layers working with iron and oxidized bearing bush × 300

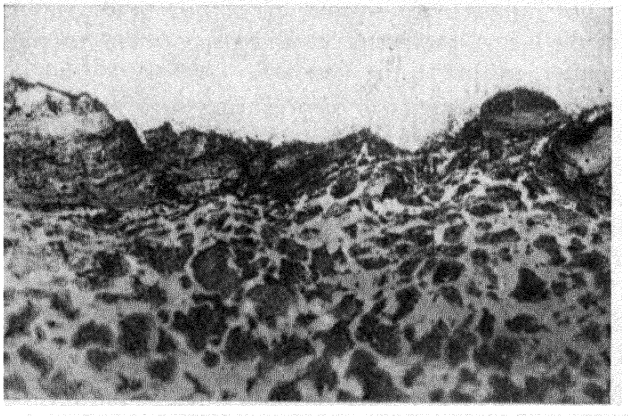

Figure 3. Structure of outer roller layers working with cast-iron bush without covering × 300

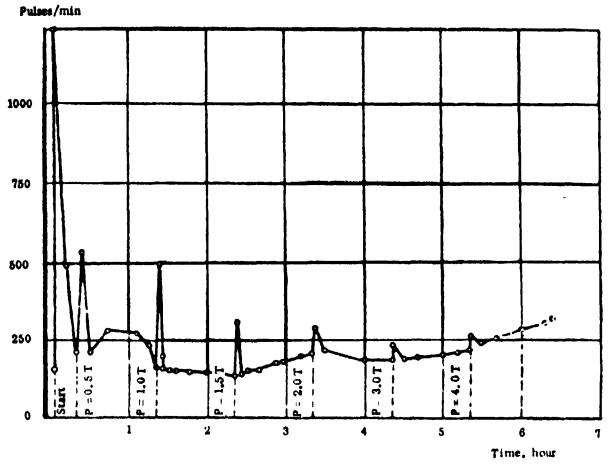

Figure 4. Wear of bush having lead-indium covering

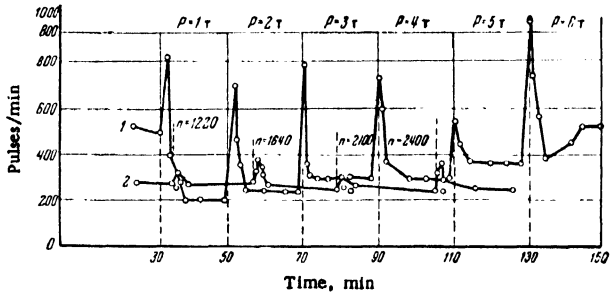

Figure 5. Wear of silver bush without coating

When constructing the filters consideration was given to their working capacity, size, obstructiveness, filtering ability of material, that is, ability of material to effectively detain the wear products not washed out, minimum ability of filter material to absorb β-radiation.

On the basis of additional investigations it was found that felt is an effective filtering element for wear particles in kerosene.

General installation set-up is given in Fig. 7.

Special filters may be included in the general set-up in two ways, as shown in Fig. 8.

Including the filter directly in the liquid current coming out of the machine is done in those cases when the quantity of out-flowing liquid in the system does not exceed the filter capacity. Otherwise the filter is installed parallel to the main current. It is best to install several filters in the current, connected in parallel to each other.

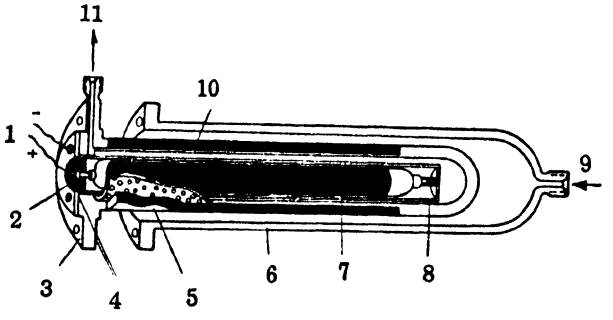

Figure 6. Filter meter: (1) wiring to registering apparatus; (2) isolator; (3) top of filter; (4) packing bush; (5) filter element; (6) filter body; (7) Haygar meter; (8) meter body; (9) oil outlet; (10) frame with holes; and (11) oil outlet

INVESTIGATING THE WEAR OF INTERNAL-COMBUSTION ENGINE DETAILS

In a study of the running-in process of aviation engines, rational conditions of piston ring running-in were determined in a one-cylinder motor.

Activation of the rings was done by way of electrolytical sediment applications of radioactive Zn^{65} in narrow channels.

Measuring the activity was done in the lubricant circulating system (Fig. 9).

The aim of the investigation was to determine the influence of rotation, load (revolving moment), temperature of oil and cylinder head, coefficient of surplus air and type of oil, and fine mechanical treatment of chromium-plated cylinder mirror on piston-ring wear.

The graph (Fig. 10) illustrates the dynamics of wear in the running-in process of motor piston rings with various revolving speeds. It was found that running-in under a heavier load is more rational.

The results permitted establishing the right conditions for the motor and for running-in, cutting the running-in time 28%, lessening oil usage and greatly increasing the wear-resistance in following working hours of engine.

Investigations on Quality of Air-Cleaning by the Tractor Air-Cleaners (Work Done by D. L. Visotski, I. G. Beloglasov)

One of the main factors affecting long life of automobiles and tractor engines is dust penetrating together with air into the engine cylinder and causing abrasive wear of the cylinder surface, pistons and rings.

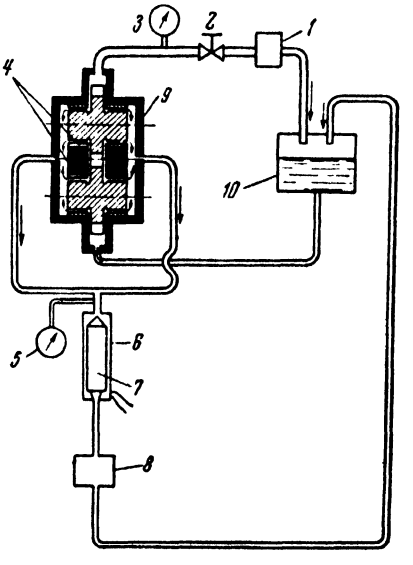

Figure 7. Apparatus scheme for investigating the wear of hydro-aggregate bearing: (1) discharge meter; (2) tap; (3) pressure gauge for 150 atmospheres; (4) bearing; (5) pressure gauge for 10 atmospheres; (6) special filter; (7) Haygar meter; (8) oil discharge meter; (9) hydroaggregate; and (10) discharge tank

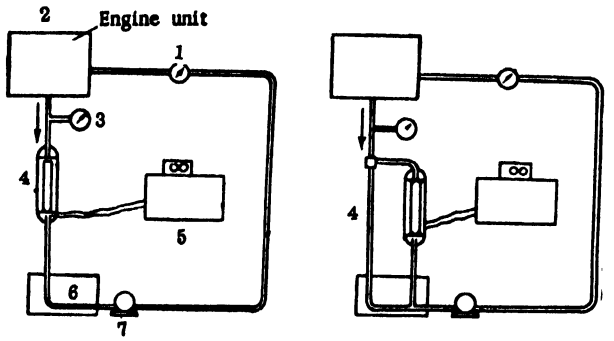

Figure 8. Scheme of measuring detail wear by method of radioactive isotopes together with filters: (1) discharge meter for liquids and lubricants; (2) aggregate engine; (3) pressure gauge; (4) special filter and Haygar meter; (5) measure apparatus; (6) oil tank; and (7) oil pump

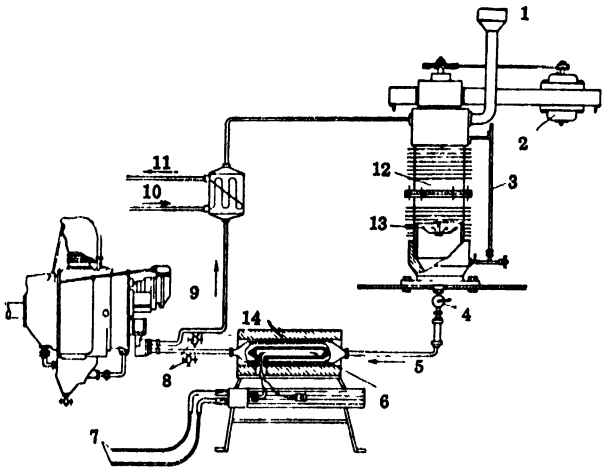

Figure 9. Scheme of a testing installation oil-main: (1) pouring in oil; (2) motor for putting mixer in motion; (3) measuring tube; (4) lock tap; (5) in the motor; (6) counting tube; (7) wiring to counting apparatus; (8) discharge tap; (9) from motor; (10) inlet for cooling water; (11) water outlet; (12) oil tank; (13) mixer; and (14) lead shielding

An effective air-cleaner seriously influences the long life of an engine.

Modern methods applied for testing air-cleaners and in investigating processes taking place in them are not perfect; they demand much time, do not guarantee exact results and cannot be applied in air-cleaners working in alternating conditions.

A final estimation as to the suitability of this air-cleaning construction is given only after testing the engine in road conditions for some length of time (10,000 km run).

Application of the radioactive isotope method in solving these problems cuts testing time down to 15 minutes and increases result accuracy about 20 times.

The existing system of dosers has shown itself useless in carrying out speed tests of air-cleaners. It does not provide reliable air filtration in alternating conditions and does not give sufficient accuracy and speed in measurement. In connection with this the necessity of elaborating a new system of dosers became obvious. A general view of the dosers can be seen in Fig. 11.

The air-channel of the doser is a glass socket whose construction was figured on creating a turbulent air-current in the reception chamber where the working end of the dustload tube enters, as well as on the doser discharge connected with the air-receptor of the tested air-cleaner.

In the dust-load tube there is a special fabricated radioactive dust pencil. The pencil is put into motion (progressive) by a gear and screw drive. Opposite the pencil and moving towards it is a high-speed electric motor spindle at the end of which is a crystal-corundum abrasive of cylinder form. Thanks to the high-speed revolving abrasive (18,000 rpm) the

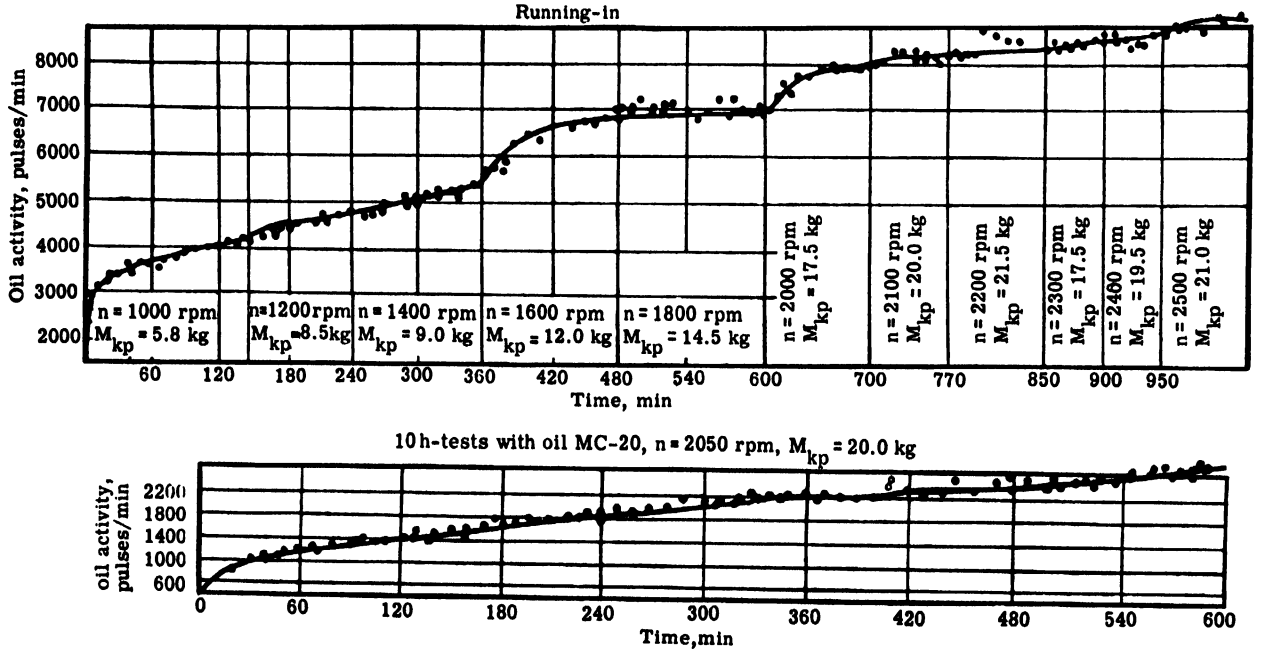

Figure 10. Determining the conditions of piston ring running-in into cylinder mirror in internal-combustion engines

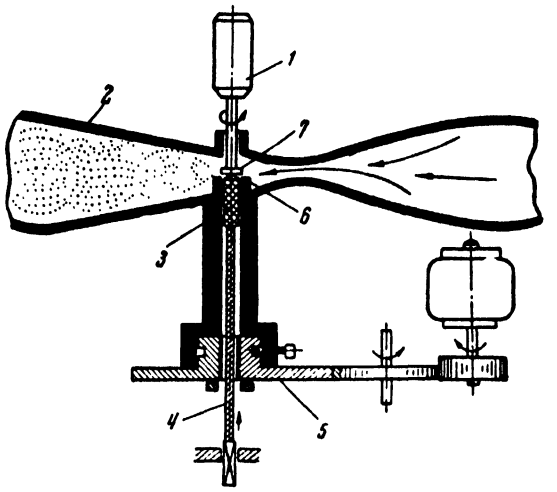

Figure 11. Dust doser for testing automobile air-cleaners (scheme): (1) electric motor; (2) glass socket; (3) dust pencil; (4) stock; (5) drive; (6) tube; and (7) abrasive

pencil is rubbed and the dust is caught up by the air-flow and enters the air-cleaner.

Changing the speed of the moving pencil changes the concentration of dust.

The radiometric installation for testing air-cleaners is designed for using air equal to $\frac{1}{10}$ of the largest amount of air to be used passing through the automobile air-cleaner and is also designed for possible investigation of the standard air-cleaner element type "Cyclon."

Air is sucked into the apparatus air-line and enters the doser where it is mixed with radioactive dust. The air-flow saturated with dust then goes through the air channel of the dust collector. In the dust-chamber, part of the air is caught by a funnel turned towards the air-current; the air then enters the dust-collector reservoir of the radioactive metric registrator and is sucked back into the general current. A counting tube is placed under the bottom of the dust-collector which registers the quantity of gathered dust.

The air-current passing through the air-channel of the dust collector finds itself in the air-cleaner's filtering element and then enters the dust-catcher with whatever dust remains. After the current goes through the dust-catching chamber it enters the filters where radioactive dust is collected.

Measurement of irradiation in the dust-collector is controlled by regular dust saturation of air-current entering the tested cleaner. Measurement of dust irradiation in dust-collector and in absolute filters illustrates the quality of work done by the air-cleaners.

In Fig. 12 is given the graph of activity in the dust-collector; the linear graph illustrates the regularity of dust saturation in the air-current.

According to the described method, comparison of air-cleaning tests were made with the air-cleaning element "multicyclon" using a smooth and pulsating air supply of 20 m^3/hour. The results of the tests are shown in Fig. 13. It was found that in the pulsating condition, the air-cleaner worked with much less effect. The curve steepness in this case enlarged considerably showing the increase in the amount of dust coming out of the pulsating cleaner.

Comparison tests were carried out according to the above method on filters of various construction and the most rational ones picked out.

Application of radioactive dust for the investigation of filter elements (packing, etc.) greatly helps in the study of dust distribution in the filter element oil.

Tests have shown that dust getting into the engine sharply increases the wear of cylinder-piston group details. And so, 20–25 grams of dust introduced during 15–18 hours fully disables the ring and bush sleeve. The biggest wear is caused by 20–80 μ sized particles of dust.

INVESTIGATING ANTI-WEAR QUALITIES IN LUBRICATING OILS

U. S. Zaclavski, G. I. Shor and others elaborated the method of determining anti-wear qualities in various oils and the influence of various additives on these qualities.

Investigations have shown the possible application of this method for high-speed determination of anti-wear qualities in oil. Nineteen different lubricants were tested.

When investigating the higher compression rings on a one cylinder motor of 3 hp, they were activated by irradiation of Fe^{59}. Wear products activity was measured by taking samples.

An example of applying this system is the data given in Table 1, in which are the comparisons of wear-speeds of the higher piston ring in engine during application of various oils.

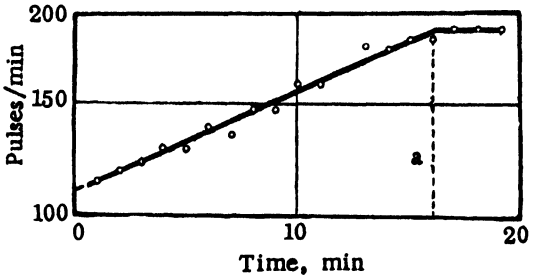

Figure 12. Increasing activity in dust-collector: dust supply stopped

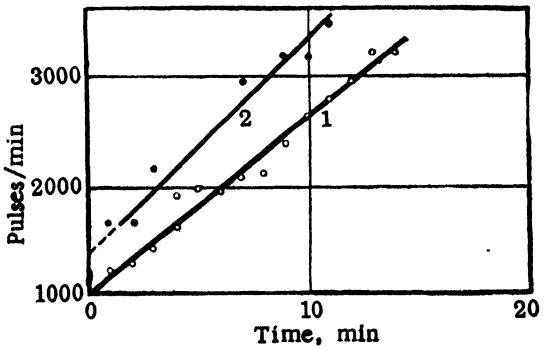

Figure 13. Accumulation of dust not caught by multicyclon element during: (1) smooth and (2) pulsating character of air-current. Air consumption 20 m^3/hr, initial dust content of the air 0.11 gm/m^3

Table 1. Comparative Anti-wear Qualities in Various Motor Oils in Water-Cooled Low Temperatures

No.	*Name of oil*	*Relative speed of wear in rings*
1.	AC-5	1.0
2.	AC-5 plus 3% additives "NACS"	0.5
3.	Motor SU	0.61
4.	SU plus 2% additives A	0.30

Ring wear-speed of oil AC-5 was conditionally considered as unity.

Analogous tests were carried out on petrols differing from each other according to the amount of sulphur content (see Table 2).

Table 2. The Influence of Sulphur Contained in Fuel on the Wear

Sulphur content	*Speed of wear, mg/hr*
0.084	0.92
0.153	1.0
0.598	1.22

SOME THEORETICAL QUESTIONS

Among the questions that are of importance when studying friction and wear are: determining the actual contact space in rubbing surfaces, investigating the influence of lubricant-film thickness on metal wear, investigating physico-chemical interrelations of oil and surface friction.

In the experimental approach to these questions the radioactive isotope method was applied (galvanic precipitation of oxidized metal on one of the friction surfaces).

In laboratory conditions, low-speed sliding (12 cm/sec under pressure of 1000–5000 gram/cm^2) and temperature of 18–20° was used.

A study was made to determine the effect the thickness of a lubricant film has on the wear of polished samples.

It was found that with an oil-film thickness of less than 2 mc friction takes place in conditions of boundary lubrication. The wear smoothly decreases with the increase of more than 2 microns in the thickness of film lubrication.

Other experiments have shown that when starting and stopping the engine friction wear depends upon the time it takes to stop, and the wear is the lowest if the stop takes place in a second; if it takes three minutes, the wear is the highest. Taking still more time for stopping does not affect the wear more. That is explained, it seems, by the fact that further oil spreading stops and the lubricant film reaches its thinnest condition.

Work that has been started in determining the actual contact space has shown the perspectiveness in applying, in these cases, the radioactive isotope method.

In order to study the mechanical action of anti-corrosion substances to oil, investigations of kinetic formations of preventive films on various metals were carried out.

A study was also made of substance-diffusion in the depth of the metal surface. Substances in oil were activated by S^{35} and P^{32}. It was found that temperature affected to quite an extent the formation of preventive films on various metals.

Sulphur diffusion in the surface on lead plates reached 30–40 microns. On lead-bronze the depth of diffusion was still more—up to 50 microns.

A great deal of work was done on investigating the wear of cutting instruments according to the conditions of cutting which allowed the solving of several theoretical cutting problems.

CONCLUSION

In the USSR a great deal of experience has been accumulated in applying the radioactive isotope method when solving various problems of friction, wear and lubrication in engines. That experience shows that these methods included into engineering knowledge are extremely fruitful and in some cases necessary, thanks to the exceptionally high sensitivity and the possibility of establishing continuous registration of the wear process.

Brief Review of Applications of Isotopes in Process and Quality Control

By Masao Kato,* Japan

For the past several years the availability of radioisotopes in industry has been generally recognized in this country, and various researches and applications are now being carried out.

Beta gauges are used for manufacturing thin steel sheets, aluminium foil and gum sheets, and for measuring the plating layer. Gamma-ray liquid level meters are used in two factories producing artificial fertilizer. The measurement of the thickness and density by gamma rays is yet to be put to practical use. Gamma-ray radiography is now very widely used in this country. Typical studies in these fields are, for instance:

ON THE SEPARATE TRAVERSING OF A RADIATION SOURCE AND AN IONIZATION CHAMBER OF BETA GAUGE FOR WIDTH DIRECTION SCANNING

This paper by H. Miwa presents a method of giving a free geometrical arrangement of a radiation source and an ionization chamber. The object of this work is to enable width direction scanning of some wider sheets by traversing the radiation source and the detector respectively on the two separated I beams which are placed exactly parallel instead of traversing such a long U frame as in conventional beta gauges.

The error introduced by the deviation of the center axis of the radiation source from that of the ionization chamber can be minimized by making the sectional area of the radiation flux intercepted by a surface of the detector window very small in comparison with the whole window area.

But this arrangement introduces an error due to the pass level deviation. Such an error can be eliminated by employing a beehive-type scattered radiation eliminator.

By combination of these two methods excellent experimental results were obtained.

Thus, with a center axis deviation of $\pm$ 6 mm and a pass level deviation of $\pm$ 10 mm, the error of instrument response was kept less than 0.5%.

GAMMA-RAY LIQUID LEVEL METER

For measuring liquid level of high-pressure tanks, etc., it is known that there are a few level meters taking advantage of gamma rays emitted from radioisotopes. This paper by T. Watanabe is concerned with a level meter having a characteristic of linear relationship between the liquid level and the indication of radiation detector. By arranging many gamma-ray sources inside or outside the tank and selecting a proper distance from the detector and a proper intensity of radiation respectively, we got a gamma-ray liquid level meter having the characteristic described previously, which covered the whole range of liquid level, from empty to full.

Another experiment was made on dynamic character of the level meter in case of combined use of G-M counter and counting rate meter. According to the results, in order to make small the fluctuation of the indication which would be caused by statistical deviation of radiation of the source, and further to lessen the indication lag of the lever meter, it is necessary to increase the counting rate by intensifying each radiation source.[1, 2, 3]

More than a few applications are made of radioactive tracing for process control: for example, the measurement of diffusion of molten glass in furnace, the determination of transit times and distribution of materials through the steaming pipe where the starch is saccharified, the measurement of desulphurization of vinyl chloride by washing, etc.

Further, there are many examples concerning the mechanism of reactions.

STUDY ON THE BEHAVIOUR OF SILVER IN COPPER ANODE USING RADIOISOTOPE Ag^{110}

The object of this experiment by M. Kato, K. Taketani, Y. Sasaki and T. Yamamoto was to quantitatively trace, with radioisotope Ag^{110}, the behaviour of a slight amount of silver included in copper anode in an electrolytic refining of copper. The experiment was performed in two terms, because it was necessary, on the one hand, to confirm the reproducibility of this experiment and, on the other hand, to reconfirm an equilibrium point in potential between copper ion and silver ion which was observed in the experiment done in the first term.

In this study, first an adequate amount of tagged silver was added beforehand to a copper anode of extremely high purity, which was subjected to electrolysis using copper sulphate of high quality to quantitatively trace tagged silver dispersing into the electrolytic solution, slime and cathode by measuring

* Dr. Eng., Assist. Prof., Metallurgy Division, Inst. of Industrial Science, Univ. of Tokyo, Chiba.

radioactivity. Then a similar experiment was performed, in this case the copper cathode being used as an anode. By repeating a series of such experiments, silver in the electrolytic solution, cathode and slime all gradually decreased. When equilibrium in potential was reached, at a silver concentration in electrolyte of the order of 10^{-6} gm Ag/l, no more dispersion of silver into the slime took place. In addition, by such a procedure the silver content in refined copper may be lower than 0.01 gm Ag/ton Cu.

Furthermore, by using Ag^{110} the solubility of AgCl in copper electrolyte was determined. The solubility was measured, the content of copper sulphate being kept at 40gm Cu/l, the composition of a standard electrolyte, while composition of free sulphuric acid and of free hydrochloric acid was changed. The solubility of AgCl in the electrolyte of copper is $1\text{–}7 \times 10^{-3}$ gmAg/l at a range of 50–300 gm/l in concentration of free sulphuric acid and of 30–70°C in temperature. It is about 20% in average lower than in pure water at the same temperature. Addition of about as much as 500 gm/m^3 of hydrochloric acid to the electrolytic solution of copper tends to decrease the solubility, while, on the contrary, addition of more than 1000 gm/m^3 tends to increase it. The minimum is 2×10^{-4} gmAg/l. Decrease in solubility is due to influence of common ions and its increase is due to the formation of some hydrochloroagentic acids.

STUDY ON THE KINETICS OF DESULPHURIZATION OF MOLTEN IRON BY SLAG UNDER REDUCING CONDITION

The process of desulphurization of molten iron by slag may be analyzed through the following three steps: Diffusion of sulphur in molten iron, transfer across a metal-slag interface and diffusion in molten slag.

Diffusion coefficients and the rate of transfer of the sulphur were determined by T. Saito and Y. Kawai by the use of radioactive sulphur as the tracer. In the experiments, iron sulphide prepared from barium sulphide containing S^{35} was used.

The results obtained are as follows:

(1) Diffusion coefficient of sulphur in molten iron saturated with carbon at 1500°C is about twenty times greater than that in molten $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag. Dependence of diffusion coefficients on temperature was expressed as follows:

D (in molten iron) $2.4 \times 10^{-4} \exp(-7000/RT)$

D (in molten slag) $1.4 \exp(-49{,}000/RT)$

(2) The rate of transfer of sulphur from metal to slag increases rapidly with increasing basicity of slag and with rising of temperature, while that from slag to metal does not change appreciably with change in slag composition and temperature.

From this study it was concluded that the net rate of desulphurization is mainly controlled by the diffusion of sulphur in molten slag.

ON THE ADSORPTION OF ADDITION AGENTS ON AgBr IN THE PHOTOGRAPHIC EMULSION

To elucidate the mechanism of sensitizers or fog-inhibitors on AgBr, the adsorption phenomenon of thiourea, N,N-diethyl-thiourea, 2-amino-4-methyl-thiazole and 2-diethylamino-4-methyl-thiazole on the surface of AgBr crystal were investigated by S. Suzuki, T. Toriu, K. Kimura and N. Saito. Quantitative measurements of these adsorbed compounds were made by the traced method using S^{35}.

The solution of addition agents were prepared in various concentrations. Each time a certain fixed amount of AgBr was added to a certain constant volume of the solution, and then the adsorbed amount of addition agents was measured. From these results the curves of the adsorbed amounts of the addition agents vs. residual concentrations were obtained.

This AgBr, on which the addition agent was adsorbed, was added to a certain constant volume of distilled water and the desorption of addition agent adsorbed on the surface of AgBr was examined.

An attempt was made to find whether or not the addition agents once adsorbed on AgBr could be replaced by the sensitizing dye, when the AgBr was put into the dye solution. Conclusion: Both thioureas react chemically with AgBr, producing the double compound, and 2-amino-4-methyl-thiazole shows the typical monomolecular adsorption on AgBr surface, while 2-diethylamino-4-methyl-thiazole is not adsorbed so strongly.

ON THE ADSORPTION OF ETHYL-AEROFLOAT ON SULPHIDE MINERALS

Aerofloats are being used often in the belief that they collect iron sulphides less strongly than they do copper or lead, but the evidence on this problem is not conclusive. By tagging ethyl-aerofloat ($(C_2H_5O)_2$ PSSK) with radioisotope S^{35}, the interaction of collector with chalcopyrite, galena or pyrite was investigated by T. Ohyama in a pH range of 2–11.

Regarding the variation of adsorbed amounts of collector against pH, distinct difference has not been recognized unexpectedly between chalcopyrite and pyrite, the adsorption having similarly decreased over pH 6. In flotation operations, the recovery has sharply decreased over pH 8 in the case of galena, while chalcopyrite was very floatable in wide pH range. From the above experimental results, it may be considered that the depressing action of OH^- ion alone, besides the adsorbed amounts of collector, affects remarkably the flotation of sulphide minerals.

Probably, the selectivity of aerofloats depends on the fact that the so-called critical pH in which the adsorption begins to be retarded is comparatively low in the alkaline range.[4]

STUDY ON ELECTROPOLISHED ALUMINIUM SURFACE IN PHOSPHORIC ACID SOLUTION

The investigation by T. Nakayama on the mechanism of electropolishing of aluminium in 80%

phosphoric acid solution tagged with radioisotope P^{32} (specific activity 0.20 mc/gm) was carried out with the following results:

In every case, within a certain range of low current density showing such surface appearance as etched the number of counts was zero or nearly so, and when a bright surface began to appear it suddenly increased up to maximum value followed by gradual decrease, and for the same current density, the lower the temperature the larger the number of counts was measured.

Moreover, the number of counts of specimen electrolytically polished by vibrating anode method being suitable to get smooth surface was larger than that by static anode method.

The activity was proportional to the thickness of the anodic film formed at the surfaces, which was determined by means of dissolving off in phosphoric-chromic acid solution, and also with the degree of the colouring of anodic films by dyeing.

Thus, it was certified that on a well electropolished aluminium surface the anodic film was formed, the phosphorous content of which was from 0.2 to 0.6% by weight for any condition.

Researches in application of radiation chemistry have just started, an example of which is given below.

EFFECTS OF GAMMA-RAY IRRADIATION ON FIBERS

Changes of strength of such fibers as Nylon, Vinylon, rayon, cotton, wool, etc., were examined by T. Hisada, R. Mineo, T. Watanabe, A. Aino and T. Kaminishi by the Instron Tensile Testing Instrument when gamma-rays from 160 mc source of Co^{60} irradiated these fibers with an intensity of about 100–1000 r/hr for six months. The radiation dose given to each sample was determined by calculation. Results of the examinations showed remarkable changes of the strength in some of the fibers, that is, in Nylon 110 d its ultimate load and elongation decreased to about 30% of that before irradiation through a dose of about 7 million roentgens, and cotton and rayon fibers showed almost the same results as in Nylon, too. But in Vinylon the change recognized was not so marked and in wool no change even through a dose of about 4 million roentgens. In repeating tensile test, the same results of the decrease of strength of fibers were found. By statistical procedure of a number of data concerning gamma-ray irradiation on fibers, it was found that fibers have a tendency to decrease in their strength and that the effective dose of gamma rays is of the order of a million roentgens.[5]

Studies on the effects of radiation on electric discharge have been advanced, and led to the practical uses today of TR tube and ATR tube.

The leak detection by radioactive gases remains in the stage of laboratory test.

In addition, techniques of radioautography are being used for researches in metals, alloys and non-metallic materials. For example, the segregation of sulphur in the welded portion of steel, the behaviour of a slight amount of iron in aluminium and zinc in brass which is affected by casting, working and heat-treatment, etc. In connection with these applications, the studies on fundamental techniques and nuclear-type emulsion for beta ray radioautography are also being performed.

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Some Industrial Uses of Radioisotopes in Norway

By U. Been and E. Saeland,* Norway

The investigations described in this paper were carried out in Norwegian industrial plants. They are mainly based on the use of radioisotopes as tracers, and were undertaken to solve definite problems in connection with the operation of the plants. The planning and performance were in each case carried out in close cooperation with the firms' own staffs.

The methods used are not very specific for the respective plants. All insignificant constructional details of the plants are therefore omitted in this paper in which we have tried to describe the general principles and results of the isotope investigations. The investigations are as follows:

CONTROL OF FLOW OF MATERIAL IN ROTARY CEMENT KILNS

The A/S Christiania Portland Cementfabrik is operating a large cement plant at Slemmestad near Oslo. In this plant Portland cement is produced by feeding a wet mixture of limestone and clay into the tops of slightly inclined rotary kilns. A blast of air charged with oil, which forms an intense flame, is injected into the lower part of the kilns. As the raw materials are transported along the kilns, cement clinker is formed. In order to control the production process it is of great importance to establish exactly the conditions in the kilns. It has been a difficult problem to determine the flow rate of the charge, and therefore tracing the materials with radioisotopes was suggested.

First of all a suitable tracer for this purpose had to be found. If this could be achieved by activating the kiln feed it would be an advantage as a radioisotope of a foreign substance might have another rate in the kiln than the raw material. Preliminary tests indicated that this procedure was feasible. The sodium content of the raw meal amounts to 0.2% which proved to give a suitable activity when irradiated in the JEEP reactor.

First the total time for the material to pass through the kilns was established. This was done by adding about 130 grams dried and radioactive raw meal to the slurry at the inlet end of the kilns in equal portions over a period of 2 hours. Sampling of cement clinker at regular intervals was started three hours after the initial addition of radioisotopes. Each sample was weighed and measured for radioactivity with a scintillation counter. The results of the measurements were corrected for decay in activity during the experiment, and for variations in weight of the samples. To find the velocity for different sizes of clinker, the samples were screened and the fractions measured separately. When the clinker activity is plotted against time, curves as Fig. 1 appear. The maximum values are taken as the average time for the charge to pass through the kilns. The diagram also shows that the materials are thoroughly mixed on their passage through the kilns. Materials fed into a kiln at the same time have different rates in the kiln. Furthermore the rate of materials show considerable variations from one kiln to another—variations which cannot be attributed to differences in the kiln's speed or diameter.

The next step was to determine the flow rate of the charge in various sections of the kilns. In these experiments radioactive raw meal was added to the slurry in a single portion. Then the tagged materials were followed along the kiln by measuring the gamma-radiation through the kiln shell at points 10 metres apart, cf. Fig. 2. A scintillation counter was used and emphasis was laid on fixing the time when the activity peaks passed the measuring points. The results, given for one kiln in Fig. 3, showed that the material rate in various sections of the same kiln is quite different. The rate increases gradually as the materials move from the chain section and reaches a maximum in the calcination zone. Thence the rate decreases and attains a minimum in the burning zone.

All the kilns in the cement plant have been studied by the above method. The results obtained have been carefully analysed and the effect of various factors deduced.[1] The conclusions arrived at in this way are in full agreement with the observations made in kiln burning. These investigations have therefore contributed to a better understanding of the various factors influencing kiln operation.

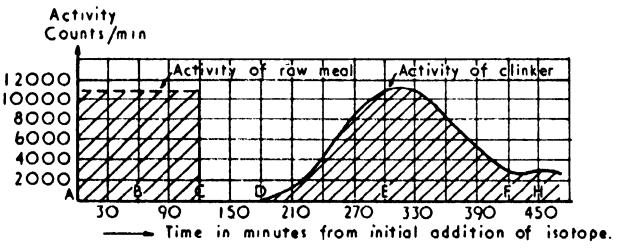

Figure 1

* The Joint Establishment for Nuclear Energy Research, Kjeller near Lyllestrom.

INVESTIGATION ON THE LOSS OF CATALYST MATERIAL IN THE INDUSTRIAL PRODUCTION OF NITRIC ACID

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab is manufacturing nitric acid on a large scale by the catalytic oxidation of synthetic ammonia. In this well known technical process a mixture of ammonia gas and air is passed through a converter containing platinum (or platinum-iridium) gauzes in contact, the platinum acting as a catalyst. During production there is a significant material loss from the catalyst gauzes. This material is believed to disperse on the pipelines, boilers, economizers and absorption towers of the production system, and the products. A greater part of the lost material is recovered when the production units are revised from time to time, but some of the loss could not be accounted for. In order to recover as large amounts as possible of the costly platinum, it was suggested to trace the loss with radioisotopes.

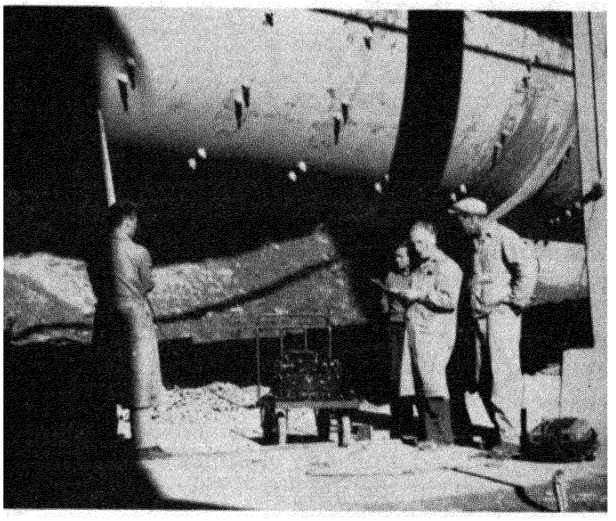

Figure 2

A piece of platinum-iridium gauze was activated in the JEEP reactor up to a total activity of approx. 1000 mc. The obtained Ir^{192} activity proved to be suitable for the investigations with its 74 days half-life. The radioactive piece of platinum-gauze was mounted in one of the plant converters which was then put into ordinary operation.

The loss of radioactive material in the products and waste products was determined by concentrating platinum metals in samples and counting the activity. This was done regularly since the material loss appeared to change with the total time of operation. Thence a curve could be drawn for this course. The amounts of radioactive material being deposited in the several items of the production system were determined by regular measurements with a scintillation counter in a number of places. One of these setups is shown in Fig. 4.

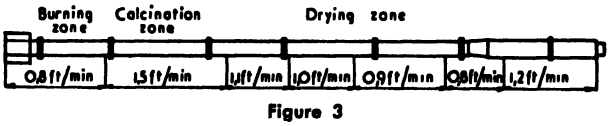

Figure 3

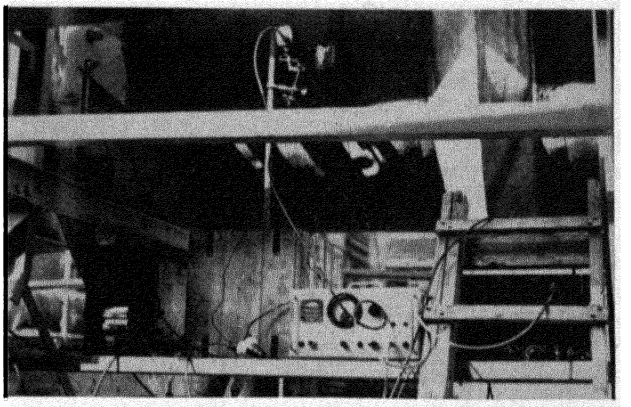

Figure 4

The operational period of the converter was four months. After this time a material balance for the loss of radioactive material from the test gauze was worked out. This was done by integrating the product activity over the total production for the period, and adding the activity in the production units integrated over the total area of the system. The material balance for the platinum obtained in this way was in good agreement with the recovery yields for platinum usually obtained at the plant.

After the operational period the investigation was continued for a time in order to include a study of the fate of "old" deposits of catalyst material; whether these were stationary or moving outwards in the production system. In this way therefore the platinum lost in one operational period was located, and important data obtained about its later movements. This could not have been investigated by any other method.

STUDIES OF THE WEAR OF FRANCIS TURBINES DUE TO CAVITATION EFFECTS DURING OPERATION

The company Aktieselskabet Hafslund is operating several hydroelectric power stations. One of them is the Vamma Power Station on the River Glomma with a capacity of 104,000 kw. The station is equipped with horizontal double runner Francis turbines, and the oldest machines are exposed to severe corrosion due to cavitation effects during operation. This means that the turbines have to be taken out of operation from time to time for repair work which results in a reduction in the station's power output. The corrosion concerns mainly the paddle-wheel of the turbines, and depends primarily on the operational load on the turbines. To reduce the effects of inoperative periods it is therefore of great importance to find the maximum load at which a high power output can be combined with long operational periods. To establish this optimum value the corrosion effect was studied as a function of turbine load by means of a method utilizing radioisotopes.

In one of the turbines the areas on the paddle-wheel which are most heavily exposed to corrosion were painted several times with radioactive paint. The paint used was previously found to show a suitable wear effect during turbine operation. It was

made radioactive by the addition of small amounts of radioactive arsenic (As^{76}, penetrating gamma radiation, 26 hours half-life).

After a drying period the turbine was prepared for operation. When the turbine was not loaded the radioactivity on the paddle-wheel could be measured exactly with a scintillation counter placed on the outside of the machine. A series of test runs was started where the turbine was loaded for short periods at changing loads. Between each run the radioactivity on the paddle-wheel was measured. With regular intervals reference runs at a chosen load were performed to obtain the necessary correction as the amount of paint on the wheel was reduced. In this way the rate of corrosion of the paint was established as a function of the load on the turbine.

The absolute corrosion rate is, of course, not the same for paint and iron, but this is not important as the relative rate of corrosion at different loads is the main interest. The loss of material proved to increase rapidly when the load factor for the turbine was nearing its maximum value. To obtain long operational periods it is therefore of great importance to avoid operating the turbine at a maximum load. This is of great practical interest for the operation of the station.

The painting on the exposed areas of the paddle-wheel is shown in Fig. 5 and the corrosion effect is indicated in Fig. 6. The efficiency curve for the turbine is also shown in Fig. 6. It is interesting to notice that the cavitation effect increases rapidly when the load on the turbine is increased beyond the point of maximum efficiency.

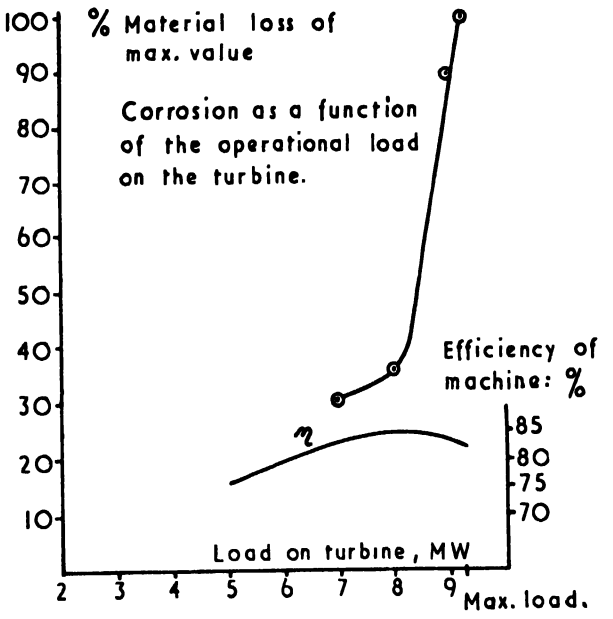

Figure 6

STUDIES OF THE EFFICIENCY OF INDUSTRIAL MIXING EQUIPMENT FOR THE PRODUCTION OF CARBON PASTE FOR SÖDERBERG ELECTRODES

Fiskaa Verk is an electrometallurgical plant located near Kristiansand and operated by Elektrokemisk A/S. Among the products is carbon paste for Söderberg electrodes which is supplied to most of the Scandinavian electric smelters and also other European and overseas works operating this electrode system. To produce this paste, raw materials, mainly coal and pitch, are mixed at elevated temperatures in special industrial mixing machines. One of the most critical factors in the operation of this process is the time necessary to obtain a uniform product. In order to investigate this an experiment was carried out in connection with the production of a typical batch of carbon paste.

Figure 5

The mixing machine was first loaded with raw materials, and operated for a few minutes. Then 10 mc of Na^{24} as sodium benzoate was added to the charge in one single portion. The mixing operation was then started. At regular intervals the machine was stopped and a number of samples taken at definite locations in the machine. This procedure was continued until the mixing was complete. Then the samples were measured for radioactivity.

The results obtained were used to calculate the statistical variation of the samples in each set. The variation expresses the inhomogeneity of the samples as a function of time. As the mixing time is increased the variation decreases until, at uniform paste, it remains constant and equal to the variation caused by measuring errors. With this method the time to obtain uniform paste is found in a fairly simple way.

The investigation could have been carried out by means of chemical analysis. This procedure would, however, be extremely time consuming due to the nature of the material. By the radioisotope method used, considerable time and effort were saved.

INVESTIGATION ON THE DEPOSITS OF FLUORINE COMPOUNDS FROM THE STACK GASES OF A LARGE ALUMINIUM FACTORY

At Årdal in Sogn the A/S Årdal og Sunndal Verk operates a large aluminium factory. The plant which has an annual capacity of 25,000 tons is situated in a narrow valley. Aluminium is produced by electrolysing a heated smelt of cryolite with dissolved

aluminium oxide. During production considerable amounts of waste gases are evolved. These are drawn off and treated with milk of lime in two washing towers. This washing process removes nearly all fluorine compounds from the waste gases. A small part, however, is leaving the works through the stacks and might contaminate the areas around the factory. This has caused several complaints especially from the farmers living in the valley. To establish the degree of contamination and the damage caused the company has started several investigations. One of these dealt with the spreading of fluorine compounds from the stacks, and was carried out by means of radioisotopes.

Fluorine has no suitable radioisotope and therefore an accompanying element had to be used. Part of the fluorine which leaves the stack is in the form of metal fluoride and it was decided to activate sodium fluoride and use the obtained Na^{24} activity as a tracer. The Na^{24} activity was very convenient with its 15.0 hours half-life, as long lived radioisotopes could not be used for security reasons. Now the part of sodium fluoride in an oven which reaches the stack is very small and it was therefore not practical to add the activity to the ovens. To utilize the activity it had to be distributed directly with the stack gases. This was done by dissolving the activity in relatively large amounts of water, and spraying the solution into hot stack gases over a couple of hours.

The amount of sodium fluoride deposited in different areas was determined by placing a number of sample sheets in each place. The sample sheets were pieces of cloth, 0.25 m^2 covered with a special glue in order to retain the dust falling on the corresponding area. Several samples were taken at different times in each place. The sheets were folded to small parcels of standard size and measured for radioactivity with a scintillation counter. In this manner 70 samples were easily controlled during a day's time and the deposits calculated. In places where no net activity was found the maximum limit of the deposits could be defined. Thus it was possible to imagine how the spreading of fluorine compounds takes place under the prevailing weather conditions.

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Portable Isotopic X-Ray Units

By R. G. Daggs,* USA

The value of diagnostic radiographs was well recognized soon after the discovery of X-rays by Roentgen in 1895. Even though improvement in technique and equipment was rapid it soon became evident that the bulky heavy stationary equipment was not practical in emergency and disaster situations. Portable field X-ray units were developed but they are still cumbersome and heavy and require electric power, not always available.

For emergency and disaster situations, such as road accidents, train wrecks, airplane crashes, explosions and natural catastrophes, as well as for medical work in remote rural areas, the need still exists for portable units light in weight, flexible and independent of electric power and water supply. Life and welfare of the victim often depend on the immediate localization of foreign bodies or a knowledge of the extent of fractures before moving the patient.

The advent of radioisotopes brought hope of achieving the desired mobility and independence of X-ray units for disaster work. Naturally radioactive elements like radium and thorium had been used in industrial radiography and the artificially produced cobalt-60, iridium-192 and cesium-137, emitting high energy gamma radiation, widened the field. The discovery and availability of isotopes emitting or producing radiations able to differentiate between bone, muscle tissue and fat could be expected to promote diagnostic radiography in the same manner as the application of gamma emitting isotopes had stimulated isotopic therapy.[1]

In order to be used as an efficient source for clinical diagnostic radiography an isotope or isotope-design should meet, as closely as possible, the qualities of a diagnostic X-ray tube. The isotope should emit radiation in the energy range of 30 to 100 kev (1 kev $= 1.59 \times 10^{-9}$ erg). It should have a high specific activity and a reasonably long half-life. Various isotopes meet these criteria and emit radiographically applicable X- and gamma radiations in the natural decay process. Other isotopes with appropriate specific activities and acceptable half lives are the pure beta emitters. These can be used as radiographic sources since the beta rays excite X-radiation upon bombardment of different target materials.

GAMMA SOURCES

Representatives of this group of isotopes are xenon-133, cesium-134, cerium-144, europium-155, thulium-170, and americium-241. The decay scheme of these isotopes is relatively complicated and the radiation spectrum becomes still more confused where beta rays are emitted in the decay process. The beta rays produce, when hitting matter, the so called "characteristic X-radiation" and "bremsstrahlung." These extra radiations can be used for radiography as will be discussed under the section on beta sources.

Pioneer studies on suitable X- and gamma radiation emitting sources were done as early as 1948 by Spangenberg[2] and in 1950 and 1952 by Mayneord.[3] They were followed by investigations of West,[4] Dennis and DeLuca[5] and others. Mayneord was the first to use thulium-170 for radiography of teeth and body parts. He, as well as Spangenberg who used cesium-134, placed the isotope within body cavities and recorded the shadows on films placed outside the body.

Based on these earlier studies the development of portable isotopic X-ray sources using X- and gamma radiation emitting isotopes became primarily a technical problem of operating parts, exposure controls and shielding. Different solutions of the problem have been offered by the Army Medical Research Laboratory, the Argonne National Laboratories and others, all using thulium-170 as the radiation source (84-kev gamma-ray; 53-kev X-ray).

The device developed at the Army Medical Research Laboratory by Carpenter and coworkers[6] uses an activated thulium pellet 4 mm in diameter and 4 mm thick, sealed in aluminum and shielded by lead. Figure 1 shows a cross section of the portable device which uses for exposure control a spring loaded remote controlled gold shutter.

The weight of the present design (Fig. 2) is approximately 40 pounds. It can be strapped to the back of an aide, set up quickly on removable tripod legs and used in any of the above mentioned emergency situations.

The portable unit consists of the source (Fig. 2) in combination with a self-contained non-dark-room cassette. Pictures are taken on photo sensitive paper with the use of an intensifying screen and are developed in the cassette using the "dry" development technique (Polaroid type of process). Exposure

* Army Medical Research Laboratory. Including work by A. T. Krebs, A. W. Carpenter, R. R. Heer, Jr., L. H. Krohn, J. G. Kereiakes, E. W. Coleman and F. J. Boyer, Army Medical Research Laboratory.

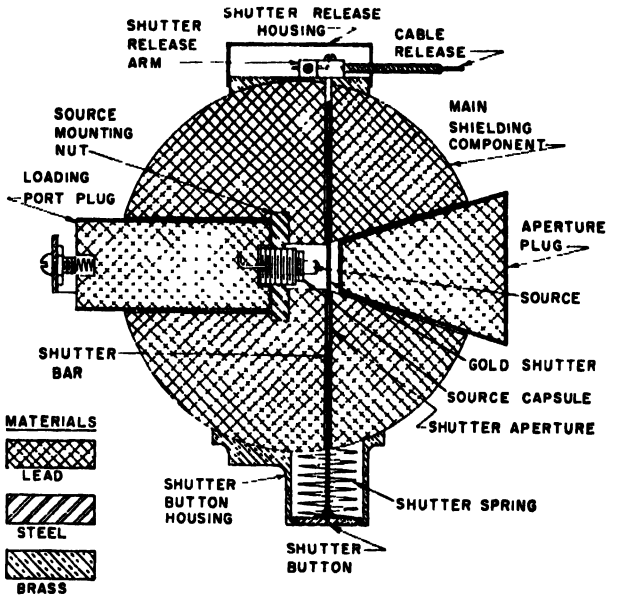

Figure 1. Hemi-sectional sketch of portable isotopic X-ray unit

times with the present source (strength about 40 curies) range from 20 to 50 seconds with an 18-inch source-specimen distance. The exposure dose varies from 10 to 160 mr. This compares favorably with the doses applied in standard radiography with conventional X-ray equipment. Special studies by Storer, Simonson and Krohn[7] using mice showed the relative biological effectiveness of thulium-170 radiation and 250 kvp X-radiation to be approximately the same. Pictures taken with this portable unit (see Fig. 3) show contrast and definition sufficient for emergency diagnosis.

Improvements in the unit and technique are possible by arrangement of different isotopes in a revolving system for selection of the proper radiation (softer or harder) for the prevailing situation. The limitations are given by the shielding requirements and by the half-lives of the isotopes. The half-lives should be sufficiently long so as to guarantee economical use of the unit before replacement of the isotope becomes necessary. In the case of thulium-170, with a half-life of 127 days, replacement is recommended after a period of three or four half-lives.

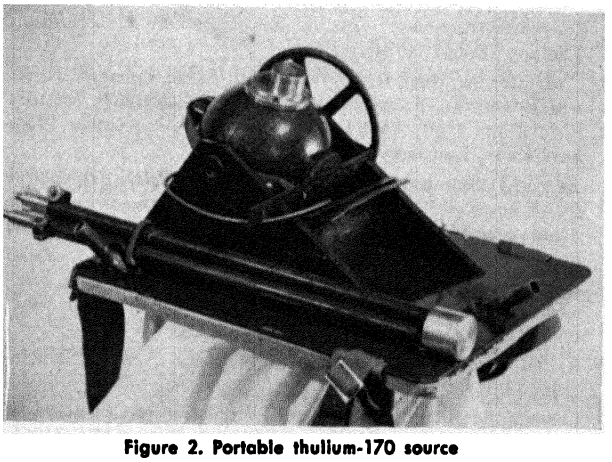

Figure 2. Portable thulium-170 source

BETA SOURCES

The applicability of pure beta emitters in diagnostic clinical and technical radiography is based on the principle of beta ray excited X-radiation which was described as early as 1910 by Rutherford and his coworkers. Gray and Chadwick of this group bombarded different target materials with beta rays from the radioactive elements RaC and RaE and investigated the X-radiation produced. In this phenomenon the beta rays interact with the target material producing characteristic X-radiation and "bremsstrahlung" (internal and external "bremsstrahlung") in a manner comparable to the production of X-rays in an X-ray tube by impingement of the accelerated electrons on the anode (target) of the tube.

The production of pure beta emitting isotopes with different characteristics in modern piles and reactors has stimulated new research in this field. Recent experiments with modern scintillation equipment show a discrepancy between the theories developed earlier by Bethe, Heitler, Knipp, Uhlenbeck, Bloch, Morrison, Schiff and others and the experimental results. The experimental yields of X-radiation produced in different target materials by beta emitters are significantly higher than the values predicted by the theory thus explaining the successful attempts by Kereiakes and Krebs[8] and Reiffel[9] to use beta emitters as sources for diagnostic X-rays.

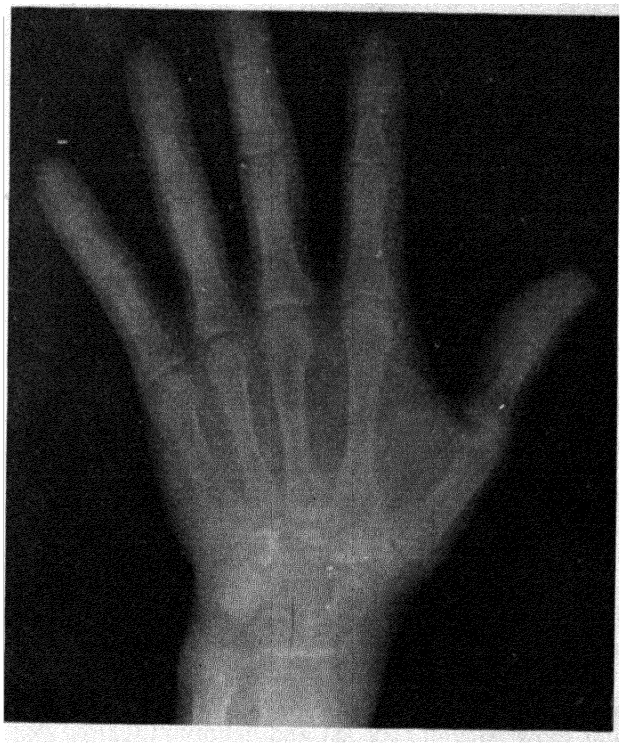

Figure 3. Radiograph of hand taken with portable thulium-170 unit 18 in. distance, 20 seconds source strength 40 curies

Among the isotopes emitting only beta radiation in the natural decay are nickel-63, strontium-90, promethium-147 and thalium-204. Kereiakes and Krebs[8] used a simple strontium-90 medical appli-

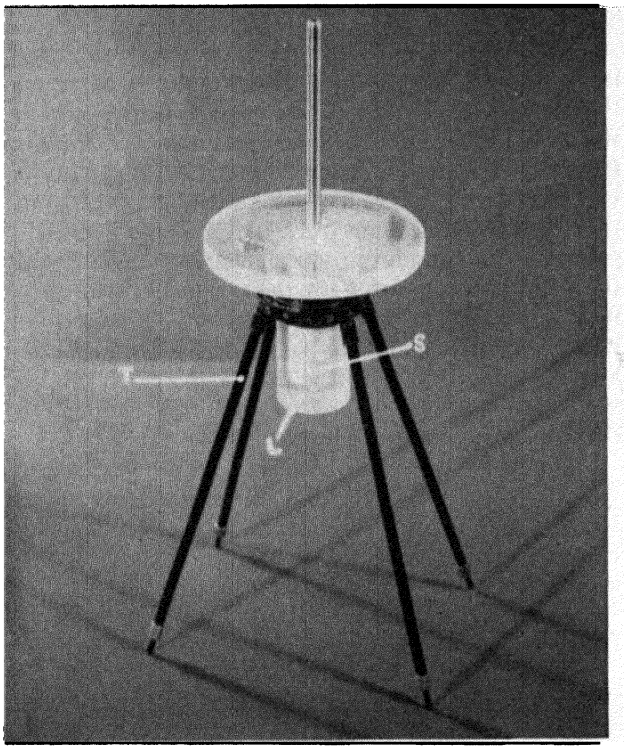

Figure 4. Portable strontium-90 source

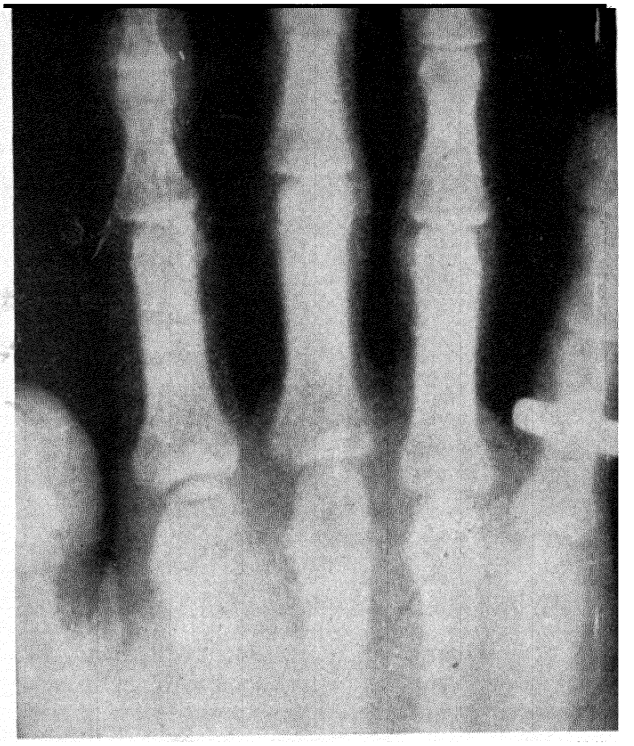

Figure 5. Radiograph of hand taken with portable strontium-90 unit 10.5 cm distance, 5 minutes, source strength 300 mc

cator for their first studies. In this device the beta rays are emitted by strontium-90 in equilibrium with its decay product yttrium-90 (strontium beta with E_{max} 0.537 Mev, strontium half-life about 20 years; yttrium beta with E_{max} 2.18 Mev, yttrium half-life 62 hours). They produce in the source as well as in the encapsulating material (2 mils stainless and 10 mils aluminum) the radiographically applicable X-radiation. A concept of the spectral distribution of this excited X-radiation may be obtained from the measurements made by Reiffel[9] using lead targets and from those of Leboeuf and Stark[10] using tin targets.

In the portable beta isotopic unit used at the Army Medical Research Laboratory the source S is surrounded by a lucite cap L for absorption of the undesired beta radiation and kept in position by the tripod T. (Fig. 4.)

Radiographs taken on Eastman "Blue Brand" film using intensifying screens above and below the film show enough contrast and definition for the desired purpose (see Fig. 5).

Improvements in the beta unit are possible. The application of selected image intensifiers, of focusing devices, and the use of different target foils in a revolving shutter-like system with only one beta emitting isotope as the source are challenging possibilities. Such a unit delivering X-rays of proper energies for various tissues, being independent of power supply, water supply and dark room facilities would be very light in weight, flexible and portable.

Present radiographs taken with portable isotopic sources are without doubt inferior to radiographs taken with modern standard X-ray equipment. Considering, however, that it has taken more than 50 years to achieve the improvements from the first picture of a hand taken by Roentgen to modern radiography, the future of isotopic clinical diagnostic radiography looks very promising.

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The Development of Gamma Radiography

By W. S. Eastwood,* UK

HISTORICAL

The earliest known use of gamma rays, as opposed to X-rays, for radiography is the experiment made by Becquerel in 1896.[1] By placing a piece of silver between some radioactive ore and a photographic plate the outline of the silver was shown on the developed negative. Radium and mesothorium were found to be the active constituents of the ore. Sources of these elements have been used for radiography but to a rather limited extent owing to their high cost.

The earliest use of artificially-made radio-isotopes for this purpose was probably made by Tenney using the cyclotron at Ohio State University in 1943. Several sources including Na^{22} and Cu^{64} were tried. In 1946 Tenney[2] working at Los Alamos made comparisons between the performance of radium, tantalum and cobalt sources. Three years later Eastwood at Harwell reported[3] on a survey of suitable isotopes for gamma radiography. The survey introduced for the first time the medium energy gamma emitter, iridium-192. The results appeared so promising that the Isotope Division at Harwell began a production programme of radiographic sources standardising on three sizes and using a special container capsule. Data sheets for Co^{60}, Ir^{192} and Ta^{182} were issued giving all the relevant information on exposure times, screens, protection and suitability of penetration in steel.[4]

Up till now no soft gamma emitter had been found suitable for thin sections or light examination. In 1951, West at Harwell announced the use of thulium-170,[5] and in a later paper the transuranium element americium-241 and europium-155.[6] Meanwhile caesium-137, as a longer-lived substitute for iridium-192 was being investigated by Dutli and Taylor at Los Alamos and also Eastwood at Harwell. In 1954 the Radiochemical Centre at Amersham started production of sources of caesium-137 for radiography.

SOURCES AVAILABLE AND THEIR SUITABILITY

Although a large number of gamma-emitting isotopes have been tried for radiography the types in practical use boil down to six or eight. For the rest either the half-lives are too short or the specific activity is not concentrated enough or it can only be made by a cyclotron reaction and is therefore not adapted to routine production.

The best classification is made by grouping together those sources with similar penetrating power —that is according to their emitted gamma energy.

Isotope	*Half-life*	*Gamma rays*
Sodium-24	15 hr	1.4 + 2.8 Mev
Lanthanum-140	40 hr	2 5 + 1.6 etc.
Radium	1590 yr	Av. 0.8 max. 20.
Cobalt-60	5.22 yr	1.1 + 1.3
Tantalum-182	111 d	1.2
Iridium-192	74 d	up to 0.6
Caesium-137	33 yr	0 66
Caesium-134	2.3 yr	up to 0.7
Thulium-170	129 d	84 kv + X-rays
Americium-241	470 yr	60 kv + X-rays
Europium-155	1.7 yr	87 kv + X-rays

The most penetrative pair sodium and lanthanum are both of such short half-lives that they are usually specially prepared for a particular job. The most concentrated sodium salt is the fluoride which can be compressed to a small pellet. Lanthanum-140 can be made by $(n\gamma)$ irradiation or extracted from fission products. The former is the preferable method. There is a component of hard radiation in radium which allows it to be used in this class but only using long exposure times.

In the 1 Mev class cobalt-60 is now used rather than either radium or tantalum. The points in its favour are a much higher specific activity and two quanta emitted at each disintegration. Even taking into account the cost of re-irradiation to maintain its activity it undersells sources of radium. Tantalum has a very similar performance and may be more speedily activated than cobalt but has a half-life sixteen times shorter than cobalt. Tantalum sources are seldom prepared now except for special orders.

The use of iridium-192 introduced a new factor into radiography. Inspection of pipe welds and steel plates of thickness between ¼ in. and 1 in. is not well carried out with radium since its radiation is too penetrating to give the required sensitivity. Iridium and the other isotopes in this class are better. Constructors of boilers, platework and pipework have been quick to employ this new technique. The rapid demand for iridium is shown in the figures given in the next section. Caesium-137 is a fission product which, though fairly new is useful as an iridium substitute. In its favour is its long half-life. It does not have quite the latitude in range of thickness shown by

* Isotope Division, Atomic Energy Research Establishment, Harwell, England.

iridium. Another isotope caesium-134 has a longer life than iridium and a similar performance. With a high flux pile it may be possible to produce a higher activity per unit volume than with fission caesium.

There is a shortage of isotopes having soft gamma rays of about 100 kev. The best so far is West's thulium-170. Some very elegant radiography has been done with thulium but the isotope has a decay scheme which yields only one gamma ray per every ten disintegrations. The exposure times thus tend to be long. Sources made from sintered thulium oxide have been in routine production at Harwell for two years. The demand will probably increase when higher specific activities are obtained in Harwell's new Heavy Water Pile.

Americium-241, the transuranium element, has been used successfully. There are not large quantities of this material available and we have had to use our sources when they can be spared by the chemists and metallurgists!

Europium-155 has similar radiations to thulium. Fission product material is useless for this purpose as it is always contaminated with the two other europium isotopes -152 and -154 having approximately 1 Mev gammas. It may be prepared however in an expensive way by irradiating separated samarium-154.

HARWELL'S PROGRAMME AND STATISTICS

When the programme for mass-producing radiography sources began in 1949 several standard sizes of source were chosen and a special capsule designed. The sizes were comparable to the focal spot of an X-ray tube and for convenience of manufacture were cylinders having a length equal to their diameter. Cylinders of 6 × 6 mm, 4 × 4 mm and 2 × 2 mm are still the three normal sizes although for special work 1 × 1 mm and ½ × ½ mm have been made. A stock of various activities in these sizes can usually meet most requests without having to prepare each source to order. Bulk production is in fact more convenient for us and allows a reduction in price of manufacture.

The standard capsule is made of an aluminium alloy resistant to sea water and is shaped with a tail-tag which both carries the serial number and provides a means of securing the source in a holder. The capsule design has been adopted by both Norwegian and French Atomic Energy Projects and is under consideration as the approved design by the British Standards Institution.[7]

There are now five different makers of radiographic source containers built to accept our standard capsules and sources. Between them over a dozen models can be bought varying from comparative simplicity to instruments with eleborate remote control arrangements. The containers have had quite a wide sale outside the United Kingdom, in many cases the source is transported in its container after being loaded at Harwell.

Source production over the past three years is shown in Table I. It will be seen that there is a rising demand for iridium sources while the output of cobalt sources remains roughly constant. Some consideration of half-life should be made in interpreting the figures since a user of iridium usually wants his source changed every 3–6 months. The figures for caesium sources are not quoted as production is comparatively recent.

Table I. Radiographic Source Production at Harwell

Year	*Number of sources sent out per year*		*Quantity of curies sent out per year*
1952	Iridium	650	810
	Cobalt	231	110
	Thulium	0	0
1953	Iridium	901	2099
	Cobalt	228	185
	Thulium	28	10
1954	Iridium	1295	3489
	Cobalt	201	213
	Thulium	43	9

Sources have been sent to 21 countries which are listed in Table II. In most cases they are used for welding or casting inspection, but there are a number of other unusual applications too varied to allow details.

No production figures are available from Russia, but we believe our source output easily exceeds that of any other country.

FUTURE TRENDS

It seems doubtful if any new isotopes will be found for radiography that have not already been tried. The weakest range is in the 100 kev class which is badly needed for non-destructive testing of light alloys or thin metal plates and assemblies. A recent paper by Reiffel has aroused interest in the possibility of exciting the emission of characteristic X-rays and bremsstrahlung by bombardment of a suitable target with beta rays. If this method works it should provide a choice of X-ray sources from about 10 to 90 kev energy.

Both Eastwood and Morison have tried using strong iridium sources to give fluoroscopic viewing, but with limited success. Fluoroscopic screens are not very well excited by radiation as hard as this and very strong sources are necessary. More likelihood of improvement will come from adaptation of the image tube developed by Philips. Even without weak thulium sources the outlines of dense objects could be perceived with this tube. Using thulium with standard methods Mayneord has shown how it may be used in medical diagnosis. Unconventional pictures can be made by placing a source inside body

Table II. Countries Using Harwell-made Radiographic Sources

Portugal	Denmark	South Africa
Mexico	Switzerland	Spain
Norway	Australia	Italy
Sweden	New Zealand	Ireland
Germany	Japan	Yugoslavia
France	India	USA
Holland	Pakistan	Austria

cavities and radiating from "inside out."[8] The time of exposure precludes the use of thulium for stomach and chest radiography but for bone fractures, particularly in places far from a hospital, thulium could be useful.

It was at one time hoped that Xeroradiography might make the conventional dark room obsolete. In this method instead of exposing a negative, a pattern of electric charge is built up on a selenium plate. The pattern is subsequently made visible by dusting on a powder which adheres to the charged areas. Although an intriguing process its one great failing for industrial use is that it does not provide a permanent record of the result. Underwriters or insurance companies are unlikely to accept such a transitory proof of a radiographic examination.

There are besides this other shortcomings such as the halation or shadow effect that appears at the edge of a sudden change of thickness in the specimen.

Already the trend is towards sources of higher activity in smaller sizes. We had imagined that the loss in portability would limit cobalt-60 sources to one or two curies. This is clearly not so. Sources of 10–50 curies are still a cheaper proposition than buying and running a million-volt machine.

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The Application of Radioactive Isotopes in Gamma-Ray Radiography

By S. T. Nazarov, USSR

1. INTRODUCTION

Many plants in various branches of industry of the Soviet Union are now using gamma-rays for the control of technological processes in metal working.

It is extremely important to use reliable methods for the quality control of machines working with high static and dynamic loads, i.e., jet-propulsion engines, turbines, aeroplanes, power plants, etc.

Out of other methods for the quality control of industrial production, most interesting are methods for the control of materials without destruction. The gamma-ray control is one of the most effective.

Achievements of physical science in the field of nuclear processes have made it possible to use the isotopic gamma-rays for nondestructive testing. The gamma-rays of the following isotopes are used for this purpose in the Soviet Union: cobalt-60, tantalum-182, cesium-137, iridium-192, europium-154 and others.

The beta-rays and neutrons are being introduced now for the nondestructive testing in addition to the gamma-rays. These kinds of radiation possess great potentialities as far as their use in industrial testing is concerned. Such valuable properties of the radioactive isotopes as portability and simplicity in the design of equipment, simplicity of operation, the possibility of using the radiation at any time and under all circumstances—in a shop and in the field—make them in many aspects indispensable in the nondestructive testing of materials.

Physics and electrical engineering have provided researchers with the equipment for the generation of the permeable radiation which considerably exceeds the potentialities of the isotopic gamma-radiation. The modern roentgen equipment makes it possible to generate X-rays in a wide range of energies (from 10 kilovolts up to 10–20 Mev and more) which, generally speaking, exceeds the radiation range of the radioactive isotopes and provides a research worker with great opportunities for their use in the radioscopy of various materials. But, due to the above mentioned advantages and, particularly, its economy the use of the radioactive isotope gamma-rays for the nondestructive testing of metals has won general approval.

Original language: Russian.

The cheapest design of a roentgen installation for X-rays examination of metals exceeds the price of a gamma-ray installation. Thus, for example, in the Soviet Union the cobalt-60 preparation costs hundreds of times less than X-ray equipment. To take into consideration the difference in operational expenses between the use of the roentgen and gamma-rays installations, the interest of industrial controllers in radioactive isotopes becomes quite understandable.

Two methods of gamma-ray examination, the photo- and ionization method, are now used in the industry of the Soviet Union.

The first method is most widely used for industrial control due to the objectivity and obviousness of the obtained results of research.

The second, ionization method, possesses lower sensitivity for revealing defects in the materials under examination and lower potentialities for the determination of the character of defects than the photo-method, but it has certain advantages in the control rate and may be used for the control of some articles on the production line.

According to the rules and standards of the State Inspection Committee existing in the Soviet Union, all welded boilers and pressure vessels, ship bodies, bridges, gas pipe-lines and other objects of machine-building and construction designs must undergo gamma-ray examination.

A special gamma-rays examination equipment for mass production has been designed in the Soviet Union to meet industrial demands of the country.

Methods of control by the gamma-rays of various isotopes have been worked up.

Welding is widely used in the machine-building industry and construction sites, so the welded articles present the main object for the gamma-rays examination. The testing of cast components, ingots and non-metallic materials is particularly important as well.

This paper, based upon the achievements of the Soviet research-workers, considers the most interesting problems from the point of view of practical application of gamma-ray testing in the industry.

2. SELECTION OF THE MOST ADVANTAGEOUS CONDITIONS FOR GAMMASCOPY

At the present time a radioactive isotope may be so selected for the testing of metals that its gamma-ray energy would provide the maximum sensitivity

for revealing defects in the tested metal on photographs. The sensitivity or resolving power determines the fitness of the given test method.

Two factors are taken into consideration in selection of isotopes for the examination of metals: the radiation energy of an isotope and its half-life. The first factor is particularly important as far as nondestructive testing is concerned.

Papers, in which the problem of the sensitivity of the gamma-rays examination method is considered, give the thorough study of the influence of geometric factors on the sensitivity of the method,[1] i.e., the width of the radiation source focus, focal distance, thickness and shape of material, size of defect, the position of the defect in the body as well as the influence of the radiation energy. Theoretical[2] and experimental[1, 6] study has been given to the influence of film properties on the sensitivity of the method.

Alteration of the energetic radiation spectrum during its penetration into the material and the influence of the resulting dispersed radiation on the film were thoroughly studied and discussed elsewhere.[4, 5]

The existing theoretical and experimental data have made it possible for the author of this paper[3] to study the influence of the dispersed radiation on the sensitivity of the radiographic method and work out a method of calculation for the determination of sensitivity. This method simplifies the common experimental operations on the determination of the sensitivity which absorbs much time and work.

But the calculation of the radiographic method sensitivity by analytical formulae is quite complicated.

In order to simplify the calculations of the gamma-ray sensitivity testing, the experimental data taken from the samples with slots of known size were analyzed. An empirical formula, deduced for the films used in the Soviet Union, makes it possible to determine the most advantageous sensitivity of any method using gamma-rays from any isotope. In working out the empirical formula radiations of the cobalt-60, cesium-137, iridium-192, europium-154, with the focal distance = 400–500 mm and with the application of intensifying screens were used.

The empirical formula for the steel runs as

$$\Delta d_{min} = \frac{0.005\ (2+\delta)}{\mu}$$

where Δd_{min} is the defect size in cm; $\mu = \exp(-V^{0.8}/1.35)$ is the absorption coefficient in relation to the radiation energy; 0.005 and 2 are constant factors reflecting the film and screens parameters, film blackening density and focal distance; 0.8 and 1.35 are constant factors reflecting the radiation energy and the atomic number of the steel substance under examination; δ is the thickness of the metal in cm; and V is the radiation energy in Mev.

For the radioscopy of copper $\mu = \exp(-V/1.45)$, for aluminium $\mu = \exp(-V^{0.33}/0.52)$.

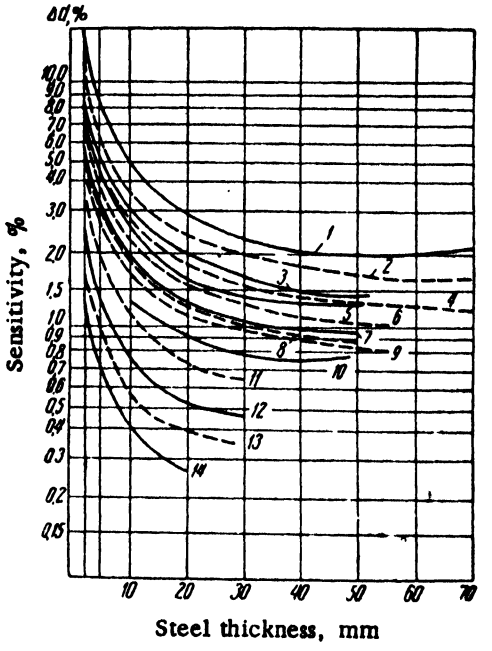


Figure 1. Sensitivity for revealing defects in steel taken with focal distance = 400 mm, with intensifying screens on films "X" and "XX." Curves: (1) experimental; (2) calculation for cobalt-60; (3) experimental; (4) calculation for cesium-137; (5) experimental; (6) calculation for iridium-197; (7) experimental; (8) calculation for europium-154; (9) calculation; (10) experimental for roentgen radiation = 200 kv; (11) calculation; (12) experimental for roentgen radiation = 120 kv; (13) calculation; and (14) experimental for roentgen radiation = 80 kv

Figure 1 provides the experimental and calculated curves of the sensitivity for the radioscopy of steel. Photographs were taken by the gamma-rays with various radiation energies; cobalt-60, cesium-137, iridium-192, europium-154 and roentgen radiation of 200 kilovolt and less.

The continuous curves represent experimental data, and dotted ones, calculated. It is evident that the calculated and experimental curves diverge within the admissible limits.

Having found the gamma-radiation energy by the main spectral line of any isotope for a given thickness of steel (up to 100 mm) or of some other metal, it becomes possible to determine with close approximation the gamma-rays sensitivity for revealing defects under the common conditions of examination.

Figure 1 also shows that the gamma-rays with the higher radiation energy, e.g., those of cobalt-60, give a low sensitivity for steels thinner than 40 mm. For instance, in case of 10 mm steel the sensitivity is 5–6%, while it is about 2% for the iridium-192 and europium-154.

For steel thicknesses between 10 and 50 mm a high sensitivity may be obtained using iridium-192 and europium-154 isotopes. The radiation with lower energy must be used in cases when the steel thickness is below 10 mm. Here the isotopes with a softer radiation, such as the thulium-170, europium-155 or some other isotopes of this sort, should be used.

The proposed method of selection of the most advantageous conditions for the gammagraphy may help specialists engaged in the industry to choose correctly a radioactive isotope with the subsequent correction of testing conditions for the given object of control.

The half-life of an isotope is of great importance for the industrial gammascopy of metals along with the radiation energy. The use of isotopes with the advantageous gamma-radiation energy, as far as the gammagraph sensitivity is concerned, but short half-life causes inconvenience in operation due to the frequent replacement of isotopes in irradiators because of the time increase of the exposure in case of a rapid activity decrease.

The results obtained by the Soviet research-workers in the field of metals gammagraphy from isotopes with different gamma-radiation energy have made it possible to give recommendations to industry controllers on the rational use of gamma-rays for controlling their objects.

3. GAMMASCOPY OF WELDED JOINTS

The selection of a suitable technology for welding various objects demands preliminary tests and researches. The main types of such tests include: the determination of the mechanical strength of a welded joint, the metallographic study of structure and some other sorts of examination of welds which secure the possibility for the selection of a rational technology ensuring working capacity of a welded construction.

But even the most thorough selection of welding technology gives no guarantee against accidental defects in welds, particularly in the cases when the welding is done by hand, where the quality of a weld depends on the skill of the welder. In cases of automatic welding there might be some defects in a weld as well, due to disturbances in the kinematic or electric circuit of the instrument. Accidental defects in the weld may lead to strength decrease of a welded construction and in some cases even to a breakdown.

Therefore, the revealing of welding defects in a finished welded object is necessary even in cases of most perfect technology.

Various types of nondestructive tests are used for the control of the welded products. To these tests belong X- and gamma-ray photography.

Rich experience has been accumulated in X- and gamma-ray tests of welded joints.

The methods of X- and gamma-rays tests of welded joints have become a commonplace operation in industrial control, and, as it was already mentioned, many now existing rules for acceptance of the welded products envisage the obligatory application of these test methods.

This rich experience seems to have brought the solution to all the problems involved.

But there are still some problems with X-ray and gamma-ray examination of welds which need solution. The most important of them are determination of sensitivity for revealing defects in welded joints of various types and the appraisal of their size by radiographs.

It is well known that gammagraphs of welded joints (in case of molten welds) may reveal macroscopic defects of a weld, such as gas pores, slag enclaves, cracks and lack of penetration. The graph data (Fig. 1) may be used for an approximate appraisal of the size of those defects which may be revealed by the gammagraph in welded joints of steel. As far as the other types of welds are concerned, such as the overlap and tee, it is necessary to make corrections for decrease of sensitivity.

The gammagraphs give a sufficient exposure of the slag enclaves and gas pores in welds. These welding defects are usually located in the weld section in such a way that in the majority of cases it is quite easy to reveal them by the radiography method. But in cases of very thick (over 100 mm) welds, the spheric gas pores and slag enclaves located on the side of the radiation source are distorted, their size being magnified or not exposed at all when their size is at the limit of sensitivity.

In case of gamma-ray examination of thin and middle-sized welds, when optical distortion of defects in their projection onto the plane of a photograph from the diverging rays has no practical importance, the spheric gas pores and slag enclaves are revealed by the photographs as spots by the diameter of which one may judge their size in the weld section. There are no peculiar difficulties in determining the depth of location of the above mentioned defects in case of thin and middle (up to 30 mm) welds. The experienced welding controllers determine the depth of the gas pores and slag enclaves location without photometric instruments by the data on the preparation of edges and the weld treatment.

The gas pores and slag enclaves are well revealed in all types of welded joints: in butt and corner welds made by various methods of welding by melting.

The revealing of the dangerous welding defects, e.g., cracks, by gammagraphy has certain difficulties.

The longitudinal cracks in thin and flat joint welds are well revealed by gammagraphy if they are sufficiently wide and deep. The cracks forming a 5–10 degree angle with the vertical axis of the weld may be revealed only if they are sufficiently wide.

The cross cracks, even if they are wide enough, may not be revealed if the given part of the weld being examined by a ray which is 10–15 degrees apart from the central one.

To reveal cracks in very thick welds is even more difficult.

The direction of cracks in the weld section may be different in very thick welds. The cracks might be parallel to the plane of the welded plates. These cracks are not revealed by gammagraphy. If the cracks in the above mentioned welds coincide with

the radiation direction and are sufficiently wide and deep but located on the side of the radiation source, their projection may be washed out, hampering a decision on the existence of a crack.

Very thick welds (over 70 mm) undergo the bilateral gammagraphic control in order that the obtained results should be more exact.

The lack of penetration in the top of joint welds is well revealed by gamma-examination. Difficulties arise in the appraisal of the lack-of-penetration extension into the depth, particularly in butt joints without an underweld. If the lack-of-penetration size constitutes less than 10% of the weld thickness, the photometric appraisal of blackening caused by the lack of penetration does not give sufficient results.

Experience proves that in case of the corner welds examination, control of tee and overlap joints is hampered even more than in case of butt welds. Due to the geometric peculiarities of these joints, the gammagraph sensitivity for a minimum defect in the corner weld is lower than that for the butt ones. Research work performed on models with various artificial welding defects, their size being preliminarily determined, has been described in a paper[7] dedicated to the determination of the sensitivity of the corner weld gamma-ray examination. In distinction to the accidental errors in the determination of the defects in the natural welds, the modelling of welds considerably increases the possibility of obtaining precise quantitative results in evaluation of gamma-ray investigations. The examination of models was performed by the gamma-radiation from the following three isotopes: cobalt-60, iridium-192 and cesium-137. The ability for revealing defects was determined by the relation of the angle of slope of the central ray to the weld.

The performed researches have proved that the gamma-ray test makes it possible to reveal cracks in the weld, lack of penetration in its apex and along the vertical tray. The ability for revealing defects depends largely on the isotope radiation energy as well as on the conditions of the gammagraph.

Figure 2 provides the dependence of the ability for revealing cracks of various width and depth on the direction of the main gamma-ray beam from the cobalt-60 and iridium-192 in a corner weld of the tee joint with the adjacent to a right angle = 30 mm.

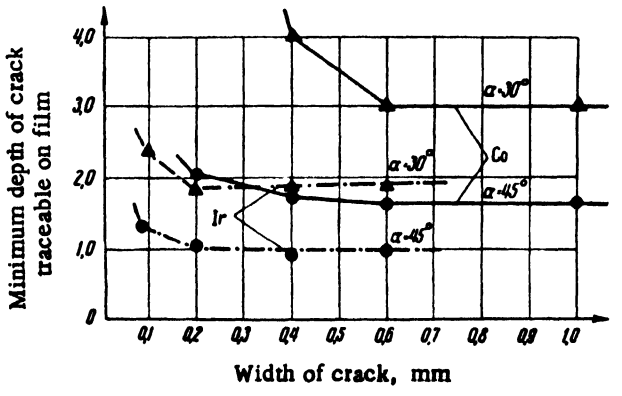


Figure 2. Ability for revealing cracks in corner welds in relation to direction of main beam for radiations of Co^{60} and Ir^{192}

As is evident from Fig. 2, the ability for revealing cracks in the tee welded joints differs for various sources of gamma-radiation. The highest ability for revealing cracks is ensured by the iridium radiation, the lowest by the cobalt one.

The rays angle of slope influence on the ability of revealing cracks and poor penetration in the weld apex has been proved by the experiments. The optimum angle in revealing cracks in the tee joints is 45 degrees.

Let us take a few examples from the machine-building industry and construction work on the gamma-ray control of welded products.

The gamma-ray testing used for the control of the welds of a boiler drum is certainly a most significant and effective case. According to the rules of the USSR State Inspection Committee for the control of boilers, all drum welds of the high-pressure boilers must undergo radiography. The gamma-ray examination of welds is performed along the whole length in the drums of the boilers with the pressure exceeding 30 atm; 20% of the total length of the welds are to be thus examined in the boilers with the pressure = 15–20 atm. Therefore, the boiler-building plants perform a great amount of work on the gamma-ray examination of the welds.

Formerly, the examination of boilers was exercised by X-ray equipment. The birth of radioactive isotopes has simplified this procedure. For instance, formerly an accidental damage of the X-ray equipment retarded the fulfilment of the plant production output program. The gamma-ray control makes such precedents unreal. A radioactive substance is always at work and there can be no troubles with it.

At a plant the gammagraphy of welds in the boiler drums is performed on special stands.

For the gamma-ray examination of welds in boiler drums with the diameter up to 1.5 m the source of radiation is placed in the centre. Thus, one exposure is enough for the examination of the whole weld. The source of radiation is placed outside and the adapter with the film inside the drum for the inspection of longitudinal welds. They are examined by separate parts 300–400 mm long.

Great demands are made of the welds in the drums of high-pressure boilers. Such defects as cracks and poor penetration revealed by the gammagraph determine waste. The admissible defects are: solitary gas pores and spheric slag enclaves. The boiler drum may be put into operation only after the welds are proved by gamma-ray examination to be fit for service.[8]

The second example of the industrial use of gamma-ray control is the inspection of welded joints in high-pressure gas pipe-lines. Radioactive isotopes provide gas pipe-line builders with a simplified and improved method for welded joints control. Due to its portability and unfailing work the radioactive

preparation is the best means of control in laying the gas pipe-lines under field conditions.

The gamma-raying of welded joints was used in all the gas pipe-line construction sites of the Soviet Union beginning with the Dashava-Kiev line.

The testing technology of gas pipe-line welded joints used in the Soviet Union consists of the following: in case of the pipe-lines, the diameter of which exceeds 400 mm, a hole is drilled in the weld; the radioactive substance is introduced into the hole along the joint centre while the adapter with the film is placed upon the weld. In controlling the welds with the diameter of pipes below 400 mm the gammagraphy of separate parts is performed through the two walls.

The application of gamma-ray examinations of welds in gas pipe-lines has made it possible to considerably decrease the inspection costs and improve the quality.

The given examples constitute only a small part of the general volume of work on gamma-ray examinations of industrial objects, but these examples speak for themselves, if one takes into account the scale of boiler production and the gas pipe-line construction in the Soviet Union.

The use of the radioactive isotopes has made it possible to reduce considerably the cost of the welded products and thus to lower their price and make their work unfailing.

4. GAMMA-RAY EXAMINATION OF CAST COMPONENTS AND INGOTS

The radiographic method using gamma-rays is still the only method ensuring the qualitative control of various cast products without the preliminary processing of their surface.

Gamma-ray testing makes it possible to reveal gas pores, voids, shrinkage cavities, slag enclaves, friabilities, cracks and other defects in castings.

The revealing of the above-mentioned defects in cast components before their processing brings down cost of production and improves the quality of the products. In addition to the qualitative control, gamma-ray testing of the cast components is aimed at the selection of a most rational casting technology. Gamma-ray examination of the cast components and ingots of the costly sorts of steel and non-ferrous alloys has great advantages as compared to X-rays. A controller may choose an isotope with the gamma-radiation energy ensuring the highest sensitivity of the gammagraph from a given mould. Like in the case of welds, the cobalt-60, cesium-137, iridium-192 and other isotopes are used for the testing of moulds at the plants of the Soviet Union.

The method of gamma-ray examination of the cast components is well developed and widely known. Certain shortcomings of gamma-ray examination of the cast members, such as low sensitivity of gammagraphs for revealing cracks in constructions of a complicated form, should be mentioned. These shortcomings make it necessary for the controllers to substitute ever more often gamma-ray testing by ultrasonic or to combine these two methods of control. But the gammagraphs are indispensable for revealing porosity in the cast members.

Gamma-ray testing is used for industrial control of steel ingots of the highly-alloyed expensive trademarks. The ingot examination is aimed at the determination of the shrinkage cavity location in order to prevent further processing of ingots before the shrinkage cavities have been removed. The ingots are examined with the cobalt-60 gamma-radiation, and in some cases with the help of the betatron. Gamma-ray examination of steel members is performed in case of their use in machines subjected to sign-changing and dynamic loads. In case of the mass control of the cast steel components, those of small size are located along the circle and inspected with an open radioactive source. The big cast components, beds of big presses, etc. are examined in sections where the casting defects are most likely to be located.

The examination of the cast steel components is mostly performed by cobalt-60 and cesium-137 isotope radiation. The cast aluminium members with thin walls are X-rayed onto the screen with the visual determination of defects. In some cases, the screen image is examined on a cathode-ray tube.

The members of big size and complicated form are tested by cobalt-60, cesium-137 or iridium-192 gamma-radiation; the thin members by gamma-rays of thulium-170, europium-155 and cobalt-60.

The work[10] bears testimony to the fact that the cobalt-60 and cesium-137 gamma-radiation have turned to be most effective for the testing of cast and welded members made out of copper alloys. The thickness of the bronze moulds being equal to 50–60 mm, the radiographs received from an X-ray installation with the tension = 250 kv are of low contrast and sensitivity, particularly in case of a casting with different walls and complicated form. In this case the cobalt-60 gamma-rays make it possible to receive photographs determining the wall thickness within the millimeter quotae and the defects in the walls having the form of cavities, cracks etc.

The amount of work on the control of the welded joints in the Soviet Union considerably exceeds that of the industrial gamma-ray examination of the cast components and ingots.

It should be supposed that many industries will use the gamma-rays testings of the cast members, though such a powerful method as ultrasonic control is already practiced.

5. INSTRUMENTS FOR GAMMA-RAY TESTING

Several types of irradiation instruments have been designed in the Soviet Union for industrial tests by the radiographic method.

As is known, industrial workers lay certain demands to installations of that sort, the most important of which is the protection of personnel from the harmful influence of the radiation. In designing the pro-

tection devices the irradiation-instrument designers follow the rules of labour protection adopted in the Soviet Union. According to these rules, the maximum permissible dose of irradiation is determined as 0.05 roentgen per twenty-four hours.

All industrial equipment may be divided into two groups on the basis of the gamma-ray activity of the applied radiation source.

Installations for sources of low activity of 0.2 0.5 curie of cobalt-60 or some other isotope's corresponding activity with the lower radiation energy enter the first group.

Instruments with low-activity sources are portable installations with small weight (25–30 kg). These instruments are used in mounting conditions, on the construction of bridges, gas pipe-lines, in ship-building yards and other enterprises for 30 mm steel examination, i.e., for metal thickness which can be radiographed by a low-activity source with comparatively short exposures.

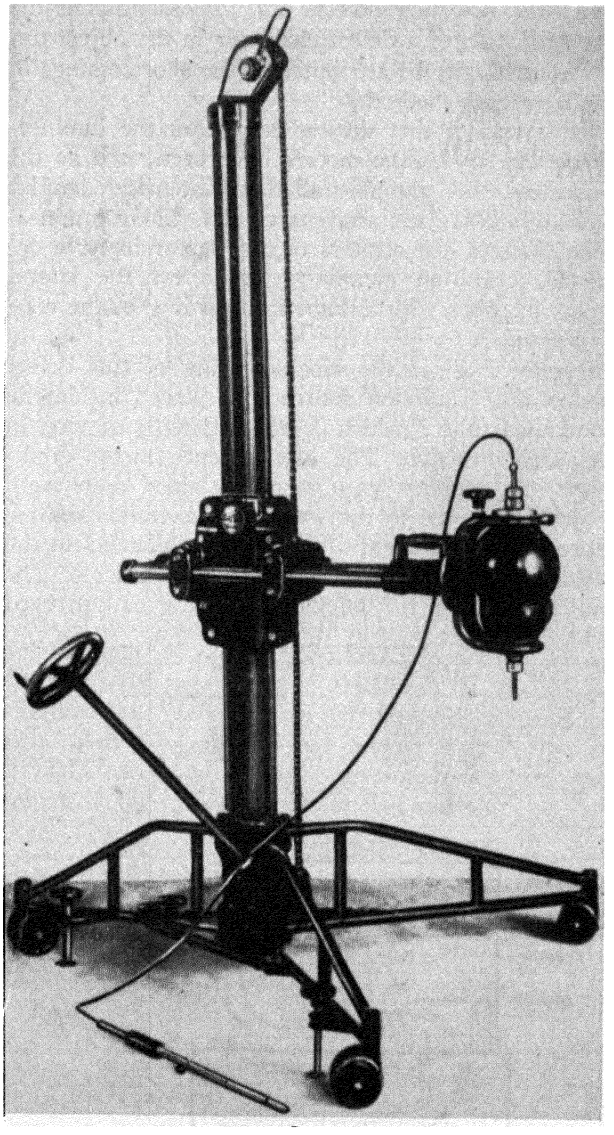


Figure 3. Outer appearance of gamma-defectoscopy instrument GUB-Co-0.5

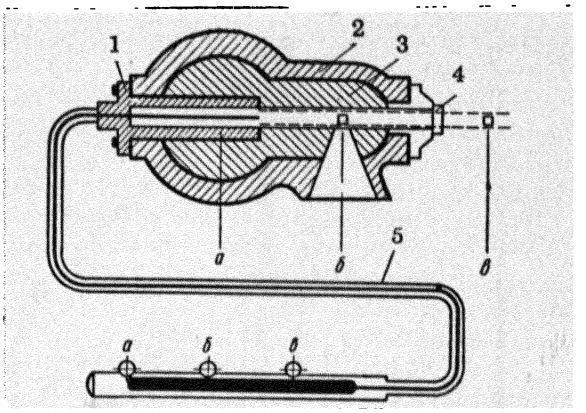


Figure 4. Constructive drawing of instrument GUB-Co-0.5: (1) portable container; (2) iron; (3) lead; (4) plug; (5) rope; and (6) crank for control of hose

The gamma-ray beam of those instruments is controlled mostly by hand by means of the rods which either open or close the gamma-ray outlet channel in the protective casing; sometimes it is distance-controlled by means of short ropes.

The GUP-Co-0.5 1 installation, which is on mass production, may serve a good example of the design of instruments for the industrial tests. These instruments are used in laboratory and shop conditions as well as for the control on the mounting of various welded constructions. Preparation of cobalt-60 with activity of 0.5 curie or of iridium-192 with the activity of 3-5 curie is used in this instrument.

The outer appearance of the instrument is demonstrated in the photograph (Fig. 3). Its protective casing is fixed on a mounting and may traverse in all directions for the gamma-ray beam to be pointed at the object.

The protective casing design is shown in Fig. 4. The cast iron external casing is pear-shaped. The internal cavity is lead-lined. The preparation conveying is performed from the distance of 3 m by means of a rope which is moving in the metallic hose. A control crank is attached to the end of the hose. The rope traversing the radioactive substance is fixed in that crank in three positions: (*a*) corresponds to the relaxation position, (*b*) to the working position when the examination is performed by a directed beam, (*c*) (after removing the cap) in case of examination performed by the open ampule. The lead cylinder containing the radioactive source together with the control rope may be extracted from the main casing by means of the special rod with the length = 1.5 m and easily carried to any place (weight ≈ 15 kg) for the testing of the hardly-accessible parts of the object under control. When the source is in the relaxation position, the working day being 6 hours long, the safety distance from the protective casing is 0.7 m.

The period of work with the portable container, its rearrangement and transference along the controlled object should not exceed 1.5 hours per working day.

The second-group instruments with higher-activity

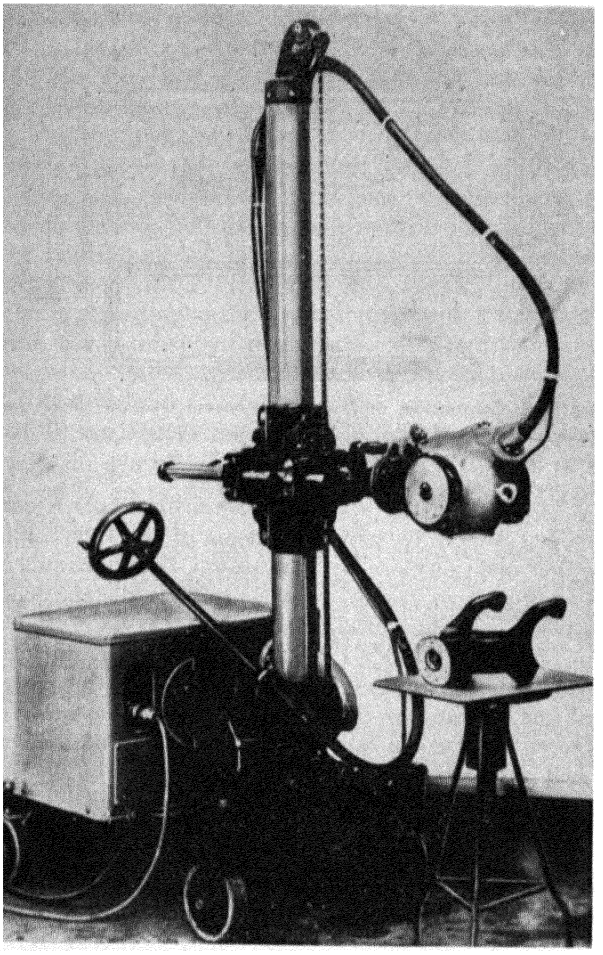


Figure 5. Outer appearance of gamma-defectoscopy instrument

preparations are destined for the examination of welds in boiler drums (with thick walls), cast parts of machines, etc., under laboratory or shop conditions.

This group may be represented by a GUP-Co-50-1 instrument with the 50-curie cobalt-60 isotope or the equivalent quantity of some other isotope with lower gamma-radiation energy.

The outer appearance of the instrument is given on Fig. 5. The instrument is mounted on a trolley and may be moved by hand or by the electrocar.

The constructive drawing of the instrument is given on Fig. 6. The instrument has the main protective casing *1* and the working one *2* which is fixed on a stand and should be placed over the object to be examined. In the relaxation position the source rests in the main casing. Being on work, the source is moved into the working casing through a flexible tube by an electromechanic device which is distance-controlled. This operation is controlled from a light portable desk with a cable of 15 m or more.

There are buttons on the control desk which set the motor in motion. This motor conveys by means of a roller *3* the rope *4* with the source from the main casing to the working one within 4 or 5 seconds.

If the conveying mechanism gets spoiled, the source may be quickly returned to the main casing by means of a device operated by hand.

The total weight of the instrument is 700 kg; the main casing weight is 350 kg, that of the working one is 65 kg.

Instruments of this type are handy in work and offer reliable protection of the personnel from the harmful influence of gamma-rays.

Special instruments for the radioactive sources of lower activity (about 5–10 curies) of the cobalt-60 isotope are turned out, their protective devices in the main casing being less powerful than those in the above described instruments.

6. IONIZATION METHOD OF GAMMA-RAY TESTING

Several researches carried out in the Soviet Union[10, 11] have proved the possibility of using some types of ionization method instruments for industrial gamma-ray inspection.

The use of this method eliminates the expenses on films and chemicals for their processing. Besides that, this method is more productive and may be used for mass control in line production. Low sensitivity for revealing defects and impossibility of the determination of a defect character in the object under control may be attributed to the shortcomings of the ionization method.

It is known that during last years the luminescence and crystalline meters have been used as the indicators of gamma-radiation intensity besides ionization chambers and gas meters. Using luminescence meters, the authors of this research[9] have designed ionization gamma-ray tests for the lateral welds in tubes with automatic recording of the control results.

Figure *7* gives the block-drawing of this defect finder. The radiation source *1* is placed inside the controlled tube *2* which is translationally moving in the axis direction. The luminescence meter (indicator) *3*, supplied with a crack-shaped diaphragm which is parallel to the weld axis, exercises the reciprocating movement which is perpendicular to the weld axis with the help of a scanning device *6*. The outlet signal of the intensity indicator is conveyed

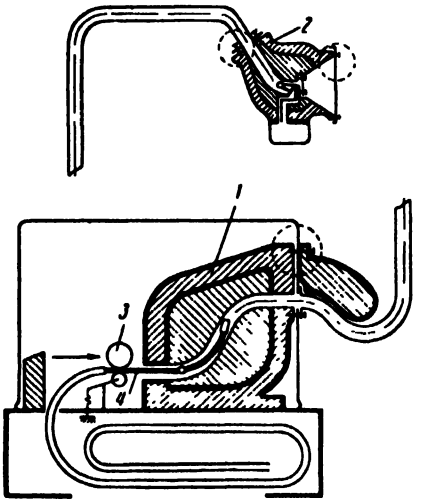
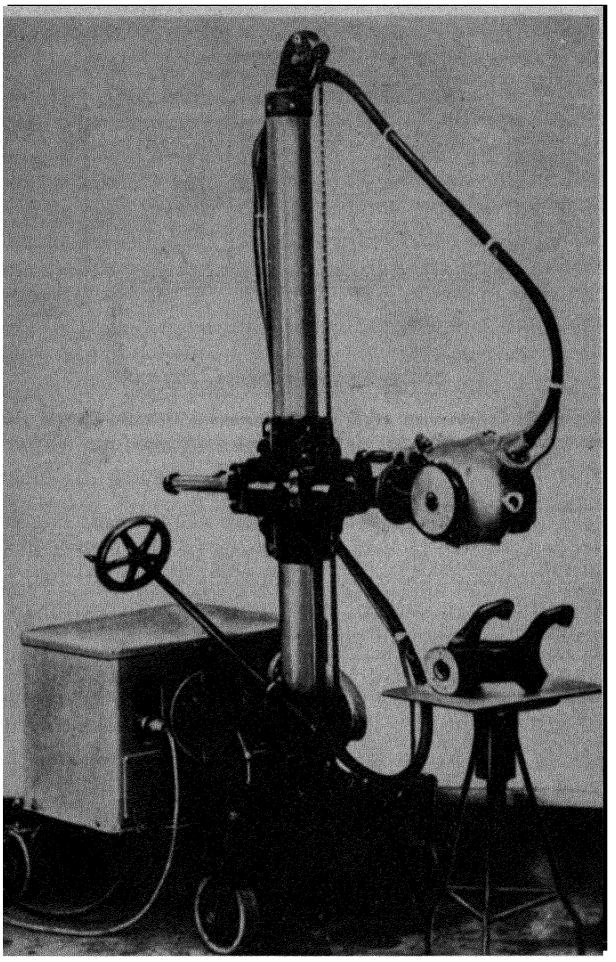


Figure 6. Constructive drawing of instrument



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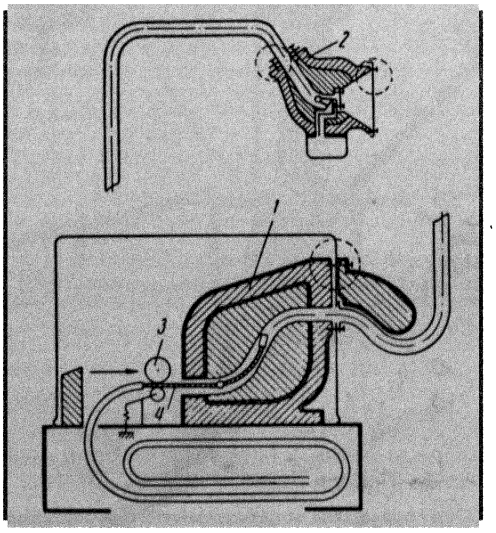

Figure 6. Constructive drawing of instrument

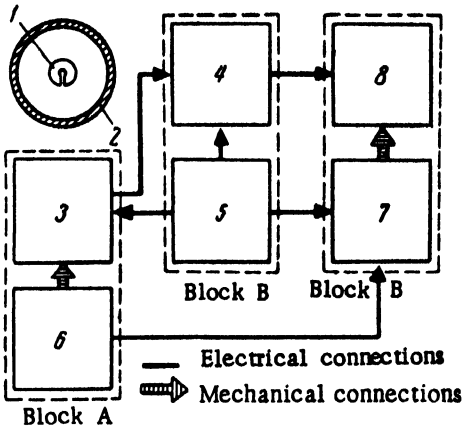

Figure 7. Block-scheme of ionization defectoscope for control of welds in tubes

through the amplifier *4* onto the recording device *8*. The indicator and the amplifier are supplied by a source *5*.

The recording device has a pen which exercises the reciprocating movement synchronous and cophasal to the indicator along a thin white paper ribbon with a graphitized underlining. The ribbon moves by dashes in the direction perpendicular to the pen movement. The pen and paper-ribbon are set in motion by means of a synchronization device *7*. The current being passed through the pen, the thin ribbon is burnt and a black strip emerges, the intensity of blackening is in direct proportion to the current. Thus, a current-graph appears on the paper, and it reflects the internal defects of the weld. The cross-scale of the current-graph depends on the amplitude of pen oscillations, while the lateral scale depends on the velocity of the ribbon movement.

A powerful source of gamma-rays with a quantum energy of 0.2–0.3 Mev is necessary to receive the sufficient sensitivity in case of controlling tubes with wall thickness = 10–15 mm. The control velocity being 1 m/min, the source activity must be 3–5 curies.

Practical tests of the above mentioned instrument have demonstrated that it is able to reveal welding defects such as cracks and lack of penetration whose size is 5–6% of the weld thickness. It should be assumed that further work on improving the ionization method of gamma-ray testing and designing special instruments may substantially widen the sphere of the industrial use of this method.

CONCLUSIONS

1. Gamma-ray testing is one of the most effective methods for controlling the quality of the industrial products where the radioactive isotopes are used more than in any other sphere of technics.

2. For the successful application of the gamma-rays in the testing of metals, it is necessary to use isotopes with various radiation energies which provide the maximum sensitivity of gammagraphs from heterogeneous metals of various thickness.

3. Methods of control by gamma-rays of welded joints and cast details made of heavy and light metals have been elaborated in the Soviet Union; rules and instructions on the radiography of the intlustrial produce have been worked up.

4. The gamma-ray testing equipment designed and made in the Soviet Union makes it possible to control various products and ensures safety of the personnel.

5. The ionization gamma-ray testing method is a prospective method for the mass control of the products of the same type in line-production.

6. The gamma-ray testing application to the quality control of the industrial products has made it possible to increase quality and to save public money.

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Industrial Inspection with Reactor Isotopes

By Eric T. Clarke,* USA

For several decades American industry has placed considerable emphasis on testing and inspection in its production of manufactured goods. Internal inspection of opaque objects in a non-destructive way is one of the important phases of such quality control operations, and of the various methods, that of radiography is one of the oldest and most widely used. Until recently, all radiographic inspection was carried out with radiations either from X-ray generators of various energies or from radium sources. Because of the widespread utility of the method, a considerable body of experience has been built up with these two basic sources of radiation, and the development of equipment and sensitive films has been carried to a high degree of perfection.

Consequently when the advent of nuclear reactors made available in quantity a wide variety of artificially radioactive isotopes, the application of their possibilities to practical radiography was not slow in taking place. After a relatively short period of experimentation three isotopes emerged from the hundreds of possibilities as being particularly suited for industrial purposes in that they possessed certain advantages over the more traditional sources of radiation. These three, cobalt-60, iridium-192, and cesium-137, can be shown to be superior to radium, both economically and in their physical characteristics, and superior to X-ray generators in some but not in all respects.

As more experience is gained and production costs of reactor produced isotopes are reduced, it becomes economically possible to utilize the characteristics of other activities for special-purpose radiography. At present, two of these show considerable promise (thulium-170 and cerium-144) though there still remains much work to be done to produce practical sources of these isotopes at high enough intensity and low enough cost to make their use economic.

It is instructive to review the reasons why both X-rays and radium sources have found application in industrial radiography. At first acquaintance one would wonder how radium or any other isotope could compete with X-ray generation in view of the unparalleled intensity and flexibility achievable with such machines as compared to the low strength and fixed energy of radioactive sources. The answer lies in the general range of thicknesses to be studied. Most applications of the radiographic techniques are on steel objects less than 2 inches in thickness, with occasional demands for inspection of heavier pieces. Since the cost of X-ray equipment is roughly proportional to the thickness of steel to be penetrated, it is generally uneconomic to purchase equipment capable of handling 10 inches of steel when the vast majority of the work can be handled by a low-voltage X-ray generator working in conjunction with a low-intensity, high-energy radium source. Radiography costs can thus be minimized by proper choice of X-ray maximum voltage and total intensity of fixed sources for any particular distribution of thicknesses.

It is clear from the foregoing considerations that the availability of specialized isotopes of various energies and costs opens up a whole new set of possibilities for the reevaluation of these economic factors, and much of this paper deals with the details of such calculations. Prices for the three most-used isotopes have dropped to the point where there is little justification for the use of radium. At the same time, a number of other advantages can be had from these artificial isotopes which make them applicable to difficult radiographic problems which were insoluble with the older media.

PHYSICAL FACTORS

Because radiography depends upon the casting of shadows, any source of radiation must be as small as possible to produce sharp, clear images. Also, the source must be as intense as possible so as to reduce exposure time. These two requirements are of course mutually exclusive, and generally a compromise must be made. Similarly, a short source-to-film distance, which reduces exposure time, also magnifies various parts of the test object unequally, depending on their distances from the film, and so here also compromises are required.

General experience has shown that the source-to-film distance should be at least six times the maximum thickness of the specimen. Also, the usual sensitivity desired is that which will make visible a flaw whose dimensions are not more than two per cent of the object thickness. Now if it is assumed that the penumbra caused by finite source size should be not more than half the image size, these geometric considerations lead to the conclusion that the source-film distance must be at least 100 times the source diameter.

Another important factor is that of sensitivity to changes in thickness such as would be presented by

* Technical Operations, Incorporated.

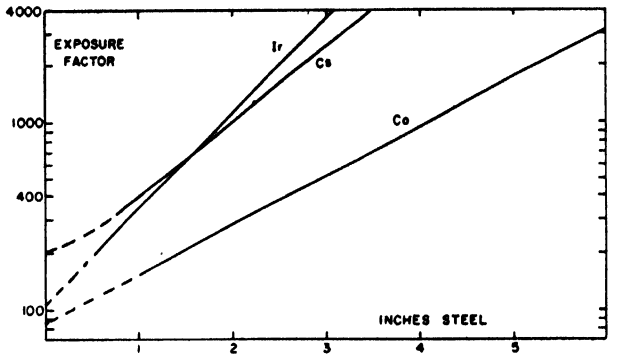

Figure 1. Exposures required to yield density 2.0 on medium speed film for three isotopes: exposure time = [(exposure factor) (source-to-film in inches)^2] /(millicuries)

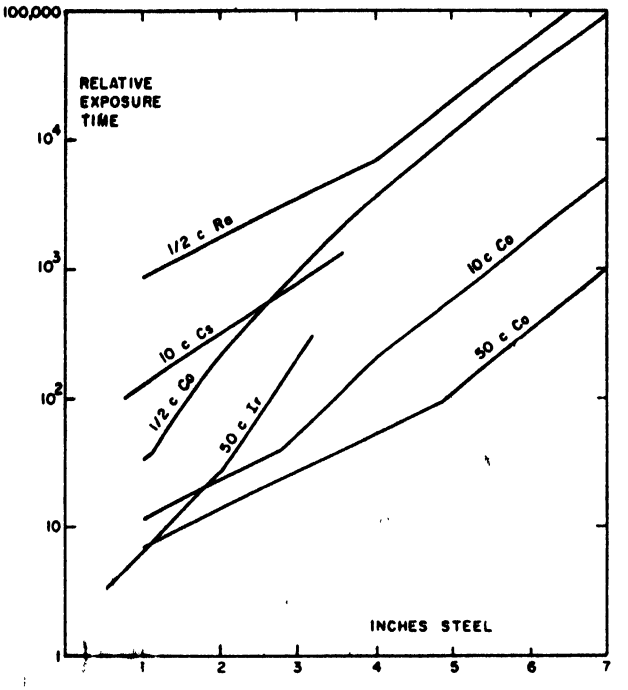

Figure 2. Relative exposure times for several sources in steel, maintaining source-film distance greater than 100 × source diameter and greater than 6 × specimen thickness. Curves extend over working range of thicknesses for each isotope

a flaw in a section of steel. Gamma rays are attenuated exponentially in their passage through matter; if this process were pure absorption, the percentage change in intensity at the far side would always be the same for a constant difference in thickness. Thus, since the eye notices percentage changes in radiation rather than absolute changes (and these changes are reproduced in the transmission of the developed film), one would expect to be able to detect flaws down to some minimum size, regardless of specimen thickness. However, gamma rays are also scattered by the obstructing matter, and the change in intensity produced by the flaw is obscured by appreciable background radiation. As a result, the visual effect turns out to be nearly proportional to percentage change in specimen thickness, except for very thin sections where the sensitivity decreases rapidly. In practice, the minimum thickness at which 2% sensitivity can be achieved is about a half-thickness for the particular radiation and material.

The over-all absorption of the radiation in the material to be radiographed therefore determines not only the exposure time necessary but also the range of thicknesses over which satsisfactory results can be obtained. Figure 1 gives typical data on absorption for several isotopes in steel. Values are expressed in terms of the relative exposure required to give constant density on a medium speed X-ray film.

In addition to radium, which has been used for a good many years in the radiography of thick sections beyond the reach of standard X-ray equipment, three reactor-produced isotopes have come into fairly active use. A number of factors have operated to make these isotopes more useful than others, and the chief points are summarized in Table I. It is apparent that their value to the radiographer derives from a composite of all these factors, rather than any one of them, though probably the one which is of most importance in distinguishing these particular isotopes from the hundreds known to exist is cost. Three sizes of cobalt-60 are included because of its wide use and because the smallest size can be compared directly with radium.

The various factors—geometry, sensitivity, and penetrability—can be combined to give an over-all view of the performance of these sources. Figure 2 gives relative exposure times required for various steel thicknesses. These relationships hold for any given type of X-ray film, since the exposure times are plotted logarithmically and film speed will enter as a factor applying to all curves. In general, film speed and grain size are proportional, so that for thin sections it is necessary to use medium or slow speed film in order to achieve the desired definition. For the thicker steel sections, high speed film can

Table I. Characteristics of Widely-Used Isotopes

Isotope	*Curies**	*Size† (inches)*	*Half-life*	*Output (rhm)*	*Equivalent X-ray energy*	*hvl (steel) (inches)*	*Cost‡ ($)*
Radium-226	½	¼	1600 yr	0.42	2500 kv	1	10,000
Cobalt-60	½	1/16	5 yr	0.67	2500 kv	1	200
	10	3/16	5 yr	13.5			600
	50	5/16	5 yr	67.5			2000
Iridium-192	50	1/8	75 d	27.5	700 kv	½	400
Cesium-137	10	¼	33 yr	3.6	1400 kv	¾	1500

* Source strengths represent practical values.
† Sizes are approximate diameters of right cylinders.
‡ Costs are representative for encapsulated sources.

be used because the size of the flaws to be detected is large; by the use of such film, exposure times can be reduced by factors of about five.

From the data of Fig. 2, it may be seen that considerable savings in exposure time can be achieved by use of these isotopes in comparison with radium. Moreover, the softer isotopes permit radiography at thinner sections of steel. Cobalt-60 and cesium-137 are both sufficiently long-lived to be useful on an intermittent basis like radium, but iridium-192 must be employed almost continuously to reach its full efficiency.

COST COMPARISONS

It is doubtful if isotopes can ever entirely replace standard X-ray equipment with their great flexibility and intensities, though for special applications the isotopes can perform in ways impossible for the lower voltage machines. Their portability and freedom from dependence on power are obvious advantages of the isotopes in field work. They can readily be used for multiple exposures where many pieces can be simultaneously radiographed; X-ray tubes are often highly directional and can accommodate only a limited area at one time. Their small size enables them to be inserted into small holes and narrow tubes and permits the radiography of an entire spherical vessel or circumferential weld in one exposure. Overnight exposures of thick pieces are no more costly in labor or operating cost than exposures of a few hours.

When comparisons are made between isotopes and high-voltage generators in the million-volt range, however, the isotopes turn out to be preferable for many general applications. Even discounting their special abilities and assuming that both isotopes and generator are operated at the same source-film distance and with the same capability for multiple exposures, the following cost analysis shows that cobalt-60 will generally produce the same results for less outlay. The reason for this ability of cobalt-60 to outperform the high voltage generator economically lies in the fact that full use can hardly ever be made of the generator's enormous radiation output. Even though the equivalent intensity of the generator is a hundred times that of the usual cobalt-60 radiography source, it is of small use when the majority of the time must be employed in setting up the work to be radiographed. This fact, together with the high initial cost of the generator, results in the conclusion that one is almost always better off in using a number of high-strength cobalt-60 sources than in operating a high voltage (1–2 Mev) generator.

In analyzing the situation, exposure times for various thicknesses of steel to produce radiographs on medium speed film were calculated, assuming a source-film distance six times the steel thickness. From this the maximum number of exposures per day was determined assuming that 20 minutes were required for each setup. This figure then yields the total number of cobalt-60 sources required to maintain any given workload up to 24 per day. It is assumed that one man can service either one high voltage generator or sufficient sources to reach this exposure rate, since he can be setting up an exposure while the other sources are in operation. Table II presents the cost assumptions.

The foregoing information is presented graphically in Fig. 3. The sloped lines representing the cobalt-60 sources reflect the increasing number of machines required as the work load is increased; the breaks in the curves of the high voltage generators occur at exposure rates where a second machine must be purchased. It may be seen that the costs per day of operation are considerably lower for cobalt-60 radiography than for the high-voltage machines. Moreover, as is usually the case, a radiographic department can start economically at a relatively low level of operation and acquire more sources as the work load increases.

It should be pointed out that these results are quite sensitive to the setup time required, and that if this can be reduced appreciably below the 20 minutes assumed, the high voltage generators will soon become more economical for high work loads. However, this will not usually be the case except under special conditions such as apply on production lines, where automatic placement of objects and films can be secured.

One can make a somewhat similar analysis to compare the direct costs of operation (exclusive of labor) of various sources and a standard 250 kilovolt X-ray machine. Here we shall again assume that setup time is 20 minutes, and calculate the

Table II. Cost Assumptions for Comparison of Isotopes and Generators

	Sources		*High voltage generators*	
	10 c Co	*100 c Co*	*1 Mev*	*2 Mev*
Equipment and source cost	$ 2500	$ 5000	$30,000	$ 90,000
Enclosure	3000	6000	25,000	50,000
Total capital	$ 5500	$11,000	$55,000	$140,000
5 yr amortization and interest	$ 1260	$ 2500	$12,600	$ 32,000
Maintenance	100	100	1600	2000
Annual cost/instrument	$ 1360	$ 2600	$14,200	$ 34,000
Labor and overhead: 1 man, 2000 hr/yr	$12,000	$12,000	$12,000	$ 12,000
Daily cost, first machine	$53	$58	$105	$184
Additional cost per machine (250 days/yr)	$5.60	$10.40	$105	$184

maximum exposures per day possible with each source at various steel thicknesses. The daily costs can be computed as shown in Table III. All these data are then summarized in Table IV. It is again clear that for steel thicknesses greater than about 1 inch, the isotopes have a decided advantage over the X-ray machine, and are always to be preferred to radium. The advantage over the X-ray machine is heightened when it is remembered that the number of simultaneous exposures by X-rays is limited by the narrow cone of radiation emergent from the 250 kilovolt generator.

ISOTOPE HANDLING EQUIPMENT

Small sources whose roentgen outputs approximate those of a curie or less of radium can be handled by the time-honored method of attaching them to a cord and using a fishpole to withdraw them from a shielded container. However, the modern high-strength source cannot be so treated since the operator will thereby receive too great a radiation dose. Consequently special handling equipment has been devised to permit the location of these multiple-curie sources by remote control, with the operator at a sufficient distance to keep his dose to a safe level.

This sort of equipment falls into two categories: those in which the source is brought to the surface of its shielding container and results in a hemisphere of radiation; and those in which the source radiates in all directions by carrying it to the end of a flexible tube running between the container and the point at which radiographic exposure is desired. The first type has been accomplished in several ways. The source can be mounted on the periphery of a disk rotating within a lead enclosure, and arranged so that one edge of the disk is at the center of the shield while the opposite edge is on the outer surface. Rotation of the disk through 180 degrees brings the source to its operating position. A second method is that of splitting the lead shield through the center and hinging it so that it can be swung open remotely. A third way involves the use of a small curved tube in the shield and employing a flexible cable to push the source from the center to the outer edge.

The second type of handling equipment is invariably built around this last principle. A curved, usually U-shaped, tube is embedded in a lead shield, with a flexible tube attached at one end and leading out to the point of exposure. A second flexible tube containing a steel cable is attached to the other end of the U-tube. The steel cable has attached to it the source, and can be driven by a mechanism located many feet away at the far end of the flexible tube. Thus, after the work to be radiographed has been set up, the operator can retire to his cranking mechanism and safely drive the source to its appointed position. Figure 4 shows a typical instrument of this sort.

Because such equipment can be made relatively cheaply to handle multicurie sources, the radiographer can afford to own a number of them and keep

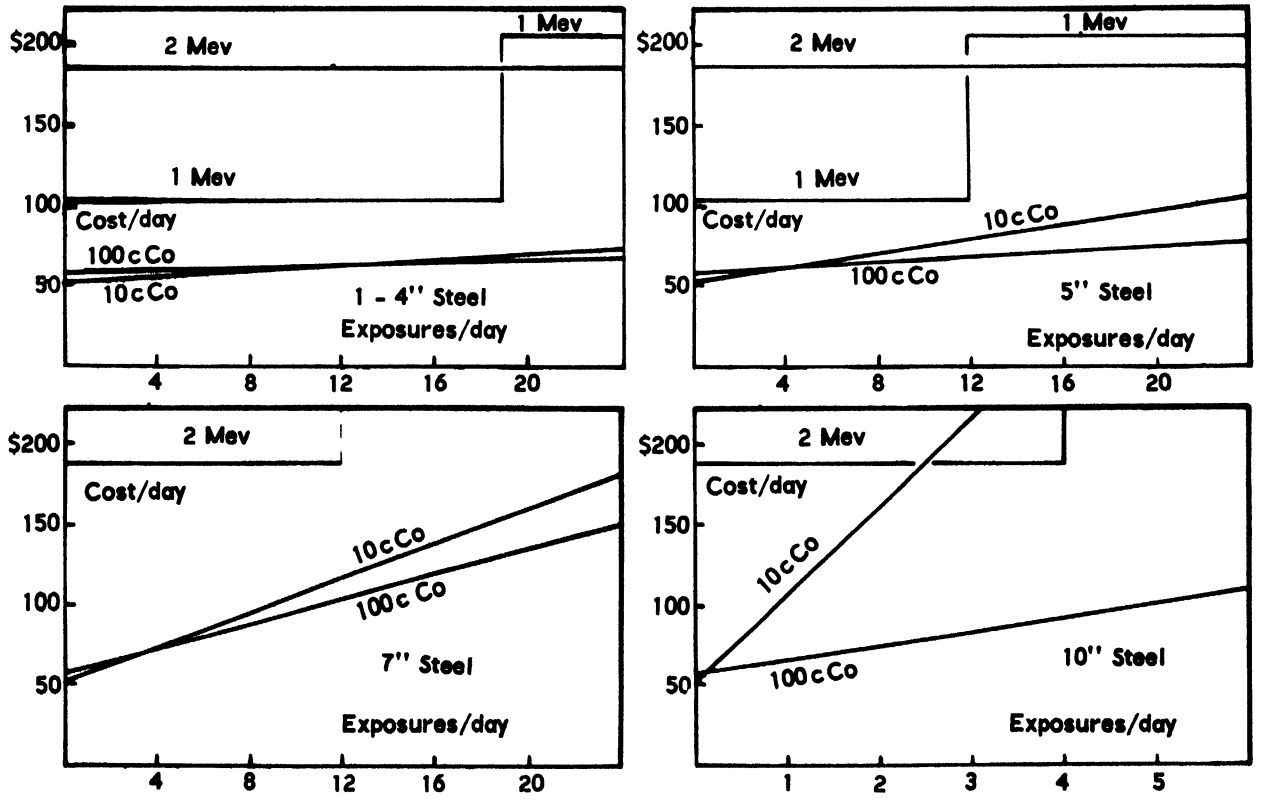

Figure 3. Cost comparison between cobalt-60 sources and high voltage generators: rising curves for sources reflect increasing number of source installations

Table III. Isotope Costs

	Handling equipment	*Source*	*Enclosure*	*Annual cost*	*Daily cost*
½ curie radium	$ 300	$10,000	$1500	$1010	$4.00
½ curie cobalt	300	200	1500	460	1.85
10 curies cobalt	1900	600	3000	1260	5.00
10 curies cesium	1900	1500	1500	875	3.50
10 curies iridium	1900	1200/yr	1500	1980	8.00

Table IV. Maximum Number of Exposures per 8-Hour Day for Various Steel Thicknesses Assuming Medium Speed Film

Steel (inches)	*½ c Ra*	*½ c Co*	*10 c Co*	*10 c Cs*	*10 c Ir*	*250 kv X-ray*
½	—	—	—	13	20	24
1	2	18	21	10	18	24
2	1	7	19	5	10	10
3	½	2	15	2	2	—
Daily cost	$4.00	$1.85	$5.00	$3.50	$8.00	$10

up with a stringent production schedule. He can be occupied in setting up his work while others are being exposed. Since he can purchase the appropriate number of units to suit his schedule, his total outlays can be made proportionate to his needs, and he can readily acquire more units should his work load increase. It is this flexibility which gives the isotope its commanding superiority over the high voltage generator for radiographic purposes.

THE FUTURE

It has been shown how these isotopes of cobalt, cesium, and iridium have been successfully applied to the radiography of steel and other relatively heavy metals. The application of isotopes to the radiography of light metals, particularly aluminum, has not had equal success. As a general principle, it appears that the minimum section that can be successfully radiographed is a half-thickness, which in the case of these isotopes in aluminum is from two to three inches. In order to bring the vast range of aluminum radiography into reach, an isotope must have a maximum energy of not more than 100 kilovolts, preferably 50.

For some time now, effort has been expended in the investigation of thulium-170, a promising isotope produced by the neutron bombardment of the rare earth element. It was chosen because, unlike most soft gamma emitters, it has few hard gamma rays accompanying its 84-kilovolt radiation, it has a high production cross section, a reasonably long half-life (130 days) and can be obtained free from other gamma emitting contaminants. It has some disadvantages also—only 10% of its disintegrations result in emission of the gamma rays, and being a heavy isotope its self-absorption is rather high—but on the whole it appeared that it could be successfully applied not only to light metals but also to special purpose human body radiography where the weight and power demands of conventional X-ray equipment could not be tolerated.

Sources have been made by sintering specially purified thulium oxide into pellets of from 50 to 200 milligrams and giving them long irradiations in the highest available neutron fluxes. Several hundred curies per source have been produced in this way, representing activation of an appreciable fraction of the atoms, but the resulting intensity has been low, less than 200 milliroentgens per hour at a meter. Fortunately, photographic film is perhaps ten times as sensitive at these energies as at 1 Mev, so that,

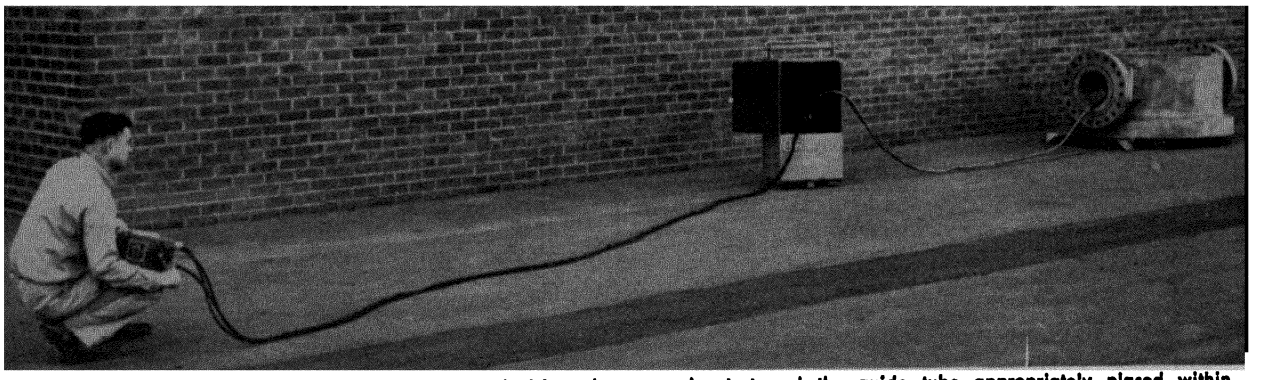

Figure 4. Panoramic projector. A cobalt-60 source is cranked from the shielded storage container (center) to the weldment to be radiographed. Film cassettes have previously been attached to the object under test and the guide tube appropriately placed within (Courtesy C. F. Braun and Co., Engineers and Constructors)

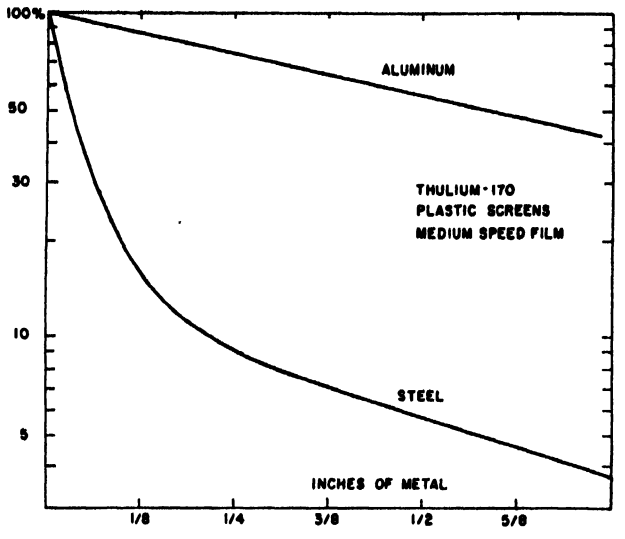

Figure 5. Per cent transmission of thulium-170 radiations through steel and aluminum. Absorption in aluminum corresponds to a gamma-ray energy of about 70 kilovolts, absorption in steel to two gamma rays of 70 kilovolts and about 350 kilovolts. Absorption in lead indicates the presence of another gamma ray of about 1 Mev

radiographically speaking, these sources are comparable with one or two curies of cobalt-60. Higher speeds can be obtained by use of intensifying screens, though with considerable loss in definition.

The half-thicknesses of these radiations in steel and in aluminum vary with the thickness. Data using film as the detector are shown in Fig. 5. It is probable that the low absorption rates at thicker sections are due to bremsstrahlung, or continuous X-rays generated by the 0.9 Mev beta rays accompanying the disintegration of thulium-170. Even so, it is apparent that thulium-170 can be usefully employed for thin sections of steel and aluminum, much thinner than is possible with presently used isotopes, and that the presence of the higher energy component is not a serious drawback. However, this radiation results in the need for considerably more shielding than had been originally anticipated on the basis of pure 84-kilovolt radiation. Preliminary measurements indicate that lead will reduce the radiation by a factor of 30 in the first inch, with a decrease of 2 per half-inch thereafter, indicating the presence of 1 Mev radiation. It is hoped that further investigation will result in methods for reducing the amount of hard radiation.

Two other isotopes also appear promising for the field of thin-section radiography—cerium-144 and europium-155. Though little work has been reported concerning their practicality for such applications, their characteristics are such that they might become useful. The predominant emission of 300-day cerium-144 is a 3 Mev beta ray and a 134-kilovolt gamma ray. It appears in high yield as a fission product, so that if it can be separated economically from the other fission products it should be readily available. Probably its chief drawback will be the presence of the small amounts of hard gamma rays as well as the bremsstrahlung generated by the hard beta rays.

Europium-155 (1.7 year half-life) has no gamma rays higher than 130 kilovolts, with the predominant radiation at 105 and 86 kilovolts. It can be obtained either by neutron bombardment of samarium or by recovery from fission products. Here the problem to be overcome is the removal of contaminating isotopes of europium and other rare earths, some of which are both long-lived and high energy. Because the beta rays of europium-155 are less than 250 kilovolts, the pure isotope should emit essentially no hard radiation.

Judging by the success already obtained in applying isotopes to radiography, there seems little doubt that in time these problems will be overcome and we shall eventually have at hand a complete spectrum of energies in practical quantities. In the meantime the three isotopes of cobalt, iridium, and cesium are being more and more widely used as their potentialities become generally recognized and facilities for their production and handling in large quantities are developed.

Radioisotopes in the Study of Fluid Dynamics

By K. O. Beatty, J. K. Ferrell and F. M. Richardson,* USA

Radioactive materials have come into widespread use as indicators for following the flow of fluids in a variety of systems both mechanical and biological in nature. In nearly all cases they have proved to be powerful tools for following movement in even intricate streams. However, it has only been quite recently that radioisotopes have been applied to the study of fluid dynamics itself and these uses, though important, are still relatively limited in number.

This paper presents a review of the types of applications of tracers in fluid flow and points out some of the many possibilities for future use of radioisotopes in the study of mechanics of fluids.

The problems in the study of flowing fluids may be divided into several groups. Radioisotopes have been used successfully in each of these groups and some applications fall into more than one group. The primary purposes of many of these experiments were not directed to a study of fluid dynamics, but information of value in this field has often been the result. Still more important, these experiments point out the possibilities of applications of radioisotopes to the study of the fundamentals of fluid flow.

The first broad class of flow studies is concerned with the simple determination of the flow path of a body of fluid; the second includes those concerned with the determination of the average velocity of a main body of fluid, and the last, those concerned with determination of relative movement of various portions of a flowing stream. Studies of this last kind are truly in the field of fluid dynamics in the usual sense of the term. It is in this category that the properties of isotopes have been least used.

TYPICAL APPLICATIONS

The first class is exemplified in the large body of tracer work in which some source of active materials is placed in a flowing stream and the movement of the material then determined. This principle is used to great advantage in determining the dispersion of many sorts of materials throughout both open and closed, natural and man-made systems, otherwise inaccessible for observation. It has also been widely used to indicate boundary locations within fluid streams. In addition, flowing tracers make possible a more refined observation of the complicated physiological flow through living organisms. The results of some of these observations have led to suggestions for a model of these flows. These uses have embodied much ingenious technique and represent the most wide and immediately important use of radioisotopes applied to flowing systems. As a whole they are straightforward involving primarily a knowledge of the initial and final positions of the active material.

Since work of this type has been so widely carried out, specific references will be omitted and several examples mentioned to illustrate the type of application dependent upon this simple principle and to indicate the problems involved in its use. The determination of the dispersion of dust or other particles through large volumes of air such as that found in factories or similar installations is an example of flow observation in semi-enclosed systems. This type of measurement is used largely in hazard detection. Here the pattern of flow is determined by wide area activity surveys in which the displacement of the activity is taken to represent the flow displacement of the air mass and any constituent particulate matter. Tracers have also been injected into suspected sources of contamination for the purpose of determining the dilution and distribution of contaminants at specified locations in rivers and streams. Another example of simple translocation is the well-known procedure of inserting a "slug" of miscible radioactive liquid between two grades of oil flowing through a pipeline in order to mark the exact location of the boundary between the two and to indicate their extent of mixing. As a means of observing dispersion, this method is quite successful provided the added tracer material satisfactorily simulates the flow of the substances one is trying to trace, and if it can be added in a quantity which can be determined accurately against background radiation.

An interesting technique using tracers for observing the onset of flow in static fluid is contained in the work of Rogers and Schilberg[1] who determined the initiation of convective flow through porous media by detecting counting rate changes in water dispersed throughout a bed of granular solids. The liquid was injected with phosphorous-32 and the entire bed heated. This application is of particular interest in that its sensitivity depends on the absorption phenomenon associated with the detection of beta radiation. The authors were able to detect incipient convective flow earlier than by visual and thermal methods.

The current activities in the field of radiation fallout from atomic explosions are a unique example in which the hazardous material may act as its own

* School of Engineering, North Carolina State College.

tracer. Such work naturally points the way to more general meteorological studies with different types of radioactive tracers.

A somewhat more complex application is presented in the use of radioisotopes to trace out the flow of several fluid phases through beds of porous solids such as are found underground in oil fields. This work is still largely in the laboratory state.

The second class of studies, the determination of velocities in various kinds of flowing systems, follows from the first principle by taking into account the time required for tracer displacement to occur. This method has proved particularly convenient in cases where more conventional types of metering are made impracticable because of size or inaccessibility. Radioisotopes have been most frequently used in velocity determinations in closed conduits.

Two simple methods for determining flow rates in pipes are in general use, both involving the rapid injection of measured quantities of tracer into the flowing stream. The first consists of timing the passage of the injected tracer between two points separated by a known volume. The flow rate is obtained by dividing the volume between the observation points by the time between the peaks of activity registered by the counters. A second technique eliminates the necessity for using more than one counter and for knowing the volume of any part of the conduit. In this case, the flow rate may be obtained from the integrated count during the passage of a known number of millicuries. By use of an easily determined calibration factor accounting for the size and construction of the pipe, the flow rate may be found from the inverse proportionality to the total count. So long as the flow rate is constant the integrated count is independent of tracer concentration along the stream.

By a procedure similar to the point-to-point survey mentioned in connection with pipe flow, the dispersion of flowing fluids through a porous medium has been determined. Counters surveying different locations in the medium register the passage of activity-bearing fluid as before. This technique is particularly useful in determining the relative movement of different kinds of fluids such as oil and water through sand and soils as well as in determining over-all flow rates. Particular use has been made of the procedure in the study of the movement of oil-bearing fluids through various geological strata.

Perhaps the most widely used and complicated applications of radiotracer techniques to flowing systems have been their application to the study of flow in metabolic systems within a living animal. By inserting a specific chemical constituent associated with the body's metabolism, it is possible to observe both the disposition and flow rate without grossly disturbing the "steady state" of metabolic process. The enormous advantage of such a process is obvious. The rate of flow of tracer through the living system is obtained by direct measurement of activity in such systems as the circulatory or by periodic sampling as in the case of tissue or similar studies. In many cases, however, the interpretation of the data thus obtained becomes extremely difficult because the absolute turnover rate measured at any specific location will be influenced by the metabolic activity in all parts of the system connected with the utilization of the specific isotope as well as by the mechanical circulation. Recently this problem has been fruitfully studied by theoretical and experimental analogy of the systems to a series of non-equilibrium hydrodynamic pools.[2]

Flow rate determinations in rivers and other open bodies of water have also been made by injecting a volume of radiotracer into the stream and measuring the passage of the diffused tracer "cloud" at some point downstream. In these cases the determinations have been limited by the kind and amount of material which can be added to the streams and to the difficulties in arranging accurate and adequate detecting devices for field testing. Interpretation of the results of the activity-time data in terms of rates and pattern are dependent upon a knowledge of the diffusive behavior of the tracer "cloud" under ideal conditions of flow and a knowledge of the stream conditions likely to cause deviations from this behavior. Under laboratory conditions the tracer cloud patterns may be observed for the various types of geometries and rates. In the simple case of streamlined flow in a circular conduit the distribution of a tracer "cloud" as it passes downstream can be predicted from theory. However, there is no mathematically exact relationship for prediction of the spread of a tracer cloud in flow through natural channels. Empirical tests on various models taking into account vertical and horizontal velocity distributions, peripheral influences, and uniformity of flow aid in interpretation. Nevertheless, because of the effect of mixing the precision of the results in many actual streams is considerably less than that obtained in conduits of known cross section.

A somewhat different method for determining flow velocities depends on the dilution of a constantly injected tracer by the main flowing stream. Samples are taken far enough downstream to insure complete mixing. If the rate of tracer injection is known, the flow rate may be determined from the dilution ratio determined from the two activity readings. This is the radioisotope analogy of the salt-addition method of flow measurement.

The last category of isotope application relates to the study of relative fluid movement and has been considerably less explored than the more general solute translocation studies just reviewed. Very generally the work in this group has been divided into (*a*) tracer determination of the relative movement of bulk volumes of fluids and (*b*) tracer determination of the relative movement of minute segments of a flowing stream. An example[8] illustrating a study of the first kind is found in radiotracer use in determining the factors affecting the performance of a large vacuum distillation column. The column con-

tained a number of bubble cap trays over which various petroleum fractions were extracted. Radiation detectors were stationed around the periphery of the trays so that the flow stream was monitored in eight different places on each tray. The results of quick injection of tracer into an adjacent reflux line were followed by each detector. The composite results of all the instruments give a picture of the distribution of fluid across the trays. A qualitative knowledge of this distribution is usually of primary importance. Information is also obtained leading to estimation of hold-up volumes and flow rates.

Mayorcas and Thring[4] have used the simple addition of a radon-air mixture into the center of an air stream in a wind tunnel to measure the dispersion of the injected tracer in directions normal to the main flow. Air samples were taken out downstream through a probe which traversed the cross section of the tunnel. Results of the experiments were used to calculate the mean mixing length for the gas flow. The authors suggest the intermittent addition of radon as a method of metering hot raw furnace gases continuously.

A similar technique has been used by Roquet[5] who introduced a jet of radon and air mixture into a turbulent air stream. An analysis of the radiation spread downstream from the jet was made by traversing the stream with a small ionization chamber. The work was originally undertaken to develop a means of measuring the degree of turbulence, however, Mlle. Roquet concluded that although the experiments provided interesting data on the diffusion of jets of compressed air, the limitations in the experimental apparatus were such that no quantitative measure of air turbulence could be obtained.

It seems, however, that a repetition of these experiments using modern instrumentation and equipment together with a more critical analysis of the data in light of present day theories of turbulence should prove a fruitful avenue of research.

Bomelburg[6] has suggested an unusual procedure for using an alpha-emitter in connection with boundary layer studies in air. He points out that it is possible to photograph a velocity profile of an air flow by means of a series of low-current electrical sparks if the interval between subsequent sparks is kept short. Each successive spark uses the ionized path of its predecessor. Photographs of sequential paths serve as a measure of the velocity profile. Interpretation of the data requires that the initial spark path be long and straight. This is accomplished by using a narrow collimated beam of alpha particles to produce an ion path. To date the experimental work has been of a preliminary nature; however, it is potentially applicable to such difficult problems as unsteady compressible three dimensional boundary layer flow.

The present authors have proposed and used a still different approach to the measurement of velocity distributions. This method has particular advantage in the study of shear flow for example in the wall adjacent region in flow in pipes. This procedure, called the tracer displacement technique, has yielded very interesting data when applied to both streamline and turbulent flow.

TRACER DISPLACEMENT TECHNIQUE

The principle of the tracer displacement technique is very simple although the full interpretation of the data may present some problems. A brief outline of the experimental technique follows. Consider a pipe or tube through which a fluid is flowing. Now consider the fluid present in a particular section of this pipe at a particular instant. As flow proceeds this fluid is displaced from the section by fluid moving in from upstream. The rate and manner of this displacement are dependent upon the velocity distribution within the fluid. If now either the fluid being displaced or the displacing fluid is made radioactive, the rate and manner of displacement can be observed externally to the conduit. From these observations, it is possible, in principle at least, to draw quantitative inferences regarding the velocity distribution.

This may be illustrated most easily by describing first the procedure and observations in laminar flow. The lower half of a long vertical tube is filled with a dilute solution of radioactive salt. (In the authors' work Na_2CO_3, sodium-24, solution of 0.2 mc/cm^3 is used.) The upper half of the tube is carefully filled with a corresponding solution of inactive salt. Care is taken to minimize mixing of the two solutions at their junction plane.

After the tube has been filled in this manner, flow is rapidly but smoothly started. Flow is maintained by continuously supplying inactive solution at the upper end of the tube from a constant-head tank.

A suitable radiation detecting device is located at a fixed position below the initial junction plane. In the authors' work thallium-activated sodium iodide crystals light-coupled to photomultiplier tubes are located at distances of 12 in. and 30 in. down from the initial junction plane. A continuous record of the output of the photomultiplier tubes is used as a measure of the amount of radioactive solution in the tube at each position at any instant after the start of flow.

When the motion of the radioactive fluid is truly laminar, the calculation of velocity distribution from the observed rate of displacement is straightforward.[7] For a strong gamma emitter such as sodium-24 and with pipes of moderate diameter (the authors used ½ in. and 1 in. diameter), the geometry between the detector and the active fluid is substantially unchanged as displacement proceeds. Consequently, thickness of the undisplaced layer of active fluid may be calculated from the ratio of the observed activity at some time, t, after the start of flow to the activity before the start of flow (i.e. when the section of the tube opposite the detector was full of active solution). For truly laminar flow in a tube of circular cross section, the thickness, y, of the annular ring of undisplaced active solution may be calculated from

$$y = \frac{D}{2}[1 - \sqrt{1 - A/A_0}] \qquad (1)$$

where D = diameter of the tube, A = observed activity at time, t, after start of flow and position, x, downstream from initial junction plane and A_0 = observed activity prior to start of flow, i.e., with the tube full.

The resolving power of the procedure is shown in Equation 1 to be limited by the ability to measure the ratio A/A_0 which in turn is limited by the magnitude of the background radiation. Amounts of activity which may be readily handled permit measurement down to values of y of 0.00001 in. or less.

A second and more important limit to the resolving power is the failure of the flow to be purely laminar on a molecular basis. With aqueous solutions of sodium carbonate, the molecular diffusion of the sodium ion becomes an important factor in attempts to measure velocities nearer than 0.015 inch from the tube wall. The use of more viscous solvents and higher molecular weight solutes have provided successful measurements to within 0.0015 inch from the wall. The results of one such run using glycerine as a solvent are shown in Fig. 1. Still closer measurements than these are possible.

Application of the tracer displacement technique to studies in turbulent flow holds much promise particularly in the wall-adjacent region. The existence of eddy diffusion as well as molecular diffusion complicates the interpretation of data. Near the tube wall where eddy diffusion is very small (or nonexistent if the laminar sub-layer theories are correct), semiquantitative interpretation of data should not be difficult. A number of mechanical difficulties arise in turbulent flow experiments that are only now being overcome. The results of some preliminary work are shown in Fig. 2. For convenience, these data have been presented on the same coordinates as the data for laminar flow. The abscissa values of y have been calculated from the activity measurements

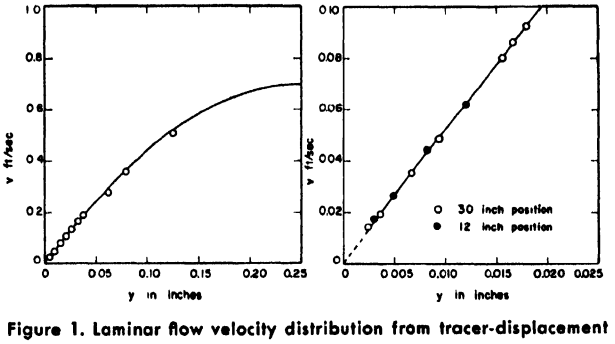

Figure 1. Laminar flow velocity distribution from tracer-displacement data. (a) An entire parabolic profile as determined using an aqueous glycerine solution with sodium carbonate as tracer at a Reynolds number of less than 1000. Data points represent values taken at both detector positions. (b) A portion of the data near the wall enlarged to show the general precision of the data even in this region. Data taken at the two detector positions have been differentiated to show the close agreement. Since data actually are obtained as a continuous curve, the data points on these figures simply represent those values selected for calculation and plotting

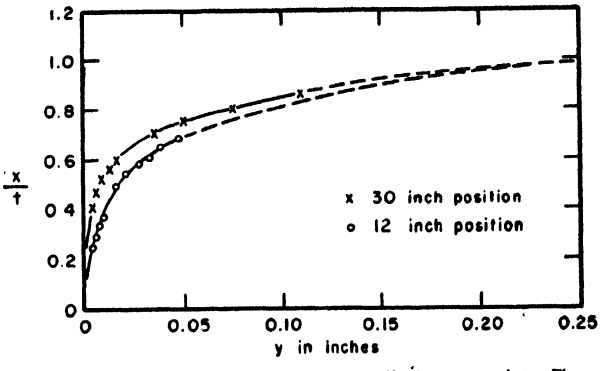

Figure 2. Turbulent flow curves from tracer-displacement data. These data were obtained using dilute aqueous sodium carbonate solution flowing at an average linear velocity of 0.87 feet per second in an aluminum tube one-half inch inside diameter. The corresponding Reynolds number is 4200. The units on the ordinate are feet per second. The smoothness of these curves illustrates the manner in which the counting technique effectively average the local eddying. The spread between the curves for the two counting positions suggest that this may well be a measure of the eddy diffusion

by Equation 1 and represent the thickness equivalent to the amount of activity remaining in the given section of tube at the time, t. The ordinate values, x/t, have the units of velocity.

The two resulting curves will require careful interpretation. They represent velocity distribution across the tube modified by the effects of eddy diffusion. The data were taken simultaneously on a single run with two radiation detectors, one located 12 in. downstream and the second 30 in. downstream from the original junction plane. It will be noted that for given values of the ordinate, the values of y are smaller for the 30 in. position than for the 12 in. position. This suggests that the divergence of the two curves may well be a measure of the magnitude of eddy diffusion in the tube.

In this experiment the average linear velocity was determined by measuring the time required to collect a known quantity of fluid. On this basis the mean velocity was calculated to be 0.87 feet per second. This is in substantial agreement with the extrapolated portion of the curves.

FUTURE USES

The review of the various techniques for the use of radioactive tracers which has been presented suggests many possible uses for this tool in the study of fluid dynamics. The simple extension of the tracer displacement technique to an experimental study of such problems as the laminar flow of liquid metals, high viscosity fluids such as polymers and greases, and the laminar flow of non-Newtonian fluids, are among the more obvious. It has been pointed out that the molecular diffusivity of the solute molecules is a limiting factor in the application of the tracer displacement technique in laminar flow. The extent of this limitation is quantitatively related to the diffusion coefficient and it appears that the technique may be adapted to provide a new method for determination of these coefficients.

Probably the most universally important problem in fluid dynamics at this time is the general study of turbulence in fluids. Specifically, this includes the study of homogeneous turbulence, turbulent shear flow, boundary layer study, and turbulent pipe flow. Due to the extreme complexity of the problem and the impossibility of a complete mathematical description of it, continued experimental work is a necessary part of any further understanding of turbulence. The use of radioactive tracers as a new tool for such studies is one which shows real promise of providing new and valuable data.

It is not yet clear which if any of the experimental methods described will prove the most effective application of radioisotopes for a detailed study of turbulent motion. It seems probably that much better techniques will be forthcoming in the future. Certainly if the uses are to be extended to supersonic flows or certain other important problems of the day, entirely new procedures will have to be employed.

Most of the present techniques make use of a gamma emitter as a tracer, and thus absorption of the radiation by the fluid is not a factor. For this reason, the detected radiation is an integrated average of the radiation from all parts of the fluid which the detecting element sees. In such a system, local velocity fluctuations or eddies may be masked since only the total amount of tracer in view of the detector is measured. This difficulty may be overcome either by variation of procedure or by use of other types of radioactivity. For example, the tracer displacement technique, which has been described in some detail, makes use of the rate of displacement of the tracer material from a given location in the tube. Consequently different portions of the fluid are observed sequentially during the displacement and information can be obtained on the behavior of the fluid at various relative radial positions.

Beta-emitting tracers, and perhaps also alpha emitters, may be used to determine the distance of the disintegrating tracer atom by measuring the absorption of these radiations by the fluid. The use of beta emitters should permit measurement of the actual velocity distribution within a boundary layer of a fluid flowing over a flat plate and of the velocities near the wall of a tube or duct. It seems reasonable that this method will also give some information on velocity fluctuations and turbulent eddies.

The recent development of scintillating liquids which can be used with an external radioactive source for excitation provides still another variation of the methods. Continuous neutron irradiation of the flowing system with subsequent counting of the activity produced may well become a practical tool as reactors become more accessible for general research.

The use of radioactive tracers and the experimental methods described are particularly well adapted to the study of mass transport or dispersion of a dissolved material in a flowing fluid. It is certain that some of the major problems in this field can be attacked by this method. In particular, the analysis of eddy diffusion should be amenable to study by the use of tracers. The authors have no feeling of prescience in predicting that the future will see great increase in the use of radioisotopes in the study of all phases of fluid flow and particularly in the field of fluid mechanics.

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Radioisotopes in Petroleum Refining, Research and Analysis

By D. E. Hull and B. A. Fries,* USA

The petroleum industry has led all others in the application of radioisotope techniques to its technological problems. The nature of its plants and processes has encouraged the development of a wide variety of radioactive methods and instruments in the scant decade since reactor-produced isotopes first became available. This paper is a survey of these applications, giving more emphasis to recently published techniques than to those better known, and also including several applications which have not yet been described in detail in the open literature.

We have attempted to include examples of all important uses of isotopes in petroleum refining, research, and analysis. The examples selected fall in four main groups:

1. The handling of liquids and fluidized solid in steel pipes and vessels, often thick-walled and heavily insulated to accommodate high temperatures and pressures, presents challenging problems of measurement and control. Many such problems have been solved through the use of radioisotopes, after other techniques had failed.

2. Keen competition in the industry puts a premium on cheaper and faster methods of testing products, and here, too, radioactive methods have met the challenge.

3. The complex mixture of the hydrocarbons coursing through a refinery complicates the problem of analytical control, but a properly chosen radiation can often single out one component from the mixture for a rapid analysis which permits control of the process.

4. Radiotracers also find use in laboratory as well as full-scale plant studies of the fundamental chemistry of petroleum refining processes and the behavior of petroleum products.

The continuous monitoring of refinery streams and processes with application to automatic control is seen as a logical development of the next decade.

REFINING APPLICATIONS

The movement of fluids through pipes is a basic operation in the refining of petroleum, as it is in many other industries. Radioactive tracers have been used to measure this flow and to provide information from which valuable inferences may be drawn concerning the fluids in the pipe or in the vessels from which they come. The flow rate of liquids in the pipe can be determined. The volume of fluids contained in holding tanks or in circulation in a complex system can be inferred. The residence times in a continuous reaction unit can be measured. Uniformity of flow in large units can be checked. Diversion of flow into wrong channels can be detected. Interfaces between different batches of process materials can be marked. The extent of intermixing and the efficacy of devices to minimize mixing between batches in a continuous process can be measured. Blending of refined stocks or separation of components being refined can be followed in process to indicate completeness of the operation.

A discrete volume of radioactive tracer is introduced into a moving mass of fluid in which it is soluble. If the fluid is a liquid in turbulent motion in a pipe, the tracer spreads in a manner that has been expressed mathematically by Hull and Kent.[1] The tracer mixes ahead and behind in the carrier stream. The random, independent movements of tracer molecules average out to a Gaussian distribution about a center which is identified with the point of injection, displaced through a distance corresponding to the average mass flow of the liquid. The mean square displacement of the tracer relative to the point of injection increases with the square root of elapsed time. At any finite time, in a pipe of unlimited length, the Gaussian distribution persists, while the concentration curve continues to grow broader and flatter. If the volume of the liquid is limited, as in a closed system, the Gaussian curve becomes obliterated and eventually the tracer comes to a uniform concentration throughout the system. By suitably selecting times and locations for measuring the radiation from the tracer, one can obtain a variety of information about the moving liquid.

Flow Rates

An elementary application of this technique is the measurement of flow rates in pipes. The tracer is observed in transit at two points on the pipe, and the time of passage of the peak of the wave is determined. The interval between the two transits is combined with the distance between the observation posts to obtain linear flow rate, or with the volume of the pipe between the two posts to obtain volume flow rate. The pipe should be of uniform diameter and free from connecting branches. The radiotracer is injected quickly, at a point close to the section in which it is to be timed, in order to obtain sharply defined peaks. By connecting the detecting elements

* California Research Corporation, Richmond, California.

together it is possible to record the tracer peaks at the two points on the same chart recorder. This method is practical in petroleum refineries only with gamma emitters, such as cobalt-60, antimony-124, cesium-134, and barium-140. Quantities of the order of a few tenths of a millicurie are adequate for pipe sizes under 10 inches. It is more difficult to measure gas velocities in this way because of rapid mixing.

Catalyst Flow Rates

The principle of timing a burst of counts from a radiotracer has also been used by Hull and Bowles[2] in measuring solid flow rates in circulating catalyst systems. In the catalytic cracking process, the speed of circulation must be controlled for safe operation, optimum yield, and minimum catalyst attrition. The circulation speed can be measured with the aid of radioactive labeled catalyst beads. A few beads impregnated with zirconium-95, about 0.5 millicurie each, are added to the circulating system. A long pipe, called the seal leg, at the top of the reactor is surrounded by two rings of Geiger counters, one near the top and the other near the bottom. A radioactive bead passing these detectors produces a burst of counts first at the top ring, then about a minute later at the bottom ring. These signals are plotted together on the same strip chart, from which the time interval may be accurately determined. Dividing the calculated capacity of the seal leg by the observed time interval gives the circulation rate of the catalyst. The deviations in a series of measurements may be considered as being distributed along a Gaussian probability curve. The bead corresponds to a single molecule which may be displaced ahead of or behind the mean bulk displacement. The experimentally observed fluctuations in a 32-foot length of pipe had a standard deviation of $\pm$ 2%.

This method has been developed in an instrument for routine plant control which automatically performs the necessary arithmetic and plots the catalyst flow rate on a chart. It does not give a continuous reading because it depends on the passage of individual beads randomly spaced in the bulk of the catalyst. In practice, however, two or three radioactive beads in a total plant inventory of 2×10^{10} ordinary beads have been found to give readings with satisfactory frequency.

Dilution Method

An alternative method for measuring flow rates which is applicable in either liquid or gas streams is to bleed in a tracer at a fixed rate. The concentration of the tracer in the pipeline is inversely proportional to the flow rate. The concentration may be determined by measuring either the beta or gamma activity in samples taken from the line at a point downstream. If a gamma emitter is used, the method may be simplified by attaching a counter outside the pipe and measuring the concentration through the wall. This avoids the sampling step and is more readily adaptable to continuous monitoring of flow rates, although it is inherently less sensitive than the measurement of samples in the laboratory. The dilution method of measuring flow rate was illustrated by the measurement of condenser water flow in a steam power plant by Karrer, Cowie, and Betz.[3] Radiosodium chloride was injected into the stream at a uniform, measured rate. Samples taken downstream were measured with a Geiger counter to determine the steady-state level of activity. The ratio of activity in the injected tracer to that in the stream, multiplied by the injection rate, gave the condenser flow rate as 33,000 gallons per minute. By this technique it is possible to measure very large flow rates with moderate quantities of activity.

Total Count Method

Hull[4] has described a radiotracer method for measuring fluid flow that eliminates the need for the second observation point and the known volume between the two points. It is based on the principle that the total number of gamma rays registered by a Geiger counter on the pipe through which a definite quantity of dissolved radioactive material passes is inversely proportional to the velocity of flow. At the same time, the integrated count is independent of the way in which the radioactive intensity varies along the stream, as long as it passes at constant speed. This principle, which can be demonstrated mathematically, was first experimentally validated in field pipeline tests. A given tracer, observed at points so far apart that extensive spreading occurred during transit from one to the other, was found to give the same total number of counts in excess of background while passing each point.

To apply the total count to an absolute determination of flow rate, it is necessary to calibrate the counting setup on the particular type and size of pipe involved. This is done by filling a cut section of the pipe with a solution of the radiotracer at known concentration and measuring the counting rate on a counter tube which is attached to the pipe in the same way as in the field measurements. The dimensions of this calibration factor,

$$\frac{\text{counts}}{\text{second}} \Big/ \frac{\text{millicuries}}{\text{barrel}}$$

can be transposed into the form,

$$\frac{\text{counts}}{\text{millicurie}} \cdot \frac{\text{barrels}}{\text{second}}$$

If the calibration factor is known and if the measurement is made in the same geometry, the total number of counts during passage of a known number of millicuries of tracer can be translated into the flow rate in barrels per second.

This method has been found useful in the measurement of a wide variety of plant streams. Water lines and various hydrocarbon streams have been measured. Pipes have been calibrated ranging in diameter from 1 to 14 inches, of different wall thickness, with and without concrete lining or magnesia insulation. A typical calibration factor is 475 in the

above units for cobalt-60 in a 4-inch pipe. Accuracies of a few per cent are obtainable in the most favorable circumstances, although in many cases corrosion or deposits in a pipe long in service introduces a larger deviation from the calibration standard.

Volume and Residence Time

Occasionally the volume of liquid in a closed system is desired.[4] It may be difficult to calculate the volume because of irregular dimensions of the container, or the calculated volume may not apply to the actual liquid volume because of foaming. If there is a mixing action, either by circulation or internal stirring, this problem may be solved with a radiotracer by a dilution method. A known volume of radioactive solution is introduced into the system and allowed to mix to equilibrium. Then, its concentration is measured in comparison with the initial concentration of the tracer. The dilution ratio multiplied by the original volume gives the desired unknown volume. For example, the volume of sulfuric acid in an alkylation plant was required. There was no well defined level because of extensive intermixing between the acid and the hydrocarbon phases. The desired information was found by adding to the system 2 millicuries of radiocesium-134 in sulfuric acid. While the tracer was being mixed, samples were withdrawn and counted in comparison with a standard prepared by dilution. From the equilibrium concentration of tracer thus determined and the total quantity added, the total volume of the sulfuric acid (24 barrels) was found.

Attrition Method

Another tracer method in which attrition is measured is applicable to tanks through which there is a known constant flow.[4] Mathematical treatment of such a case, assuming complete mixing of the tracer injected in the incoming stream with the contents of the vessel, predicts that its concentration, c, in the tank decreases exponentially. The rate of decrease is determined by the throughput rate, R, and the volume, V, as follows:

$$-\frac{d \ln c}{dt} = \frac{R}{V}$$

The alkylation plant in the previous example was also checked by this method. The radioactivity of samples taken from the system from time to time for 30 hours following the injection was measured and plotted on logarithmic coordinates. The known throughput rate divided by the slope of this plot gave the volume of the acid phase as 28 barrels.

The determination of volume by the attrition method involves a factor, the mean residence time, which often constitutes information valuable in its own right. In many chemical reactions, the time spent in the reaction vessel is important in determining the yield of the reaction. Examples might be in thermal cracking of gas oil or in alkylation processes. Whenever the mixing time is short compared to the residence time, the latter variable can be measured directly by the technique just described. Mathematically, the mean residence time is the time for attrition to a value $1/e$ of the original, or the reciprocal of $d \ln c/dt$ in the above equation.

Peak Circulation Method

The volume of a liquid circulating in a closed system can be determined by yet another method, if the dispersion volume of the tracer during the circulation time is considerably less than the total volume. The tracer is observed in repeated cycles at some convenient point in the system. The time between successive appearances of the tracer peak, multiplied by the circulation rate, gives directly the total volume of the circulating liquid. This is illustrated by a test made on a large vacuum distillation column by Gester, Lee, and Hull.[5] Cobalt-60 tracer was injected into a reflux line with heavy gas oil. A counter attached to the outside of the column showed an initial peak, followed after an interval by an attenuated peak. It was possible to observe the time interval for three or four circuits, before the tracer peaks spread out and merged into the background. This principle also has been applied to the determination of the total quantity of solid catalyst circulating in a catalytic cracking unit by noting the average time required for the complete circuit of radioactive beads through the system and multiplying it by the flow rate, determined from the same beads as described above.

Flow Paths

Sometimes the course of process materials among various possible paths inside a plant unit may be a subject of doubt or even of vigorous argument among the unit's operating crew. Radioactive tracers often make it possible to resolve the question while the plant continues in normal operation. An example of this was demonstrated in the investigation of the flow distribution in a large vacuum distillation column.[5] Bubble cap trays in the column were each divided by baffles into eight channels. Entrainment of heavy metals and color in the heavy gas oil stream raised the suspicion that not all of the bubble caps were filled. Such a condition would arise if the flow of the liquid over the trays was not uniform. The uniformity of flow was tested while the column was operating by injecting 7 millicuries of radioactive triphenylstibine into the column and observing the response on eight Geiger counters, each attached outside the column at a point opposite one of the eight channels on one tray. Four of the counters, all on the same side of the column, simultaneously showed a strong response as the tracer flowed down; the other four, on the opposite side, showed either a weak or zero response. The conclusion that the liquid was flowing over the trays on only one side, leaving the bubble caps on the other side open to pass unscrubbed vapor to the column, was verified visually when the plant was shut down for repair.

Paths in Catalyst Circulation

The flow pattern of catalyst beads in various parts of a circulating system has been determined with the use of radioactive beads.[6] A difference of opinion about the value of an intricate system of baffles for promoting uniform flow through a large sloping pipe at the bottom of a furnace was settled by this means. A pair of Geiger counters, one at each end of the pipe, was placed successively on the top, on the bottom, and on each side of the pipe. The speed and relative number of radioactive beads which followed these various paths were recorded. A large difference in both speed and number of transits between the different paths showed that the baffles did not serve their intended function. In a similar plant, the rate of bead movement down different paths near the periphery of a large, regenerating furnace was used as a basis for adjusting the orifice plates at the bottom to obtain more uniform flow. These applications of tracers have yielded valuable operating data which could not be obtained in any other way.

Leak Testing

The diversion of any fluid stream from one channel to another can be readily detected with radioactive tracers. Sometimes the extent of such a leak can be measured quantitatively. Leakage between the cross-streams in a heat exchanger offers an excellent example of this technique.[4] A radioactive tracer was introduced quickly in the heating stream inlet. Geiger counters were attached to the exit pipes of both the heating medium and process streams. When activity appeared at the counter on the process stream, it disclosed the existence of a leak. The extent of leakage was judged by the size of the tracer peak compared to the peak on the other stream. Leaks of a few tenths per cent have been detected by this method.

Interface Marking

The applications considered heretofore have dealt with tracing a single component in refining operations. When two miscible stocks are brought together, the introduction of a tracer in one of these or at the interface between them opens another field of possibilities. The position of the interface can be fixed by means of its radioactivity as long as it remains an identifiable entity. Until intermixing between the liquids obliterates the interface, the extent of the intermixing can be measured. Finally, complete mixing is shown by a uniform level of activity.

A simple application of this type is the marking of interfaces between different fuels transported consecutively through the same pipeline.[7] It is possible to distinguish between them at the delivery point, if an oil soluble radioactive tracer is injected into the stream when the interface is formed at the pumping station. Geiger counters attached to the pipe at the terminal station give a signal when the interface arrives. Antimony-124 in the form of triphenylstibine is most widely used for this purpose; cobalt-60 naphthenate is also used when long-term residual radioactivity is not a problem. The signal from the interface becomes progressively weaker the farther it is transported from the point of injection, but a millicurie or two of radioisotope provides a satisfactory signal after several hundred miles.

For several years, a system of this kind has been used routinely on a products pipeline from Salt Lake City, Utah, to Spokane, Washington.[8] This line is particularly complex in the number of different products carried and in the number of delivery points served. Reports to the dispatcher from each station as to the exact time each interface passes provide an accurate picture of the position of each batch in the 700-mile pipeline. A 3-mile line at Skagway, Alaska, used for delivering the cargo from tankers to storage, is also equipped for the routine tracing of interfaces.[6]

Interface Mixing in Pipelines

A radiotracer can be used not only to identify an interface but also to measure quantitatively the degree of intermixing of the two components across the interface.[9] This intermixing in a trip of several hundred miles extends through a volume of hundreds of barrels. To meet the rigid specifications which must be observed in some mixtures of petroleum products, such as gasoline in stove oil, and at the same time to minimize wastage, requires an accurate measure of the extent of cross-contamination. While it would be possible to label one stock with radiotracer at a uniform level and use the radioactivity as a direct measure of its concentration, Hull and Kent[1] have shown that the use of a narrow interface marker between the stocks gives a much more sensitive measure of the extent of intermixing and also requires much less tracer. Under ideal conditions, the experimentally determined plot of activity versus time during passage of the labeled interface follows the theoretically predicted Gaussian form. The counting rate at each point across the interface is proportional to the derivative of the concentration at that point. It is possible to detect the limits of the contaminated zone between two stocks with much greater sensitivity than by measuring a difference in some property which is proportional to the concentration itself, such as specific gravity, color, or dielectric measurements. Experience in operation of the Salt Lake pipeline has shown that this mathematical principle can be used to meet precisely specifications as to limits of contamination of products shipped by pipeline and at the same time to reduce very substantially the volume of contaminated interfaces returned to the refinery for reprocessing.

The intermixing to be expected at various stations in any pipeline operated under turbulent flow conditions can be estimated with the formula given by Hull and Kent[1] if the mixing coefficient is known. Taylor[10] has given a theoretical basis for calculating this from the physical properties of the system. According to his derivation, the mixing coefficient is proportional to the pipe diameter, the velocity of flow, and a logarithmic function of the Reynolds

number. His formula, well checked by laboratory experiments with small pipes, was shown to hold also for the much larger pipes in commercial use over level terrain. Mixing in two of the lines reported by Hull and Kent was consistent with the theory. The third, following a mountainous route, showed a systematic divergence from theory in the direction of greater mixing, caused by the curvature of the pipe.

Blending Efficiency

Although Taylor's[10] work provides a substantial theoretical basis for the study of turbulent mixing in pipes, very little basis exists for understanding the mixing of liquids which are stirred in a vessel. Two quantitative measures of the degree of mixing have been proposed by Danckwerts:[11] (1) intensity of segregation, which measures variation in concentration from point to point, and (2) scale of segregation, that is, the dimensions of regions of unmixed components. Both these factors approach zero as mixing proceeds to completion. If a radioactive tracer is added to one of the components, both factors can be measured by the radioactivity as a function of time, intensity along the ordinate, and scale of segregation along the abscissa (time $\times$ flow rate $=$ volume). A typical mixing curve might fluctuate between zero and the original activity of the labeled component over relatively large regions at the beginning; as mixing progresses, the intervals of zero and maximum activity must become smaller, and regions of varying intermediate activity more frequent. The activity level would fluctuate through continually decreasing amplitudes and finally settle down at the average level for the completely mixed liquid.

Some of these characteristics were illustrated in a crude way by a test made on a large refining unit.[4] A 50,000-barrel surge tank in the feed line to a thermal cracking plant received stock from two main sources, which varied from time to time in viscosity and other properties. The contents of the tank were mixed by pumping the liquid through a side loop at a rate of 100,000 barrels a day. Fifty millicuries of a soluble zirconium-95 compound was injected in a volume of 50 barrels into the tank. The effectiveness of the surge tank in minimizing variations in the mixed feed was studied by watching the activity registered by counters attached to the loop and to the outgoing line. The largest intensity of segregation observed was 0.22% of the activity of the labeled batch, but fluctuations between zero and 0.2% continued throughout the period of the test. Statistical analysis of the counting data indicated a scale of segregation of the order of 500 barrels. It was apparent that mixing was considerably less than ideal.

Mixing between Crudes in Distillation

An attempt was made to use an interface marker in the feed to a distillation battery to segregate as closely as possible the tar bottoms from two different crudes.[4] The battery comprised four stills in series. At the time of switching to the new crude, 10 millicuries of radiocobalt naphthenate was added to the feed. The tar line leaving the battery was monitored for several days with a Geiger counter. If the stocks had followed a pistonlike displacement pattern through the stills, the interface tracer would have appeared 21 hours after the injection. Actually, the activity began to appear in the outgoing stream after only two hours. The tracer spread out into a broad, diffuse wave, with a peak at 14 hours and a tail persisting into the third day. The curve to be expected if complete mixing occurred in each still was calculated, using data on volumes and throughputs supplied by the operators. It matched the observed data to a close approximation, indicating that mixing was not much short of ideal. Thus, it proved quite impractical to effect the desired sharp break between the tars from the two crudes.

Separation Processes in Refining

In contrast to the wide and varied applications of radiotracers to operations which involve movement or mixing of stocks, only a few applications have been made to operations in which components of petroleum stocks are separated. The first kind of operation requires only that the tracer be physically and chemically compatible with the stock traced, while the second requires a similarity of physical and, perhaps, chemical properties which approaches the identity of isotopic compounds. An isotopic tracer is required, for example, to measure the distribution of a compound which can occur in both phases in a distillation.

The most useful isotopic tracers for studies of petroleum processing operations would be carbon-14, sulfur-35, and hydrogen-3; but the short range of the soft beta rays emitted by these isotopes, especially by tritium, makes them inconvenient to measure even in the laboratory, and next to impossible under typical refinery conditions, viz., at high temperatures and pressures and behind thick steel walls. The development of liquid scintillation counters for routine industrial use will make the application of these isotopes much more attractive, although it will be necessary in most instances to take samples out of the plant.

Entrainment of Tar in Distillate

It is not always necessary to use isotopic tracers to follow separation processes. Many important problems exist where the component of interest exists only in one phase, and its presence in the other phase is due to an incomplete separation of the phases. In this situation, much greater latitude is allowable in the selection of a tracer material, and use of a gamma emitter makes it possible to follow movement of stocks in process during continuous operation. Such a tracer may be thought of as a phase tracer rather than a tracer for a specific material.

An example of phase tracing is the study of entrainment of tar in overhead streams in evaporators

and distillation columns. Tar cannot be tolerated in refined products; also, it must be excluded from many process streams to reduce coke formation and increase plant operating time. A plant-scale test was made of the tar entrainment in an evaporator in a thermal cracking plant. Ten millicuries of cobalt-60 naphthenate, as a tracer for the tar,[4] was injected into the feed to the evaporator. A counter, attached to the pipe carrying the still bottoms to the tar tanks, recorded the activity of the bulk of the radiocobalt, which passed through this pipe. Another counter, attached to the overhead stream from the evaporator, picked up the activity of cobalt in that stream. By totaling the counts on both streams and making corrections for different flow rates in the two pipes, a quantitative measure of the tar entrainment in the distillate was obtained. Values ranging from zero up to a few per cent, depending on operating conditions, were found. Similar studies have been made in lubricating oil fractionating columns.[6]

Level Gages

Radioactive level indicators are finding increased application in refinery technology, where liquid or solid levels must be measured and controlled in process vessels and tankage. The need for radioactive methods has arisen because of extreme operating conditions, both in temperature and pressure, in refinery process vessels, and because refinery tankage frequently contains corrosive materials, e.g. sulfuric acid, sodium hydroxide, and hydrofluoric acid. Under these conditions the usual gages, such as floats, hydrostatic pressure indicators, or thermocouples, behave unsatisfactorily or become inoperative due to coking or fouling. Radioactive level gages are not affected by the physical conditions within vessels. Their particular advantage is that levels may be gaged by measurements made completely outside the vessel. Automatic level controls may be made from radioactive level gages.

Radioactivity methods are based upon the attenuation of radiation by the vessel contents, upon differences in backscattering of radiation by the contents, or upon the movement of a float containing a radioactive source. In the float-type gage a movable detector outside the vessel locates the floating source, or use is made of the inverse square variation of response of a detector above the float. This type is useful where other radioactive gages are unsuited to the size or shape of the vessel. It suffers from the same disadvantages as other float-type gages. In backscattering gages gamma rays from a few millicuries of cesium-137 or radium strike the outer wall of a vessel, and a detector registers the scattered rays which emerge on the same side. The backscattering above the liquid level is due to the wall only; below the level, scattering is increased by the presence of the liquid, and a higher count rate is observed. While the reflection gage is completely independent of vessel size, it is limited in range to a wall thickness of about ¾-inch.

Cut-Off Level Gage

A wide variety of source-detector arrangements is employed with the attenuation gage. The simplest is an "on-off" type consisting of a gamma-ray source and Geiger tube, both located outside the vessel at the same elevation but on opposite sides. When the level inside the vessel is below the line between source and detector, the radiation is transmitted through the vessel walls and vapor space. When the level reaches this line, the radiation is greatly attenuated, and the count rate falls sharply. Vessels of many feet diameter may be gaged within an inch, using sources of cobalt-60, cesium-137, or radium of suitable strength. A recent petroleum application of this method is the measurement of the coke level within a petroleum coke drum.[12] More complex arrangements include a multiple source with a single detector, a single source with a multiple detector, and a multiple source with a multiple detector.

Depth Gage

A radioactive depth gage utilizes the absorption of gamma radiation in a vertical column of liquid or solid and measures continuously the radiation transmitted through the column of material. The detector may be located outside and below the vessel, while the source may be outside and above the vessel or in a well within the vessel. The gage is calibrated by measuring the radiation intensity at known levels. The useful range with cobalt-60 sources of several hundred millicuries strength is about 5 feet.

This gage is employed in the control of tar levels in thermal cracking units at several refineries.[6] Gasoline production is increased when the tar level is kept high, but the level must not be so high as to result in entrainment of tar in the overhead stream. Hence, operation for optimum production requires accurate level control. The cracking vessels are about 8 feet in diameter with steel walls about 3 inches thick. The tar depth is maintained up to 4 to 5 feet. A 200-millicurie cobalt-60 source is centrally located within the vessel in a well above the liquid level. With the source located inside the vessel the required source strength is reduced because the radiation need shine through only one wall thickness. Further, no provisions for radiological shielding are necessary. A Geiger tube and and count ratemeter with recorder may be used, but because the attenuation of radiation is exponential with respect to thickness, a nonlinear response in count rate and recorder reading is obtained, and at higher liquid levels the depth scale becomes tightly compressed. This inconvenience is neatly overcome by the use of a commercially available logarithmic ionization chamber in place of the Geiger tube ratemeter circuit.[13] The naturally exponential response of the ion chamber to radiation intensity, in combination with the exponential character of attenuation, produces a nearly linear chart record over a range of tar depths from zero to 5 feet.

Density Gages

In a path of fixed length through an absorbing medium, the linear absorption coefficient of gamma rays is directly proportional to the density of the medium. Based on this principle, methods have been developed for measuring the density of liquids in process lines and vessels with radioactive sources and instruments mounted outside the equipment.[14] A gamma-ray gage has been installed on a Canadian products pipeline for continuous recording of density.[15] It is used for separating batches of products received by pipeline. Cobalt-60 or cesium-137 is used for the gamma-ray sources, and pressured-argon ionization chambers serve as detectors. One source-detector couple looks through the pipe, and another couple is wired in opposition to the first to provide a null-balance reading. This provides a high sensitivity, which is further enhanced by a range adjustment to spread the differences for any set of liquids over the most advantageous portion of the scale. The accuracy of the gage increases with pipe diameter, and on a 24-inch pipe is ¼°API, equivalent to about 0.001 gm/cm^3. Beta rays could also be used for density measurements, but only on very thin liquid samples.

Maintenance of liquid level during a continuous process is one of the most basic operations of automatic control, and radioactive instrumentation has already been readily adapted to this function. Flow rate is another operating variable which may be chosen for primary control. In other processes, density of a product stream might be monitored for control. Uniformity of composition, appearance of entrained spray in a distilled product, or leakage into an undesired channel might be used for automatic cut-off of a process. These are examples of application of radioactivity to petroleum refining which may find a place in future plants as the trend to automatic control continues.

ANALYTICAL APPLICATIONS

The analytical phase of many chemical and physical studies is greatly simplified by the application of radioisotopes. Labeling a substance makes it easier to separate or isolate; its activity may be used to measure the degree of recovery or for its final determination. Studies of the kinetics and mechanisms of chemical reactions, the fate of various substances in fuels and lubricants, and the wear of activated engine parts are typical examples of this kind of analytical application. But, in addition, new applications have been developed for the analysis of specific elements by making use of the radiation properties of selected radioisotopes. Rapid, accurate analyses for sulfur and for hydrogen in hydrocarbon materials can be made by these new methods.

Sulfur by X-ray Absorption

X-ray absorption methods for the analysis of sulfur or chlorine have been used for many years, the source of X-rays being high voltage generating tubes. Because X-ray absorption is not specific for any element, the analysis is limited to simple systems of two or three elements, such as sulfur in liquid hydrocarbons. It is advantageous to select an energy at which the mass absorption coefficient for sulfur is many times greater than for carbon and hydrogen. With 25 kev X-rays (0.53Å) the mass absorption coefficients of carbon and hydrogen are equal and the attenuation is independent of changes in carbon and hydrogen content; at other wave lengths, the carbon-hydrogen composition must be taken into account. Corrections must always be applied when more than a few hundredths of a per cent of other elements is present.

As a substitute for a high voltage X-ray tube and its accessory electronic equipment, a monochromatic radioactive source of X-radiation offers a number of advantages. Constancy of radiation intensity is attained without the need for voltage and current regulation. This imparts compactness and results in considerable instrumental simplification and lower cost. Iron-55 is a radioisotope that serves this purpose. It decays with a half-life of 2.9 years and emits manganese X-rays, the Kα line of which is 6000 ev (2.1Å). At this energy, the mass absorption coefficients of carbon and hydrogen are not equal (10 and 0.5 cm^2/gm, respectively), but that of sulfur is very much greater (200 cm^2/gm). The carbon-hydrogen content of the sample being measured must be known.

Hughes and Wilczewski[16] have described equipment suitable for this analysis in the concentration range 0.05% to 3% sulfur, using a 4-mc source of iron-55. Provision is made for moving the source relative to the Geiger tube to compensate for radioactive decay. The sample cell, fitted with thin beryllium windows, holds 1.5 ml of sample. The density of the sample is determined separately. From the density, the carbon/hydrogen ratio, and count rate of the sample, the percentage sulfur is calculated using the absorbances of sulfur, carbon, and hydrogen measured with standards in the same equipment. The analysis requires only a few minutes and is as accurate as the lamp sulfur method.

Fries[6] independently developed similar equipment which has been in routine refinery use for almost two years for the measurement of the sulfur content of thermally cracked gasoline. This equipment was made rugged and semiautomatic for use by nontechnical refinery personnel. The equipment is shown in Fig. 1. For a sulfur analysis the sample is poured into the funnel, and the scaler is started by pushing a button. While a fixed count is being automatically timed, a hydrometer reading is taken on the rest of the sample. After the timer stops, the readings from the timer, the hydrometer, and the calendar are combined into a simple nomograph operation which indicates the per cent sulfur. The analyses have a reproducibility of 0.01% and an over-all accuracy of

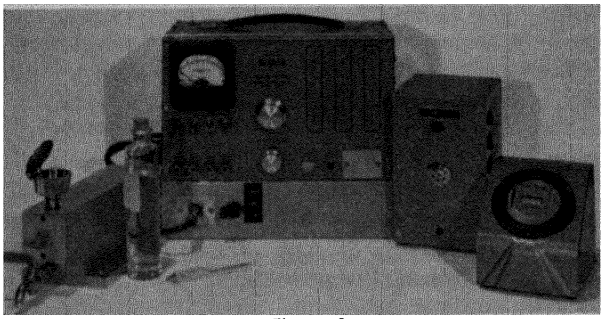


Figure 1

about 0.02%; checks with lamp sulfur analyses rarely show a disparity greater than this.

Hydrogen by Beta-Ray Absorption

The attenuation of beta rays in matter is a function of the absolute mass and the chemical composition of the absorbing material. It is nearly independent of composition because the principal interaction of beta rays is with the electrons in matter, and the number of electrons per gram of matter is approximately the same among the lightest elements. Hence, the attenuation of beta rays varies approximately as Z/A, where Z is the atomic number and A is the atomic weight. For the light elements, including carbon, nitrogen, and oxygen, Z/A is close to ½. With heavier elements, Z/A deviates from ½, and other interactions become more important, so that the attenuation becomes somewhat greater. Hydrogen, however, is unique in that it has an electron density, $Z/A = 1$, approximately twice as great as the other elements with which it is commonly found. This fact forms the basis of the hydrogen analysis. The weight percentage of hydrogen in liquid hydrocarbons may be calculated from beta-ray absorption and density measurements using calibration curves based on pure hydrocarbons. Small corrections must be made for the presence of nitrogen, oxygen, sulfur, and other heavier elements.

Two instruments are commercially available, both operating on the null principle with two opposing ion chamber detectors. In the equipment of Jacobs and Lewis,[17] the output from two chambers receiving radiation from a single 10-mc source of strontium-90 are brought into balance by a movable wedge absorber in front of one chamber. The sample cell holds about 10 ml of sample. The determination may be completed in 20 minutes with a reported accuracy of 0.03% hydrogen. This accuracy is considerably better than that obtained by conventional combustion methods (0.05%–0.1% hydrogen) and is about five times as rapid. The equipment developed independently by Smith and Otvos[18] uses two 25-mc strontium-90 sources, two liquid cells, and two ion chambers. In operation, one cell is filled with a reference liquid, the other with the unknown sample. The difference in the two ion currents is amplified and recorded. Calibration is made with liquids of known composition.

A third independently designed instrument by Fries,[6] based on this principle, uses a 2-microcurie strontium-90 source and a single Geiger tube to measure the beta-ray absorption. The sample cell is in the form of a "U" tube with a flat, enlarged section sealed with beryllium windows to form the actual cell. The "U" tube also serves as a pycnometer for density determination. The accuracy is about 0.2% hydrogen. By replacing the removable strontium-90 source with an iron-55 source, the sulfur content may be determined on the same liquid sample.

Hydrogen by Gamma-Ray Absorption

While electrons lose energy principally by ionization processes, gamma rays interact with matter in three major ways: by photoelectric, pair-production, and Compton scattering processes. In the absorption of the higher energy gamma rays from radioisotopes by hydrocarbons and their common light element impurities, such as sulfur, nitrogen, and oxygen, the photoelectric and pair-production processes are not involved and absorption is due entirely to the Compton effect. Because the scattering is proportional to the electron density of the atom, Z/A, the same uniqueness is found in hydrogen for gamma rays as for beta rays. Accordingly, the mass absorption coefficient for hydrogen is about twice that of other light elements for gamma-ray energies from about 0.5 Mev to the upper limit attainable from radioisotopes, about 3 Mev. Using this property, Fries and Barieau[6] have developed a method for hydrogen determination that is analogous to the beta-ray method but employs essentially monochromatic hard gamma-ray emitters, such as cobalt-60 and cesium-137. The sample path length is about one meter, in contrast to the 0.5-centimeter path in the beta-ray equipment.

The arrangement shown in Fig. 2 consists of a 0.5-curie source of cobalt-60 in a shielded container, a glass tube of constant volume holding the liquid sample, and a simple framework supporting a shielded Geiger tube. The tube shielding serves to reduce the background from scattered radiation. By calibrations with pure hydrocarbons, a linear relationship was established between the logarithm of the count rate and the parameter, $d(1 + W_H)/2$, where d is density and W_H is weight fraction of hydrogen. The coordinates for such diverse materials as acetone, butyl alcohol, water, and thiophene fell on the hydrocarbon curve, showing that no correction need be applied for the presence of oxygen or sulfur in the sample. The use of a radiation which can penetrate the heavy steel walls of pipes and vessels makes possible the determination of hydrogen in closed systems, such as refinery streams.

Trends in development point to the incorporation of these analytical applications of radioactivity in continuous process stream analysis and plant control. Such instruments offer further opportunities for auto-

matic control, if chemical composition of a plant stream is the important operating variable.

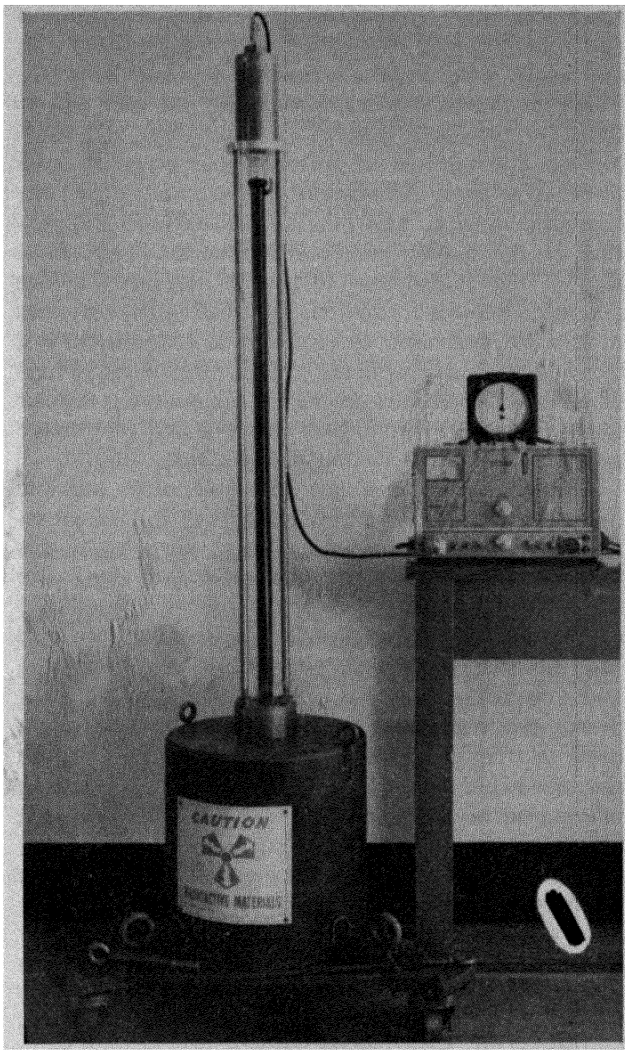
PRODUCT TESTING

The petroleum industry maintains elaborate programs for testing the qualities of fuels, lubricants, chemicals, and special products. In a keenly competitive industry, product specifications must be rigidly observed and improvements in quality or performance are constantly sought. Techniques involving radioisotopes have been eagerly taken up by petroleum research teams and now form an essential part of many test methods. New information is obtained more rapidly and at lower cost than by conventional methods. Studies of the influence of operating variables and fuel and lubricant composition make use of radioactive engine parts, such as piston rings, gears, and bearings. The deposit-forming characteristics of fuels and fuel additives are measured in relatively inaccessible parts of engines by simple methods employing radiation attenuation.

Engine Wear Studies

The use of radioactive engine parts to study wear was first proposed by Ferris[19] in 1943. At that early date, only cyclotron-produced isotopes were available, and although a successful demonstration of the technique was made by incorporating radiophosphorus in a custom-made piston ring, its fabrication was too costly to permit general use. In 1948 Pinotti, Hull, and McLaughlin[20] showed the way to an inexpensive and practical radioactive test by neutron activation of standard piston rings inside a nuclear reactor. Iron-59, formed by neutron capture, emits gamma rays and thus serves as a tracer for the metal. When the activated ring is installed in an engine, the particles worn from the ring during operation of the engine accumulate in the oil in the crankcase. Samples may be withdrawn at convenient intervals and counted to determine the amount of wear debris in the oil, or, for continuous observation of the wear rate, the oil may be circulated through a chamber in which the oil surrounds a counter.

This technique has been used to study the influence of fuels, lubricants, and operating variables on wear rates.[21] It has also been applied to field tests in ordinary passenger car service, using a radioactive ring in the top front cylinder in each car. These tests demonstrated the efficacy of a high-detergent-type oil for reducing ring wear in cars used for average five-mile trips in winter weather. The radioactive ring technique is about 50 times as fast as the weight-loss method which it has replaced. The reproducibility of wear rates has been found much better because the radioactive method, in a series of tests, records the break-in wear as a separate item. This is frequently a substantial fraction of the total wear and varies greatly depending on the exact set of a new ring in the cylinder. The radioactive analysis of the oil is also superior to the chemical analysis for iron, not only because it is cheaper, faster, and 50 times as sensitive, but also because the activity



measures the wear from one specific part; whereas a gross chemical analysis includes wear from all parts of the engine.

A similar technique was used first by Borsoff, Cook, and Otvos[22] to study gear wear using neutron-irradiated gears. More extensive results on gear wear are reported by Schwartz and Eaton.[23] The activity of circulating oil from the gear box was monitored continuously with a ratemeter. Wear rates as low as 50 mg per minute were detected. Autoradiographs were made of the working teeth of the inert gear after operation against a radioactive gear to show the quantity of metal transferred at different loads. In the latter study, the value of extreme pressure lubricants in reducing wear rates by a factor of 20–30 was strikingly demonstrated. Other examples of engine parts which have been irradiated for wear in lubricant testing are combustion cylinder liners, ball bearings, automobile shackle pins, and piston wrist pins for Diesel locomotives.

Engine Deposits

Deposits in various locations in internal combustion engines are customarily determined by dis-

assembling the engine after many hours of operation and removing the deposit by scraping or dissolving and finally weighing the recovered deposit. A method based on radiation thickness gaging has been developed by Sigworth and Fries[24] for these measurements. The surface of a removable plug is made radioactive by incorporation or deposition of a suitable radioisotope. The plug is inserted into the portion of the engine under examination. The count rate of the radioactive surface is measured before and after deposit formation. By relating the attenuation of the radiation to establish absorption curves, the deposit thickness in mg/cm^2 is determined. Plugs of various dimensions are in use for studying deposit formation in the combustion chamber and fuel intake systems of internal combustion engines.

Many radioisotopes are available with suitable half-lives and with energies convenient for the measurement of very thin films or heavy deposits by this method. Using nickel-63 (0.05 Mev beta ray) and a gas flow proportional counter, a sensitivity of 0.01 mg/cm^2 has been obtained. With sulfur-35 (0.16 Mev beta ray) and cobalt-60 (0.31 Mev beta ray) and a mica end-window Geiger tube, deposit thicknesses ranging from 0.05 to 20 mg/cm^2 are measured. Harder beta rays and gamma rays may be employed for still heavier deposits. Less than a microcurie of activity need be incorporated on the plug surface.

Radiosulfur has been incorporated as iron sulfide on the surface of an iron plug by heating the plug in mineral oil containing dissolved elemental sulfur or by placing a drop of dilute ammonium sulfide on the surface. Tests showed that this surface was stable, even in the engine combustion chamber. It is convenient, however, to protect this surface with a thin (10 micron) nickel electroplate. The plug may then be repolished and reused without abrading activity from the surface. Radionickel and radiocobalt surfaces are conveniently formed by electroplating. Where considered necessary, it is possible to apply a protective nickel plating over these radioactive surfaces.

Combustion Studies

The wear protection afforded by a motor lubricant changes in use, and the absorption of combustion products from the fuel can be a major factor in causing deterioration. Buck[25] measured the rate at which sulfur dioxide from the combustion of sulfur-containing Diesel fuel accumulated in the crankcase oil by adding sulfur-35 as di-*n*-butylsulfide to the fuel. At the beginning of a run, 0.3% of the sulfur burned in the engine found its way to the oil through absorption in the oil films on the cylinders. At the end of 200 hours' operation, this accumulation rate had diminished to 0.09%. This was shown to be caused by a reversible absorption of SO_2 in the cylinder zone oil layer, the rate of desorption increasing as the base reserve of the oil is depleted.

TRACER STUDIES IN PETROLEUM CHEMISTRY

Radioisotopes are used to explain the mechanisms and kinetics of chemical reactions. Occasionally, isotopic tracers can be used to obtain information which could not be obtained in any other way; at other times, they simplify chemical analyses. The major application to petroleum chemistry is in the investigation of catalytic reactions of petroleum hydrocarbons using carbon-14 and hydrogen-3 tracers.

Many problems in the chemistry of catalytic reactions are studied using pure compounds only or by varying a single component in a complex reaction system. Only rarely do these conditions represent actual plant operations. By suitably labeling a component of interest, its behavior in the reaction system can be followed under typical plant conditions.

Fischer-Tropsch Synthesis

An exhaustive study of the reaction mechanisms of the Fischer-Tropsch synthesis of higher hydrocarbons from carbon monoxide and hydrogen was made by Emmett and his colleagues.[26] These investigators, using carbon-14, disproved the metal carbide theory and confirmed the existence of an intermediate oxygen compound in the reaction. Further study has been made by Fletcher and Gibson.[27] The interaction of hydrocarbon and oxygenated radicals was investigated with hydrogen, ethylene, and C^{14} carbon monoxide. From specific activity measurements it was shown that one atom in every six or seven was derived from carbon monoxide among paraffin and olefin products ranging from C_4 to C_{10}. The distribution of radioactivity among different carbon atoms of propylene produced in the reaction was also studied to see whether a concentration of radioactivity occurred in any position. The central carbon atom had negligible activity, while the terminal atoms were high in activity, especially the methylene carbon atom. These results were interpreted to mean that carbon monoxide reacts to form propylene by direct addition to ethylene. All the activity is originally located at one position, but a migration of a hydrogen atom back along the carbon chain results in a shift in the double bond causing activity to appear in both terminal atoms.

Catalytic Reforming

The catalytic isomerization of cycloalkanes over several isomerization catalysts has been thoroughly explored by Kilner, Turner, and Warne.[28] Although the work was directed towards improved methods for the preparation of carbon-14 ring labeled aromatic compounds, very valuable information about the reaction mechanisms was obtained. Double labeling experiments were employed using C^{13} and C^{14} in the same molecule. The reaction products were completely degraded to determine the distribution of both isotopes. C^{14} methyl-labeled methylcyclohexane, from which toluene may be derived by dehydrogenation, is obtained by isomerization of α-C^{13}, β-C^{14} ethylcylo-

pentane under mild conditions, such as $AlCl_3$ at 0°C or 95% H_2SO_4 at 25°C. The α carbon is found entirely in the ring; the β carbon entirely in the methyl group Under more severe conditions, $AlCl_3$ at 100°C, both C^{13} and C^{14} are randomly distributed among methyl and ring carbon atoms. Over a chromia-alumina catalyst at 500°C the above labeled ethylcyclopentane is converted directly to toluene, but the rearrangement of α and β carbons is more complex. The α carbon is found principally in the ring, the β carbon principally in the methyl group.

The mode of cyclization of heptane over chromia-alumina catalyst was investigated by Wheatcroft, Tolbert, and Powell[29] using heptene-1, labeled in the 1-position with C^{14}. About two-thirds of the carbon-14 was found in the ring and one-third in the methyl group of the toluene produced.

The conversion of napthenes to aromatics by the catalytic reforming reaction has been examined on a pilot plant scale with carbon-14 by Fries.[30] Methylcyclohexane, labeled in the methyl group with C^{14}, was added to 500 ml of a typical toluene plant feed and passed over molybdena-alumina catalyst in a pilot plant. The feed consisted principally of methylcyclohexane, dimethylcyclopentanes, and n-heptane with small amounts of other napthenes and paraffins. In the reaction products, C^{14} activity was found mostly in toluene and xylenes but also in the coke, the light paraffin gases, and other paraffins, naphthenes, and aromatics. Based on specific activity determinations of the original methylcyclohexane and the recovered toluene and methylcyclohexane, it was shown that only one-half of the toluene was derived from methylcyclohexane, while the remainder must have come from dimethylcyclopentanes because the catalyst was inactive in the dehydrocyclization of heptane to toluene. Carbon-14 was found in benzene and in the benzene ring of toluene, which indicated that some isomerization occurred. The recovered dimethylcyclopentanes contained very little radioactivity, while the recovered methylcyclohexane had the same specific activity as at the start. These results were interpreted to mean that little isomerization of methylcyclohexane to dimethylcyclopentanes took place under the reaction conditions. If methylcyclohexane was an intermediate in the production of toluene from dimethylcyclopentanes, the methylcyclohexane formed did not exist in the free state but rather the adsorbed intermediate was rapidly dehydrogenated to toluene on the catalyst.

Coke Formation

Several studies have been made of the mechanism of coke formation in catalytic hydrocarbon conversions. McMahon[31] has demonstrated that all carbon atoms in heptane, octane, and octene, labeled at different positions with C^{14}, participate equally in the formation of coke during cracking. This result suggests that some of the adsorbed molecules remain on the catalyst surface where they undergo dehydrogenation and polymerization to form coke. In Fries'[30] study of methylcyclohexane, the methyl carbon atom was found to have only half the tendency to form coke shown by all the other carbon atoms in the mixed feed studied. Specific activity measurements of the coke deposited on silica-alumina catalyst during the transfer of hydrogen from naphthenes to olefins, studied with C^{14} butene by Blue and Engle,[32] showed that the naphthenes contribute a large amount to coke deposition and that tetralin more readily deposits coke than does decalin. The effect of catalyst granule size in catalytic reactions was also studied by Blue *et al.*[33] with carbon-14 butene. The amount of carbon-14 activity found in the coke deposited at various depths in chromia-alumina pellets was measured, and the relatively lower effectiveness of the interior portions was demonstrated.

Hydrogen Transfer

Isomerization reactions have been examined with both carbon-14 and hydrogen-3. Powell and Reid[34] found large amounts of hydrogen exchange between HCl and the hydrocarbon in the isomerization of the butanes over $AlCl_3$ catalyst, but very little between hydrogen and butane. Turkevich *et al.*[35] correlated the migration of the double bond in the butene-1 and butene-2 system with the exchange of tritium from the catalyst to these hydrocarbons. The same catalysts were active for both reactions, and the rates of the two processes were comparable. Stewart and Harman[36] found rapid exchange of hydrogen atoms during the alkylation of isobutane and butene-2 over tritiated sulfuric acid. The exchange occurred prior to the alkylation reaction. The kinetics of the forward and reverse reactions in the catalytic isomerization of butane over $AlBr_3$ has been studied by Otvos *et al.*[37] with carbon-14 labeled butane and isobutane.

The foregoing illustrations of radiotracer studies in petroleum chemistry cover the major amount of reported work. It is hoped that the increasing commercial availability of labeled organic compounds and the increased ease of measuring carbon-14 and tritium by means of liquid scintillation counters will provide the stimulus for increased studies of chemical processes of interest to the petroleum industry with this powerful tool. Even full-scale plant studies become possible with moderate quantities of isotopic compounds when liquid scintillators are used.[38] The continuing trend in the industry toward specific tailoring of the molecules to realize more complete utilization of petroleum for power, as well as to produce raw materials for chemicals, suggests that research of this kind will become increasingly important.

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The Field Experiment of Littoral Drift Using Radioactive Glass Sand

By Shizuo Inose, Masao Kato, Seiichi Sato and Naobumi Shiraishi, Japan

I. INTRODUCTION

After the war, the Japanese Government has facilitated the general development of Hokkaido as a part of the multi-purpose development in Japan in order to solve the over-population problems and to attain economic independence. From a viewpoint of aiming at improvement of industry and promotion of export, an industrial port is to be constructed at Tomakomai City (at long. E. 141 degrees and lat. N. 42 degrees) which is in the southern part of Yufutsu Plain. The hinterland of the harbour is rich in natural resources, for instance, the Ishikari coal field, industrial and drinking waters, a flat land for factories.

The Tomakomai harbour will be a "dug type" harbour as shown in Fig. 1, the length of east and west breakwaters are respectively 970 and 800 m, the depth of fairway is —9 m for ships of 10,000 G/T class. The area of industrial port is 1900 ha, the area of commercial port is 120 ha, the area of residential district is 4500 ha and 1,000,000 population can be expected in these districts.

The authors have been engaged in the construction of the Tomakomai Industrial Harbour since 1951, and as it is situated along a monotonous sandy beach about 120 nautical miles long, they have encountered many difficulties in the way of planning the harbour which is protected from littoral drift reasonably and economically.

But the general method of analysing the phenomena of littoral drift has not yet been found.

Since 1950, many observations have been practised in this Tomakomai coast, the authors have made a new attempt using radioactive glass sand to find the movement of the sand on seabed.

This paper is concerned with the method and results of the experiments using radioactive glass sand which were made in summer 1954. The radioactive glass sand was prepared at the radioisotope laboratory in the Institute of Industrial Science. We appreciate the kindness of the Tomakomai City; without its constant financial support, this investigation would not be presented in the present form.

And particular thanks are due to Dr. Fumio Yamasaki, Dr. Magoji Matsumura, and Dr. Yasumasa Tani for their kind suggestions and assistance.

These experiments were performed by the hearty cooperation of technical officials including Keiroku Umeki, Shoji Sato, Yoshihisa Kawakami, Muroran Construction Office, Hokkaido Development Bureau; and other technical officials including Fumio Kishida, Dr. Hideo Kikkawa, Tsutomu Kishi, Public Works Research Institute, Ministry of Construction; research members Kiyoaki Taketani, Masatoshi Kobayashi, Yoshikata Sasaki, Institute of Industrial Science, University of Tokyo.

II. SELECTION OF RADIOISOTOPE AND CONSIDERATION OF RADIATION HAZARDS

1. Selection of Radioisotope

The radioisotope to be used for such a purpose must satisfy the following conditions:

(1) It should be a gamma-ray emitter.

(2) The energy of gamma-rays should be high enough to be of a greater range in sea water.

(3) The flux density of gamma-rays should be large to raise the detectability.

(4) Its half-life should be optimum for this experiment and also in respect to the accompanying radiation hazards.

(5) It should be such an element as to be easily and strongly fixed as a chemical component in glass.

(6) It should be as cheap as possible.

Considering the above conditions, attention may be paid to the three kinds of radioisotope, Co^{60}, Ag^{110} and Zn^{65}. Co^{60} has a difficulty on term (*4*), because of its long half-life. Ag^{110} has a difficulty on term (*5*), where it is hard to be fixed in glass. Zn^{65} has a certain difficulty on term (*3*), where the gamma-rays emission is only 46% of the activity strength. In spite of the difficulty above mentioned, Zn^{65} seems to be most adapted for this experiment, since it satis-

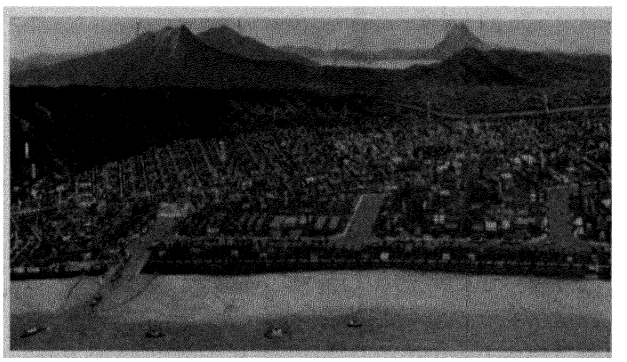

Figure 1

fies other conditions. After all, it was decided to use the radioisotope Zn^{65}.

Moreover, if the radioactive glass sand could be prepared by means of neutron irradation, it might be also a good method to use Sc^{46} as contaminant, which emits gamma-rays of high energy and decays with short half-life. However it is impossible, because there is no atomic reactor in this country yet.

The properties of the radioisotope Zn^{65} are as follows: beta-particles (positron), 0.32 Mev (3%); gamma-rays, 1.11 Mev (46%); others, k (46% and 51%).

The specification of the radioisotope Zn^{65} obtained from US AEC is as follows: chemical form, $ZnCl_2$ in HCl solution; concentration, $14.13 \pm 10\%$ mc/ml; specific activity, 129 mc/mg; radio-chemical purity, 98.0; Zn content, approx. 109 N; acidity, 0.90 N; assayed on Jan. 29, 1954.

2. Consideration of Radiation Hazards

At the beginning of planning this experiment, we discussed enough the problem of radiation hazards affected by putting the radioactive glass sand on seabed. As a result of cautious discussions, this experiment was carried out under the following considerations and precautions:

(1) The radioisotope Zn^{65} chemically fixed in glass is less soluble in sea water.

(2) When the radioactivity of a grain in glass sand is being made so as to be less than about 0.1 c, the radioactivity on the seabed shall fall into the range of background in such velocity as in proportion to dispersion of the glass sand and decay of the radioactivity.

(3) Even if fishes and shells would ingest the radioactive glass sand, it might be of the order of several grains. In this case, their radioactivity may be very weak and they may be excreted without dissolving in the digestive organs because of glassy substance.

Therefore, it seems that the radiation hazards are out of the question.

III. METHODS OF EXPERIMENTS

The principle of this observation is as follows: The radioactive glass sand, containing the radioisotope Zn^{65} which was manufactured to bear a close resemblance in specific gravity and diameter to the bed material at the observation point, was put on the seabed. It was possible to observe by a radiation measurement how the glass sand was moved together with the other bed material by waves and littoral currents.

1. Preserving the Radioactive Glass Sand

We prepared two kinds of glass sand; one is for 3 m in water depth, and the other is for beach line, and these were wrapped in a double bag made of polyethylene. Radioactivity of each bag is about 30 mc. These packets were kept in a leaden case, thickness 5 cm, at the outside of which 15 milliroentgens per hour were indicated by a gamma survey meter. It was being stored in the storing room made of concrete.

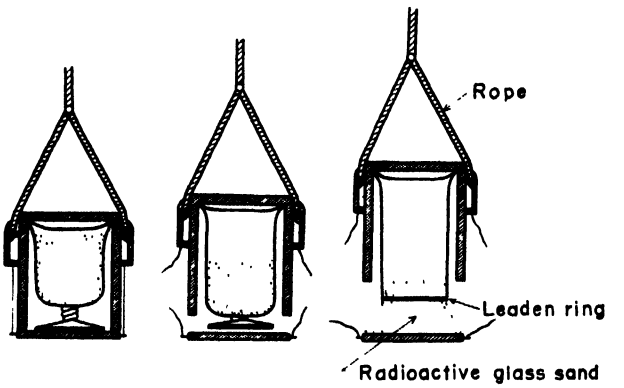

Figure 2. Schematic representation of putting radioactive glass sand into bags

2. Putting the Radioactive Glass Sand on the Seabed

At first the glass sand has to be placed into the device. During such a procedure the operators are necessarily exposed more or less to external radiation and radioactive dust. Thus the operator should put on working rubber dresses, surgical rubber gloves, rubber boots, masks necessary for health protection and dosimeters necessary for health control. Such a working method is to be adequate precaution against inhalation of fine radioactive glass sand, since the radioisotope has already been in an insoluble chemical form as a constituent of glass. The leaden case for putting the radioactive sand on seabed was a cylinder, 15 cm in inside diameter, 15 cm in length, 3 mm in wall thickness in which a polyethylene bag with a leaden ring was hung upside-down. (See Fig. 2.)

Operators put the radioactive glass sand and soapsuds in this polyethylene bag and twisted the mouth of the bag several times and put the leaden lid on the cylinder (Fig. 3).

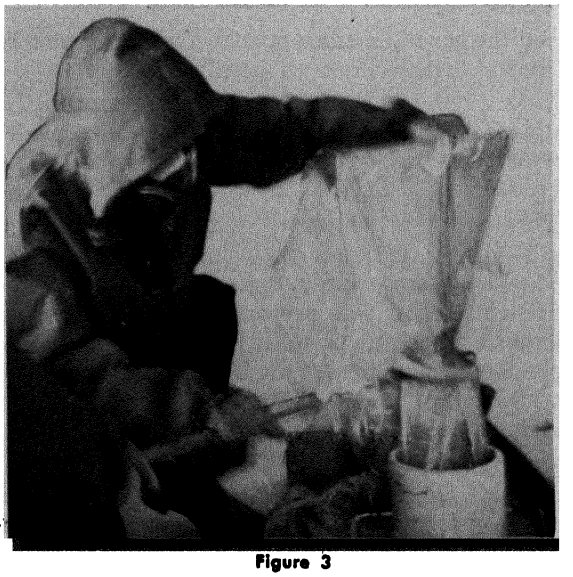

Figure 3

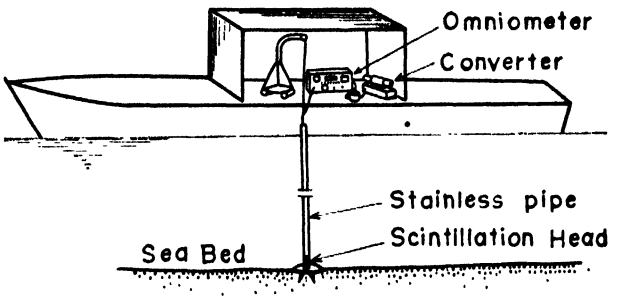

Figure 4. Method of measurement in field

The cylinder which was in a sand box, 100 cm × 50 cm × 50 cm, was carried on a boat to the observing point on the sea. When the cylinder was set, being turned upside-down on seabed, the wire fixing the lid of cylinder was cut by a diver; then the cylinder was slowly pulled up by a rope after several times of up-and-down motions. As shown in Fig. 4, the radioactive glass sand was put entirely on the seabed.

The above operations were confirmed to be possible in field by many preliminary tests. The soapsuds added to the glass sand was used for the purpose of eliminating air films surrounding the surface of sand grains to be smoothly discharged from the bag, and to be immediately wetted going down in the seawater.

3. Measuring Radioactivities in Field

To route the movement of glass sand due to waves and littoral currents, the authors succeeded in measuring the radioactivities on seabed by a radiation measuring instrument on boat.

Namely, a perfect watertight steel pipe, at the bottom of which a scintillation head was held, was made to stand vertically on the seabed from a boat. A flange was attached to the bottom of pipe so that it may not sink into the bed but may measure under the same geometrical condition. The scintillation head and scaler were connected with a cable of length 10 m.

Some defects of this method are as follows:

Difficulties in steering boat because of the handling of a large pipe hanger and a long pipe and in preventing the pipe from rocking during the measurements. Therefore the authors designed a new arrangement.

A probe of a GM counter installed in a watertight tube made of 18–8 stainless steel is directly hung from a boat, and it can be prevented from rolling with the boat.

This new equipment will be employed in the next experiments. Its details will be described later.

IV. PREPARATION OF RADIOACTIVE GLASS SAND

1. Principle of Preparation

The radioactive glass sand as a tracer must bear a close resemblance in specific gravity and sand-size distribution to the bed materials at the observation point. It must have such a specific activity and amount as may make the measurement possible, even when it disperses up to an extent of several hundred square metres.

According to the data previously investigated, the conditions required for preparing the radioactive glass sand were specified as follows:

(1) Specific gravity from 2.6 to 2.7.

(2) Sand size and its distribution:

Purpose:	*Range of distribution in mm*		*Mean in mm*
For beach line	0.11	0.55	0.246
For 3 m in water depth	0 09	0.30	0.186

(3) Amount about 1.5 litres in apparent volume respectively for each purpose.

(4) In addition to the above, the glass to be prepared should not only be homogeneous in chemical composition and radioactivity but also be free from bubbles.

2. Specific Activity

In general, two radioactivity factors remain for the discussion of the limits upon a tracer experiment. One of these is the statistics of the nuclear phenomenon and instrumentation which places a statistical limit upon the reliability of instrument response. Another is the actual yield factor which relates the amount of instrument response to the disintegration rate in the sample.

In this experiment the scintillation counter was used. The fluorescent crystal was made of anthracene and its size was 1 inch × 1 inch × 0.5 inch. The detection limit of this instrument for gamma-rays was up to 0.01 μc in case of the favorable condition.

The glass sand of 3 litres in apparent volume corresponds to a glass block of about 2 litres in actual volume. Now, supposing Zn^{65} of 100 mc was homogeneously dispersed in glass of 2 litres, the results of calculation of the activities of sand grains of 0.25 mm and 0.10 mm respectively in diameter are as follows: 0.79 μc for a grain of 0.25 mm in diameter; 0.05 μc for a grain of 0.10 mm.

Since the measurement in the field experiment must be carried out under less favourable conditions, such as protecting pipe over scintillation head, medium- and self-absorption, scattering effect, smaller geometrical factor, etc., a specific activity of this order may be necessary. Furthermore, the decay of activity must also be considered.

After all, we ordered the radioisotope Zn^{65} of 100 mc from America. The total activity of two samples was about 70 mc at the time when the preparation was finished. Further, it decayed down to about 60 mc till the field experiment was started.

3. Chemical Composition of Glass

The chemical composition of the ordinary glass is 70–72% SiO_2, 14–16% Na_2O, 10–12% CaO, and its specific gravity is 2.4–2.5. Adding of Zn to glass may be done by means of replacing some fraction of CaO with ZnO in the same content. In order to increase the specific gravity it is necessary to add PbO, as ZnO contributes less to this purpose.

To manufacture the glass, the powdered raw materials, such as SiO_2, $CaCO_3$, Na_2CO_3, Pb_3O_4 and ZnO, are homogeneously mixed and then charged in melting furnace. Besides, to remove bubbles it is preferable to add 1.5–2% $NaNO_3$ as oxidizer and degasser, and to melt at high temperature.

Hence, in the first place, the weight ratio of principal raw materials was kept constant as:

SiO_2	$CaCO_3$	Na_2CO_3	$NaNO_3$
70 gm	19.7 gm	24.8 gm	1.85 gm

Then, the combined effects of adding ZnO and Pb_3O_4 on the increase of specific gravity were assessed in order to find out the optimum chemical composition.

The results are shown in Fig. 5. By means of

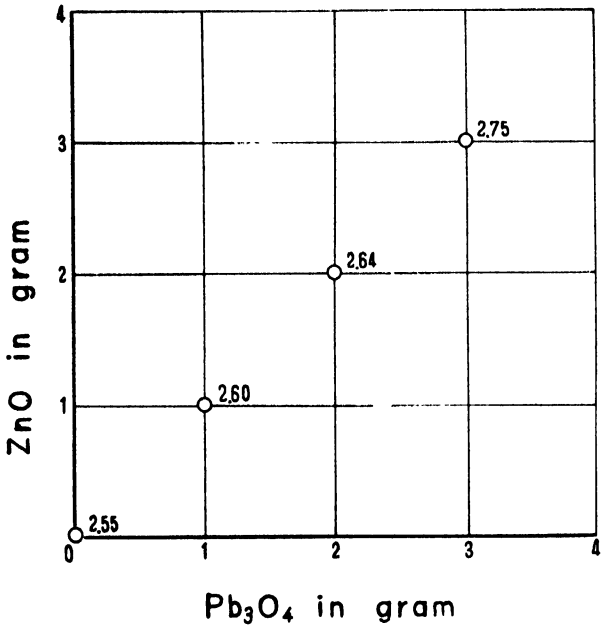

Figure 5. The increase of specific gravity of glass by adding ZnO and Pb_3O_4

such procedure the weight ratio of raw materials was finally settled as follows:

SiO_2	$CaCO_3$	Na_2CO_3	$NaNO_3$	Pb_3O_4	ZnO
70 gm	19.7 gm	24.8 gm	1.85 gm	2.0 gm	2.0 gm

4. Preparation of Radioactive Glass Sand

The first question to be investigated was to determine the method to fix the radioisotope Zn^{65} homogeneously in glass, since it was received in a chemical form of an aqueous solution of $ZnCl_2$. The first method is to convert this $ZnCl_2$ in solution state to ZnO in powdery state, which might in the next be mixed with stable ZnO as carrier. However, it seemed advisable to prefer the following method to the above method in order to disperse the radioisotope Zn^{65} more homogeneously as well as more safely in glass.

This second method is to add the aqueous solution of $ZnCl_2$ to the powdery mixed raw materials which turn into a porridge-like state, and then to mix it enough.

The authors tried this method. The porridge-like material solidified after being kept at room temperature for a day. Then, by gradual heating, free or combined water vaporized. Furthermore, by going on with heating up in oxidizing atmosphere $ZnCl_2$ turned to ZnO and it was fixed in glass. In this case, it was necessary to confirm whether Zn^{65} ran away from the melt or not, since $ZnCl_2$ is easy to vaporize during heating. As a result of experiment using tracer technique, it was confirmed that Zn^{65} did not run away. That is to say, $ZnCl_2$ was wholly oxidized and chemically combined in glass. Therefore, a half of ZnO weight ratio specified above was replaced by equivalent $ZnCl_2$, which was tagged with Zn^{65} of same chemical form and added to raw materials in aqueous solution. Moreover, in melting practice the raw material subjected to the preliminary treatment was charged together with a beaker into the pot in furnace, and hence the specific gravity of glass produced was about 2.63, which was somewhat smaller than 2.64 shown in Fig. 5.

After heating up to about 1650°C the molten glass was slowly cooled down to about 1550°C and was being held at that temperature for three hours until the bubbles were entirely removed, and then drawn out from the furnace. The molten glass was not solidified in a pot but poured into quenching water bath, so that it was pulverized to particles and next crushing operation became easy. The crusher (Fig. 6) was of a rotary type and provided the automatic sieving device which facilitated safe manipulation of the radioactive materials.

To obtain the required sand-size distribution, the

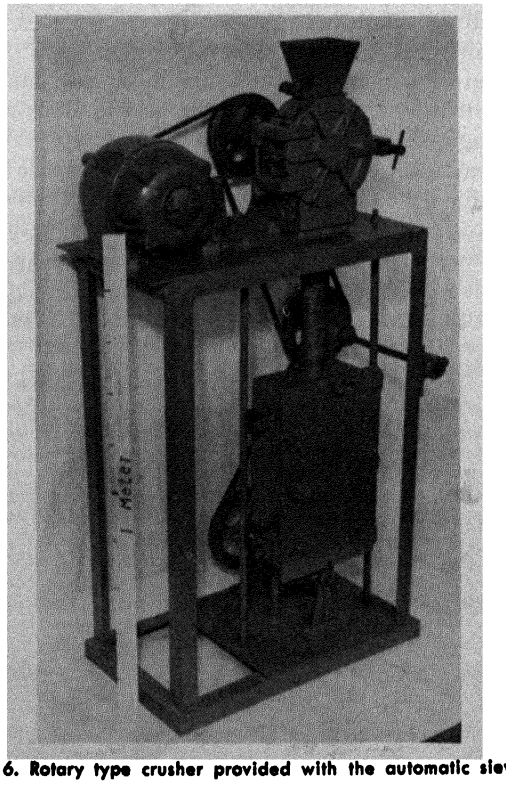

Figure 6. Rotary type crusher provided with the automatic sieving device

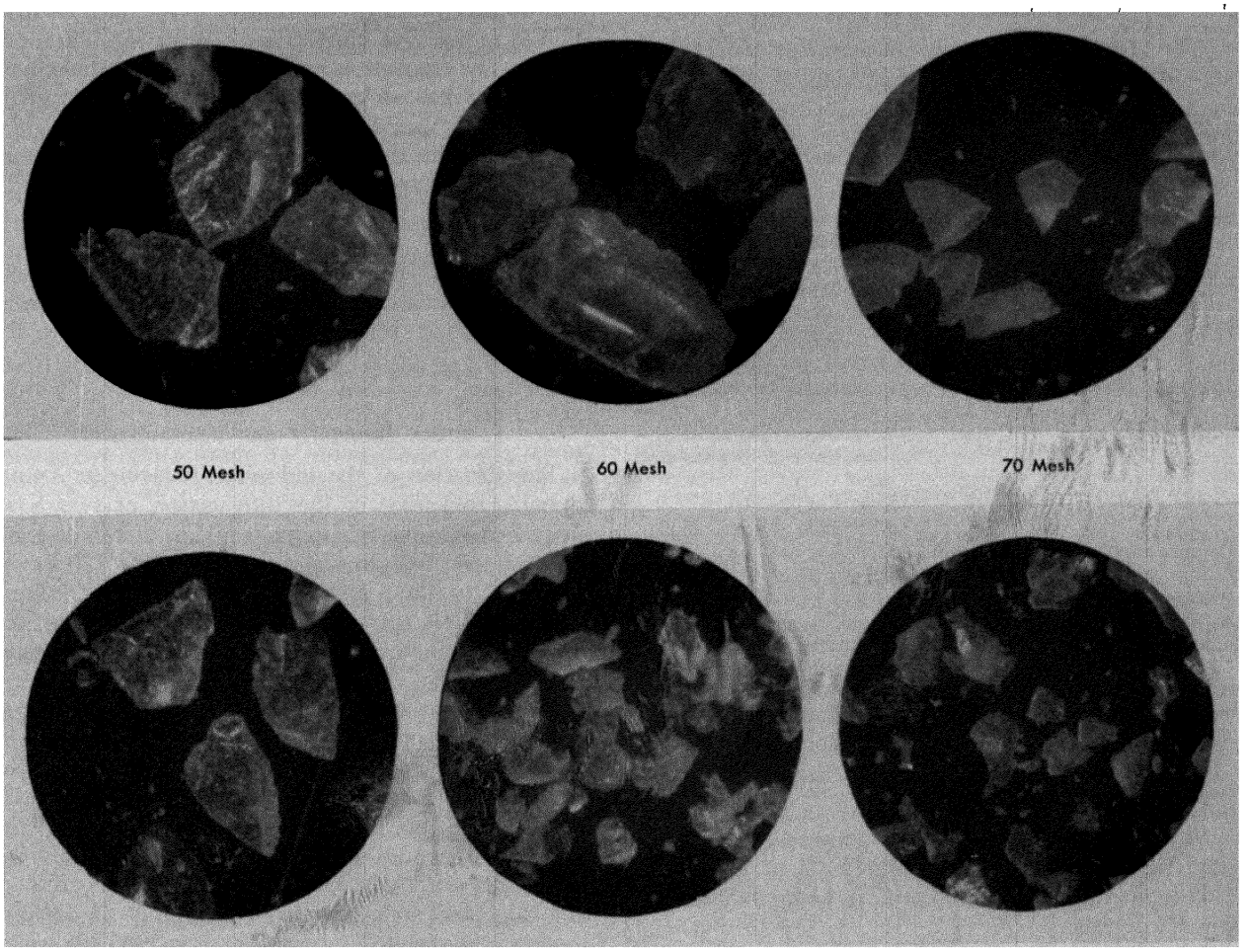

Figure 7. Microphotograph of sand grains: magnification × 180

crusher was previously adjusted through many tests with non-radioactive glass. The glass sand was simultaneously sifted to seven sorts of meshes by six sieves piled on. These were further divided to proper quantities and synthesized to two kinds of samples respectively in nearly the same quantity.

5. Properties of Samples

After finishing the radioactive glass sand was inspected in regard to the homogeneity of specific gravity and specific activity.

(1) Specific gravity: The results of measurement by random sampling were as follows:

Sample	*a*	*b*	*c*	*d*	*Mean*
Specific gravity	2.63_1	2.62_8	2.62_7	2.63_6	2.62_8

(2) Specific activity: The results of activity measurement by random sampling were as follows:

Sample	*a*	*b*	*c*	*d*	*e*
cpm	6873	2654	2241	2272	3489
Weight, gm	0.4285	0.1599	0.1363	0.1502	0.2458
cpm/gm	15950	15675	16120	14900	14200

Therefore, the deviations from mean value were ± 7%.

(3) Sand-size distribution is shown in Fig. 8. The numerals in the figure are weight per cent against the total amount.

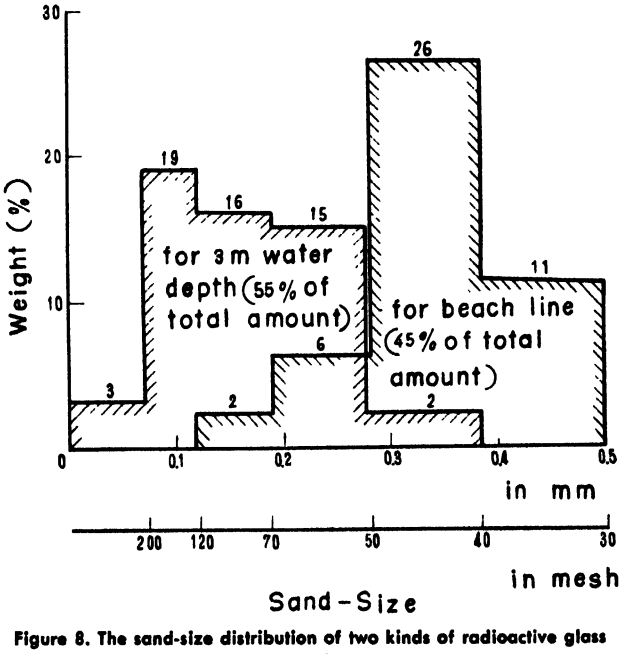

Figure 8. The sand-size distribution of two kinds of radioactive glass sand

V. INSTRUMENTS AND EQUIPMENT

The type of radiation measuring instruments should be determined by what kind of experiment using radioisotope is carried out. Thus the instruments provided for these experiments are as follows:

Description	*Amount*	*Remarks*
Scintillation counter*	1 set	Omniometer (RCL, Mark 15, Model 15) Scintillation head (RCL, Mark 10, Model 10) (With cable of length 10 m)
Gamma survey meter*	1 set	the type of Beckmar (Mark 11, Model 23)
Dosimeter and charger*	4 and 1 sets	the type of Victoreen
GM counter†	1 set	the probe was protected by a case made of 18-8 stainless steel (Kobe Kogyo Corp.) (With cable of length 20 m)
Portable survey meter†	1 set	(Kobe Kogyo Corp.)
Rotary convertor†	1 set	changing dc to ac
Voltage regulator†	1 set	
Battery	6 sets	12 v
Tongs	2	for use with radioactive materials
Working dress	5 sets	rubber dresses, surgical rubber gloves, rubber boots, masks.

Then, the main equipment for manipulation of radioactive materials is as follows:

(1) Storage of radioactive glass sand is in a watertight room made of concrete, 2 m in length, 1 m in width, 0.8 m in depth. It is surrounded by wooden fences.

(2) The wooden room for classifying radioactive glass sand has an area of about 10 square metres.

* Instruments made in Radiation Counter Laboratories, Inc. USA.

† Instruments made in Japan.

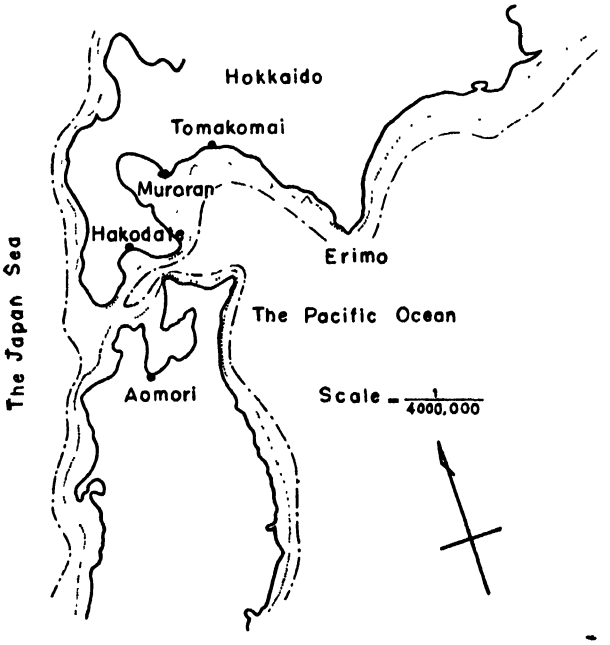

Figure 9. The situation of the Tomakomai harbour

The replacements of radioactive glass sand or division of radioactive samples are operated in this room.

(3) The wooden room for measuring radioactivity of samples has an area of about 20 square metres. The wall is mortar finishing, the surface of which is painted with decontamination paints. A ventilator and a washer are installed in this room.

VI. EXPERIMENTAL RESULTS

The authors performed the first field experiment using radioactive glass sand along the Tomakomai coast from 28 June to 11 Aug. 1954. Before the results are described an outline of characteristics of Tomakomai coast will be given.

1. Beach Geometry and Bed Materials

The situation of the industrial harbour at Tomakomai, Hokkaido, is the intersection of two bow-shaped coasts, one side extends 60 km to WSW-ward to the Cape of Chikyu and the other side 120 km to SE-ward to the Cape of Erimo. There is infinite fetch from SE through S to SSW (Fig. 9).

The bed material is fine sand and its specific gravity is 2.6–2.8. The contour lines of seabed are nearly parallel with beach line and the sandridges are found about 150 m off the beach line. The change in the ratio of the mean sand-size with the water depth in the direction of the perpendicular to the beach line is shown in Fig. 10. Namely, the mean sand-size is approximately 0.13 mm off the sandridge, and it becomes larger near the crest of sandridge and approximately 0.22 mm at the trough. It increases abruptly with the approach to the beach line.

2. Winds

As shown in Fig. 11, it is seen that stronger winds from sea are predominant in June, July, Aug., and Sept., and that winds from land are frequent in winter. Winds from E and W, being parallel with the beach line, are comparatively weak through the year. In consideration of the longshore component of the wind through the year, it is westward in summer, eastward in winter and through the year the westward trend is prominent.

3. Waves

It is considered by wave hindcastings and observations that waves approaching from SE through S to SSW are prominent in frequency and energy through the year as shown in Fig. 12.

In summer, waves approaching from SE through S to SSW are frequent and a maximum wave-height in deep water is estimated approximately at 7 m. In winter, the sea is rather calm and waves approaching from SW are somewhat frequent. The maximum wave-height in deep water is estimated approximately at 4 m.

The first field experiment was performed at 2.8 m in water depth, ashore or sandridge. This location was selected to be out of the area sheltered by the

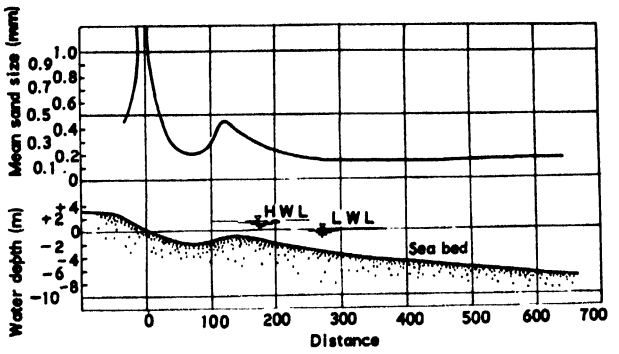

Figure 10. Relation between sand-size and water depth

breakwater of this harbour. After 1.5 litre of the radioactive glass sand, its radioactivity being about 30 mc, was put at this location on the seabed on 28 June, the observation of sand movement was continued to 11 Aug. 1954. The measurements of radioactivity on seabed using a scintillation counter were performed radially from this location to the regions where the counts were equal to those of the background, and thereby the graphs of equi-count-line were obtained. The background on seabed of this region was 15 cpm. The results of observation done on 29 June, 13–14 July, 24 July and 11 Aug. 1954 are shown in Fig. 13. The characteristics of winds and waves during the experiment are shown in Fig. 14.

4. On the Observation on 29 June

From the observation of this time, the glass sand was scarcely dispersed, and crowded near the original point. Initial activity at this point was tens of thousands of counts per minute which decreased to 1041 cpm on the following day.

5. On the Observation on 13–14 July

From the observation of this time, the glass sand had a tendency to approach gradually to the beach line and was scarcely moved parallel with beach line. This sand movement seems to be induced by waves, about 1 m in wave-height, on 6 July.

6. On the Observation on 24 July

After 13–14 July, it was noticed that waves of 0.7 m in wave-height, SW in the direction of wave approaching on 11 July and of 0.75 m in wave-height, SE in the direction of wave approaching on 19 July, were prominent. Waves from SE were frequent on the whole. From the observation on 24 July, the glass sand seems to move perpendicular to beach line and simultaneously to west along the beach.

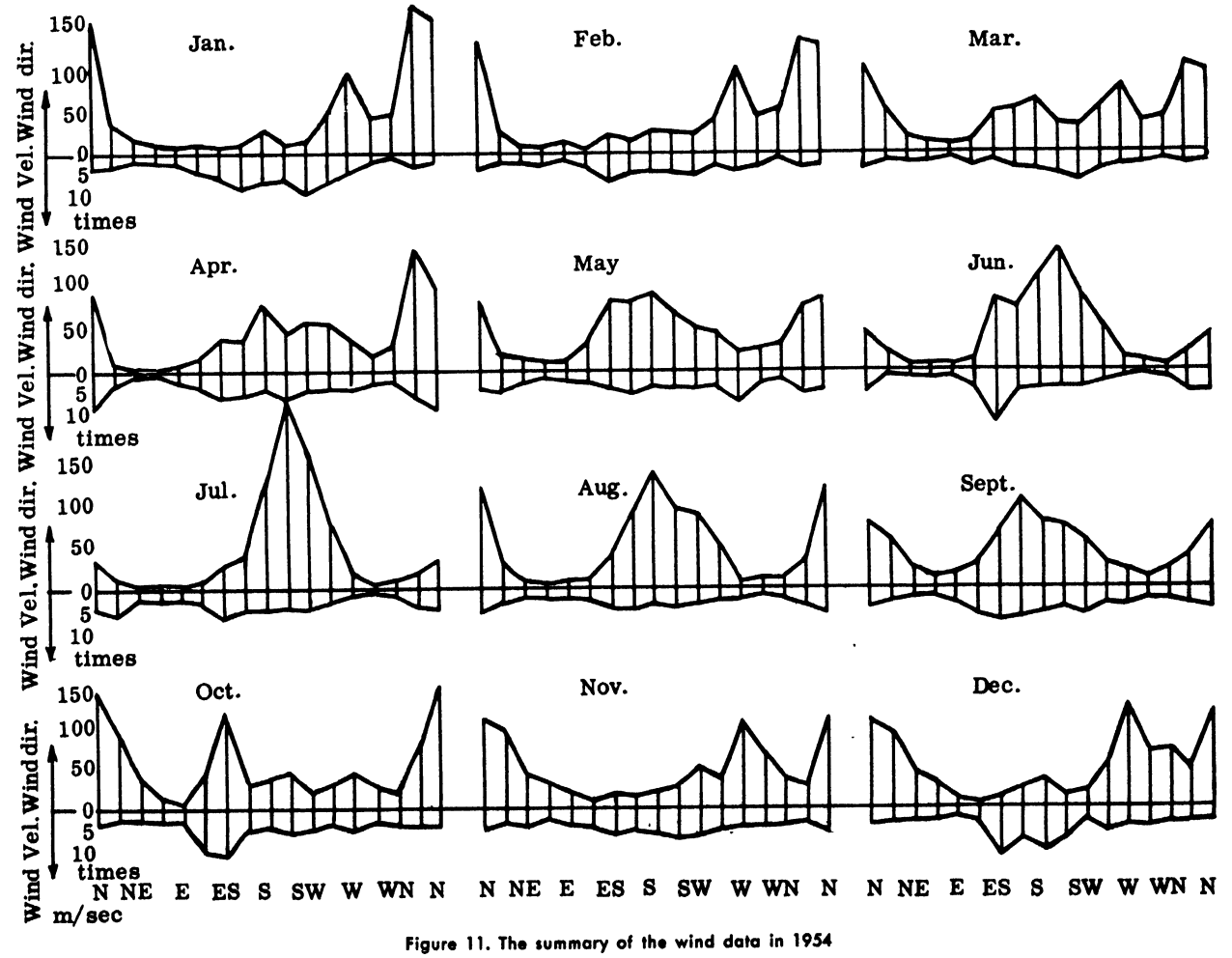

Figure 11. The summary of the wind data in 1954

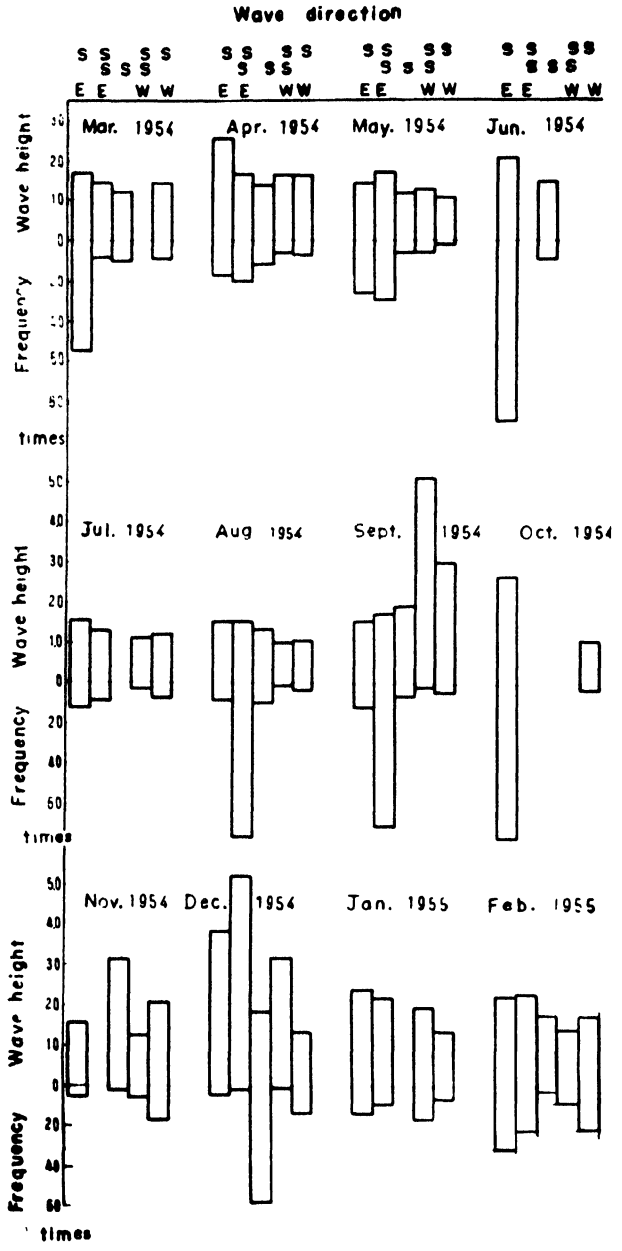

Figure 12. The summary of the wave data in 1954

7. On the Observation on Aug. 11

Since 13–14 July, waves of about 1.6 m in wave-height on 26 July, 8 Aug. were prominent and waves from SE were frequent on the whole. The sand seems to disperse extensively and move to the west.

Assuming that the location of maximum counts was the mean position of sand movement under consideration, for the period from 13–14 July to 24 July, the glass sand was moved to landward, showing a tendency of shoaling and after this period the glass sand was moved offshore, showing a tendency of erosion. The wave steepness for the period of the former was about 0.01 and smaller than that of the latter. Accordingly, it seems to suggest a certain correlation between shoaling, erosion and steepness of the waves.

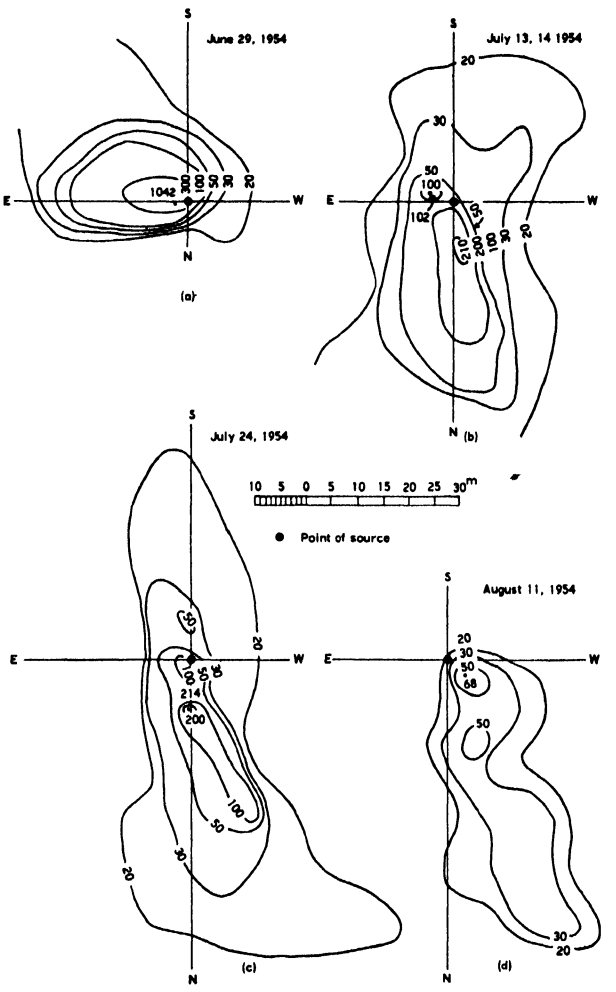

Figure 13. Dispersion of radioactive glass sand is shown by equi-count-lines: the origin of coordinates is the putting-point

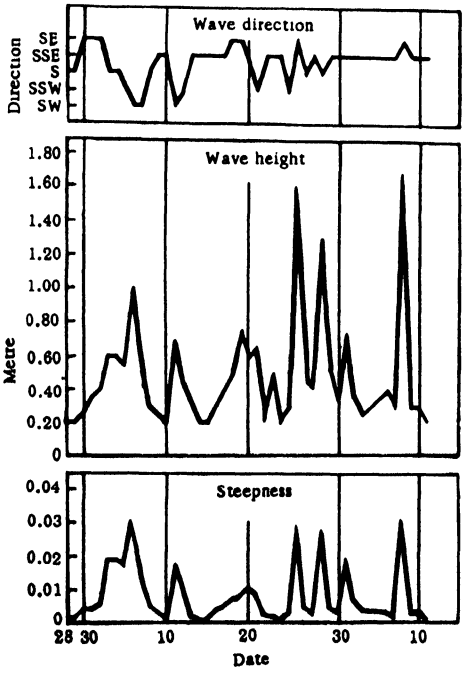

Figure 14. The characteristics of winds and waves during the experiment

The data obtained in this experiment seems to be significant and hence useful, in view of the fact that the observation of the sand movement was possible to be continued for a long time.

Next, on 31 July 1954, we put the glass sand (about 30 mc) at the beach line of the mean sea level eastward 7000 m from the main breakwater, in order to observe the zig-zag motion of beach sand. Soon, the first wave attacked a beach, 30 minutes later, glass sand rolled westward about 8 m, and quickly dispersed in the sea.

At this time, wave-height was 1 m, wave direction was SE, and period was about 5 sec.

According to the later observation, we could not find any radioactivity at the beach line.

VII. CONCLUSIONS

In conclusion, then, the results of this field experiment make clear that this method is available to reveal skilfully the substance of littoral drift, a complicated phenomenon. The authors believe that this method is better than any conventional one for the investigation of littoral drift and could be applied to any coast in the world. But we do not know if the radioisotope Zn^{65} is the best suited or not for this experiment. The radioisotope Co^{60} seems to be suitable for the observation of a long period, and the radioisotope Sc^{46} would be suitable to investigate exactly the characteristics of littoral drift for a short time. Moreover, in view of our empiric experiences, it seems that the radioactive substance used for this method can be manipulated with few biological hazards. We expect that this method shall be developed and utilized everywhere in future.

Now we are arranging for experiments to determine the depth, where the bed materials moving is practically little, and to observe a movement of littoral drift along the breakwater and a permeability of the mound breakwater for sand. These experiments are expected to start from May 1955.

Applications of Radioisotopes to Research and Industrial Problems in Japan

By Kenjiro Kimura,* Japan

In post-war Japan, the application of radioisotopes to research and industrial problems was resumed in April, 1950, by the use of an isotope, Sb^{125}, which was presented to Dr. Yoshio Nishina through the courtesy of the American Philosophical Society. Since then, various kinds of radioisotopes have been extensively utilized in every field of natural science. These isotopes, with the exception of a few produced in Japan, were imported from the United States, Canada, the United Kingdom, and Norway. This review covers a few interesting instances of application of radioisotopes which have attracted considerable attention from Japanese scientists.

THE STUDY OF THE DISSOCIATION OF STRONTIUM AND BARIUM OXIDE UNDER ELECTRON BOMBARDMENT

It is very important to study the effect of electron bombardment on the secondary emission power of oxide-coated cathodes. The result of the recent study by S. Yoshida and his co-workers at the Electrical Communication Laboratory, Nippon Telegraph and Telephone Corporation, Tokyo, shows that a part of the barium oxide on the cathode is decomposed into barium and oxygen by electron bombardment. While it was already confirmed by other workers[1, 2] that the oxygen atoms produced by the bombardment is liberated from the surface of the oxide, the behaviour of barium atoms formed was not clear until very recently. The reason is that the amount of barium is too small to be detected by the conventional analytical procedures. S. Yoshida and N. Shibata, at the above-mentioned laboratory, applied radioisotope techniques to this problem and were successful in determining the amount of liberated atoms from the surface of strontium- and barium oxide under electron bombardment.

Experiments on Strontium Oxide

In Fig. 1, A is a nickel sleeve ($\phi = 2$ mm) partly coated with strontium carbonate containing Sr^{89}. One gram of strontium carbonate contained about 0.2 mc of the isotope. This sleeve is attached by Pt-Pt Rh thermo-junction ($\phi = 0.05$ mm).

F is the primary electron source, and C is the nickel plate (2.5 × 1.5 cm) to collect the strontium atoms evolved from A. In order to minimize the contamination of the collector plate C by radioactive strontium evaporated from A during evacuation, activation, and aging processes, the circumference and the upper and lower sides of those electrodes are shielded by the nickel and mica plates, respectively. The decomposition of strontium carbonate into oxide is carried out at a pressure lower than 2.5×10^{-5} mm of mercury. Specimen A is aged about one hour at 900°C before bombardment. S, in Fig. 1, is a movable shield which is removed only during the bombardment. Upon completion of the bombardment, the experimental tube is opened and the activity of Sr^{89}, deposited on C, is measured by a Geiger-Muller counter (1.4 mg/cm² mica window) which is shielded by lead 5 cm thick on all sides in order to reduce natural counts. As the temperature of strontium oxide depends on the input wattage (bombarding current × voltage), it is adjusted to a constant value by means of a back heater, even though the bombarding current is varied at a given bombarding voltage.

Experiments on Barium Oxide

The experimental tube is similar to that shown in Fig. 1, except that A is a rectangular nickel sleeve (4.0 × 1.0 mm). One gram of the barium carbonate contained about 0.9 mc of Ba^{140}. The decomposition, activation, and aging processes are also similar to those in the case of strontium oxide.

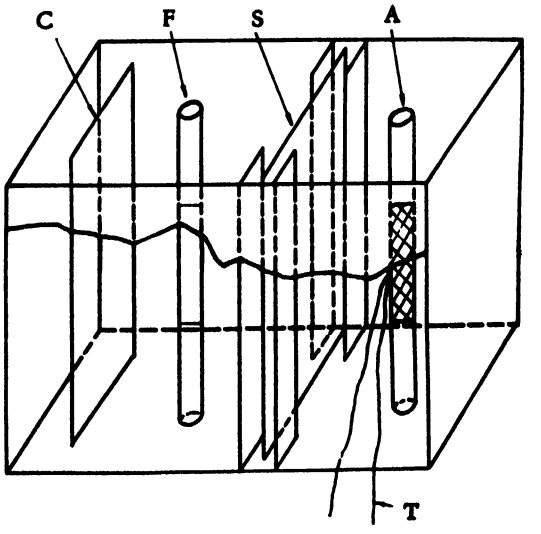

Figure 1

* Professor, Department of Chemistry, Faculty of Science, the University of Tokyo.

Ba^{140} of a half-life of 12.8 days, decays to La^{140} which has a half-life of 40 hours. If the total activity of an initially pure Ba^{140} is measured as a function of time, it gradually increases due to the growth of the daughter nuclide, La^{140}. After a certain time, the ratio of the numbers of atoms of parent and daughter becomes constant, and the rate of decay of total activity will follow the half-life of Ba^{140}; that is, the so-called radioactive equilibrium is attained between two isotopes. In order to measure accurately the quantity of barium evolved, it was necessary to allow the collector *C* to age for approximately two or three weeks after the completion of a bombardment. Thereafter, the mass of barium on the collector *C* could be determined by a comparison of its activity, extrapolated to a given date, with that of a standard specimen.

From the above experiments, the following results are obtained:

Strontium Oxide

The quantities of Sr^{89} on *C*, under various bombardment conditions, are shown in Table 1, as a function of bombarding currents, times, and voltages. The experimental errors are about 1.5% at several hundreds, and 3% at scores of cpm. The total mass of strontium evolved from *A* is calculated easily from the quantities on *C*. The factor (1.6×10^{-8} gm/cpm) which is used to convert cpm value into weight of strontium, is calculated from the counting rate of the standard specimen.

Figure 2 gives a few examples of the curves, showing the quantities of Sr^{89} deposited on *C* at several bombardment conditions as a function of bombarding time.

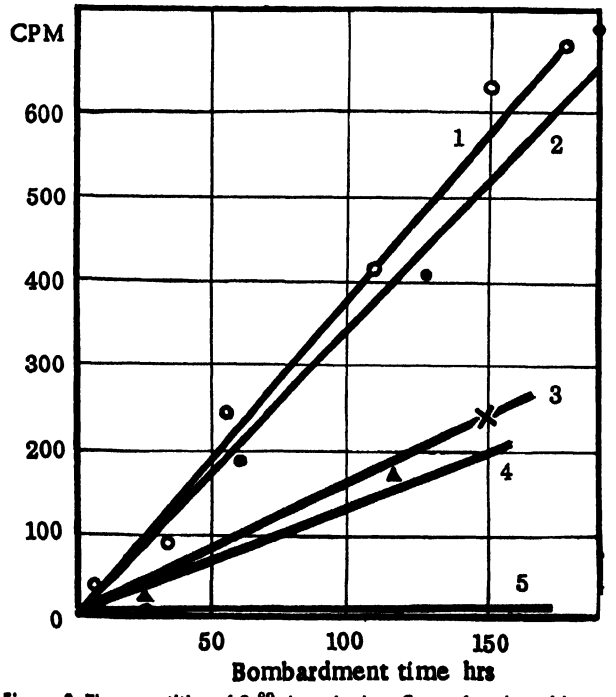

Figure 2. The quantities of Sr^{89} deposited on C as a function of bombarding time at several bombardment conditions: (1) 3.5 ma, 750°K; (2) 2.5 ma, 750°K; (3) 2.5 ma, 700°K; (4) 1.0 ma, 750°K; and (5) 1.0 ma, 560°K; (bombarding voltage is 150 ev)

Table 1. The Quantities of Sr^{89} Deposited on C

Bombardment conditions				
Voltage (volt)	*Current (ma)*	*Temperature (°K)*	*Time (hour)*	*cpm*
150	3.5	750	6*	26.4
150	3.5	750	6	26.8
150	3.5	750	34	95.1
150	3 5	750	57	222.2
150	3.5	750	100	141.9
150	3.5	750	110	415.1
150	3.5	750	140	637.2
150	3.5	750	150	627.8
150	3.5	750	180	682.1
150	2.5	700	6	11.4
150	2.5	700	150	233 6
150	2.5	750†	43	230.6
150	2.5	750†	60	190.3
150	2.5	750†	128	412.5
150	2.5	750†	191.5	699.8
150	1.0	560	21	0.2
150	1.0	560	122	1.3
150	1.0	750†	21	17.7
150	1.0	750†	120	179 9
500	1.0	750	6	0
500	1.0	750	34	3.5

* Strontium oxide was heated at 1070°K for 5 min after each bombardment which lasted for 10 min.
† Temperature was adjusted, using a back heater.

Although there are some irregularities in the experimental results obtained, the following general conclusions may be drawn:

(1) When the voltage was kept at 150 volts and the current was varied (as 1, 2.5, and 3.5 ma), the rate of evolution of strontium from the oxide increased linearly with the number of primary electrons, provided the temperature of the oxide remained constant.

(2) The rate of evolution increased exponentially with the rise of the temperature between 560° and 750°K. The activation energy is about 0.8 ev at 150 ev (cf. Fig. 5).

(3) When the input wattage is equal, the evolution by 500 ev electrons is far less than that by 150 ev electrons.

(4) The efficiency of the evolution, or the number of strontium atoms evolved per one primary electron, is around 1.1×10^{-5} at 150 ev and 750°K.

Barium Oxide

The quantities of Ba^{140} deposited on *C* under various bombardment conditions are shown in Table 2. There are two kinds of experimental errors: One is due to the extrapolation of observed counting rates to a given date, and the other is due to statistical fluctuation of radioactive disintegration. The total experimental errors are about 5% at two hundreds and 10% at scores of cpm. The factor (1.5×10^{-9} gm/cpm), which is used to convert cpm value into weight of barium, is also calculated from the counting rate of the standard specimen.

Figure 3 gives a few examples of the curves, showing the quantities of Ba^{140} deposited on *C* as a function of bombarding time. The bombardment conditions are illustrated in each figure. Figure 4 gives the relation between the specimen's temperature and

Table 2. The Quantities of Ba^{140} Deposited on C

Bombardment conditions				
Voltage (volt)	Current (ma)	Temperature (°K)	Time (hour)	cpm
150	2.5	600	10	2.0
150	2.5	600	50	8.4
150	2.5	600	100.5	38.1
150	3.5	640	10	6.5
150	3.5	640	30	26.0
150	3.5	640	50	30.0
150	3.5	640	95	68.3
150	4.5	670	10	8.3
150	4.5	670	29	35.9
150	4.5	670	71	146.1
150	5.5	710	18	57.4
150	5.5	710	42	154.1
150	5.5	710	77	294.0
500	1.0	620	29.5	—
500	1.0	620	68	5.6
90	3.0	540	26	3 2
90	3.0	540	91	15.2
150	1.0	670	65	19.1
150	1.0	670	120	33.7
150	3.5	670	55.5	32.0
150	3.5	670	101	118.7
500	1.0	670	24	—
500	1.0	670	44	3.1
90	3.0	670	20	27.6
90	3 0	670	77	101.4

the quantities of Ba^{140} evolved at two different bombarding voltages.

From the results obtained, the following conclusions may be drawn, which are qualitatively very similar to those for strontium oxide:

(1) When the voltage was kept at 150 volts and the current was varied (as 1, 2.5, 3.0, 3.5, 4.5, and 5.5 ma), the rate of evolution increased linearly with the number of primary electrons, provided the temperature of barium oxide was constant.

(2) The rate of evolution increased exponentially with the rise of the temperature between 600° and 710°K. The activation energy is about 0.7 ev at 150 ev (cf. Fig. 5).

(3) When the input wattage is equal, the rate of evolution decreases exponentially with the increase of square root of the bombarding voltage (cf. Fig. 6).

(4) The efficiency of the evolution, or the number of barium atoms evolved per one primary electron, is approximately 6.7×10^{-7} at 150 ev and 750°K.

STUDY ON THE VOLATILIZATION OF INDIUM FROM THE ELECTRODE IN SPECTROGRAPHIC ANALYSIS

In spectrographic analysis, it is often necessary to know the mode of volatilization of the tested substance from the electrode. In other words, precise knowledge on the mode of volatilization of substance, especially that of a minor constituent in a sample, is required to determine the optimum condition for analysis. For such purpose, many studies have been made, which were based on the time variation of the intensity of the spectral line on the photographic plate during the arc excitation. But, the measurement of the density of spectral line cannot always provide the data on the amounts of volatilized substance.

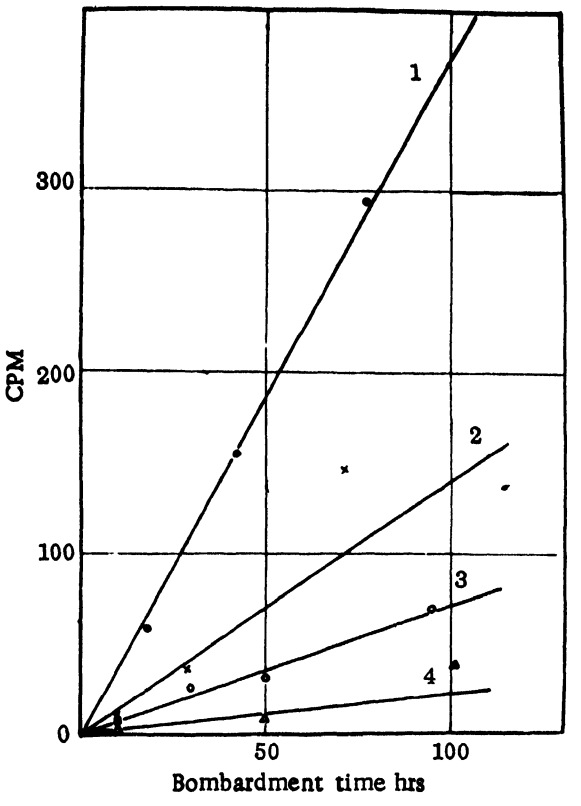

Figure 3. The quantities of Ba^{140} deposited on C as a function of bombardment time at several bombarding conditions: (1) 5.5 ma, 710°K; (2) 4.5 ma, 670°K; (3) 3.5 ma, 640°K; and (4) 2.5 ma, 600°K; (bombarding voltage is 150 ev)

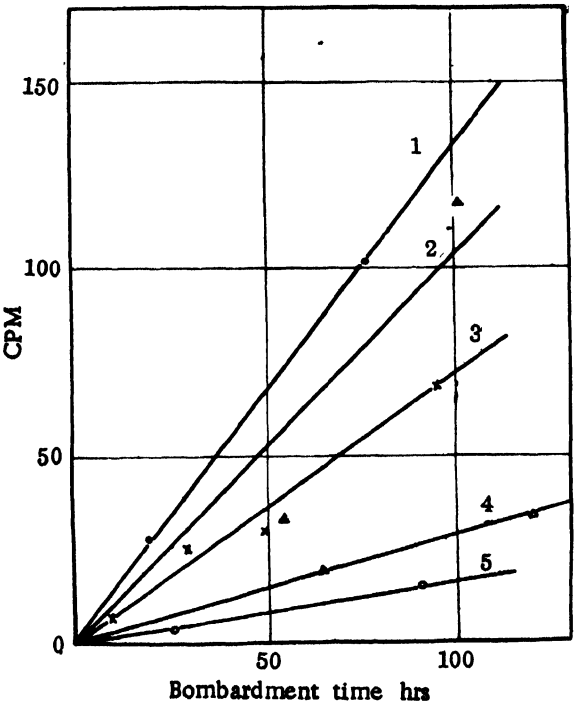

Figure 4. The relation between the specimen's temperature and the quantities of Ba^{140} evolved (bombarding conditions): (1) 90 ev, 3.0 ma, 670°K; (2) 150 ev, 3.5 ma, 670°K; (3) 150 ev, 3.5 ma, 640°K; (4) 150 ev, 1.0 ma, 670°K; and (5) 90 ev, 3.0 ma, 540°K

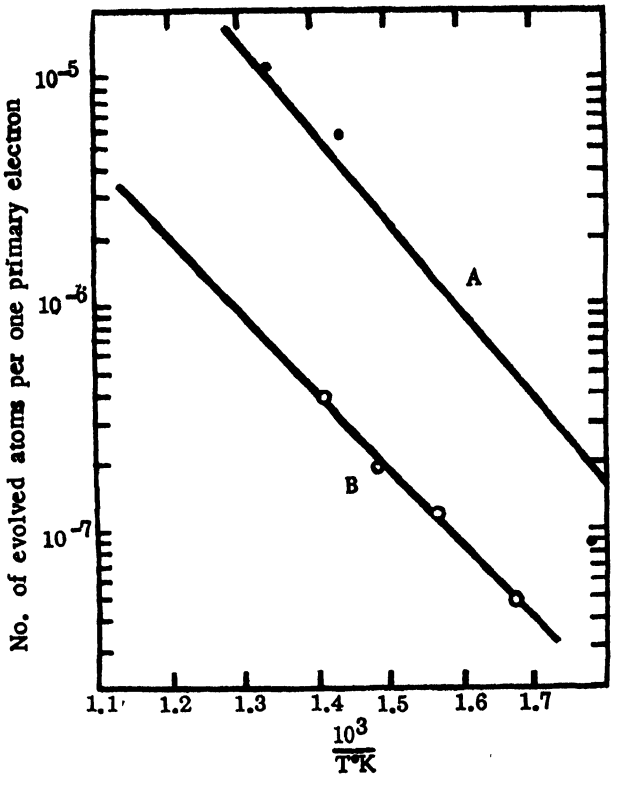

Figure 5. The rates of evolution of Sr and Ba from Sr- and Ba-oxide as a function of reciprocal temperature: (A) Sr-oxide, (B) Ba-oxide

For example, there are some limitations on the linearity between the density of spectral line and the intensity of spectral emission. And, in some cases, spectral lines cannot be recorded on the photographic plate because of rapid volatilization of test substances.

K. Kimura at the Department of Chemistry of the University of Tokyo, in collaboration with N. Saito, K. Saito and N. Ikeda, applied radioactive tracer technique to this study and the volatilization of indium from the carbon electrode was successfully traced by a radioisotope, In^{113m}.

The principle of the method can be described as follows:

Radioactive indium, In^{113m}, is the daughter of radioactive Sn^{113}. Emitting both γ-rays and internal-conversion electrons, it decays to the stable nuclide of indium with the short half-life of 105 minutes. Consequently, its activity becomes almost negligible within 10 hours after its separation from the parent. Therefore, this short-lived indium is very suitable for the investigation of the above problem, because there is little danger of undesirable radioactive contamination to the spectrochemical laboratories as well as to the workers.

If the known amounts of labeled indium compound are mounted on the lower electrode, and the arc is lighted for some time under definite conditions, the decrease in the activity of indium on the electrode after the arc excitation will indicate the rate of volatilization of indium from the electrode, provided the observed activity is corrected against decay.

The experiment is carried out in the following way. The preparation of indium tracer is performed by a new extraction method,[3] in which indium is leached out from stannic sulfide containing Sn^{113} by repeated washing with 1/100 normal hydrochloric acid solution saturated with hydrogen sulfide. To this extract is added, 0.1 cm^3 of dilute hydrochloric acid solution containing 0.1 mg of indium, and hydrogen sulfide is driven off by heating. Then, iron or aluminum is added as the carrier, in the form of ferric chloride or alum respectively, and hydroxide of iron or aluminum is precipitated from this solution with ammonia solution. The precipitate is filtered off, dried, and divided into several portions. Of these portions one portion is used as the control, while another is transferred into the cavity of the previously weighed carbon electrode. The carbon electrode is fixed on the supporter and the arc is lighted under various conditions.

After the arc is extinguished, all of the residue in the cavity of the electrode is spread on the stainless steel counting dish, which is directly placed in the ionization chamber, and the radioactivity is measured by a Lauritsen electroscope in the same geometry as in the case of the control. Throughout this procedure rapid operation is quite necessary because of the short half-life of In^{113m}. Although different geometry of the sample in the counting dish has considerable effect on the precision of the experiment, constant geometry in the strict sense can be scarcely attainable in such rapid procedure. Therefore, correction of the experimental data is performed on the assumption that the intensity of radioactivity is proportional to the weight of the sample within a given range. Since the relationship between the activity and the weight of sample shows good linearity as expressed in Fig. 7, the assumption mentioned above seems fairly valid in our experiments.

The percentage of the remaining indium on the electrode after arc excitation can be expressed by B/D, where B is the corrected, initial activity of

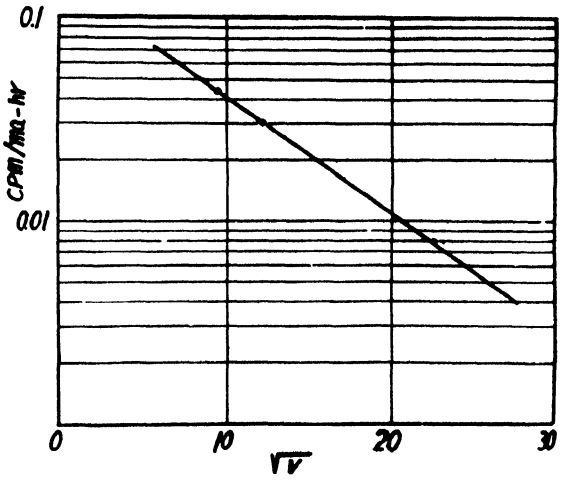

Figure 6. The quantities of Ba^{140} deposited on C as a function of the bombarding voltage

Table 3*

Time (min)	A (div./min)	B (div./min)	C (mg)	D (div./min)	B/D (%)	Time for excitation (sec)
0	0.7	—	9.6	—	—	0
35	0.57	0.60	8.9	0.65	94	10
50	0.31	0.46	8.2	0.60	77	20
63	0.23	0.36	10.3	0.75	48	30
75	—	—	7.8	0.57	0	50

* Ratio of amount of indium to that of iron, 1:1000; arc current: 4 amp; Voltage between electrodes: 30v. Time for arc excitation is varied for each experiment.

sample before arcing, and D is the corrected, initial activity of the equal amount of the control.

Two different arc sources are used in this experiment. One is the lasting arc, while the other is the interrupted one. A 110-v-accumulator of large capacity is used as the electric source.

The results obtained with the lasting arc are shown in Table 3, where the symbols, A, B, C and D, indicate the activity of the remaining indium after excitation, the calculated initial activity, the amounts of sample mounted on the electrode, and the activity of the control,* respectively.

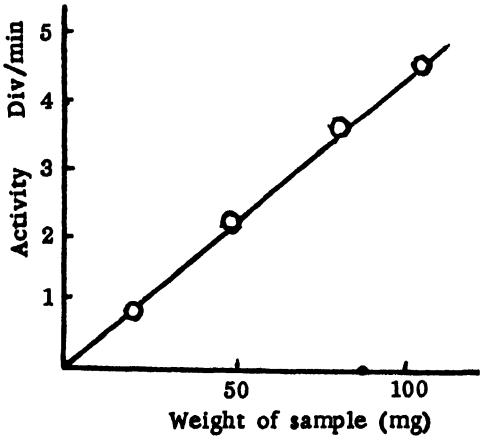

Figure 7

In Table 4 are shown the results of the experiments using the interrupted arc. The time for excitation and the time for net excitation mean the total time for arc excitation and the effective time for arc excitation, respectively. The symbols, A, B, C, D, etc., are used in the same way as in Table 3.

From this data, the following conclusions may be drawn:

* Activity for the amount equal to the sample; $D = C \times 0.7/9.6$ in the case of Table 3.

(1) In the ordinary lasting arc method, indium in the sample volatilizes at early stage of arc excitation. With a sample which contains 0.01% of indium, indium does not remain in the electrode after 50 seconds' excitation. Since the time of exposure in ordinary spectrographic analysis is usually thirty to forty seconds or so, this result confirms the adequateness of the time of exposure in the ordinary experimental procedure.

(2) In the interrupted arc method, the volatilization of indium is very slow, so that more than half of the initial amount of indium still remains after about one minute's effective arc excitation. Usually, the effective time for excitation used in the analysis is approximately more than twice that of the lasting arc. Now the actual effectiveness, as well as the significance of such prolonged excitation, is confirmed by the present technique.

SUMMARY OF SOME OTHER APPLICATIONS OF CONSIDERABLE INTEREST

H. Goto at the Tohoku University used some tracers (Fe^{59}, Co^{60} and Sb^{125}) to determine the dissociation constants of several complex salts, such as the tartrates, citrates, malonates of iron, cobalt and antimony.

The mechanism of the formation of chromate film on the zinc-plated specimen was studied by T. Hayashi at the Governmental Industrial Research Institute, who used Cr^{51} as a radioactive tracer. It was confirmed that the ions contributing to the film on the zinc-plated specimen are not Cr^{+3}, but CrO_4^{-2} ions in solution. T. Hisada and co-workers at the same institute studied the absorption of hydrogen sulfide in rubber. Using hydrogen sulfide containing S^{35}, they confirmed that the amount of absorption increases rapidly when the quantity of hydrogen sulfide passing through rubber tubing exceeds a certain value. T. Watanabe and collaborators, also at the same

Table 4*

Time	A (div./min)	B (div./min)	C (mg)	(D (div./min)	B/D (%)	Time for excitation (sec)	Time for net excitation (sec)
105	1.6	2.66	9.2	—	—	0	0
125	1.6	3.0	10.6	3.1	100	30	10
134	1.1	2.7	11.1	3.2	85	60	20
148	1.5	3.2	13.2	3.8	80	90	30
175	0.84	2.4	12.7	3.8	67	150	50

* Ratio of amount of indium to that of iron, 1:2000; interruption factor = (lighting period of arc/ extinguishing period of arc); 1:2; Period of interruption: 1.2 sec; peak current: 5 amp.

laboratory, prepared vulcanized linseed oil as well as oleic acid labelled with S^{35}.

The removal of such oils from the surface of bakelite, aluminum, lead, copper, glass, nickel, soft steel, and cast iron was studied by measuring residual S^{35} activity after the surface was smeared.

K. Kimura and co-workers at the University of Tokyo used Ra^{224} (ThX) to measure the flowing velocity of water through the pipe of a hydroelectric power station. S. Iwai and his collaborators at the Kyoto University were successful in studying the magnitude of turbulent mixing and the detention time in hydraulic structures such as pipes, open channels, and tanks by using I^{131} as a tracer.

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2. Asakasu, K., and Imai, T., *J. Appl. Phys.* 24, 107 (1953).
3. Kimura, K., and Ikeda, N., *J. Scientific Research Institute* (Tokyo) 45, 133 (1951).

Record of Proceedings of Session 22C

FRIDAY AFTERNOON, 19 AUGUST 1955

Chairman: **Mr. J. V. Kurdiumov (USSR)**
Vice-Chairman: **Mr. E. Estermann (Switzerland)**
Scientific Secretaries: **Messrs. I. D. Rojanski and C. A. Sastre**

PROGRAMME

P/463 Development in thickness gauges and allied instruments.....J. L. Putman
P/164 The versatility of radiation applications involving penetration or reflection.....C. E. Crompton
P/704 Application of radioisotopes to control technological processes .....G. G. Jordan *et al.*
DISCUSSION
P/383 Studies and industrial applications of bremsstrahlung from the beta rays of yttrium-90.....P. Lévêque *et al.*
P/462 Application of radioisotopes to leakage and hydraulic problems.....J. L. Putman and S. Jefferson
P/707 The use of artificially radioactive isotopes in the study of the processes of the production of steel and iron.....A. M. Samarin
P/713 The use of radioactive isotopes in the study of wear of machine parts .....B. D. Grozin
DISCUSSION
P/1054 Brief review of applications of isotopes in process and quality control..... M. Kato
P/882 Some industrial uses of radioisotopes in Norway.....U. Been and E. Saeland
DISCUSSION

The CHAIRMAN: At today's meeting, we are to consider a series of papers on the use of radioactive isotopes in industry for the control and analysis of production processes. The papers submitted review the various uses of isotopes. They show that isotopes have already found large-scale application in engineering in a number of countries. Instruments have been developed for controlling the thickness or density of articles in production, recording changes in the level of liquids in closed vessels, making rapid analyses of certain elements in oil, etc. The production of portable sources of X-rays, on which information is given in a number of the papers submitted, is a particularly interesting development. Radioactive isotopes are being widely used in engineering as tracers. They are already being used in metallurgy for the study and control of the wear of the lining of blast, open-hearth, and electric furnaces and for the study of the hydrodynamics of molten steel, of crystallization in the conventional and continuous casting of steel and aluminium and of the thermodynamics and kinetics of metallurgical processes. We will also hear today about the use of tracers for the detection of flaws in piping, the investigation of silt movements in rivers and many other uses.

Mr. J. L. PUTMAN (UK) presented paper P/463.
Mr. P. AEBERSOLD (USA) presented paper P/164.
Mr. NAZAROV (USSR) presented paper P/704.

DISCUSSION OF PAPERS P/463, P/164, P/704

The CHAIRMAN: We can now discuss these three papers, on which there are a number of questions.

Mr. GIANELLA (Switzerland): I should like to know something about checking weldings on steel linings in hydro-electric plants—that is, the steel linings of penstocks. I should like to know whether such a check is possible by reflection; in other words, entirely from the inside.

Mr. PUTMAN (UK): I think in fact, that the tubes can be checked from the inside. We have not yet developed an instrument which will do that. Provided, however, that a suitable mounting can be made so that the radioactive source is pressed against the metal to be measured and so that one can concentrate on a small part of the inside surface of the tube, and provided that the tube is of sufficient diameter to accommodate a scintillation counter—or at least a

crystal and a light guide—this should certainly be possible.

We have also done some measurements using neutron scattering for the measurement of the water content of soils. In those measurements we have used a neutron source in connexion with a boron trifluoride counter. One of the difficulties which we expected to encounter in some soils was related to the absorption of neutrons by possible contaminants of the soil, such as chlorine, arising from salt contamination or rare earths. Would Mr. Aebersold like to comment on the effect which soil contaminants that absorb neutrons may have on the accuracy of such measurements?

Mr. AEBERSOLD (USA): Strong neutron absorbers would certainly interfere with this test. The devices that I mentioned were developed for highway engineering and also for use before strips of concrete on airfields were put down. The soils were of rather ordinary types. I can imagine that very salty soils, or the soils one would encounter in oilfields, would create many interferences. As I have said, however, these devices were for ordinary road and airport construction measurements.

Mr. EATON (USA): An alpha-ionization manometer was introduced in the United States a few years ago. It was of the type described in Mr. Nazarov's paper (P/704). It did not, however, find much application. Could he tell us what are the principal advantages which, in his experience this type of device has over other types of manometers?

Mr. NAZAROV (USSR): Alpha particle manometers for the measurement and control of gases at low pressures have advantages over other methods, their principal advantage being the accuracy (± 2 per cent) with which they register pressure and the consistency of the readings obtained. I should explain that they have not yet found wide application in the Soviet Union and are mainly used in research laboratories and scientific-research organizations.

Mr. GOMBERG (USA): I am interested in the pipe seam exploration device. I should like to know what degree of resolution can be achieved with the device. How small a defect can be found, both in size and in density change? How close does the scintillator have to be to the pipe circuit?

Mr. NAZAROV (USSR): The paper states that the ionization method of detecting flaws in welded seams is less sensitive than the usual X-ray method. With the X-ray method, flaws of the magnitude of 1.5–2 per cent can be detected in 10 mm welded seams. With the ionization method, flaws of the magnitude of 6 per cent up can be detected. The defects in question are mainly non-fusion and cracks running along the seam. Spherical defects in the form of gas vapors and slags are less easily detected. Since comparatively insensitive control instruments occasionally have to be tolerated in industry and since the X-ray method is costly and of low efficiency, the ionization instrument is quite acceptable in mass production. The counter is placed 22 mm away from the welded seam.

Mr. MEDVEDEV (USSR): I have a question for Mr. Putman. What is the ratio of direct to back-scattered gamma radiations in the instruments using gamma-ray reflection?

Mr. PUTMAN (UK): We have not done direct measurements of the proportion of actual numbers of radiations, but, because the efficiency of the system is greater for low-energy gamma rays than for high-energy gamma rays, the counting rates obtained from the direct radiations and from the back-scattered radiations are comparable. It is probably worth adding that one instrument has now been developed which, by using a small crystal, is less efficient for the high-energy direct radiations and manages to make the measurements I have been describing without the use of electronic discriminators.

Mr. MEDVEDEV (USSR): Is amplitude discrimination used at all in industrial plants?

Mr. PUTMAN (UK): In the device I was describing, which is in industrial use, we do use amplitude discrimination, so that we pick out only the responses for the back-scattered radiations, but in the commercial gauges which are being developed it is likely that this discrimination will be avoided by the use of small crystals which are more sensitive to the back-scattered radiations than the direct ones.

Mr. P. LÉVÊQUE (France) presented paper P/383.

Mr. J. L. PUTMAN (UK) presented paper P/462 as follows:

Radioisotopes, especially those which emit gamma rays, are particularly useful in problems of flow in relatively inaccessible conditions, as for example in buried pipes. We have been concerned during the past few years in a number of such problems, both for basic measurements of liquid flow in pipes and for specific tests of a more practical nature. Some of these are described in the written version of Paper P/462 which I am now presenting.

In this verbal account, I should like to confine myself to two projects in which we have been concerned. These are (1) the detection of leaks in buried water and oil pipelines, and (2) the tracing of mud movements on the bed of a river estuary.

When new water mains are being laid, it is often desirable to refill the trenches which have been dug for the water mains with earth almost as soon as the pipes are jointed. One obvious reason why this is necessary is that if the mains pass close to a main road great inconvenience to the public may result from leaving the trenches open. The practice, however, of covering a main immediately after jointing and before testing with a meter or more of earth, used to be rather risky because if subsequent tests showed that a leak existed in the main it was very

difficult to find. Generally, sections of main not longer than about 300 or 400 metres can be isolated by orthodox pressure tests by which leaks, if they exist, can be found in the relatively short sections, so that the usual problem is to find a leak in a section not longer than this. Generally speaking also, the pipes themselves, since they are new pipes, are intact and only the joints are suspected of leaking.

The commonest method which we have used for radioactive testing is to fill the suspect length of main with a uniform solution of sodium-24 in the form of sodium bicarbonate. The chemical form is not very significant: we used sodium bicarbonate because it dissolves easily in water in the field. The main, then, is filled with a uniform solution containing sodium-24 and we raise it above the working pressure of the main to be tested to encourage the radioactive solution to leak out into the soil. It is left in this condition for about half an hour.

After this the radioactive solution is moved along to another section of the main by replacing it with fresh water, and now only the radioactivity which has leaked out is still present in the soil. Meanwhile, bar holes have been prepared in the ground close to each joint in the main, and detectors enclosed in steel tubes are pushed down these bar holes into the vicinity of the suspect joints (Slide 1). These may be Geiger counters or scintillation counters: we have in fact used both types. If radioactivity is found in the soil, then a leak is probably present in the main. There is one condition in which apparent radioactivity could be found there when there is some adsorption of the radioactive material inside the pipe. To guard against such false indications we also made it possible to take samples of water for assay from the same bar holes by using a specially adapted tube containing a sponge. This method is rather tedious to use but it is still much quicker than tests which involve taking up long lengths of the main. The level of activity used is 0.8 microcuries per litre (that is about one-tenth of the international tolerance level for sodium-24 in drinking water). Leaks of 5 millilitres per hour or more can be detected. In fact on one occasion we detected a leak which was as low as two millilitres per hour. Generally the kind of leaks in which we are interested are of the order of 100 millilitres per hour and are easily found.

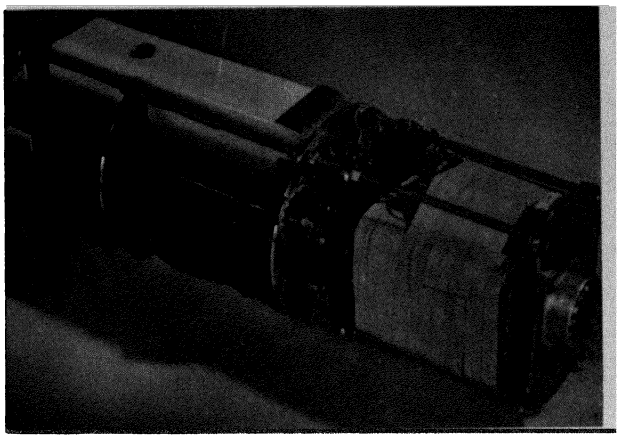
Slide 1

For longer sections of main, up to a few kilometres, a different method is used. The main is closed at both ends and a short section about 2 or 3 metres long is exposed. In the middle of this section a small volume of rather more highly radioactive solution is injected and the pressure behind this injection is maintained with a pressure pump. If there is a leak in the main the radioactivity then flows towards the leak and is at once detected by one of two Geiger counters placed on either side of the injection point. By applying this method successively the leak can be localized to a short section of main.

There is another method which we have used when the leak rate is high. By making small volume injections into the main and closing up all known exit points the main is still maintained under pressure and the radioactive solution then flows along the inside of the main under the action of the leak. By measuring its velocity in the main from measurements on the outside one can find the leak, because the flow velocity changes appreciably when the leak is passed. Unfortunately it is essential to have a turbulent flow to use this method, otherwise the radioactive solution gets badly spread, and to produce turbulent flow in a main of ten centimetres diameter one needs a leak of the order of 500 litres per hour.

Generally mains to be tested are not yet connected to public water supplies, but when they are every care is taken to ensure that the radioactivity cannot reach the public even though the activity is well below the danger level, or even below the tolerance level. Close liaison is maintained with public health authorities whenever there is any question of possible outlet to public water supplies to make sure that this does not occur. Those who attended Dr. Seligman's lecture earlier in the week will have seen some of these gentlemen standing around the scientists making the measurements. In addition, any solutions injected into the main in this way are very heavily chlorinated, for two reasons: first, to guard against bacterial infection and, secondly, to make these radioactive injections so unpalatable that no one is likely to drink them.

Leaks in oil pipelines, which may stretch for much further—tens or hundreds of kilometres—without access are quite a separate problem. In these we have found it convenient to detect the radioactivity from the inside of the pipeline. A section of line is filled with a radioactive solution and this is pumped along under pressure, followed by clear water or oil.

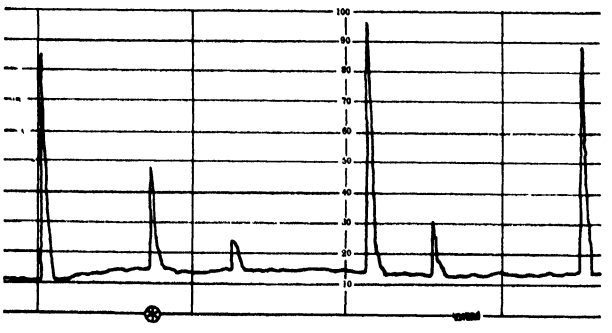


Slide 2

After a delay of about an hour a detector unit, shown in Slide 2, enclosed in a sealed container is passed into the pipeline and is drawn along the pipeline by a standard type of pipe scraper, pushed by the flow of water or oil. Wherever radioactivity has leaked out in passing along the pipe line this following detector unit detects it with the four Geiger counters, two of which you can see, and the impulses from these are fed to a small portable wire recorder. At the far end of the main the unit is extracted and the wire recorder is played back into a rate meter which gives an indication on a paper chart of the activities passed.

The peaks in Slide 3 show in fact leaks in the pipeline. The pipelines do not usually leak so frequently, but we made them do so artificially. The larger pulses are due to small pieces of cobalt-60 wire of about 200 microcuries placed on the outside of the pipeline as distance markers. This unit has been used at present for measuring leaks in lines up to about 20 kilometres and it is confidently expected that by slowing down the portable wire recorder we shall be able to extend its range to 100 kilometres or more.

So far we have dealt with fluids under control. Siltation on the bed of a tidal estuary is an example of a system not under control—or at least not under as much control as we might wish. In the estuary of the Thames, dredging is carried out by the Port of London authority to keep the waterway free for shipping. Some millions of tons of mud and silt are removed per year from the dock areas and mostly dumped out to sea. It appeared, however, from measurements that about five times as much silt was being removed from the river as could be accounted for by the mud brought down by the river. The Hydraulics Research Station made flow measurements which indicated that a counter current of salt water could flow upstream on the bed of the estuary and might be carrying mud with it. At the request of the Port of London Authority a joint experiment was made by the Hydraulics Research Establishment and Harwell to find out if this is happening. The silt in question is known to be transported by a thin mud about the consistency of thin porridge which is known as liquid mud. After deposition this latter solidifies in the form of solid mud on the river bed. The liquid mud consists of a mixture of organic material with very fine sand, and to trace it we found the best material we could use was powdered glass to simulate the sand. As a radioactive marker for the powdered glass we used scandium oxide in solid solution. For the pilot experiments about 85 grammes of glass, containing 5 per cent of scandium oxide, was ground to the required size and then irradiated to obtain a total activity of about 4 curies of 85-day scandium-46.



Slide 3

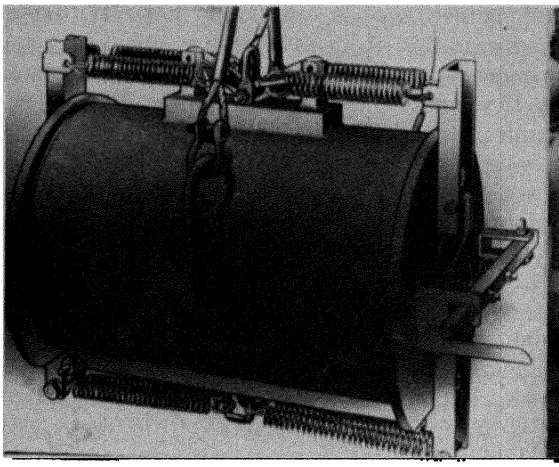
On the deck of a boat this was mixed with about 40 kilogrammes of mud in a container (Slide 4). That was done in the open air without screening at a distance of about 2½ metres (Slide 5).

The radioactive glass powder is in fact being put into a hole at the top of the drum (Slide 6) which is finally closed by a lid held down by springs and operated by rather crude remote control. The whole container is then slung overboard and lowered to the bed of the river, where the two ends of the drum can be released with a trip wire pulled from the deck of the boat. Having injected in this way in the pilot experiment, the mud was followed for about two weeks. We injected at low tide to make sure that in this pilot experiment the activity went upstream.

The results showed that the radioactivity did in fact follow the liquid mud and could be followed with Geiger counters for about two weeks. They also showed that a higher activity would have been desirable, and samples of mud taken from the river bed of the most active areas showed that this would be quite safe. Therefore, after making a thorough survey of background counting rates, a full-scale experiment was started on 5 July of this year and is still in progress.

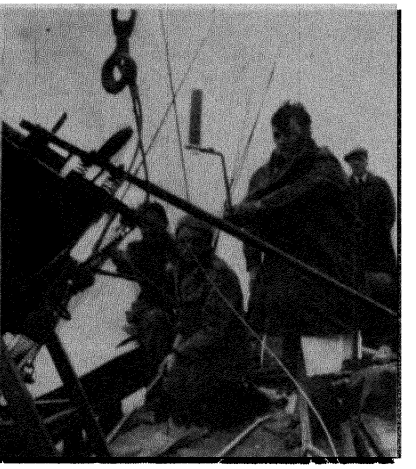
In this case about 30 curies of scandium-46 were used in 750 grammes of ground glass. This was injected into the river near Tilbury in a similar way to the one I have described but this time at high tide.

As expected, the active mud was swept down the estuary and was detected on the river bed up to 9 kilometres downstream at low water. No activity appeared upstream for the first full tidal cycle, but after two days, activity gradually began to appear



Slide 4

Slide 5



Slide 6

(Slide 7), first in Long Reach 11 kilometres upstream after about 9 days. Then, after sixteen days, it appeared at Barking Reach, which is 20 kilometres upstream. It is still present at Barking Reach according to a telephone conversation held today. It has disappeared from the area downstream but it is still strong in Gravesend Reach.

By this experiment we have confirmed that upstream movement of mud is taking place. The Port of London Authority will be able to reconsider their dredging techniques in the light of this evidence.

What may prove to be more important still is that the use of radioactive tracers is now established for general full-scale measurements of siltation in tidal estuaries up to the size of the Thames. The details and actual equipment from this investigation are shown at the Palais des Expositions.

A similar investigation is planned later this year to measure movements of sand on the seabed as part of an investigation of coastal erosion.

Finally, this is intended to be a technical paper but it is perhaps worthwhile to stress the economic significance of the two projects I have been describing. The importance of measuring and controlling the siltation of navigable rivers is of fairly obvious economic importance.

Radioactive water leak detection, as applied now on a small scale to freshly laid water mains, has already saved many thousands of pounds in engineers' time. If this is developed eventually on a large scale and used in existing mains as well, it may save millions of pounds a year in Britain alone in conserving our vital water supplies. It is difficult to see how either of these projects could have been undertaken by other than radioactive means.

The CHAIRMAN: Before we go any further, I should like to hand over the Chair to Mr. Exterman, the Vice-Chairman of this session. Mr. Exterman, I should be glad if you would take over the conduct of the meeting.

The VICE-CHAIRMAN: The next paper deals with the use of radioactive isotopes in the study of the process of steel and pig iron production. I call on Mr. Samarin.

Mr. A. M. SAMARIN (USSR) presented paper P/707 and paper P/713.

DISCUSSION OF PAPERS P/383, P/462, P/707 AND P/713

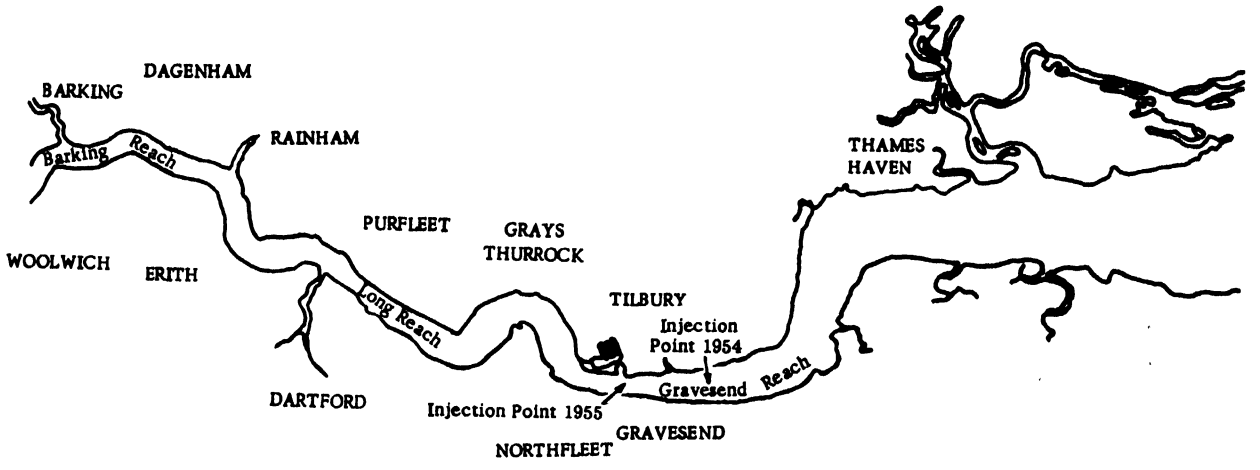
Mr. SAELAND (Norway): I should like to ask Mr. Lévêque a question on the bremsstrahlung sources. When the activity of beta emitters of the source is increased, the gamma yield declines. There must, therefore, be a practical limit to the total gamma activity. Could you give us some idea of the maximum gamma activity obtainable assuming that the source is not too large to permit radiography?

Mr. LÉVEQUE (France): If the source is larger, I believe that a process of auto-absorption occurs within the source itself. To provide a source for radiographic purposes, however, strontium activity of the order of 1 curie is probably required, which, under optimum conditions, represents a weight of approximately 5 milligrams of strontium at most.

Mr. EATON (USA): I have the following question on the first paper presented by Mr. Samarin. How representative or typical of the behaviour of refractory brick do you consider the calcium carbonate and calcium oxide used as tracers in the study of inclusions in steel?

Mr. SAMARIN (USSR): We introduced the calcium isotope into the refractory material before it was moulded into bricks, thus ensuring that the isotope was evenly distributed in the refractory ware and hence that the behaviour of a lining filled with isotope-containing bricks would be identical with that of a lining filled with ordinary bricks. Consequently the wear of the bricks and the degree of contamination of the steel by particles of the refractory lining can be determined from the activity of the particles of non-metallic inclusions separated out in the electrolytic dissolution of steel specimens.

Mr. AEBERSOLD (USA): I wish to commend the USSR delegates for the very excellent papers they have presented. Those papers have given evidence of a very large use of isotopes in industry in the USSR. As I understand it, radioisotopes such as phospho-



Slide 7. Port of London

rus-32, calcium-45 and cobalt-60 are used daily as a matter of routine in steelmaking, and a certain amount of radioactivity perhaps gets into the products sold to the public. I appreciate that this amount is quite small, but I wonder just what levels of activity are permitted in isotope uses in industry in the USSR. For instance, what levels of activity would be allowed in steel that is sold to the public?

Mr. SAMARIN (USSR): We have no specific regulations on this, but the amounts of isotopes we are adding to steel are completely harmless to any one. If a small ampoule of radioactive cobalt-60 is incorporated in the lining of a blast furnace, the amount of the isotope that finds its way into a 2000-ton mixer is insignificant, and, if the proportion of molten cast iron in the cast iron used in the smelting of steel in open-hearth furnaces is taken into account this ampoule would be distributed over approximately 4000 tons of steel.

Mr. GOMBERG (USA): I was particularly interested in the reference to the use of autoradiographic methods for studying inclusions in steel and the sectioning used in order to study their distribution. What special techniques have been used for locating these inclusions? I am referring particularly to autoradiographic techniques. Furthermore, what practical resolution limits have been found for this work?

Mr. SAMARIN (USSR): I am not sure if I quite understand the question in translation. The autoradiography method is an excellent method of locating non-metallic inclusions in smelted steel. With the contact autoradiography method, particles of from 16–40 microns can be clearly located in steel.

Mr. GOMBERG (USA): This may have to be resolved by a private discussion. What I had in mind was the use of the radioactive material and the photographic film simultaneously, so that one gets not only the quantity of radioactive material but also the exact location of the inclusion, all in the same pattern.

Mr. SAMARIN (USSR): There is a detailed discussion of this particular point in a paper by S. M. Gnuchev, which was published in the transactions of the session of the Academy of Sciences of the USSR on the peaceful uses of atomic energy. We can talk about this more fully after the meeting.

Mr. EATON (USA): This question relates to the second paper presented by Mr. Samarin. Could he tell us a little more about the method of preparing the very interesting electrolytic iron oxide coating which gives the superior bearing surface of which he spoke?

Mr. SAMARIN (USSR): This is not an electrolytic iron oxide coating, but a coating obtained by chemical methods.

Mr. LÉVÊQUE (France): The statement frequently appears in papers on wear, that the sample products of wear are measured in the same geometric conditions as the control. The control is, however, in liquid form, whereas the samples are in solid form. At the Soviet exhibition I saw, *inter alia*, the measuring of the radioactivity of filings which are the products of wear, and I should like to ask Mr. Samarin how accurate this method is.

Mr. SAMARIN (USSR): In the work we have done we have attained an accuracy of not less than 5–10 per cent.

Mr. LÉVÊQUE (France): I am not so much asking a question as making a comment. For the purpose of gauging the efficiency of filters, Mr. Labeyrie of the French Atomic Energy Commission has used a slightly different method of marking. He makes use of the fact that the products of radon decay, which are solid, settle on dust. Radioactivity can thus be obtained directly from this dust and the need to use a different dust is eliminated.

Mr. SAMARIN (USSR): That seems to me to be quite a good method.

Mr. BASSETT (UK): If I understood Mr. Samarin correctly, he said that the amounts of cobalt-60 in steel would not be such as to have any effect on personnel using it. Would he care to say whether there would be sufficient activity in the steel to affect photographic material placed on shelves made of it?

Mr. SAMARIN (USSR): I do not think that the presence of cobalt in such concentrations would affect photographic material. For example, in the case of cast iron containing 0.3 mc of cobalt-60 per ton, very slight darkening of photographic paper was observed over a period of 100 days—not more than 30 per cent more than the fog normally formed.

Mr. GOMBERG (USA): I should like to ask Mr. Lévêque if, in his bremsstrahlung sources, he has made any tests using a tungsten target or enclosure. I do not recall seeing tungsten as one of the test metals.

Mr. LÉVÊQUE (France): We have not used tungsten as an absorber. We have confined ourselves to lead.

Mr. M. KATO (Japan) presented paper P/1054.

Mr. U. BEEN (Norway) presented paper P/882.

The CHAIRMAN: I should like to thank Mr. Been for his paper. The papers in this third group are now open for discussion.

DISCUSSION OF PAPERS P/1054, P/882

Mr. AEBERSOLD (USA): I have a question for Mr. Been. In the last three studies which he described, tracers were used which differed chemically and physically from the material being traced. What sort of assurance have you, Mr. Been, that the tracer represents the true behaviour of the material being traced? Specifically, could the sudden rise in the paint erosion which you showed in one of your last charts be characteristic of the yield strength of the paint rather than of the steel?

Mr. BEEN (Norway): We are aware of the fact that the radioactive material used in the latest investigations might exhibit a somewhat different behaviour from that of the materials being traced. However, we did not consider this a very serious drawback to the investigations, as to a large extent the results could be verified during the subsequent operation of the plants. Direct methods were not feasible in these investigations, and to obtain indications as to the different effects we tried to reproduce the true conditions in the best possible way. In the turbine experiments, for instance, several kinds of paint were tested to find one with a suitable wear effect. As far as we have seen the results obtained in these isotope investigations agree with the operation experiences.

Mr. AEBERSOLD (USA): This question is directed to Mr. Kato. In your complete paper, you mentioned a radioactive tracer for process control in determining the transit time through steam or steaming pipes. I should like to know if this is a routine procedure that is done for continuous process control or is this just for research purposes? Could you comment some more about this particular type of use?

Mr. KATO (Japan): This experiment was carried out on a semi-industrial scale in our institute. Therefore, it is rather research purpose.

In this saccharifying process, the paste which is a mixture of powdered potato and phosphoric acid solution is continuously fed into the steaming pipe. We made up the paste of one litre tagged with phosphorus-32 of 50 microcuries. In the midst of the process, we added such a tracer material. Then we measured activity at the outlet of the steaming pipe which was 20 metres in length and 5 centimetres in diameter. Thus we determined the transit times and the spread of raw material in the steaming pipe.

Mr. GOMBERG (USA): In the test of the cement kiln operation, what particular advantage do you gain by adding the tagged cement-fed material over a period of two hours rather than putting in one batch at a given time?

Mr. BEEN (Norway): In the cement experiments, for statistical reasons the radioactive materials were added to the kiln feed over a period of two hours. The rate of the various particles differs considerably in the kilns, and to obtain an average value for the material rate and a picture of the rate distribution we found two hours to be a suitable period.

Session 23C

FISSION PRODUCTS AND THEIR APPLICATIONS

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The Effect of Gamma Radiation on Some Chemical Reactions of Possible Industrial Importance

By Leigh C. Anderson, Bruce G. Bray and Joseph J. Martin,* USA

For the past four years this laboratory has been investigating chemical reactions promoted by gamma radiation. The work has been carried out as part of a broad program to find uses for the large amounts of radioactive fission products that are expected to be made available from the operation of nuclear reactors. However, because development programs for packaging and shipping fission product sources have not been completed, the studies have been conducted with artificial cobalt-60.

Two cobalt-60 sources of gamma radiation have been employed in this investigation. The first source is an aluminum-clad hollow cylinder of cobalt about 3.5 cm in diameter and 35 cm long. It was activated by neutron radiation in the pile of the Brookhaven National Laboratory and was given a nominal rating of 1000 curies. Later calibration indicated its true radiation strength to be about one-third this value. The cylinder of cobalt was mounted in a heavy lead container so that objects to be radiated were simply placed in the center of the cylinder. This permitted only small volumes to be treated at any one time. A second cobalt-60 source was installed which made provision for radiation of large volumes of material. This source consists of 100 aluminum-clad rods of cobalt about 0.6 cm in diameter and 25 cm long. These rods are mounted in two close concentric circles in an aluminum rack of about 15 cm internal diameter. The whole unit is stored under water about 5 meters deep. When it is to be used, the unit is raised by remote control into a chamber where the various materials to be radiated have been stacked. The radiation chamber is constructed with concrete walls about 1.2 meters thick. The cobalt rods were activated in the pile at Chalk River, Canada, and were nominally rated at 10,000 curies; though, as with the other source, calibration indicated the radiation strength to be about one-third this amount.

In selecting chemical reactions to be studied in the presence of gamma radiation, emphasis has been placed on those which might have commercial applications. When a reaction was found to be promoted only minutely by radiation, it was discarded in favor of other reactions that proceeded vigorously. Two classes of chemical reactions that result in appreciable yields of products in the presence of gamma radiation are (1) polymerizations, and (2) chlorinations. In the former category this paper presents information on the polymerization of ethylene. In the latter category the chlorination of a series of aromatic compounds is considered. Also the economics of a plant to chlorinate benzene are presented and a comparison is made between the use of ultraviolet and gamma radiation.

I. POLYMERIZATION OF ETHYLENE

The gas-phase polymerization of ethylene has been studied in the presence of alpha radiation,[16] ultraviolet radiation,[2, 12] and gamma radiation.[9, 13, 14, 15] The data presented here were taken in a continuation of the work of Lewis,[13, 14] and cover a pressure range of 50 to 100 atm and temperatures from 6 to 220° C.

Experimental Work

The high pressure stainless steel reaction vessel of Lewis was used in all runs. This reactor, shown in Fig. 1, could be maintained at any desired high temperature by a set of electrical resistance heaters which fitted around the outside. A uniform procedure of loading and cleaning was followed in each test. The reactor was sealed at the flanges and pressure tested with nitrogen at 1000 psi for 12 hours. The nitrogen was vented and the reactor evacuated, after which ethylene gas was charged at room temperature. The loaded vessel was placed in the radiation chamber and controlled to the desired temperature before raising the ten-kilocurie cobalt-60 source to initiate the reaction. Runs in the one-kilocurie source could be made only at room temperature as there was no room for the electrical heaters on the outside of the reactor. During the runs pressure and temperature measurements were made at various intervals. At the conclusion of the run the reactor was removed from the radiation field and the excess ethylene was vented. The flanges were opened and the polymer product was removed mechanically and weighed. The reactor was cleaned by washing with boiling xylene, acetone, and distilled water. The ethylene was about 97% pure with a gas analysis showing it to contain 1.7% N_2, 0.8% C_5H_{12}, 0.37% CO_2, 0.05% CO, and 0.02% O_2. The amount of ethylene charged to the reactor was determined from the measured temperature, pres-

* University of Michigan.

sure, and volume by means of the thermodynamic properties of ethylene.[20] The radiation received by the reactor during a run was calculated by the dosimetry techniques of Lewis, et al.[14, 15]

Product Yields

A summary of the reaction conditions and the polymer yields is given in Table I. White, curdy, solid polymers were formed at reaction temperatures from 6 to 130°C. A white wax formed at about 160° C and above this the product was an opaque liquid that separated into two layers after standing awhile. The top layer was colorless and the bottom layer contained a finely divided solid. The yield of polymer is presented as the *A* value,[13] gm-moles of ethylene reacted/(metric ton of ethylene charged) (megarep of gamma radiation). The rep is based on the absorption of 93 ergs per gram. From the scatter of the data it is difficult to determine the effect of temperature on the yield since largest yields were at 39 and 217° C.

Evaluation of the Polymer Products

Melting points of the solid and waxy products were measured on a melting point bar.[3] Melting points of the liquids were observed in small tubes of the polymer which were allowed to warm up after being frozen in a dry ice bath. Because each product is a composite of polymers of varying molecular weights, a range of melting points was found. The points at which melting could first be detected have been plotted as a function of the reaction temperature in Figure 2.

Solid products produced in appreciable quantity were pressed in a one-compartment mold at 1500 psi and 150° C for 5 min. Specimens were punched from the molded polymer and placed in an Instron Tensile Test Machine. The measured tensile strengths are presented in Table I. Densities of the solids were determined by the Archimedes principle while those of the liquids were measured by weighing in a calibrated pipette. Fig. 3 shows the densities as a function of the reaction temperature. Crystallinities or the degree to which the molecules are arranged in parallel positions were determined from the densities,[11] and these are also shown in Fig. 3.

Melt viscosities of solid products were obtained in a parallel plate plastometer at about 137° C. Viscosities of liquid products were determined in a modified Ostwald pipette. Molecular weights were estimated[4] from the viscosities and are shown in Fig. 2 as a function of reaction temperature. The molecular weights are not considered very accurate, but the general trend is indicated.

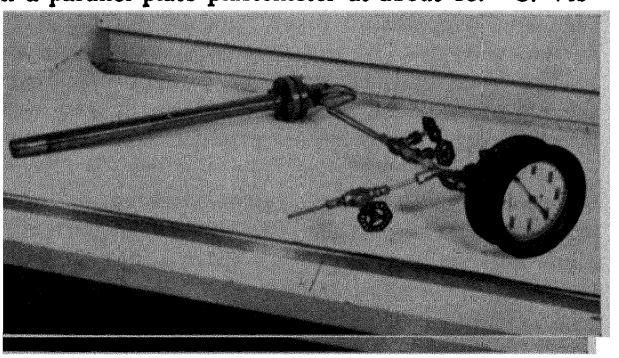

Figure 1. High-pressure polymerization reactor with fittings

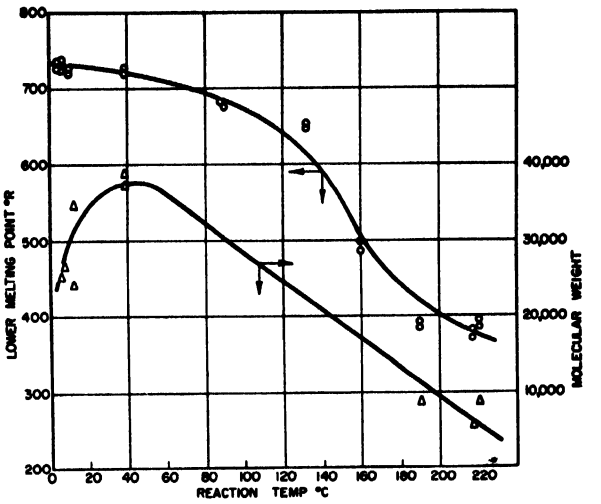

Figure 2. Melting point and molecular weight of polyethylene

From the above results it is clear that a wide variety of polymers of ethylene may be produced in the radiation reaction. The yields are sufficiently high to consider the process feasible for commercial applications. At this stage economic studies are in order to determine the possible competitive position of polyethylenes produced by radiation processing with those produced in conventional processes.

II. CHLORINATION OF SOME AROMATIC HYDROCARBONS

In general chlorination of an aromatic hydrocarbon may result in three possible reactions: (1) substitution of chlorine for hydrogen in the benzene ring, (2) substitution in an alkyl group attached to the ring, and (3) addition of chlorine to the ring. Friedel-Craft catalysts promote substitution in the ring; high temperature in the absence of catalyst favors substitution in the alkyl group; and radiation appears to favor addition to the ring. Ultraviolet,[5, 6] roentgen rays,[17] alpha radiation,[1] and gamma radiation[7, 8] have been employed to promote the addition reaction. In this laboratory Harmer[7] initiated a study of the chlorination of benzene and toluene in the presence of gamma radiation. This has been extended to include xylene, mesitylene, and ethyl benzene.

Experimental Work

Figure 4 is a flowsheet of the equipment developed by Harmer for carrying out chlorinations in the presence of gamma radiation. The glass bulb is the reactor which holds the aromatic liquid to be chlorinated. This was equipped with inlet and outlet tubes for passage of gases, a steel cooling jacket, glass baffles to promote mixing, and a thermocouple

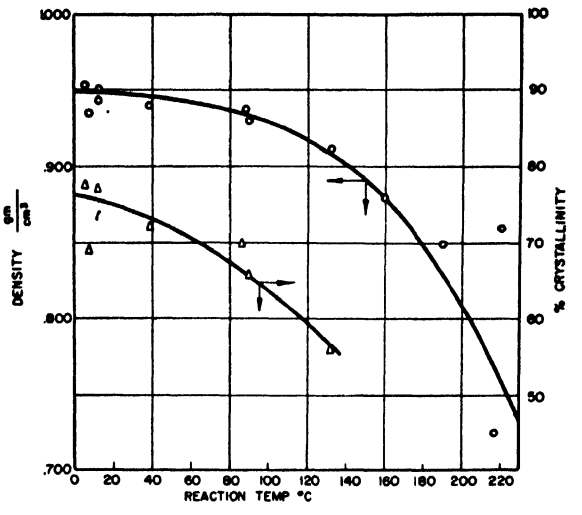

Figure 3. Density and crystallinity of polyethylene

well. Constant temperature was maintained by circulating cold methanol through the cooling jacket. The temperature of the methanol was controlled by a thermocouple potentiometer which governed the periods of operation of heaters and cooling coils. The reactor unit was placed in a portable hood in the ten-kilocurie radiation chamber and connected to the cooling and gas analysis equipment by glass tubing that passed through ports in the concrete shielding wall.

In starting a run nitrogen was passed through the system to sweep out all air. Then the chlorine flow was started and the cobalt-60 source was raised into the radiation chamber. The reaction time was measured from the moment the source was raised to the mid-point of the period during which a sample of gas was collected. Radiation dosages were determined by the time and dosimetry calibrations.

Rates of reaction between chlorine and the aromatic hydrocarbons were determined by chlorine balance. The amount of chlorine into the system was measured with a rotameter. Excess chlorine was passed through the reactor at all times to maintain saturated conditions. At certain intervals samples of the exit gas were absorbed in a solution of 0.2*N* sodium arsenite and 3.0*N* potassium hydroxide. The amount of free chlorine was determined by titrating the excess arsenite with ceric sulfate and total chloride ion was measured by the Volhard method. In this way the amount of substitution and addition could be determined.

Results of Chlorinations

Benzene, toluene, xylene, and mesitylene reacted vigorously with chlorine in the presence of gamma radiation. Addition of six chlorine atoms to the ring and alkyl substitution appeared to be the primary reactions. The ratio of addition to substitution was different from that obtained in chlorination reactions without radiation. In general this ratio appeared to be increased by radiation and decreased by increasing the temperature. The radiation yield is reported as *G* value (molecules chlorine reacted per 100 ev of radiation absorbed) in Table II. For some reason radiation had little effect on the reaction with ethyl benzene. Whether this is due to inherent inactivity or to inhibiting impurities is not known. Harmer[9] demonstrated the inhibiting properties of small amounts of benzyl chloride and oxygen in the chlorination of benzene and toluene.

Radiation chlorination of benzene takes place so quickly that temperature control is difficult. Also the production of the solid addition product tends to plug up the reactor unless the benzene is diluted with carbon tetrachloride. Toluene, xylene, and mesitylene do not react quite so fast and may be charged to the reactor in a pure condition. However, in all cases reaction under gamma radiation takes place so rapidly as to make it very attractive for commercial application. This is particularly true where the addition product might be desired, for radiation favors the addition reaction. Chlorination of many other compounds may also be accelerated by gamma radiation.

III. ECONOMICS OF RADIATION CHEMICAL PROCESSING

The laboratory studies on the polymerization of ethylene and the chlorination of aromatic hydrocarbons have demonstrated the feasibility of promoting chemical reactions with gamma radiation. It is of

Table I. Products from the Irradiation of Ethylene

Run	*Reaction temp. °C*	*Reaction pressure, ave. psia*	*Total radiation dose, megarep*	*Radiation yield A**	*Polymer state*	*Tensile strength psi*
839	6	755	4.20	1340	Solid	3050
833	8	985	5.46	1630	Solid	3075
800	13	1145	4.10	1530	Solid	3350
801	13	875	5.28	2270	Solid	3100
807	39	1380	4.47	3040	Solid	2520
808	88	1325	1.90	490	Solid	
812	90	1300	5.85	433	Solid	
845	132	1700	4.05	955	Solid	
712	160	1490	2.76	945	Wax	
848	190	1125	2.88	1300	Liquid	
814	217	1100	3.77	4030	Liquid	
813	220	1175	4.86	1400	Liquid	

* A = gm moles reacted/(metric ton charged) (megarep).

interest to examine the costs of such radiation processes. The chlorination of benzene is well suited to cost estimation and comparison because the reaction is presently conducted as a commercial scale using ultraviolet radiation.

The addition product of benzene and chlorine is technically known as 1,2,3,4,5,6 hexachlorocyclohexane, but it is usually referred to as benzene hexachloride. The gamma isomer of this compound is a powerful insecticide[10, 21] which is sold under various trade names. In the usual radiation reaction this isomer constitutes about 12% of the total addition product. The present commercial process utilizes small quartz equipment necessary for transmission of the ultraviolet. The following calculations are made for the gamma radiation process using a single larger reaction vessel made of nickel alloy. Costs are estimated for four different gamma radiation sources derived from fission products.

Design of a Chlorination Process Using Gamma Radiation

In a typical batch run at 20°C and 62 kilorep/hr of radiation, Harmer[7] obtained 63.6 gm of benzene hexachloride in 0.333 hr from a charge of 20 ml of benzene and 80 ml of carbon tetrachloride. The theoretical yield is 65.6 gm based on the benzene density of 0.88 gm/ml. Neglecting the actual increase in volume of the reactor contents, the benzene concentration decreased from 20 to 0.6% by volume. Assuming the reaction is first order with respect to benzene concentration C, the rate is $dC/d\theta = -kC$, with k being the reaction velocity constant and θ the time. Integrating this from the beginning to the end of the batch reaction gives $In\ (20/0.6) = -k\,(0.333)$, or $k = 10.6\ \text{hr}^{-1}$.

As a basis it will be assumed a plant is to be designed to produce 454 kg/day of the gamma isomer. This corresponds to a production of 541 gm moles/hr of mixed isomers. A cylindrical agitated flow reactor is to be employed with a uniform benzene concentration of 80%. The gamma source is to be placed in a center hole according to the scheme shown in Fig. 5. The source is to be of such strength that the mean reaction velocity constant is 1.0, so the reaction rate is (1.0) (0.8) ml benzene/hr-ml solution. This is equivalent to 9.02 gm mole benzene/hr-liter solution. Since a gm mole of benzene makes a gm mole of product, the volume of the reactor is 541/9.02 or 60 liters. This volume may be realized in a cylinder 50 cm high and 50 cm in diameter, with a hole 20 cm in diameter for the radiation source and cooling coils circling the inside of the walls.

The reaction velocity constant is assumed to vary directly with radiation intensity I (Harmer[8] showed the chlorination of toluene to vary as $\sqrt{I}$) which is conservative for intensities less than that of the laboratory experiment. Thus, $k = mI$, or $k = 0.171\ I$ from the fact that $k = 10.6$ at $I = 62$. For rough estimation assume the cylindrical reactor is the equivalent of a 25 cm radius sphere with a point source

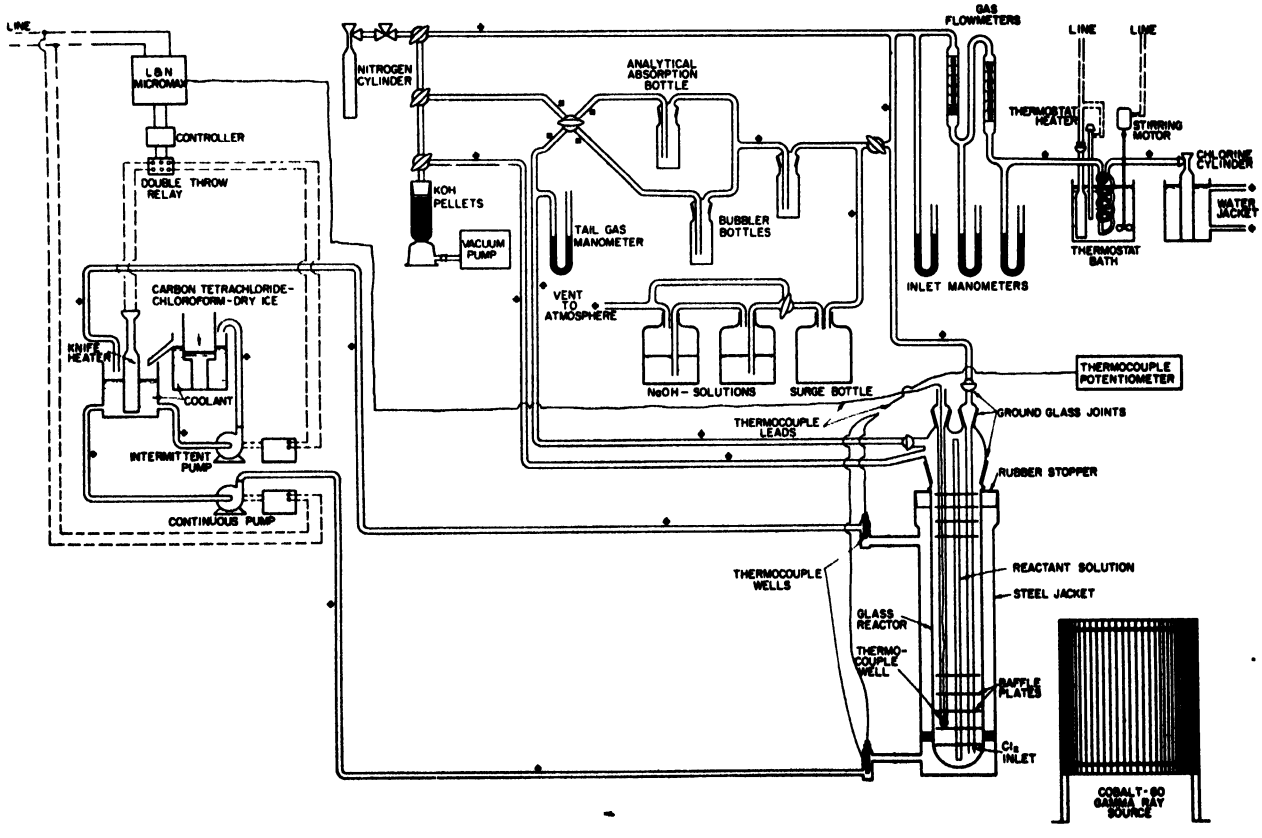

Figure 4. Schematic diagram of laboratory equipment for aromatic chlorinations

Table II. Chlorination of Aromatic Compounds with Gamma Radiation

Run	Aromatic chlorinated	Temp. reaction, °C	Dose rate, kilo-rep/hr	Cl_2 addition moles/liter	Cl^- substitution moles/liter	Average G* addition	Average G* substitution
1.	30% Benzene	20	61.0	35.2	—	234,000	—
2.	20% Benzene	20	61.0	32 6	—	252,000	—
3.	10% Benzene	20	61.0	33.3	—	90,000	—
4.	30% Benzene	−10	61.0	13.7	—	90,000	—
5.	10% Benzene	−10	61.0	32.7	—	57,000	—
6.	Toluene	20	14.0	17 42	7.54	523,000	226,000
7.	Toluene	−5	14.0	14.12	6 59	900,000	420,000
8.	Toluene	35	14.0	10 35	6.12	812,000	480,000
9.	Toluene	20	None	3.23	.85	—	—
10.	Xylene	20	13 7	5 90	3 48	462,000	272,000
11.	Xylene	−5	13.7	7 45	2 94	448,000	177,000
12.	Xylene	20	None	3.20	2 63	—	—
13.	Mesitylene	20	13.7	4 20	15 10	210,000	827,000
14.	Ethyl benzene	20	13 7	1 81	.47	137,000	35,000
15.	Ethyl benzene	20	None	1.61	.13	—	—

* G = molecule reacted/100 ev absorbed (based on chlorine).

of radiation at the center. There will be a spherical hole of 10 cm radius at the center to account for the volume occupied by the actual source. If the radiation intensity on the surface of the hole at 10 cm from the center is 50 kilorep/hr, and if the intensity decreases according to the inverse square law and the exponential absorption law, the average k throughout the reactor volume may be calculated as

$$k_{ave} = \int_{10}^{25} \frac{0.171(50)(10)^2 e^{-0.640(0.88)(r-10)}(4\pi r^2)dr}{r^2(4/3\pi[(25)^3 - (10)^3]} = 1.0$$

Here 0.064 is the gamma absorption coefficient and 0.88 is the density of the benzene. In order to obtain an intensity of 50 kilorep/hr at 10 cm from the center for a fission-product source, about 1250 curies would be required.[8] This is multiplied by a factor of four to account for self-absorption, absorption by the wall and the agitator between the source and the benzene, and losses of radiation from the cylinder through the hole. Therefore, 5000 curies will be taken as a conservative estimate.

The radiation chamber housing the reactor will be made 3 meters square to provide adequate working

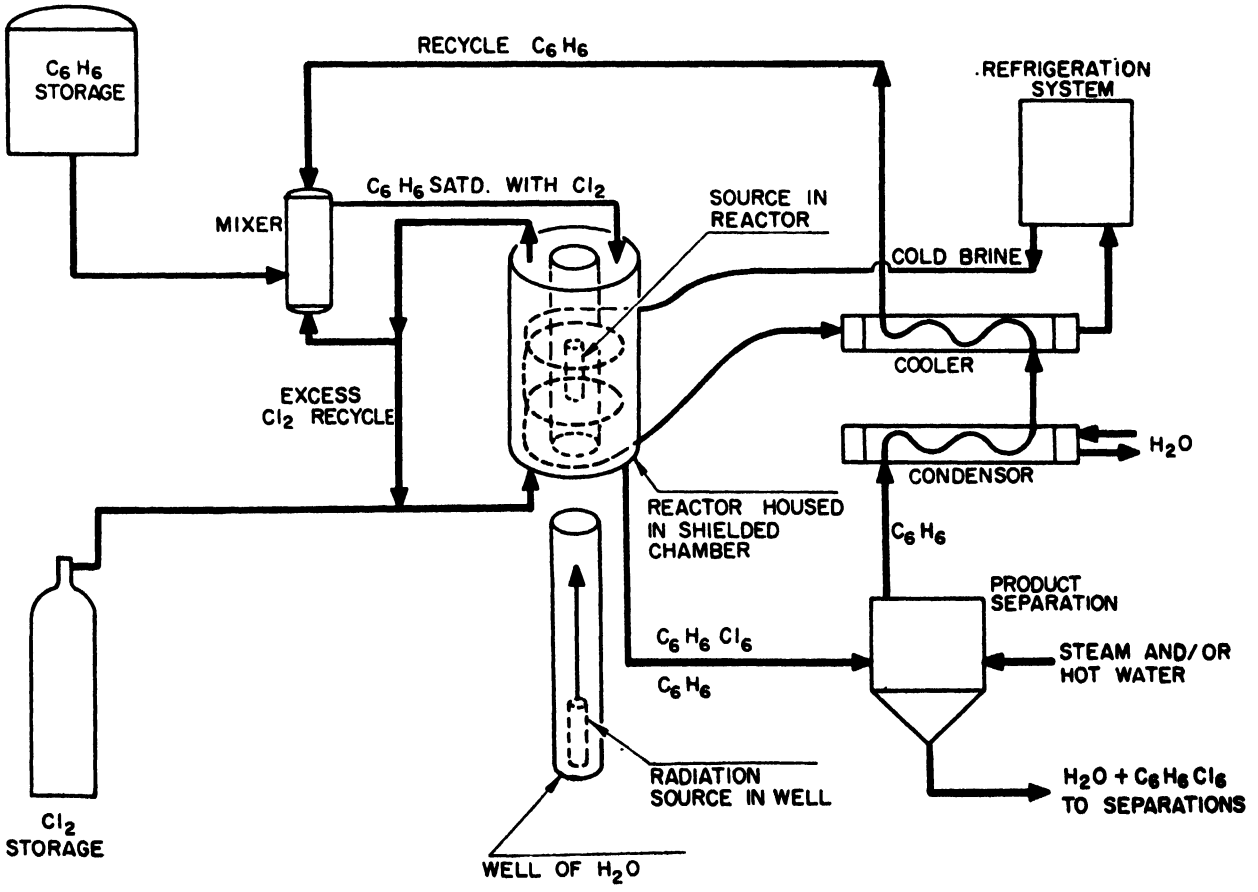

Figure 5. Flowsheet of proposed plant design for producing benzene hexachloride

space. To insure that the intensity of radiation is less than 0.5 millirep/hr outside this chamber with a 5000-curie source, the concrete walls must be 85 cm thick.[19] The other units in the system are calculated by conventional means. The process is straightforward with the benzene being saturated with chlorine before entering the reactor and excess chlorine bubbling through the reactor to keep the contents saturated. The product from the reactor is flashed to separate out the solid benzene hexachloride. The benzene is condensed and returned to the chlorine saturator. Refrigerated coolant is required to maintain the reactor feed and contents at 20°C.

Cost Estimations

The costs of fission-product sources are not yet available. Therefore estimations are made for a range of values that seem reasonable. Because of varying half-life of different sources, it will be assumed that charges are made approximately according to the radiant energy delivered. Since the energy E of a radioactive source is given by $\int I_0 e^{-\lambda\theta} d\theta = I_0(1 - e^{-\lambda\theta})/\lambda$, at large values of time θ the energy varies inversely as the disintegration constant λ. But λ is the reciprocal of the half-life, so the energy varies directly as the half-life. The costs will therefore be selected in proportion to the half-life. The cost of long half-life sources is to include shipping. Short half-life sources would involve excessive shipping costs and are assumed to be used in the vicinity where they are produced. If the source intensity is not to fall below say 80% of its initial strength, short half-life materials will require frequent replacement. These factors have been considered in Table III, where the costs of producing the mixed isomers of benzene hexachloride are given as a function of the type of radiation source. In estimating the total radiation required, the source is to be composed of five sections. Whenever the intensity falls off 20%, one section is replaced with fresh radioactive material. In the case of cesium-137, it is apparent that no replacements are necessary. In fact, at the end of a five-year period, the cesium activity is still more than 90% of its initial value. In selecting costs for radiations sources, ten-fold ranges were estimated for each case, but only the highest value is given in the table. It is noted that the variation in costs of radiation actually has only a small effect on the product cost.

The costs of benzene and chlorine are taken from the latest trade journals. These also give the cost of commercial benzene hexachloride as $1.90 to $3.00 per kg of gamma isomer in 12% mixture with the other isomers. The gamma radiation process evidently can compete with the ultraviolet process for making this compound. Of course, the true comparison between the two should be made on the basis of the comparative costs of the reactors and radiation sources, since all other equipment is the same. What this comparison does show, however, is that gamma radiation processing is not out of line with other processing methods and that it should be given serious consideration by industry.

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Table III. Cost Estimate for Producing 454 kg/day of Gamma Isomer of Benzene Hexachloride with Four Radiation Sources

	Radiation source			
	Gross fission product 0.5-yr	*Gross fission product 1-yr*	*Gross fission product 2-yr*	*Cesium-137*
Half-life, years	0.2	0.3	1.1	33
Total curies reqd in 5 years	84,000	57,000	19,000	5000
Selected high cost/curie, $	0.05	0.10	0.25	5.00
Radiation cost 5 yr, $	4200	5700	4800	25,000
Initial investment in radiation source	250	500	1250	25,000
Radiation chamber cost, $	22,000	22,000	22,000	22,000
Process equipment cost, $	49,000	49,000	49,000	49,000
Total investment, including radiation	71,250	71,500	72,250	96,000
Annual charges on investment at 80%, depreciation, taxes, interest, maintenance, etc.	57,000	57,200	57,800	76,800
Annual radiation replacement cost	800	1000	700	0
Salaries of workers, $/yr	21,000	21,000	21,000	21,000
Chlorine & benzene, $/yr	109,000	109,000	109,000	109,000
Utilities, $/yr	3000	3000	3000	3000
Sales and marketing, $/yr	8000	8000	8000	8000
Total annual cost, $	199,000	199,000	200,000	218,000
Annual production, 290 working days, kg gamma isomer	131,500	131,500	131,500	131,500
Cost/kg. gamma isomer, in 12% mixture, $	1.51	1.51	1.52	1.66

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Recent Developments in the Irradiation of Long-Chain Polymers

By A. Charlesby,* UK

The use of high-energy radiation as a method of effecting changes in materials is likely eventually to become a technique of considerable industrial importance. Although the study of radiation effects is still in a very early stage, several fundamental discoveries have already been made, promising very novel applications. Among these the possibility of modifying polymer structures has received considerable attention, since many of the changes produced cannot be readily achieved, by other means. We may indeed consider such recent developments as only the first steps in a new industrial process whose eventual scope it is as yet difficult to envisage.

The investigation of radiation-induced changes in polymers is not only of interest to polymer scientists; the effects produced are of considerable scientific interest in radiation research. Long-chain polymers constitute one of the most convenient systems in which to investigate radiation damage, and reactions first traced in such systems have subsequently been found to occur in simpler organic molecules. Moreover a comparison with results obtained in the field of radiobiology reveals many points of similarity, so that in this field too one may hope to apply conclusions derived from the chemically much simpler polymeric systems.

The use of long-chain polymers to study radiation effects has several outstanding advantages. The molecules have a relatively simple structure, and modifications in their chemical constitution can be readily produced. They may be irradiated in the form of solids, liquids or in solution, and reactions can be readily followed by simple means such as solubility, swelling or melting. Considerable changes in the physical properties can be obtained with relatively small radiation doses, and these changes can be readily measured and interpreted. The effect of additives and protecting agents can be studied, and it is interesting to note that their behaviour in irradiated polymers is closely parallel to that in biological systems, which are very much more difficult to assess quantitatively.

Two major effects have been observed in long-chain polymers exposed to high-energy radiation. The first is termed cross linking and corresponds to the formation of bridges or links between molecules, such links consisting of new primary bonds. As a result a specimen is transformed from an assembly of separate linear or branched molecules held together by weak secondary forces into a three-dimensional network, each atom being linked to the others by primary bonds. The whole specimen now consists of a single gigantic molecule which cannot be melted, and whose properties depend on the density of these links. It is therefore possible to modify to any desired extent the physical properties of such materials, merely by varying the radiation dose. The formation of these crosslinks has been ascribed to the fracture of side chains, leaving an activated molecule or radical which can then attack a neighbouring molecule and form a permanent link with it. At first this only results in an increase in the average size and complexity of the molecules initially present, but further radiation forms links between parts of the same molecule and eventually leads to a network structure.

The phenomenon of crosslinking only occurs in a certain number of polymers. In others the effect of radiation is to break the main chain; if the two fragments formed can be stabilised by a rearrangement of a few atoms, a permanent break results, and the average molecular weight is reduced. By repetition of this process it is possible to reduce a high molecular weight material which is solid at room temperatures down to a very viscous liquid. The average molecular weight of the irradiated material is directly dependent on the number of breaks, i.e., on the radiation dose.

In certain polymers both processes, i.e., main chain and side chain fracture, occur simultaneously. It is of general interest to discover why irradiated polymers behave in these two alternative ways. As a general rule polymers with two side-chains tend to suffer main chain fracture while those with one side chain or none crosslink. In this connection hydrogen (which can readily diffuse away) is not considered as a side-chain. However there are certain exceptions to this general statement, and these are now being studied.

A third possibility has recently been investigated theoretically. If the two fragments produced by main chain fracture of a molecule are assumed not to become stabilised, but to be capable of attaching themselves to neighbouring molecules, a three-dimensional

* T.I. Research Laboratories, Hinxton Hall, Cambridge.

network can be produced; the statistics of formation of such a network are very similar to those resulting from side-chain fracture. It is not therefore certain (as has been assumed hitherto) that gel formation is in fact due to side-chain fracture; it may equally well result from main chain fracture. The distinction between polymers which when irradiated undergo side-chain fracture and those which suffer main chain fracture then disappears, and becomes one between polymers which when fractured in the main chain are capable of attaching themselves to neighbouring molecules, and those which cannot do so.

In the study of radiation-induced polymerisation reactions, the effect of radiation is to produce radicals which then react in a manner typical of the conventional chemically-produced processes. The final product is identical with one which would have resulted under the same conditions had these radicals been produced in some other manner. In crosslinking or main chain fracture this similarity does not hold, and the effects produced by radiation do not necessarily follow the pattern to be expected from their chemical structure. For example, the process of main chain fracture and depolymerisation, induced thermally, is quite different from that which results from radiation. Chemical bonds with low binding energies are often more resistant to radiation changes than stronger chemical bonds. It is therefore not possible to predict purely on chemical grounds the course of such reactions, and it is necessary to study anew the chemical stability of molecules when reactions are initiated by radiation. There is a growing body of evidence to show that such reactions occur in at least two separate stages. In the first of these excited or ionised molecules or radicals are formed at random, simultaneously with the passage of the ionising radiation through the specimen. A relatively long period of time may then elapse during which the energy captured can travel freely throughout the molecule (possibly in the form of an unpaired electron) during which time the molecule may suffer an atomic rearrangement. Only after this will the final reaction take place.

This need to consider a radiation—induced reaction as falling into separate stages is demonstrated by the possibility of modifying such reactions (even in the solid phase) by the addition of small amounts of inhibitors which cannot directly absorb an appreciable proportion of the incident energy, yet which can profoundly affect the nature of the final product. It can only be assumed that these inhibitors play their part in the subsequent processes, by collecting this energy from neighbouring molecules, which are thereby protected from radiation damage.

An experiment which demonstrates this multistage process concerns the irradiation of polyisobutylene at various temperatures. This polymer suffers main chain fracture and reduction in molecular weight as a result of exposure to high-energy radiation. The energy absorbed per main chain fracture is about 20 electron volts at room temperature, an energy far greater than is required to break a C–C bond. The energy per fractured bond varies with the temperature of the specimen during irradiation—a surprising observation since it would appear unlikely that a temperature change corresponding to only a few thousandths of an electron-volt could seriously affect a reaction requiring about 20 ev. It must be concluded that the final reaction leading to decomposition must take place after an interval of time sufficient for the molecule to have returned to thermal equilibrium with its surroundings. The observed temperature variation of main chain fracture of polyisobutylene follows very closely the trend found in the inactivation of certain bacteriophage by radiation, indicating that in this latter case the temperature dependence is not due to a biological factor, but occurs as a fundamental process in radiation damage.

In published work on the effect of radiation on long-chain polymers, attention has been wholly concentrated on the changes produced when such polymers are irradiated in the solid. Such studies of solid state reactions demonstrate the value of radiation as a research tool. Research on radiation effects in liquids has been largely directed to the elucidation of the fundamental processes involved and has usually been confined to small molecules. It is possible, however, to obtain valuable information from the irradiation of solutions of long-chain polymers, which can be gelled at concentrations as low as 0.5%. The radiation dose needed to induce gel formation is found to decrease with decreasing concentrations, so that polymer molecules further apart in the solvent are apparently more readily linked together.

The explanation of this apparent anomaly depends on the possibility of both direct and indirect effects, often studied in radiobiology. In the former case radiation affects a polymer molecule directly, while in the latter case it operates on a solvent molecule which is thereby rendered active in some way. This active solvent molecule can subsequently react with a polymer molecule, rendering it in its turn active. The direct effect is of course independent of concentration, while the indirect effect will be more important in dilute solutions, when there will be fewer polymer molecules available to share the activated solvent molecules. In either case the polymer molecules activated either directly or through the intermediary of the solvent molecule can attach themselves to neighbouring polymer molecules to form a gel structure as in the solid. In very dilute solutions this process does not take place as the polymer molecules are too far apart to link and form a network; presumably this activity is dissipated in other ways, e.g., by internal linking.

The study of such polymer-solvent systems offers a very useful method of comparing direct and indirect action, the effect of polymer separation on the crosslinking process, the relative susceptibility of different

chemical groupings to attack, and possibly the nature of the interaction between active solvent molecules and the polymer. Such polymer-solvent systems offer a useful analogy to certain biological systems, but have the great advantage that the concentration of solute can be varied over a wide range and that the changes produced can be readily measured because of the structural simplicity of the polymer molecule. The action of certain additives which in very dilute concentration inhibit or reduce the effect of radiation has also been investigated. In this manner it is possible to decide whether the inhibitory action applies only to the indirect effect, the direct effect, or whether it interferes with the subsequent process of cross-linking and gel formation.

Among such inhibitors oxygen plays a prominent part. It is known that oxygen greatly affects the radiation resistance of biological systems, and it is of interest to note that these polymer/solvent solutions are often equally sensitive to the presence of oxygen. A quantitative analysis can indicate the role played by oxygen in the radiation processes.

In this short review it has only been possible to outline briefly some of the possible lines of research into radiation effects in polymers, which appear to be of purely scientific interest in other fields of radiation research. From the more applied aspect, the modification of polymeric materials as an industrial process will need considerable quantities of high-energy radiation at an economic cost. Such radiation can be obtained from suitably designed atomic piles, fission products, radioactive isotopes, or from electrical accelerator equipment. In assessing the economics of atomic power, account must be taken of the high-energy radiation which can be simultaneously produced, and which may offer a valuable financial contribution to the cost of operating atomic piles. The uses to which such radiation can be put are already manifold but the price at which it is offered must be competitive with that of the electrical accelerators. From the economics of existing and projected accelerators it is possible to deduce an upper limit for the cost at which high-energy radiation obtained from atomic energy sources can be sold.

Progress and Problems in the Development of Cold Sterilization of Foods

By B. E. Proctor and S. A. Goldblith,* USA

HISTORY OF DEVELOPMENT OF RADIATION STERILIZATION

The preservation of food is one of man's greatest blessings. It has permitted him to carry the harvest over from one season to another and thus defy the ever-present law of nature according to which foods begin to spoil as soon as they are removed from her protective fold.

Preservation of man's food dates back to antiquity. The largest single means of preservation today, thermal processing, dates back to the Napoleonic era, and scientific heat processing originated at the turn of the present century.

Radiation sterilization also has a history, comparatively brief but dating back, on a fundamental basis, to the discovery of ionizing radiations by Roentgen[1] and Becquerel[2] in 1895 and to the initial researches on the bactericidal properties of these radiations which occurred shortly thereafter.[3, 4]

The developments in radiation sources made in the 1930's and 1940's disclosed new potentialities for the beneficial uses of such types of energy sources.

In 1943, research experiments were initiated at the Massachusetts Institute of Technology in Cambridge, Mass., that were destined only a decade later to result in a multi-million dollar research effort in numerous laboratories in the United States. These investigations may lead to practical applications of ionizing radiations as a means of sterilization in the food, drug, and pharmaceutical fields. In fact, such application is already on the verge of commercial utilization in the pharmaceutical field.

From 1945 until 1948 research on the microbiological effects of ionizing radiations was limited to a small number of laboratories in the United States. In 1949, a research center in Great Britain became active in this field. In 1950, under the sponsorship of the United States Atomic Energy Commission, research activity in the peacetime uses of the atom for sterilization and preservation purposes increased, and a number of excellent laboratories began applying their skills in their several particular disciplines toward solving the problems facing commercial utilization of radiation sterilization.[5]

Our discussion of the various phases of this development is based largely on investigations conducted by our group at M.I.T., and citations are directed to publications that may amplify the necessarily brief factual data that can be encompassed in this report.

SOME RESULTS OF RESEARCH STUDIES

Early in our own research we were able to demonstrate the ability of these radiations to destroy all types of microorganisms in every conceivable type of package, so long as the dimensions of the package did not exceed the limitations imposed by the particular type and energy level of radiations used. In addition to these findings, we have been able to demonstrate that the species of organism is the prime factor in determining the magnitude of the sterilizing dose[6-8] (see Fig. 1). This fact has since been confirmed by many other investigators.[9, 10]

Later research has shown the importance of environmental factors in the survival ratios of microorganisms exposed to ionizing radiations.[11, 12]

More recently we have obtained interesting data on the microbiological factors involved in radiation sterilization. These data indicate the hazards in applying any one set formula for the use of ionizing radiations to destroy all species of microorganisms

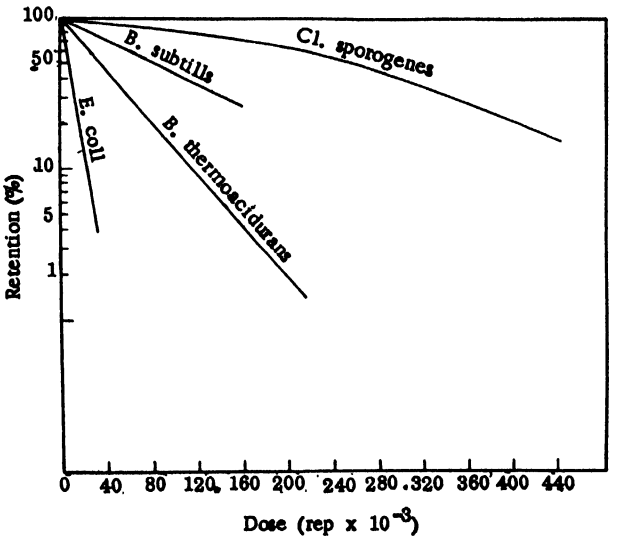

Figure 1. The relative radiosensitivities of four species of bacteria[6]

* Department of Food Technology, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA.

that may contaminate a food. They also demonstrate the necessity of time-consuming, tedious research under the particular experimental conditions to be encountered in processing with each particular contaminating species.[13]

The examples cited above relate to experiments conducted with *B. subtilis* spores and with *E. coli*[14-16] (see Figs. 2 and 3). The data obtained for these two organisms illustrate one of the interesting facets of the microbiological effects of radiations. The data obtained for *E. coli* might well have been predicted theoretically, from the qualitative standpoint at least. The results obtained with *B. subtilis* spores, on the other hand, were quite contrary to accepted theory and could not have been predicted.

Research on the microbiological effects of radiations may be considered to be further advanced than research on some other aspects. Studies are in progress at present on the complementary effects of heat and radiation, which may greatly reduce radiation requirements for particular species of organisms.[17]

Studies in our own laboratories are underway on applying, to radiation processing, certain fundamental nutritional and environmental factors known to speed germination of spores. These studies may well lead to other means of obtaining increasing economy in the doses of radiation used.

The chemical effects of ionizing radiations on foods have not been overlooked in these pioneering experimental years.[12, 18]

Early in our experiments it was observed that radiations affect isolated components of a mixed solution of nutrients *in vitro* to a greater or less degree, dependent on the particular component, its concentration in solution, its purity, and the radiation dose. *In vitro*, each particular nutrient might be classified as to its relative radiosensitivity (Table I). The types of effects that might be observed include (where applicable) decarboxylation, deamination, cleavage of aromatic rings, oxidation of sulfhydryl groups, and many others. With niacin and para-aminobenzoic acid, radioactive tracers have been used to study the nature of the effect.[20, 21]

These indirect effects of radiations, which occur as the result of the absorption of large amounts of energy in the radiation sterilization process, exhibit not only the phenomena associated with dilution, rate of reaction, and temperature dependence to be expected according to the indirect action theory but also the phenomenon of protection in mixed systems[22] (see Table II). The comparison given in Table III, which shows that vitamins in pure solutions are relatively more radiosensitive than vitamins in foods, illustrates the protective nature of the complex food material.[8, 18] A further illustration[23] of this protective action is given by the comparison in Table IV. These data demonstrate that nutrients may be affected by ionizing radiations, but that the effect is dependent on the phenomena mentioned above.

Table I. Relative Radiosensitivities of Amino Acids in Aqueous Solutions*

Amino acid	*Specific inactivation dose* (D_0/C) (*rep/gm/ml*)
dl-phenylalanine	1.18×10^9
l-histidine	1.25×10^9
l-cystine	2.40×10^9
l-tyrosine	2.60×10^9
l-leucine	3.60×10^9
dl-tryptophan	10.00×10^9

* From Bhatia.[19]

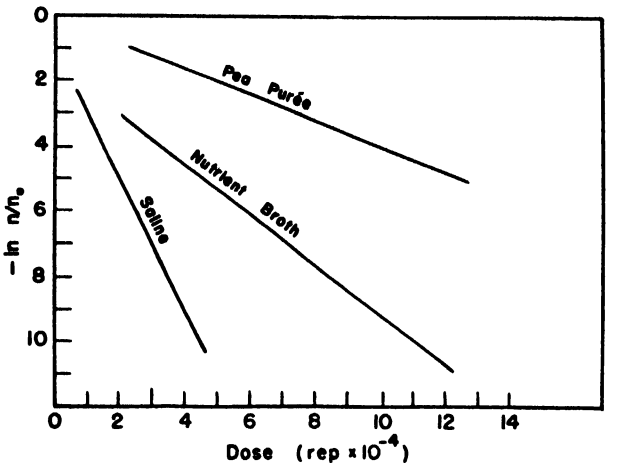

Figure 2. Comparative effects of gamma radiation from cobalt-60 on saline, nutrient broth, and pea puree suspensions of *E. coli* in air atmosphere[13]

Table II. Effect of High-Voltage X-rays on Solutions of U.S.P. Niacin, U.S.P. Ascorbic Acid, and on Mixtures of the Two with Dose = 125,000 r*

Solution	*Concentration before irradiation*		*Retention after irradiation*	
	Niacin (γ/ml)	*Ascorbic acid* (γ/ml)	*Niacin* %	*Ascorbic acid* %
Niacin	50	--	86.0	—
Ascorbic acid	—	500	—	66.6
Niacin-ascorbic acid mixture	50	500	44.0	83.6

* From Proctor and Goldblith.[22]

Because enzymes are, for the most part, protein molecules, they might well be expected to react to ionizing radiations as do proteins or other solutes. They exhibit the same phenomena associated with dilution, temperature and protection that are observed with proteins, amino acids, and other molecules of biological importance. As a consequence, enzymes are not completely inactivated by sterilizing doses of ionizing radiation. In fact, under a number of conditions enzymes are neither completely inactivated nor even inactivated to a desirable extent by doses of ionizing radiations ten to twenty times the magnitude of those doses required for sterilization.

Because the spoilage of certain foods occurs partly through enzymatic action, it is usually necessary that these biological catalysts be inactivated. In most thermal processes the amount of heat used for sterili-

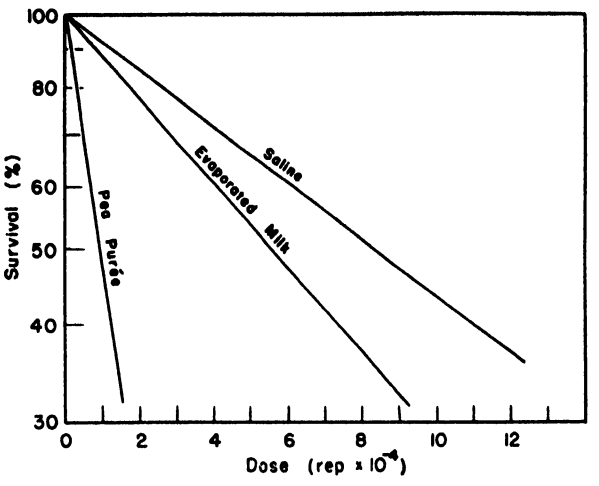

Figure 3. Comparative effects of high energy cathode rays on spores of *B. subtilis* suspended in physiological saline, evaporated milk, and pea puree[13]

zation is sufficient to inactivate the enzymes, but in radiation sterilization ("cold sterilization") some other means for enzyme inactivation could be used to advantage. The possibility of applying high frequency electronic heating is intriguing. Such application may well prove to be feasible, as it is a rapid, efficient, and satisfactory method for this purpose. The properly controlled use of microwave heating results in even heating throughout the mass of food and thereby avoids overheating of the exterior surface while producing only the minimal quantity of heat needed for enzyme inactivation in the interior of the food mass.

PROBLEMS IN RADIATION STERILIZATION

Some indirect effects of ionizing energy have given rise to the greatest problems existing today in radiation sterilization, namely, changes in color, texture, and flavor of irradiated foods. The fundamental studies mentioned above have suggested several technological means of obviating these undesirable side-reactions. These include (*a*) irradiation of food in the frozen state, (*b*) irradiation in inert atmospheres, and (*c*) addition of free-radical acceptors.

It may be that all three of these technological means are really one and the same fundamentally, that is, a means of reducing the indirect effect of radiation, leaving only the direct effect for destroying microorganisms.

Table III. Specific Inactivation Doses of Ascorbic Acid and Riboflavin Irradiated Per Se and In Evaporated Milk

Irradiated medium	*Specific inactivation dose, D_0/C (r/gm/ml)*
Ascorbic acid, pure solution*	1.19×10^9–3.6×10^9
Ascorbic acid, evaporated milk†	$2\ 4 \times 10^{10}$
Riboflavin, pure solution*	2.6×10^9–5.2×10^9
Riboflavin, evaporated milk†	3.7×10^{11}

* From Proctor and Goldblith.[8]
† From Kung, Gaden, and King.[18]

Fundamental investigations are being conducted today to study the basic changes that take place in food materials when irradiated. The premise is made that once the type(s) of changes in complex food materials is known, the possibility of finding means of avoiding or minimizing these should logically follow.

In addition to the chemical changes occurring in the protein components of irradiated foods, modifications in the structure of carbohydrates are observed. The changes in lipoidal material have been studied by several investigators, with interesting results.[30] The data obtained indicate the complex interaction that takes place among the many components of which foods are comprised.

The basic effect of ionizing radiations responsible for destruction of nutrients is probably also the simultaneous cause of changes in flavor, and any means of reducing the one effect will, *a priori*, be a means of reducing the other effect.

These same indirect effects have also given rise to speculation as to whether any compound of a toxic nature might be produced by these radiations. The United States Food and Drug Administration has given its views on the required testing procedure.[24] This testing is not easy or inexpensive, and details of the procedure are frequent subjects of controversy. For instance, it has been stated that laboratory animals should be fed with irradiated food material in such an amount that a positive answer (if there can be one) should be obtained.

In other words, to determine the factor of safety, it is stipulated that one should ascertain what irradiation dose will produce changes of a toxic nature in foods. The procedure suggested to accomplish this is to over-irradiate a food by a dose ten times, for example, as great as the sterilizating dose.[24] Such a procedure, however, may cause certain fallacies. For instance, let us assume that compound *B* is a toxic compound produced by irradiation from compound *A* (precursor compound) in a food. Increasing the irradiation dose may produce more of compound *B* but it may also have an entirely different effect, that of producing compound *C* from compound *B*. Compound *C* may be entirely innocuous. Such a combination of circumstances might result in a false and mis-

Table IV. Effect of Cathode Rays (Dose 5,700,000 r) on Amino Acids in Haddock Fillets*

Amino acid	*Change in amino acid*	
	Loss %	*Gain* %
Phenylalanine	6 10	0.00
Tryptophan	6.92	0 00
Methionine	4.68	0.00
Cystine	0.00	0.00
Valine	0.00	6.36
Leucine	0.00	2.74
Histidine	0.00	8.11
Arginine	0.00	4.12
Lysine	4.23	0.00
Threonine	5.95	0.00

* From Proctor and Bhatia.[23]

leading sense of security. This example points out the difficulties in this particular problem alone.

In two toxicity studies that have been published to date,[25, 26] evidence has been lacking that ionizing radiations produce compounds of a toxic nature in foods. Destruction of nutrients has been noted, but this occurs even with conventional heat processing and is not unexpected.

Research to study this important point thoroughly is being conducted today in many laboratories in the United States under sponsorship of the Quartermaster Corps of the Department of the Army and with the scientific supervision of the Office of the Surgeon General. Not only are animal feeding studies and chemical studies underway, but also feeding studies with humans.

A problem closely related to that of wholesomeness or toxicity of irradiated foods is that of a possibly induced radioactivity in irradiated foods. This may be stated theoretically to be a function of the type of radiation to be used, the energy level, the cross-section of the precursor element, and its relative isotopic abundance. With fast electrons or gamma rays, induced radioactivity should theoretically not occur below 8 to 10 Mev (million electron volts). Studies are in progress in our laboratories at the Massachusetts Institute of Technology and elsewhere to ascertain the particular energy level of fast electrons necessary to produce induced radioactivity, the particular species of isotope, and the quantity of the isotope (if any) produced.

Recent research (thus far unpublished) on the sterilization of milk in these laboratories has indicated that many of the undesirable changes taking place in irradiated foods occur almost immediately. Therefore, any efforts to avoid these undesirable changes must, *a priori*, be made during or before the irradiation process. This research has resulted in a technique for obtaining an organoleptically acceptable milk product treated by ionizing radiations in doses up to 10^6 rep (roentgen-equivalent-physical).

Concurrent with the developments just mentioned, great strides have been made in the design, fabrication, and utilization of radiation sources. Multi-kilowatt sources of fast electrons are now available at increasing energy levels, and kilocurie isotopic sources have been developed. Designs for reactors for this purpose, as well as megacurie isotopic sources, are now in fabrication. All this has been partly instrumental in enabling increases in the research effort in this field.

There are problems relating to the use of these sources of radiation, however, just as there are problems relating to irradiated foods. For example, there is a continually occurring economic loss in the use of an isotopic source because of its nuclear disintegration and the necessity for replenishment of the source.

Theoretically it would be most efficient if this nuclear energy could at all times be absorbed by foods requiring sterilization. Since many food plants are widely dispersed in location and their operation is often highly seasonal in nature, this is not possible. Plants that operate 24 hours daily throughout the year are in the minority, and many now work only one 8-hour shift per day, five days a week. Even from the standpoint of location alone, it would be difficult for such plants to tie in with projected future nuclear power stations, which are unlikely to be established in the most flourishing rural agricultural regions.

The use of particle accelerators presents problems as well. These relate to the tremendous amount of development necessary to produce machines of high output reliably delivered over extended periods of time during the harvest season.

Packages also present certain problems, because during storage a food material can be of no better quality than the functional properties of the package in which it is contained. Plastic containers have been suggested for use in the radiation sterilization of foods and drugs. Some of these containers require study to determine the effect of the radiations on them. It is known, for example, that certain plastics degrade on irradiation whereas others crosslink. The question arises whether these changes affect the functional properties of the containers. In studies conducted in our laboratories on certain plastics, no such effects have been observed. Further study is necessary with other plastics.

Because, in general, the penetrability of radiations into foods is related to the product of thickness and density of the packaging material, it is obvious that a metal container as thin and of as low a density as possible is desirable. The metal containers designed for use in this field of research need not be so rigid as those used for thermal processing, because they need not withstand the heavy pressures of retorting. Hence savings in metal containers may result.

Today the accelerated research on food sterilization in the United States, alluded to above, has made it possible for many research investigators well skilled in their several disciplines to become associated with those already active in the field of radiation sterilization and to participate in solving many of the important and difficult problems facing radiation sterilization. Over thirty research laboratories throughout the United States are now active in this field. Both food and pharmaceutical industrial laboratories are also playing an important role, and the outlook for more complete understanding and possible utilization of radiation sterilization is improving.

APPLICATIONS OF RADIATION STERILIZATION

Certain limited applications appear today to be possible. For example, it seems possible that pharmaceuticals such as ointments, antibiotics, and other products of microbial metabolism that are heat labile and certain parenterally administered products such as steroidal compounds may be sterilized by ionizing radiations. Because pharmaceuticals or mixtures

thereof are relatively simple compounds as compared with foods, they lend themselves more readily to tests for chemical changes induced by ionizing radiations. Also the changes produced in pharmaceuticals by irradiation are less in degree than those in foods. These facts, combined with the relatively greater cost of pharmaceuticals, the economic structure of drug distribution, and the smaller overall mass of a drug per unit package cause us to predict again that the first industrial application of radiation sterilization may be with pharmaceuticals.[31]

This research has also resulted in another interesting and important application of ionizing radiations, namely, the sterilization of segments of human aortae for subsequent surgical transplant in persons suffering from coarctation of the aorta. Although this is a relatively small-volume application of ionizing radiations, it is one of great importance and one that has already been of great value in saving lives.

Another promising application of radiation sterilization is in the field of surgical sutures. Irradiation will do away with separate heat sterilization of suture and ampoule and aseptic handling of the suture through the filling stage. This will result in a better product with respect to tensile strength.

Ionizing radiations may also be used for the sterilization of the surface of certain foods, to increase shelf life. Such foodstuffs as comminuted meats in casings may have their shelf life greatly increased if cathode rays of low energy level are used to reduce their surface contamination.

The research of Doty and Wachter[27] has pointed to the fivefold increase in shelf life of meats irradiated with low doses of gamma radiation (less than 10^5 rep).

Research at the Department of Food Technology of the Massachusetts Institute of Technology has shown that by the application of free-radical acceptors, the irradiation dose may be increased to 800,000 rep without detectable side reactions, and the shelf life of irradiated comminuted meats at 36° to 40°F may be increased from 5 to 7 days for the control sample to three months for the irradiated product. Similar promising results in preservation have been obtained with other meat products.

It has been found[28] that insects can be destroyed by relatively low doses of ionizing radiations (less than 50,000 rep). This finding points out one of the more promising applications of ionizing radiations and one that may be a means of saving many millions of dollars now lost annually because of destruction of cereals by insects. The relatively low dose of radiation required for insect eradication in grain products results in a comparably reduced cost of preservation.

The recent work of Sparrow and Christensen[29] has shown that ionizing radiations successfully inhibit sprouting of potatoes at low doses (approximately 20,000 roentgens) and thus the storage life of these potatoes is increased by many months. Whether this method can compete with chemical means of inhibition is as yet unknown.

SUMMARY

Summing up the activities of the decade now drawing to a close, one might say that the horizons have been scanned in respect to the many factors relating to a possible new method of food preservation using ionizing radiations and a method providing an extension of food storage life for perishable foods, accomplishments that may have a pertinent influence on the food processes of the future.

That foods, pharmaceuticals, and tissues may be adequately sterilized by ionizing radiations is now an established fact, and the levels and types of radiation that may accomplish this sterilization are known.

For this method to be successful for a wide variety of foods, extended research will be required into many specific and fundamental factors, largely chemical in character, which are severally and simultaneously affected by the extent and magnitude of radiation exposure. This is because the concomitant results of other changes, such as changes in flavor, color, and texture which sometimes occur during the sterilization period, may necessitate modification by some additional treatment.

On the assumption that the above difficulties may be alleviated as the result of sufficient application of research and subsequent process control, economic establishment of the available radiation sources is obviously necessary if these sources are to be put to optimum use. Because the processing of fruits, vegetables, and fish in the United States is highly seasonal and the processing plants are widely separated geographically, atomic radiation sources would be used only a relatively small portion of the year and thus would be unused and depreciate during the remainder of the year. The processing of meats and dairy products is not limited to the same extent, although the quantities of raw materials for these products may vary greatly during different parts of a given year.

If research is continued at present levels toward solution of the problems cited above, it would seem conservative to predict the initiation of commercial processes for irradiation sterilization of some pharmaceuticals, foods, tissues, and packaging materials in the present decade. To accomplish this will require the best type of scientific cooperation, diligence, and interchange of ideas, in the splendid manner that this meeting has made possible through the combined activities of the many participating nations, whose scientists are attending. May we look forward to more such meetings in the future.

ACKNOWLEDGEMENTS

Many of the studies quoted have been excellent examples of team research. In our own instance, research in the field of ionizing radiations would have been impossible without the combined efforts and co-

operation of our colleagues in the Physics Department and the Electrical Engineering Department at M.I.T., namely, Dr. John G. Trump and Dr. Robert J. Van de Graaff, to whom we express our thanks. In addition, the many research investigators in our own department have been greatly instrumental in our progress in this field. The valuable and continued cooperation of our colleagues, Professor John T. R. Nickerson and Professor Ernest E. Lockhart in the Department of Food Technology, is specially acknowledged.

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Prevention of Human Helminthic Diseases by Gamma Radiation of Food, with Particular Reference to Trichinosis

By H. J. Gomberg* and S. E. Gould,† USA

The control of trichinosis, a prevalent and typical food-borne helminthic disease, through the irradiation of the larvae encysted in meat, has been under study for several years. The effectiveness of X-rays, gamma rays from cobalt-60 and gamma rays from mixed fission products have been evaluated and the results are summarized. In addition, the effectiveness of the newly available pure cesium-137 gamma rays for breaking the trichinosis cycle has been successfully proven. The results of the study demonstrate the use of ionizing radiation as a means of eradicating this particular food-borne helminthic disease and also suggest the use of radiation as a new approach to the world-wide problem of control of all food-borne helminthiases.

SOME IMPORTANT FOOD-BORNE HELMINTHIC DISEASES

In Table I, a listing has been compiled of the principal helminthic diseases of man, the causative organisms of each, the form in which the parasite is ingested by man, and the incidence and geographic distribution of the parasite or disease. All the diseases listed are contracted as a result of eating raw or inadequately cooked foods. Thus, trichinosis, beef or pork tapeworm infections, pork cysticercosis, and hydatid disease are acquired as a result of eating raw or undercooked infected meats; fish tapeworm infection and clonorchiasis (Chinese liver fluke), through eating raw infected crabs or crayfish; fascioliasis (sheep liver fluke), fasciolopsiasis (intestinal fluke), and ascariasis (in some cases), through eating vegetables or raw fruit contaminated with infected soil.

In a number of countries of the Orient, the use of night-soil as fertilizer is an age-old, widespread and firmly established practice. This practice is responsible for contamination of fresh fruits and vegetables, leading to infestation with sheep liver fluke or intestinal fluke.

In each case thorough cooking could destroy the parasite and break the disease cycle. However, the natural food flavor and texture preferences and the established eating habits of the population groups involved has made this approach ineffective.

It may, however, be possible to break these disease cycles by irradiating the food with doses which, while preventing parasite growth and reproduction, does not affect flavor and texture.

This principle of breaking a parasitic disease cycle by inhibiting continued reproduction has been rather completely explored in the case of *Trichinella spiralis*, the causative agent of trichinosis.

THE TRICHINOSIS CYCLE[1]

The cycle of trichinosis takes approximately the following course. On ingestion of meat containing encysted trichina larvae (*Trichinella spiralis*), the muscle fibers and cyst walls that enclose the parasites are digested, liberating the larvae. In the small intestine, the larvae mature in two to four days[2] to adult worms and then copulate. Beginning with the sixth day,[2] gravid females partially embedded in the mucosa of the intestine give birth to young larvae of the second generation. The larvae enter the blood stream and are carried into the general arterial circulation. The young larvae leave the capillaries and penetrate skeletal muscle fibers and encyst there. At this point, the course in man ends, although the encysted parasites may remain alive in a latent state for the rest of the life of the infected person. In hogs, however, the parasitic cycle is continued when inadequately treated meat of a trichinous pig is eaten by another pig. A secondary avenue lies through consumption of infected meat by rats which then become infected and, in turn, are eaten by pigs.

METHODS OF CONTROL

Man may be directly protected by killing the trichina larvae in the meat by adequate cooking, by suitable refrigeration, or by ionizing radiation. Adequate cooking which raises the temperature of all parts of the meat to 137°F will kill the larvae, but is a precaution that must be taken by the consumer and is not suited for public health control measures.

Holding the meat at 5°F (temperature of meat, not of refrigerator) for 20 days[3] or sharp chilling to −35°F for a few minutes will also kill the trichinae, but this method of control is expensive and results in changes in the meat texture.

The information available from our work to date on breaking the trichinosis cycle through the use of radiation is discussed in the following section.

* University of Michigan.
† Wayne County General Hospital.

Table I. Some Important Helminthic Diseases of Man Acquired Through Food

Causative organism	*Form in which ingested by man*	*Disease produced in man*	*Natural host*	*Incidence and geographic distribution*
Trichinella spiralis	Cysts in raw or undercooked pork	Trichinosis	Hog. (Rat, man, carnivorous animals)	Cosmopolitan. In 16% human autopsies in U.S. (p. 370).* In U.S. 1.5% of all hogs are infected (p. 370)* 27.8 million people†
Clonorchis sinensis	Metacercariae in fresh-water fish	Clonorchiasis (Chinese liver fluke)	Man, dog, cat, hog. (Snails and fish are intermediate hosts)	Japan, China, Formosa, Korea, French Indo-China. "Disease is equally prevalent in poor and the prosperous, in illiterate as well as the educated," because of custom of eating raw fish (p. 650)* 19 million people†
Ascaris lumbricoides	Ova in raw vegetables. (Principal mode of transmission is infected soil)	Ascariasis. (Intestinal obstruction in children, pneumonia)	Hog, man	Cosmopolitan. In surveys of U.S. Southern states, 1 to 60% in children (p. 447).* In Shantung, China, 23 to 44% in children 644.4 million people†
Fasciolopsis buski	Metacercariae on raw fruit or edible water plants	Fasciolopsiasis (intestinal fluke)	Man, hog. (Snail is intermediate host)	Central and South China 10 million people†
Taenia saginata	Cysticerci in meat	Beef tapeworm	Man. (Cattle are intermediate hosts)	Cosmopolitan. 0.38% of persons infected in Peiping, China. Incidence in cattle: U.S. 0.37%, Holland 3.3 to 5 6%, S. Africa 5% (p. 578).* 38.9 million people†
Taenia solium	Cysticerci in pork	Pork tapeworm; cysticercosis in tissues	Man. (Hog is intermediate host)	Cosmopolitan. Incidence of tapeworm in man: Russia 0 2 to 1.5%; incidence of cysticercosis in man: 2.9% Mexico (p. 575).* Incidence in hogs: S. Africa 25%, Mexico 4.3%. 2.5 million people†
Diphyllobothrium latum	Plerocercoid larva in fresh-water fish	Fish tapeworm anemia resembling pernicious anemia	Man, dog, cat. (Fish is intermediate host)	N. America, Europe, Tropical Africa, N. Asia, S. Asia. In Finnish Army 14.5% (p. 548).* About 20% of pickerel and pike in Lake Winnipeg and Lake Manitoba are infected (p. 549).* 10 4 million people†
Paragonimus westermani	Crabs or crayfish containing metacercariae	Paragonomiasis (Oriental lung fluke)	Man, dog, cat, many other animals. (Snail and crab or crayfish are intermediate hosts)	Japan, Korea, Manchuria, Formosa, China, other countries of Orient; Africa, S. America. Adult parasites have been found in mammals in Canada and many states of U.S. 3 2 million people†
Fasciola hepatica	Encysted cercaria in water cress, lettuce	Fascioliasis (sheep liver fluke)	Man, sheep. (Snails are intermediate hosts)	Cosmopolitan, in sheep-raising areas of world. Incidence in Estonia 57% in sheep, 72% in cattle; in Transcaucasia, 48% in sheep; in Southern Texas, 21 to 32% of rabbits (reservoir hosts for new infections) (p. 629)* 100,000 people†

* Page numbers have reference to Belding, D. L.: *Textbook of Clinical Parasitology*, 2nd Ed., New York: Appleton-Century-Croft, 1139 pp.

† Stoll, N. R.: "This Wormy World," *The Journal of Parasitology*, 1947, Vol. 33, p. 15.

IRRADIATION OF MEAT FOR THE CONTROL OF TRICHINOSIS

The effects produced by irradiation of trichinous meat may be summarized as follows:

1. Killing the Trichina Larvae in the Meat

This can be done by exposing the meat containing the trichinae to about 1,000,000 rep.[4, 5, 6] This value applies for 250 kv X-rays, and for cobalt-60 gamma radiation of about 1.3 Mev energy. However, a radiation dose this large produces highly objectionable flavor changes, making the pork rancid and sour.[7]

2. Inhibiting Maturation of the Trichina Larvae

The primary danger from trichinosis occurs as a result of multiplication of trichinae in the intestinal tract, about 1500 young being produced for every female adult worm. Any measure which prevents reproduction can be effective in trichinosis control.

About 18,000 rep of cobalt-60 gamma radiation[8, 6] or 15,000 rep of 250 kv X-rays[5] will inhibit the development of the larvae that are liberated from the meat by digestion. These dose levels produce no detectable change in flavor, texture or appearance of the pork.[8]

3. Sexual Sterilization of the Trichinae

Adult female trichinae, developing from larvae which were exposed to 15,000 rep of cobalt-60 gammas[8, 6] or 5000 rep of 250 kv X-rays,[5] are completely sterile. A normal gravid adult female trichina worm, photographed at the instant one of the larvae emerged from the vulva is shown in Fig. 1a. A female worm which developed from an irradiated encysted larval form is shown in Fig. 1b. The complete degeneration of the reproductive system is apparent.

While the evidence is not yet conclusive, it appears that the males have likewise been rendered

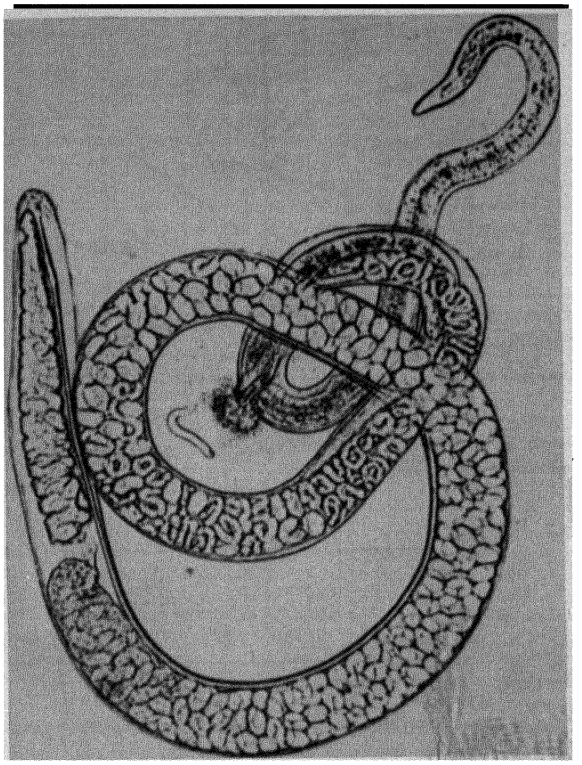

Figure 1a. Nonirradiated adult gravid female *Trichinella spiralis*: note numerous young embryos in anterior portion of uterus and a newborn larva that has just been expelled from the vulval opening (× 250)

sterile by these doses of radiation. This sterilizing effect is significant, since for purposes of trichinosis control, it can serve as a second line of protection in processing intended to inhibit maturation of the larvae.

Based on these results, a dose of 30,000 rep of cobalt-60 gammas, or its equivalent, delivered to pork will serve as a method of preventing and eradicating trichinosis.

SECONDARY CONSIDERATIONS IN CONTROLLING TRICHINOSIS BY MEAT IRRADIATION

1. Enteric Phase of Trichinosis[9]

While the muscular phase of trichinosis is usually the most serious, in the case of infection with large numbers of larvae, a violent enteric reaction may be produced, sometimes with fatal results. In tests, 12,000 larvae fed rats weighing between 200 and 250 grams killed 12 out of 12 animals within 24 days. A similar group fed 12,000 larvae which received 10,000 rep survived the test period of 31 days although six developed a transient diarrhea. In a third group of ten fed 12,000 larvae which received 18,000 rep, all survived with no diarrhea and continued to show weight increase during the test period. A fourth group fed 24,000 larvae which received 18,000 rep fared as well as the third group.

It is expected that consumption of pork containing larvae exposed to 30,000 rep will not result in any intestinal disturbance.

2. Immunity[9]

A small dose of trichina larvae, producing a mild infection, can also produce immunity to further reinfection. It has been found that experimental feeding of larvae exposed to 10,000 rep of cobalt-60 gamma rays will produce a marked immunity, although not as effective as that produced by unirradiated larvae. An exposure to 18,000 rep destroys the ability of larvae to induce immunity.

3. Selection of a Radiation-Resistant Strain of Trichina Larvae[9]

When doses approaching but not equal to the total sterilizing dose of radiation are applied, the progeny of the unaffected trichinae appear to breed normally. These were tested to determine if the young produced by trichinae which were not sterilized were in any sense more resistant to radiation than others not so selected. There is no indication as yet that the young produced by survivors of the sterilization process differ in radiation resistance from the controls.

4. Induced Radioactivity[10]

There is no induced radioactivity in food treated with cobalt-60 gamma rays or radiation of lower energy. Thresholds for photo-neutron reactions which would result in induced radioactivity occur at much higher energies.

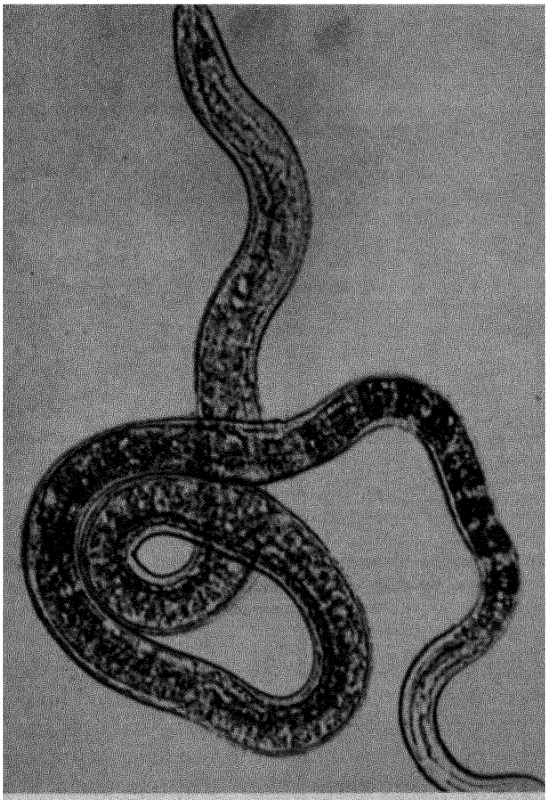

Figure 1b. Sterile adult female *Trichinella spiralis* (× 250) showing stunting of growth and degenerative cellular changes. This female developed from a larva that had been exposed to 10,240 rep cobalt-60

Among the secondary effects examined, there is no indication of deleterious side effects which would contraindicate on medical or biological grounds the use of radiation as a means of trichinosis control.

EFFECTIVENESS OF CESIUM-137 GAMMA RAYS FOR IRRADIATION OF PORK

While the tests run to determine the effectiveness of cobalt-60 and 250 kv X-rays in breaking the trichinosis cycle yielded positive results, it was felt that definitive tests using cesium-137, the principal long-lived gamma emitting fission product, as the radiation source were necessary. Arrangements were made with Dr. Marshall Brucer of the Oak Ridge Institute for Nuclear Studies for the use of the cesium therapy unit being installed at the medical division of the Institute. It was possible to use the unit before its installation for human therapy use was quite completed and so, first irradiation tests using a pure cesium-137 radiation source were made at Oak Ridge on March 25, 1955.

CESIUM-137 IRRADIATION TECHNIQUE AND DOSIMETRY

A ham, weighing about 30 pounds after being trimmed of the fat and which came from a hog which had been fed 10,000 trichina larvae about 21 months before sacrifice, was transported to Oak Ridge by air. The ham formed a roughly rectangular meat slab which, when irradiated was about 11½ inches tall, 15 inches long and 6 inches wide. It was centered under the cesium irradiator which was adjusted so that the radiation emerged vertically downward.

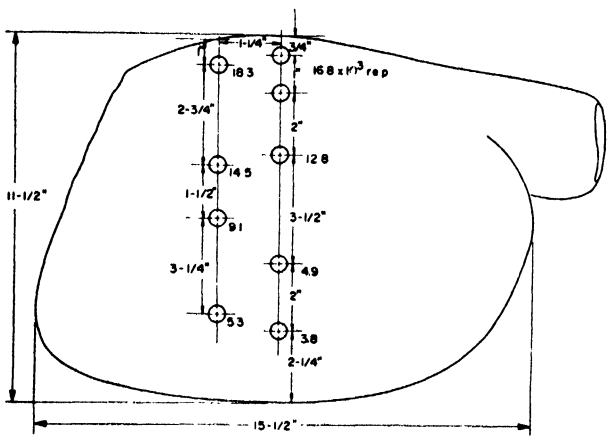

Figure 2. Location of ferrous sulfate dosimeters and corresponding dose recorded: readings indicate center line of meat and radiation beam did not coincide

The top surface of the meat was 27¾ inches below the cesium source within the irradiator housing. Dosimeters consisting of small glass vials containing ferrous sulfate were inserted in the meat at intervals, starting one-half inch below the top surface and working down. The dosimeters were placed chiefly in the cone of direct radiation, although a few were placed in peripheral positions. The relative position of all elements is shown in Fig. 3.

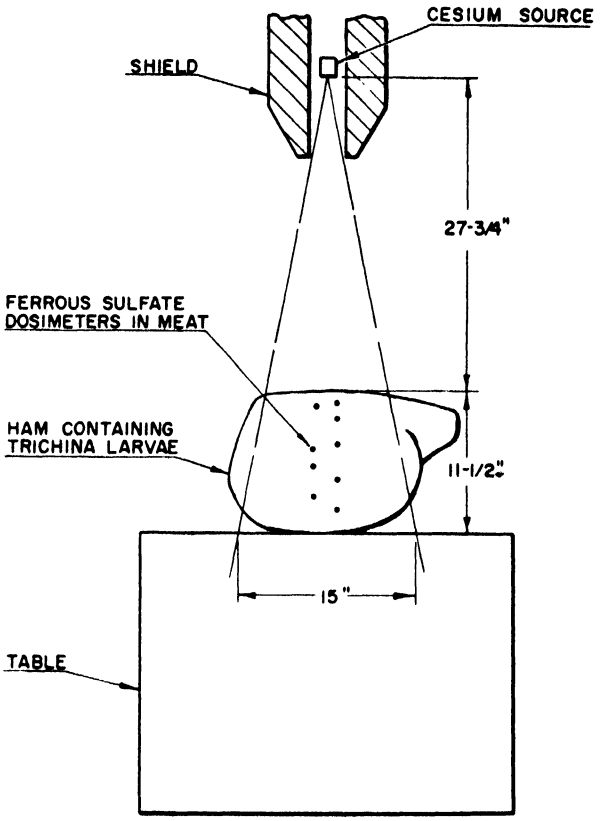

Figure 3. Arrangements of cesium-137 source and meat during irradiation

The radiation cone had previously been monitored with a Victoreen Roentgen rate meter and the relative position of the irradiator and meat chosen so that the center of the top surface received 11.5 r per minute.

Irradiation continued for 23 hours and 40 minutes. The radiation source was then closed and the meat and dosimeters returned to Ann Arbor.

Radiation dose was measured, using a Beckman D U spectrophotometer, after return to Ann Arbor. Checking control dosimeters which had been left behind with control dosimeters which had been carried along, no difference was found. The indicated doses were then accepted as correct. The location of the dosimeter in the meat and the corresponding dose is shown in Fig. 2. The variation in dose with depth in the meat has been separated into that caused by geometry (Inverse Square Law) and that caused by geometry plus absorption. The half value layer for cesium-137 radiation in meat as found from this data is 6¾ inches.

As in previous experiments using cobalt-60 gamma rays,[8] small blocks of meat were cut from sites surrounding the dosimeters. It was assumed that, on the average, all the trichina larvae in the meat in a single small block had received the same dose. The larvae in each sample block were recovered by digestion of the meat and then 5000 larvae fed by stomach tube to each of a number of test rats. In addition, control specimens of meat taken from unirradiated

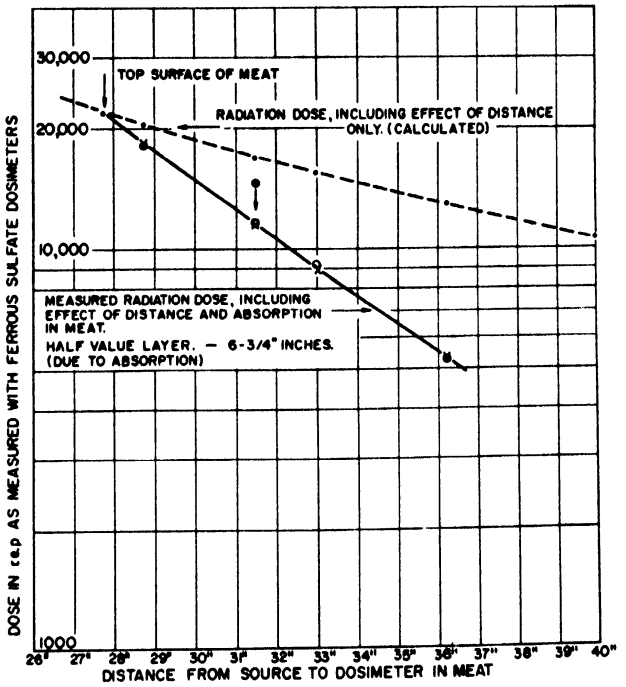

Figure 4. Dose of Cs^{137} gamma radiation at varying depth in irradiated meat as measured with ferrous sulfate dosimeters and calculated dose in air at same points for ORINS Cs^{137} irradiator

portions of the same hog carcass were processed and the recovered larvae fed to rats intended to serve as controls on the infectivity of the larvae.

CESIUM IRRADIATION RESULTS

The results have been evaluated in two ways: first, the ability of the radiation to sexually sterilize the female larvae, and second, the dose needed to prevent the larvae from remaining in the intestine of the test animal in the presence of normal or violent intestinal clearance. The results are summarized in Figs. 5, 6, and 7.

First, in Fig. 5, determination was made of the per cent of adult female trichinae with young, recovered from the gut of test rats 6 days after feeding irradiated larvae. This curve is quite similar to those found previously for cobalt-60 and waste fission product irradiation.[8] The points are scattered somewhat more than previously, but the trend and cut-off point is clear. About 14,000 rep from cesium-137 apparently sterilizes more than 99 per cent of the female trichinae larvae.

Second, a more significant test is the measure of the number of second generation larvae recovered from the muscle tissue of the test rat 35 days after feeding 5000 larvae. This is shown in Fig. 6. The very rapid drop in number with small doses of radiation and the general logarithmic decrease in number with dose, again checks previously observed results from cobalt-60 quite well. Implied in this and previous results is the effectiveness of "one hit" in preventing growth of eggs within the female, or at least in preventing encystment.

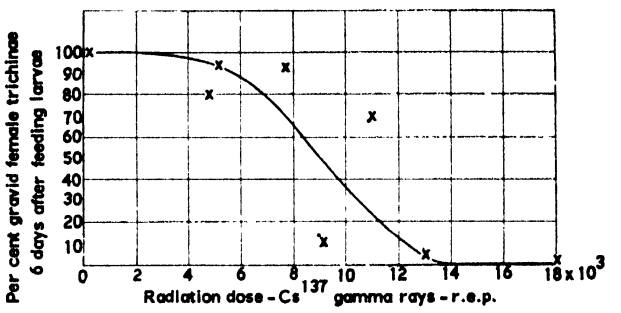

Figure 5. Sexual sterilization of trichinae by irradiation of the immature larvae, as measured by examination for maturing eggs in 100 adult female trichinae recovered from intestine of test rat 6 days after feeding irradiated larvae

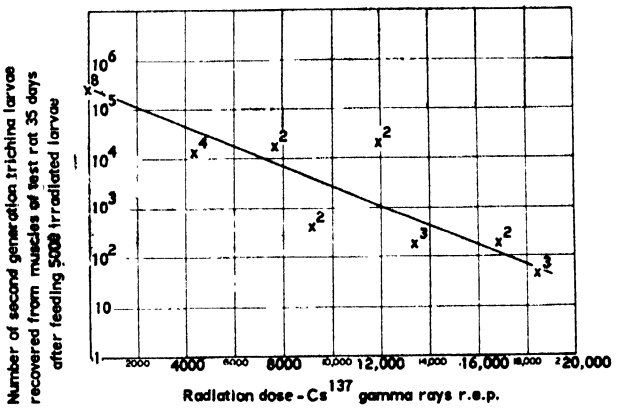

Figure 6. Sexual sterilization of trichinae by irradiation of the immature larvae, as measured by reduction in number of encysted second generation larvae found 35 days after feeding 5000 irradiated larvae. Numbers at test points show number of rats used to obtain larvae count

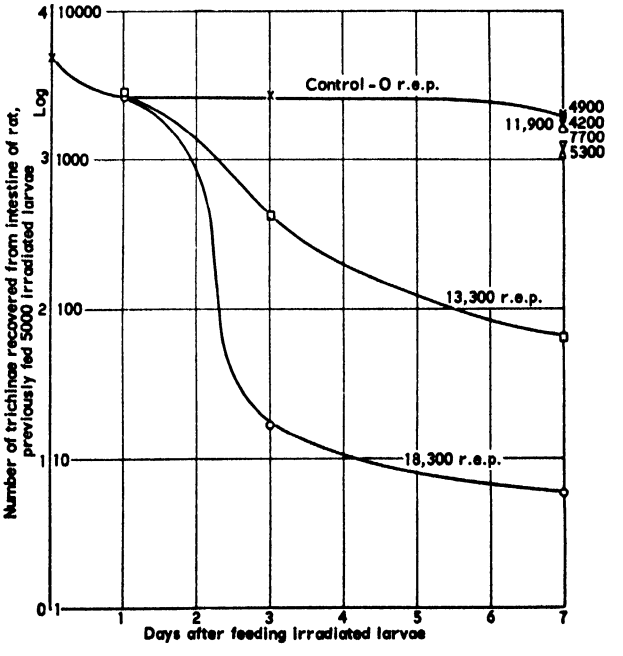

Figure 7. Effect of irradiation on ability of larvae to remain and mature in intestine of rat

Of equal importance is the measure of intestinal clearance rates for the rats fed 5000 larvae. This is shown in Fig. 7. The number of developing larvae or adults remaining after 1, 3, and 7 days was determined for groups of rats fed trichinae larvae which had received different radiation doses. About half the larvae are lost in the first day regardless of whether they are irradiated or not. However, following radiation doses as high as 11,900 r of cesium-137, the ability of the trichinae to grow and hang onto the intestinal wall is not seriously impaired. Thus, even though largely sterilized as shown by the results in Figs. 5 and 6, the trichinae remain in the intestine. However, beyond about 12,000 r the ability to grow or at least to remain attached to the intestinal wall is rapidly lost. At 18,300 r, practically all the larvae have been cleared out (or digested) in seven days. These results correlate directly with the observed disappearance of the enteric phases of the disease when larvae receiving 18,000 r cobalt-60 radiation are fed even in massive numbers.[9]

It would appear that, except for a reduction in half value layer from about 8 inches to 6¾ inches in meat, the cesium-137 gamma rays are equally as effective as cobalt-60 in breaking the cycle of trichinosis.

TECHNIQUES OF IRRADIATION

Based on the trichinosis results, the general use of irradiation as a method of parasitic disease control appears worthy of consideration. While the dose to be used to inhibit development of other parasites remains to be determined, the general problems of mass food handling applicable to pork will be characteristic of most other foods. The effectiveness of food irradiation for large-scale use anywhere in the world will be governed by the technical feasibility of setting up the necessary facilities, not only in large technically advanced communities, but also in less well developed areas, even those without basic utilities such as electricity and running water.

Two basic sources of high energy radiation are available: (1) electric converters such as X-ray machines and particle accelerators, and (2) radioactive materials, particularly by-products of nuclear reactors such as cesium-137. Small nuclear reactors could also be used, but for the application proposed here, they do not appear sufficiently simple or inexpensive, and also because they involve fissionable material, their use may not be politically feasible at this time.

In the case of trichinosis, the simplest mode of treatment would be the irradiation of whole animal carcasses. The thorough penetration of all parts requires the use of fairly high energy gamma rays. Radiation from cobalt-60 and from cesium-137 have been demonstrated as capable of providing adequately uniform penetration of all sections of the split carcass of a 450-pound hog.[8] Using a 1 to 3 Mev X-ray machine, similar results would be obtained.

However, the technical complications of operation of such a system would be great. One great advantage of the radioactive sources is that they require no external power supply. However, they cannot be turned off and so must be adequately shielded at all times.

The safe operation of a food irradiation unit energized by a radioactive source can be assured by indoctrination of semi-skilled personnel in safety procedures and simple methods of radiation monitoring. No complex ultra-high-voltage power system, radio frequency generator or vacuum systems are involved.

A facility for processing pork carcasses or other foods, for parasite control, can be built from simple material. Given the radiation source, the rest of the facility such as the conveyor belt, source storage pit, handling system and shielding could be built and improvised from materials available almost anywhere. Central facilities of a permanent nature in urban and population centers could serve large groups and have high handling capacities. Facilities to handle 2000-hog carcasses per day for operation in conjunction with a modern American style packing plant have been studied and designed.[11]

Smaller units with lower capacities, and even portable or mobile plants, which could serve a number of communities on a rotating basis when slaughtering is in progress are technically feasible although no detailed design studies have been made. Where fish or fresh produce are to be irradiated, simple conveyor belt systems could carry the food past radiation sources. A recent study of a potato irradiation plant showed that bulk food items could be irradiated with 10,000 rep from cesium-137 at the rate of 270 bushels per hour, using a 150,000 curie source made up of 20 individual rods.[12]

Sufficient radioactive material for many radiation sources is already in existence in the waste storage pits of chemical processing plants of the United States Atomic Energy Commission. Similar supplies exist in other parts of the world wherever large-scale reactor operation is in progress. And as the use of atomic energy for electric power generation expands, suitable radioactive supplies will be even more abundant.

COSTS OF PLANT CONSTRUCTION AND OPERATION

In a detailed cost study of a plant designed to process 2000 hog carcasses per day and allowing costs for the radioactive source which are believed to reflect the developing technology of chemical processing, it was found that the meat could be treated at 30,000 rep for less than one-fourth cent per pound.[11]

Processing the meat (or other food product) in a more compact package than the split and spread carcass could lead to further reduction of cost. On the other hand, increased costs of the radioactive sources could raise the price of processing. The potato plant,[12] mentioned previously, would cost $0.066 per bushel or about $3.91 per ton of bulk

food to operate provided it operates 16 hours per day, 260 days per year.

Smaller plants may, in general, be expected to operate at somewhat higher costs than the reference design unit. The construction and test operation of a pilot plant could contribute substantially to our information in this and other areas.

CONCLUSIONS AND RECOMMENDATIONS

The technical feasibility of breaking the trichinosis cycle by irradiation of pork has been established. No undesirable secondary effects from this method of processing have been discovered. Present estimates, based on admittedly meager data on costs of radioactive sources, indicate that the cost of such processing can be a tiny fraction of the value of the product.

In addition, the principle of using moderate amounts of radiation to break the life cycle of parasites by treating food or other materials they infest appears to be well established. Additional applications, particularly where uncooked food such as fish is involved, are worth consideration. If the potential for growth of the parasite when lodged in the intermediate host is destroyed, the disease can be eliminated.

Radiation doses of the size previously shown to be capable of inhibiting development of the parasite (*Trichinella spiralis*) does not affect the taste or texture of the food so treated. Thus, the normal eating habits and dietary preferences of population groups need be altered to only a minor degree.

Further work along the following lines is either under way in our laboratories or is recommended for consideration by the cognizant authorities:

1. Determination of the sensitivity to radiation of the parasites carried by food to man or his essential livestock.

2. Establishment of the technical feasibility of carrying out the processing where it is needed.

3. Possible erection of pilot plant facilities in those world areas where the need for control of food-borne parasitic disease is greatest. The implementation of this recommendation might best come through consultation with the World Health Organization and other cognizant United Nations groups. It is planned to investigate this aspect of the problem in more detail.

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Sterilization of Medical Supplies with Gamma Radiation

By L. E. Brownell and J. J. Bulmer,* USA

INTRODUCTION

Sterilization of Various Types of Medical Supplies

The application of gamma radiation to the sterilization of medical supplies is believed to be one of the most promising uses of the fission products. There are fewer obstacles to this application than in the radiation sterilization of food. In the case of medical supplies the problem of "off" flavor (a major problem in food sterilization) is nonexistent. The question of toxicity is only a consideration with certain pharmaceutical products such as antibiotics and vitamins which are taken into the human body orally or intravenously. Bulk medical supplies such as dressings, cotton gauze, cotton swabs, sutures, instruments, and special items such as human "bone-bank" bone can be sterilized on a mass basis as soon as suitable irradiation facilities are put into operation.

For several months lyophilized human bone for the "bone bank" at the University of Michigan Hospital has been sterilized by gamma irradiation in the Fission Products Laboratory. Highly successful bone grafts were first made in dogs.[1] Since then over 30 human patients have received successful grafts of lyophilized human bone sterilized with gamma radiation. Dr. Paul H. DeVries, M.D., Section of Orthopedics, Department of Surgery, University of Michigan Medical School, and his associates state that gamma radiation has already revolutionized their procedures in bone grafting. Laboratory cobalt-60 sources are adequate for processing human bone, aorta, or similar material for use in surgery.

The sterilization with gamma radiation of most of the important antibiotics and a number of other pharmaceuticals without loss of potency has been demonstrated using solutions of these products packaged in glass ampoules.[2] Although these products have great dollar value, they have small volume, and the daily production of any one pharmaceutical manufacturer could be sterilized with a radiation facility not much larger than the radiation "cave" in the Fission Products Laboratory.[3, 4]

Sterilization of Cotton Products and Other Bulk Medical Supplies

The greatest volume of medical supplies that are sterilized is found in the cotton, gauze, adhesive bandages, surgical dressings, and other bulky materials used for medical purposes in the home, in the doctor's office, and in the hospital. Every year the American public spends about $100,000,000[5] for these items. This large amount of money is spent with the knowledge that these materials have been sterilized and as a result are free of microorganisms which could possibly initiate the spread of infection. The sterilization measures and protection against subsequent contamination are costly operations performed by the manufacturer in the interests of public health and customer acceptance of his product. The current sterilization practice employs steam under pressure as the sterilizing agent. Although procedures vary somewhat, in the method employed by one large manufacturer a number of pallet loads of these materials are placed in a chamber batchwise and subjected to pressurized steam for a period of time sufficient to kill any microorganisms present. The success of this method is contingent on the ability of the steam to penetrate the cartons and packages of materials to provide enough heat to destroy these organisms in the material.

A new method of sterilization is proposed which consists of the application of a sterilizing dose of gamma radiation to the materials after packaging and prior to shipment to consumer markets. This new method has several distinct advantages and eliminates many of the disadvantages of the present practice of steam sterilization.

Advantages of Gamma-Ray Sterilization of Bulk Medical Supplies

It is quite natural to consider gamma rays as a sterilizing agent for bulk medical supplies such as surgical dressings when examining the extensive work that is presently being conducted on the pasteurization and sterilization of food using gamma rays. The advantages offered by gamma-ray sterilization can affect economies of operation while still producing a product free of microorganisms.

1. Gamma radiation is extremely penetrating and can pass through several pallet loads of materials producing death for microorganisms in its path.

2. Complete sterilization could be assured in even

* From a study by J. J. Bulmer submitted in partial fulfillment for the degree of Master of Science in Nuclear Engineering, University of Michigan. Including work by J. J. Bulmer, L. E. Brownell, Fission Products Laboratory, University of Michigan; J. Controulis, Parke, Davis and Company, Detroit, Michigan; P. H. DeVries, Department of Orthopedic Surgery, University of Michigan Medical School; L. L. Kempe, Department of Bacteriology, University of Michigan Medical School; W. W. Meinke, Department of Chemistry, University of Michigan; J. V. Nehemias, Fission Products Laboratory, University of Michigan.

the most tightly packed containers, thus could produce savings in packaging materials.

3. The restriction to certain types of packaging materials would be eliminated; this alone could accrue tremendous savings.

4. Manufacturers could exercise a wider choice of packaging-material colors which would have a greater psychological sales appeal.

5. Economies could be accrued by elimination of the salvage due to the irreparable damage to heat-sensitive materials by the steam. Gamma irradiation produces no appreciable temperature rise in the materials.

6. Continuous processing lends itself to more efficient and economical materials-handling methods as compared to the present system of batch operations.

Effects of Gamma Irradiation on Bulk Medical Supplies

The question arises as to what effects, other than killing microorganisms, gamma radiation will have on the materials so processed. In experiments[6] conducted at the University of Michigan, studies were made on the radiation dose required to sterilize food wrappers. Using two bacteria, *E. coli* and *B. stearothermophilus,* it was found that a dose of 2,000,000 rep was sufficient to affect complete sterilization. No visible damage, such as color change, embrittlement, clouding, etc., was observed in any of the samples of plastic, cloth, or paper irradiated in the course of the work. Also, Seaman[7] has indicated that the dose of radiation necessary to cause damage to cellulose and similar materials far exceeds that required for sterilization. Excessive doses of radiation are known to decrease the tensile strength of cellulose products but more information is needed on such effects.

In addition to queries on the effects on the physical properties of materials, others are concerned with the possibility of induced radioactivity. Meinke[8] has studied the problem as related to food and has obtained negative results when investigating 24 elements that occur in food. This would indicate that induced activity would not be a problem in the sterilization of surgical dressings.

DESIGN OF A GAMMA-IRRADIATION FACILITY TO STERILIZE BULK MEDICAL SUPPLIES

Selection of Radiation Source

Electrical machines such as Van de Graff generators and linear accelerators produce ionizing radiation in the form of high-speed electrons that have been used extensively for research investigations on radiation sterilization. These machines show great promise in the sterilization of small items such as ampoules of pharmaceuticals. The penetration of high-speed electrons is quite limited, and the authors do not believe that high-speed electrons from such machines are suitable for the sterilization of bulk medical supplies, especially when these supplies are handled as is the customary practice on pallets 4 × 4 × 4 feet. Therefore, gamma radiation was chosen as most suitable in the proposed design for such a facility.

If a gamma source were used, the irradiation could take place after the materials had been packaged and just prior to shipment to distributors. This is possible because of the great depth of penetration of the gamma rays. Since the materials would already have been packaged, there would be no danger of possible recontamination before use by the customer. Gamma sources are becoming available as by-products of the atomic energy program and are considered suitable sterilizing agents in this proposed facility. The gamma source specified consists of twenty fuel elements which have been removed from a nuclear reactor. The fuel elements were chosen over the fission products or cesium-137 as gamma sources since they are presently available. Their availability is contingent on the unloading schedule of a reactor and the subsequent chemical processing schedule.

In the operation of a nuclear reactor, fission products and transuranic elements are formed from the uranium contained in the metallic fuel elements. After these materials have accumulated to certain concentrations or because of considerations of damage to the fuel elements, the fuel elements must be processed chemically in order to provide uranium suitable for refabrication into new fuel elements. It is current practice to hold the fuel elements, which have been removed from the reactor, for a period of time sufficient for the intense radioactivity to be degraded and for the neptunium formed to decay to the valuable element plutonium. Except during periods of experimentation, the radioactivity from the fuel elements at present is being dissipated in storage wells using water as a shield. This operation is expensive because of the large inventory costs associated with the fissionable material. If some of these fuel elements were used as a radiation source, part of the cost of the delay period before chemical processing would be defrayed. Thus, it is easily seen that use of the fuel elements as commercial sources of radiation is conveniently and economically adaptable to the present scheme of chemical processing operations.

The requirements in the United States for fuel elements for the irradiation of bulk medical supplies would not be great since there are very few manufacturers in this field large enough to sponsor such an endeavor. Although reactor fuel elements were selected for this use in the United States suitable radiation sources could be fabricated using fission product wastes for use in those parts of the world where fuel elements may not be available.

Determination of the Optimum Number of Passes

The reactor fuel elements proposed for use in this facility have a very high gamma activity but a very rapid decay rate. It is recommended that each fuel element be used for a period of two months and then replaced with a new fuel element. If the replacement schedules for different fuel elements are staggered greater uniformity of radiation flux will be possible.

However it will probably be necessary to make adjustments in the material flow rate through the facility during the period of operation to compensate for the decay of the fuel elements. The irradiation of a large volume of materials necessitates continuous operation involving the use of a conveyor system to pass the materials into the chamber, past the radiation source, and out of the radiation chamber. Efficient operation requires that the total thickness of materials being conveyed through the chamber should absorb most of the radiation.

The amount of radiation absorbed naturally depends on the absorption characteristics of the materials being irradiated. To explore this aspect of the problem the absorption coefficients were evaluated for a series of bulk medical materials normally sterilized by steam. These materials included sterilized cotton, cotton swabs, cotton balls, roll bandages, gauze pads, and plastic strips in tin cans. The thickness of materials required to absorb half the gamma radiation (half-value thickness) was measured using gamma radiation from the cobalt-60 source in the radiation "cave" of the Fission Products Laboratory. The average half-value thickness for all the materials except the sterilized cotton and cotton balls was found to be approximately 22 inches, whereas for these materials it was approximately 45 inches. The cobalt-60 used in these measurements emits gamma rays of 1.17 and 1.33 Mev. The presence of many different fission products in the fuel elements would cause them to have a spectrum of energies with an average energy of about 0.7 Mev. This lower energy would normally result in a lower half-value thickness but due to the phenomenon of multiple scattering, a build-up of the radiation occurs when treating thicknesses of materials as those proposed in this design. In absorption studies on meat,[9] using gamma rays of different energies, this phenomenon was observed. It was therefore decided to use the half-value thicknesses obtained from the cobalt-60 determinations as approximately correct for the lower-energy gammas of the fuel elements corrected for multiple scattering.

In this design it will be assumed that the materials to be irradiated would be loaded on pallets to a thickness of 42 inches. One pass of such an absorber would theoretically result in the absorption of 73 per cent of the radiation normal to the surface of the materials. This was calculated from the relation:

$$I = I_0 e^{-\mu x} = I_0 e^{-0.693 \frac{x}{(X_{1/2})}} \qquad (1)$$

where I = intensity of radiation passing through thickness, x, I_0 = original intensity of radiation, μ = broad beam absorption coefficient, inches^{-1}, x = thickness of material, inches, and $(X_{1/2})$ = half-value thickness of material, inches.

$$\frac{I}{I_0} = e^{-0.693 \frac{(42)}{(22)}} = e^{-1.3} = 0.27$$

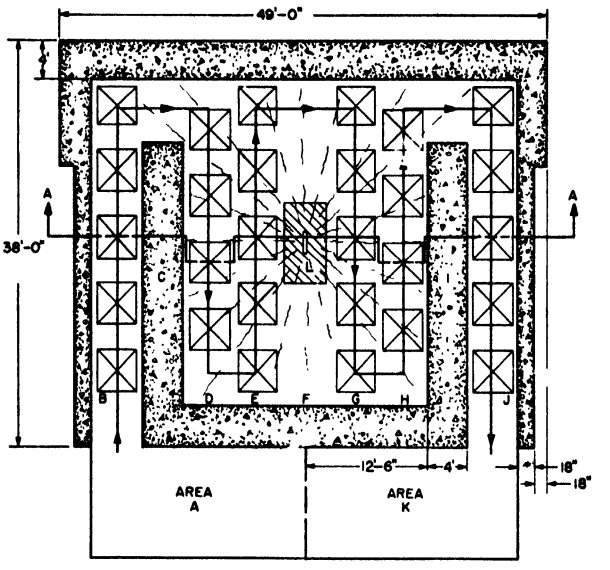

Figure 1. Plan view of irradiation facility

The spacing between the pallet loads as they progress through the chamber will reduce the per cent of the radiation absorbed. This is partially offset by the greater total thickness the materials offer to all the radiation not normal to their surface, such as that from the extremities of the source. Consequently, the materials were considered 80 per cent efficient as an absorber. Thus each 42-inch pallet was considered to absorb 73 per cent × 80 per cent or about 58 per cent of the radiation flux.

To provide a uniform radiation dosage, the first pass of the conveyor was placed 3 feet from the source. The second pass was farther away but because of the normal attenuation of the radiation with distance, the spacing was kept at a minimum. Knowing the radiation flux and the absorption coefficients of the material, the absorption of the radiation in the first pass was calculated. The radiation flux at the second pass was reduced both by absorption in the previous pass and by the distance to the source. After a number of passes, the radiation would be reduced to the point where it was no longer economically feasible to add another pass. In this design, because of the width of the pallet and the large amount of absorption in each pass, only two passes on each side of the source were specified.

Description of Design

Figures 1 and 2 show the plan and elevation views, respectively, for the proposed radiation chamber using 20 reactor fuel elements as a source of radiation. As shown, the materials to be sterilized will be conveyed by racks holding three pallet loads on a monorail conveyor system. This particular design arose out of considerations for maximum ultilization of the radiation field which emanates in all directions from the radiation source.

Referring to Fig. 1, material handlers will deliver to area A pallet loads of materials from production

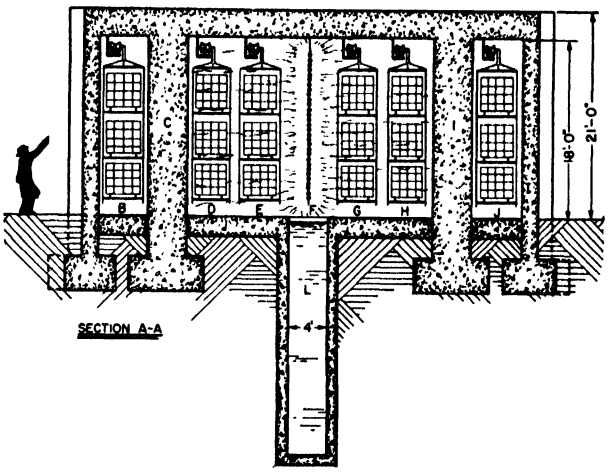

Figure 2. Elevation view of irradiation facility

areas. Here the loaded pallets will be raised by fork lift trucks onto the racks ready for irradiation. The racks will travel on the monorail system through the labyrinthine passage *B* and into the chamber past barrier wall *C*. The materials then make two passes, *D* and *E*, on one side of the radiation source *F* and two passes, *G* and *H*, on the other side. This arrangement will provide a more uniform radiation dose for the materials by irradiating both sides of the pallet loads. After a sufficient dose of radiation is obtained in the chamber, the materials pass around concrete barrier *I* and out the labyrinthine passageway *J* to the unloading and removal area *K*. From area *K* the sterilized materials could be loaded into railroad cars or sent to accumulation areas awaiting shipment.

Provided in the chamber is a well *L* which would be filled with water and would be used to store the radiation source when not in use. It will be necessary for the operator to enter the chamber for such things as routine maintenance, change of radiation source, or recovery of spilled materials from the pallets. The presence of the well will permit this access simply by lowering of the source beneath the protective shield of water. Since there is no residual activity in the chamber after the source is lowered into the water, the operator could perform all necessary duties and leave the chamber without danger.

Each horizontal pass of the conveyor would be driven by sprockets connected by a common shaft or a chain drive to keep them moving at the same rate. If arcs were provided at the end of each pass, the spacing required between the individual racks and the successive passes would be more than could be tolerated. The most efficient operation would naturally have minimum spacing between each rack to maximize the amount of absorption per pass and the minimum distance between successive passes to reduce the attenuation due to distance. This may be accomplished by installing an oscillating transfer mechanism at the end of each pass for lifting the racks as they reach the end of the pass from one monorail and placing it on the next monorail where it would be conveyed past the source as previously. The transfer mechanism would have to be synchronized with the driving mechanism of the passes to insure smooth transfer of the racks. Guides would be used to maintain the racks in a vertical position while traveling along each pass and from one pass to another to prevent spillage. The spacing between each pass and between adjacent racks was set at 2 feet.

Source Distribution and Radiation Dose

The decision was made to specify 20 reactor fuel elements as the source of radiation after considering the radiation flux available from one fuel element and the amount of radiation required to affect complete sterilization. The dose of radiation selected as a sterilizing dose was 4,000,000 rep which is greater than the amount generally considered as necessary for sterilization. The productive capacity for the radiation chamber is a function of this required dose and also a function of the radiation field provided by the source.

The radiation field will, of course, vary with the geometry of the source. If the fuel elements were arranged side by side with no distance separating them, the radiation field would vary in all directions and would appear as if emanating from a plaque source of uniform concentration. This type of source was previously found to be inefficient.[10] A more efficient design would be to distribute the activity of the source in such a way as to provide a uniform radiation field in one direction. In the case of the fuel elements, the activity may be distributed by spacing of the fuel elements. Since the materials were to be transported on racks through the chamber on a monorail in a number of horizontal passes, it was decided to establish a uniform radiation field in the vertical direction. This would mean that although the materials traveled in a varying radiation field in the horizontal direction, the uniform vertical field would insure that the materials on the top pallet would receive the same dose as those materials located on the bottom pallet.

The uniform vertical field could be accomplished by aligning the long axis of the fuel elements in a direction parallel to the direction of the four passes. In addition, the elements would be arranged with vertical spacings as shown in Fig. 3. The smaller

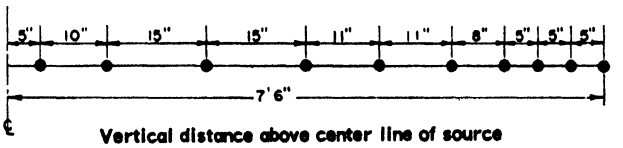

Figure 3. Elevation view showing spacing of one half of fuel elements for irradiation facility

pitch of the fuel elements near the floor and ceiling is used to produce a more uniform radiation field at the extremities of the source.

The optimum spacing of the fuel elements was determined by trial and error by calculating the dose

rate in air at certain positions and then plotting the dose rate versus vertical distances for a definite horizontal distance from the source to ascertain the effect of a particular spacing scheme.

The procedure for calculation of the dose rate in air was quite extensive because of the irregular spacings of the 20 different components of the source contributing to the flux at any arbitrary point. The total flux at a point is a scalar sum of the contributions from each of the fuel elements. The calculations were simplified by assuming that at a sufficient distance from the fuel elements the source may be considered as being comprised of 20-line segments. The dose rate contribution of one of the fuel elements is given by:

$$I_1 = \alpha(H_a + H_b) \tag{2}$$

where α = concentration coefficient for each fuel element.

The calculation of the radiation flux at any point in a given plane parallel to the face of the group of source rods will be demonstrated. The values of H_a and H_b for one fuel element are obtained at any point p from the general equations:

$$H_a = \int_0^{l_1} \frac{dx}{x^2 + y^2 + d^2} = \left[\frac{1}{\sqrt{y^2 + d^2}} \tan^{-1} \frac{x}{\sqrt{y^2 + d^2}} \right]_0^{l_1} \tag{3}$$

$$H_b = \int_0^{l_2} \frac{dx}{x^2 + y^2 + d^2} = \left[\frac{1}{\sqrt{y^2 + d^2}} \tan^{-1} \frac{x}{\sqrt{y^2 + d^2}} \right]_0^{l_2} \tag{4}$$

where all distances are in inches and x = length along the horizontal axis of the 24-inch (assumed) fuel element, y = horizontal distance from plane of source rods to parallel plane containing point p, d = vertical distance from point p to the fuel element, and l_1 and l_2 = lengths along the axis of the fuel elements between the base of a perpendicular from point p and the extremities of the fuel element.

For a particular solution, consider, for example, a plane located 3 feet from the face of the source rods and a point p located in this plane 2 inches above the horizontal center line and 6 inches to the left of the vertical center line as shown in Fig. 4. For convenience, Fig. 4 shows only the fuel elements on either side of point p and the two elements at the extremities of the source holder. In this example the distance d_{10} from point p to fuel element no. 10 was determined from Fig. 3 and the contribution of fuel element no. 10 would be:

$$I = \alpha_{10}(H_{a10} + H_{b10}) \tag{5}$$

$$H_{a10} = \int_0^{6} \frac{dx}{x^2 + (36)^2 + (3)^2} = \left[\frac{1}{\sqrt{(36)^2 + (3)^2}} \tan^{-1} \frac{x}{\sqrt{(36)^2 + (3)^2}} \right]_0^{6} \tag{6}$$

$$H_{b10} = \int_0^{18} \frac{dx}{x^2 + (36)^2 + (3)^2} = \left[\frac{1}{\sqrt{(36)^2 + (3)^2}} \tan^{-1} \frac{x}{\sqrt{(36)^2 + (3)^2}} \right]_0^{18} \tag{7}$$

The contribution to the flux at point p of the other fuel elements is determined by insertion of the proper vertical spacing d into these equations and subsequent multiplication by the concentration coefficient α. Following this procedure for each fuel element the total flux at the point p would be

$$I = I_1 + I_2 + I_3 - - - - - - - I_{20} \tag{8}$$

The concentration coefficients, which depend on specific activities and other properties of the fuel elements, were not known. However, a value of the dose rate opposite one fuel element and 3 feet from it was estimated to be approximately 10^6 roentgens per hour.

Since the concentration coefficient for each fuel element would be approximately the same, the function H was integrated and plotted as a function of distance from a fuel element. The values of the function were first normalized to 1×10^6 roentgens per hour at 3 feet where the value of the dose rate had been estimated. The immediate problem was then reduced to summing the ordinates of the function H at the distances of the 20 fuel elements from the point at which the dose rate was desired. With the spacings as shown in Fig. 3, the values of the radiation intensity were calculated for the points opposite the center line of the sources and 2, 4, and 6 feet above the center line. The dose rate calculations on the center line were made for horizontal distances

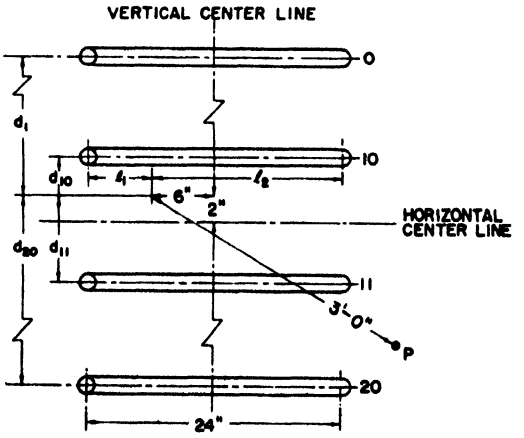

Figure 4. Dimensions for example calculation of radiation field

of 3, 5, 8, and 12 feet from the source. The results of these calculations are depicted in Fig. 5. As Fig. 5 indicates, the radiation field resulting from the distribution indicated in Fig. 3 provides a very uniform radiation field in the vertical direction. As the source is symmetric with respect to the center line, the uniform field would extend over the entire height of the racks transporting the pallets.

Capacity Calculations

The dose rate was calculated for many arbitrary points throughout the chamber using the fuel element spacings shown in Fig. 3. The dose rates at these points were then plotted to produce the isodose curves shown in Fig. 6. These isodose curves denote the levels of the radiation flux in air and must be corrected for the absorption which takes place when the chamber is in operation.

The materials located at the center of any pallet will receive the minimum dose of radiation. The materials on the side of the pallet closest to the radiation source will receive a higher dose due to less shielding and nearness to the source. Since the pallets do not reverse in their travel past the source, the edge closest to the source on the right side becomes the farthest away on the left side of the chamber. This compensates somewhat for the high dose received on one side of the source. Figure 7 is a plot of the dose rate corrected for absorption as a function of distance traveled in the irradiation chamber for materials located at three different positions on a pallet. Curve *A* shows the radiation field traversed by the materials on the edge of the pallet nearest to the source; curve *B*, the central portion;

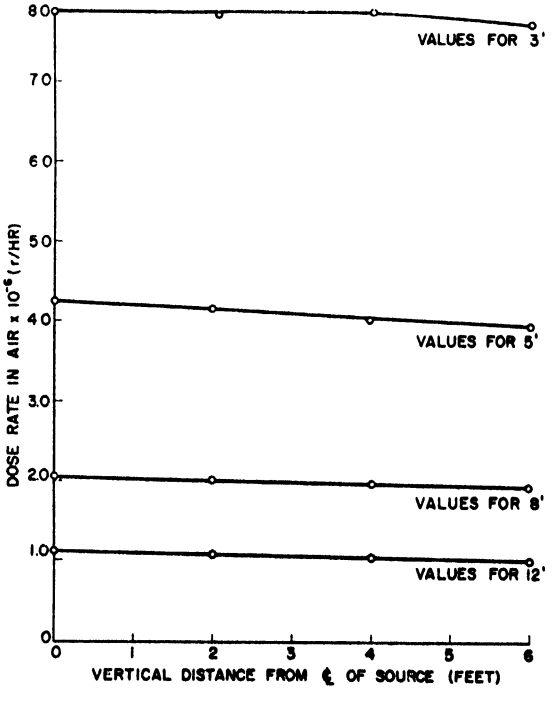

Figure 5. Radiation flux versus vertical distance for selectively spaced fuel elements

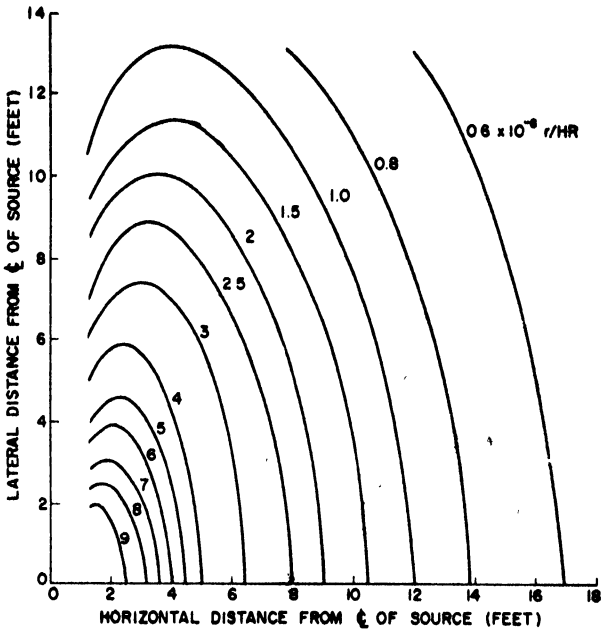

Figure 6. Isodose curves in horizontal plane perpendicular to source at center line for one quadrant of radiation chamber

and curve *C*, the materials on the pallet farthest from the source. The area under the curves represents the dose received by the materials located at these positions as they travel through the chamber. The curves have been drawn for only one half a traverse since the path of travel is symmetrical for both sides of the chamber. The total dose received by materials located at the center portion of the pallet would be twice the area under curve *B* while for the materials on the outer edge, the total dose would be the sum of areas under the curves *A* and *C*.

Twice the area under the curve *B* was determined to be equal to 11×10^7 rep-feet per hour. This value was then divided into the dose required for sterilization and multiplied by the feet of travel to obtain the time required to completely sterilize the materials.

$$\frac{4(10)^6 \text{ rep}}{11(10)^7 \text{ rep-feet/hour}} \times 118 \text{ feet} = 4.3 \text{ hours/cycle}$$

This time was calculated to be 4.3 hours. Since the fuel elements will also be decaying during the time they are in use as gamma sources, a variable speed drive would be needed to alter the conveyor speed as required.

In each cycle there would be 20 racks transporting three pallet loads per rack. The capacity per hour would then be:

$$\frac{20 \text{ racks}}{\text{cycle}} \times \frac{3 \text{ pallets}}{\text{rack}} \times \frac{\text{cycle}}{4.3 \text{ hours}} \cong \frac{15 \text{ pallets}}{\text{hour}}$$

Thus, in an 8-hour day the radiation facility could handle a normal day's pallet production of 100 to 120 pallets. The radiation chamber could easily handle extraordinary production rates by scheduling two shift operations.

Other Calculations (Summarized)

Shielding calculations were made which indicated that 4 ft 0 in. of concrete would be required. A cost estimate was prepared which indicated that the radiation chamber could be constructed for $57,900. An estimate of $55,000 per year was made for anticipated operations costs. This cost will depend in a major part on the rental charges for fuel elements. These charges were unknown. Therefore, the estimated cost for the construction of the radiation chamber is considered more reliable than the estimated annual cost for operations.

CONCLUSION

The sterilization of medical supplies by gamma irradiation appears promising considering both the limited experimental work and the present feasibility studies. A preliminary design has been presented for the radiation sterilization of bulk medical supplies in pallets 4 × 4 × 4 feet using cooling-reactor fuel elements as a source of radiation. The estimated capacity of 120 pallets per 8-hour day is sufficient to handle the production of a large manufacturing plant, and the estimated cost of operation compares favorably with known costs for steam sterilization.

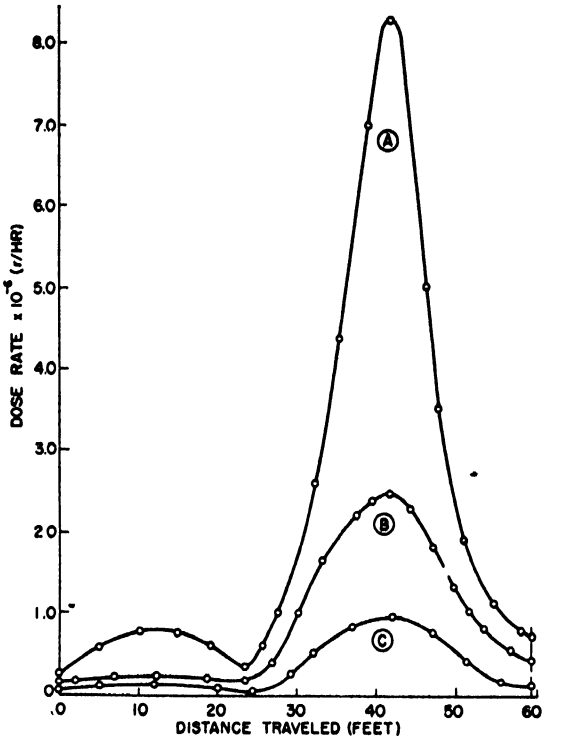

Figure 7. Dosage rate as a function of distance along path of travel in radiation chamber

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Ionizing Radiations for Meat Processing

By D. M. Doty, B. S. Schweigert, C. F. Niven, Jr., and H. R. Kraybill,* USA

The food industries are constantly evaluating new processing methods and improving existing methods. Currently there is widespread interest in the application of high energy radiations to the preservation of meat products and other materials that are subject to microbial deterioration. When considering this method, one must first recognize the fact that an ideal technique or techniques for food preservation must eliminate microbial spoilage without having any adverse effects on color, odor, flavor, or other palatability and nutritional factors. Certainly our present methods of food preservation (dehydration, heat processing, cold storage and freezing, and the addition of chemicals such as salt or acids) are not completely satisfactory when judged on this basis. Thus, the importance of evaluating the possible application of high energy radiations to meat preservation becomes apparent.

There is ample evidence to show that food spoilage microorganisms can be killed in pure cultures and in foods by ionizing radiations at dosage levels of 10^5 to 3×10^6 rep. Unfortunately, undesirable changes in color, odor, and flavor of some foods (especially high protein foods such as meat and milk) are induced by this radiation dosage. Some means for preventing these changes must be developed before ionizing radiations can be widely used for the sterilization of meat and other food products. As the first essential step in the solution of this problem, we have attempted to elucidate the nature of the chemical reactions induced when meat, particularly raw beef, is subjected to gamma irradiation. Also we have studied the factors influencing the radiation sensitivity of some meat spoilage microorganisms so that realistic irradiation dosages may be established for the preservation of different meat products under various conditions of storage.

No attempt will be made here to report previous work relating to this subject since it has recently been reviewed by Schweigert *et al.*[1] and by Hannan.[2]

MATERIALS AND METHODS

Irradiation of meat and other materials for study in our laboratories was done in an experimental cobalt-60 source with a radiation intensity of approximately 90,000 roentgens per hour, or in a more intense gamma ray source at Arco, Idaho, USA. Unless otherwise indicated, the products were irradiated at approximately 5°C.

* American Meat Institute Foundation, University of Chicago.

The meat used was ground lean beef unless otherwise indicated.

Details of the chemical and bacteriological methods used are given with the results or have been presented in other reports from our laboratories.

CHEMICAL NATURE OF UNDESIRABLE ODORS FORMED BY GAMMA IRRADIATION OF BEEF

Batzer and Doty[3] have reported that when ground lean beef was irradiated at a dosage of 5×10^5 rep or above, there was an appreciable reduction of soluble protein and a simultaneous corresponding increase in the non-protein nitrogen compounds in the meat. It was also shown that glutathione present in the meat or added to meat was partially destroyed by gamma irradiation.

More recent experiments have shown that the pH of the meat and the carbonyl compounds present are increased by gamma irradiation. The loss in glutathione and the increase in pH and carbonyls are directly related to irradiation dosage (Table I).

Table I. The Effect of Gamma Irradiation on Glutathione, pH and Carbonyls in Beef

Dosage rep $\times 10^4$	*pH*	*Glutathione mg/100 gm*	*Carbonyl moles* $\times 10^{-6}$*/gm*
0	5.68	13.5	12.7
2	5.70	9.0	43.1
4	5.72	6.3	66.0
6	5.80	4.1	86.3
8	5.97	4.5	112.0
10	5.99	4.0	115.0

These changes suggest that the protein fraction of meat and possibly the fat are influenced by irradiation. The nature of the primary undesirable odor of irradiated meat suggests further that sulfur compounds may be involved. Actually, Batzer and Doty[3] reported the presence of hydrogen sulfide and methyl mercaptan in irradiated meat and suggested that these compounds might be responsible, in part at least, for the undesirable irradiation odor. Since that time a rather sensitive method for the quantitative estimation of hydrogen sulfide has been developed[4] and used to measure the hydrogen sulfide present in irradiated meat. The results obtained show that the hydrogen sulfide produced is influenced by the irradiation dosage and the fat content of the meat (Table II). It is of interest that subjective evaluation of the odor of irradiated meat indicates that less objectionable odor is developed in meat containing large amounts of fat than in meat with less fat.

Table II. The Effect of Irradiation Dosage and Fat Content of Ground Beef on Hydrogen Sulfide Produced (Results are expressed as moles $\times 10^{-7}$ H_2S per 100 gm meat)

Dosage level 10^6 rep	Fat content 20%	Fat content <10%
0	0	0
2	9.4	22.6
4	—	23.9
6	3.5	30.9
8	13.6	38 4
10	16 0	20 2

Attempts are now being made in our laboratories to develop a satisfactory method for estimating the amount of methyl mercaptan in irradiated meat. Also, investigations are in progress to identify other odoriferous compounds that develop during gamma irradiation, particularly at radiation dosages above 2×10^6 rep.

Changes Induced in Meat Fats by Irradiation

Meat fats (beef tallow or pork fat, rendered or unrendered) increase in peroxide content during irradiation, particularly in the presence of oxygen (Table III). There is accelerated production of peroxides during storage of irradiated fats at refrigerator temperature (5°C) in the presence of air as compared to non-irradiated controls. In some cases also, carbonyl compounds and free fatty acids are increased in meat fats during irradiation and storage in air.[5]

We have not detected off odors in irradiated fats; however, chemical changes in fats may influence the production of off odors or chemical changes in meat pigments when meat is irradiated. These aspects of the problem are now being investigated.

The Effects of Irradiation on Myoglobin

One of the undesirable side reactions induced by irradiation of fresh meat is the change in color. Studies on myoglobin, the principal pigment of fresh meat, and changes associated with irradiation have been reported by Ginger *et al.*[6]

These studies on chemical changes in meat pigments have revealed that the myoglobin may be oxidized to metmyoglobin during irradiation (oxidation of ferrous iron to ferric iron) or may be changed to a green pigment (as revealed by work with water extracts of meat or purified myoglobin) determined by spectral measurements. Thus, when crude extracts of meat are irradiated, they may turn brown, red brown, green, or green brown or remain red, depending somewhat upon the conditions of exposure. Spectral curves on such extracts showed these colors to be related to the amounts of metmyoglobin (brown), oxymyoglobin (red) and the green pigment (absorbing light at 610 mμ) present.

Spectral analyses of extracts from irradiated meat and reflectance measurements on meat indicate that these same changes occur in the pigments when meat is irradiated. However, it has been found that the undesirable changes are reduced by minimizing the amount of oxygen present. Thus, observations on irradiated meat in sealed cans with minimal air space or in oxygen impermeable casing do not show any appreciable change in color from non-irradiated meat even after several weeks' storage. On the other hand, meat irradiated and stored in oxygen permeable casings discolored during irradiation and continued to darken (metmyoglobin formation) during storage after irradiation. The addition of 0.05 and 0.5% ascorbic acid to meat was ineffective as a protective agent against discoloration during irradiation and storage in the presence of oxygen.

BACTERIOLOGICAL STUDIES

Since the ultimate aim of any food sterilization process is to destroy the spoilage microorganisms present, it is essential that factors influencing the sterilization sensitivity of spoilage microorganisms most commonly present in the food be carefully considered. This has been done by bacteriologists in our laboratories.

A detailed physiological study of 39 bacterial cultures isolated from spoiled beef samples held at 0 to 2°C demonstrated that virtually all belonged to the genus *Pseudomonas*. They appeared to be closely related to *Pseudomonas geniculata* and have tentatively been placed in this species. Consequently, studies have been made to determine the radiation sensitivity of those microorganisms and to establish the factors that might influence their resistance to gamma radiation.

These fresh meat spoilage bacteria were shown to be very sensitive to gamma radiation. The mean lethal dose (dose required to kill 63% of the population) was found to be approximately 1370 rep when these bacteria were irradiated in nutrient broth (1.0% tryptone, 0.5% yeast extract). In contrast, *Staphylococcus aureus* requires a mean lethal dose of 8900 rep and *Clostridium botulinum* spores require approximately 30,000 rep. The sensitivity of the *pseudomonads* to gamma radiation was not changed appreciably by the addition of ascorbic acid, nitrite, glutathione, cysteine, or thioglycollate or by varying the pH of the suspending medium.

However, some unidentified substance(s) in meat juices did increase the irradiation resistance of *Pseudomonas geniculata* (Table IV).

Also, it should be noted that the organism was less sensitive to gamma radiation when high initial populations were employed. The protective effect of high

Table III. The Influence of Irradiation and Storage on Peroxide Values of Beef Fat

Dosage 10^6 rep	Container	Peroxide value: Irradiated	Peroxide value: Stored 4 weeks; 5°
0	Visking casing	0.4	0.4
2.1	Visking casing	2.0	18.7
0	Saran casing	0.5	0.6
2.1	Saran casing	1.6	2.6

Table IV. The Radiation Sensitivity of *Pseudomonas geniculata* Suspended in Different Media

Suspension medium:	Nutrient broth	Phosphate buffer	Meat juices
Initial population, log	Mean lethal dose rep		rep
8.5	9830	7440	13,900
7.5	3600	1640	6580
6.5	3290	1640	4940
4.5	1640	1640	3600

populations was not due to the presence of killed cells. High populations of viable *Staphylococcus* did not decrease the radiation sensitivity of small numbers of *Pseudomonas*. Thus, the protective factor in high populations is apparently not the result of liberation of a substance from dead cells or from viable *Staphylococcus*.

It was found that ferrous ion in 0.001*M* solution as $FeSO_4$ or $FeCl_2$ increased the resistance of the *Pseudomonas* suspension to radiation. This was true, however, only if the ferrous ion was autoclaved with glucose or tryptone and if citrate was used as a solubilizing agent (Table V).

Reducing sugars other than glucose exhibited a similar effect. The protective effect was independent of glucose concentration within a range of 0.5 to 2.0%, but the effect was enhanced by an increase in the Fe^{++} concentration (Table VI).

Although neither the protective substance(s) in meat juices nor the product of the glucose-ferrous salt reaction has been identified, it is possible that these substances are similar.

When we consider the potential role of radiation in the preservation of cured meats, the picture is quite different from that for fresh meats. The curing salts added and the heat processing to which cured meats are usually subjected greatly limit the important types of spoilage microorganisms for these products. The spore forming rods that survive processing and various lactic acid bacteria, micrococci, yeasts and molds that contaminate the product after processing are of primary importance. These microorganisms represent a wide range with respect to

Table V. The Effect of Ferrous Ion and Glucose on the Radiosensitivity of *Pseudomonas geniculata*

Suspension medium*	Mean lethal dose, rep	Dose necessary for 99% destruction, rep
Nutrient broth	1640	7240
Nutrient broth + 10^{-3} *M* Fe^{++}	5750	22,700
Glucose + 10^{-3} *M* Fe^{++} (autoclaved together)	4600	14,700
Glucose (autoclaved) + 10^{-3} *M* Fe^{++} (filtered)	1640	7550
Glucose (filtered) + 10^{-3} *M* Fe^{++} (autoclaved)	1640	6570
Glucose	1640	8220

* Contained sodium citrate in all cases.

Table VI. Effect of Ferrous Ion Concentration on Radiosensitivity of *Pseudomonas geniculata*

Ferrous sulfate conc. in medium* molarity	Mean lethal dose rep	Dose necessary for 99% destruction rep
5×10^{-2}	4120	19,700
10^{-2}	5750	20,200
10^{-3}	4080	16,400
10^{-4}	1640	8220

* Contained sodium citrate and glucose.

radiation resistance, but all of them are generally much more resistant than the pseudomonads, which are the major spoilage organisms of fresh beef.

From a practical standpoint then, the possibility of extending the shelf life of cured meat products by irradiation at low levels is not good. Work in our laboratories has shown that low dosage irradiation (<100,000 rep) can extend the shelf life of fresh beef under refrigeration (5°C) at least fivefold. At this irradiation dosage, no objectionable changes in color or odor are produced. However, such low dosage irradiation would be of little value in extending the shelf life of packaged cured meats because the spoilage microorganisms present would not be destroyed to a sufficient extent.

PROTEOLYTIC ENZYME STUDIES

Radiation sterilization cannot be applied generally to foods unless enzyme systems that may catalyze undesirable changes during extended storage are inactivated also. In this connection, Doty and Wachter[8] recently reported the effect of gamma radiation on the total proteinase activity in beef muscle tissue.

Since preliminary studies had indicated that the optimal pH for proteolysis in beef muscle tissue was near pH 4.5 and the optimal temperature for a reaction time of 24 hours was near 40°C, test conditions of pH 4.6, a temperature of 37°C, and a reaction period of 24 hours were selected for measurement of enzymatic activity. For all enzyme tests, ground meat, extracts from ground meat, or residues from extracted meat were used at a level equivalent to 7.5 gm or 15 gm raw meat in 50 ml acetate buffer, pH 4.6. When casein was used as an added substrate, it was added at the level of 1.0 gm per test. For maximum activity, particularly with added casein, all test suspensions were stirred or shaken continuously during the incubation period.

One ml of a preservative consisting of 1 part fluorotoluene, 1 part ethylene chloride, and 2 parts butyl chloride was used to prevent microbial growth in all test suspensions during incubation. After incubation the solutions were filtered, the residue washed thoroughly at pH 4.6, and tyrosine determined in a suitable aliquot of the filtrate.

Irradiation at a dosage level of 1.6×10^6 rep reduced the activity of the proteinase and also reduced the amount of extractable tyrosine present (Table VII).

At a lower dosage level, 0.5×10^6 rep, these effects were not apparent. Even at the higher dosage level,

Table VII. The Influence of Gamma Radiation on the Proteinase Activity of Extracts (pH 9.6) and Residues of Beef*

Sample No.	Extract		Residue	
	Non-irradiated	Irradiated	Non-irradiated	Irradiated
	mg/gm	mg/gm	mg/gm	mg/gm
2†	0.085	0.019	0.087	0.080
3†	0.046	0.012	0.059	0.037
5‡	0.035	0.035	0.062	0.056
6‡	0.034	0.030	0.063	0.058
7‡	0.037	0.021	0.076	0.075
8‡	0.028	0.033	0.076	0.076

* Incubation at 37°C for 24 hr at pH 4.6 with casein substrate. Results are expressed as tyrosine liberated.
† Samples 2–3:1.6 × 10^6 rep.
‡ Samples 5–8:0.5 × 10^6 rep.

the residual proteolytic activity probably would be sufficient to catalyze proteolytic changes in raw meat if attempts were made to sterilize meat by irradiation and store it for long periods of time without refrigeration.

DISCUSSION

The work reported here does not supply solutions to the many problems involved in the application of ionizing radiations for food sterilization. However, it does furnish much information that can be used effectively for the solution of these problems. With some understanding of the chemical changes that occur during irradiation of meat, it will be possible now to study pre- and post-irradiation treatments with objective rather than subjective methods for evaluation of results. The influence on meat quality of such factors as radiation source (beta or gamma rays), radiation dosage, radiation intensity, the presence or absence of oxygen, the use of protective substances such as ascorbic acid, the type of meat (beef, pork, lamb), and the composition of the meat (especially fat content), can be more completely and precisely evaluated. Thus, from a practical standpoint, the investigations described here may be of value in explaining and correcting some of the undesirable organoleptic changes that occur when meat is subjected to ionizing radiations for preservation.

SUMMARY

Meat is one of the foods most sensitive to acceptability changes induced by ionizing radiations. Considerable progress has been made in determining the nature of the chemical changes that occur in meat (fresh beef) during irradiation and in quantitating these changes. The chemical changes noted when meat is irradiated at dosages above 1.5 × 10^6 rep include a loss in soluble protein and a corresponding increase in non-protein nitrogen, a loss in glutathione, the formation of simple odoriferous sulfur containing compounds (hydrogen sulfide and methyl mercaptan), an increase in carbonyl compounds, a reduction in total proteinase activity, destruction or modification of tyrosine, conversion of the red pigment, myoglobin, to a green compound that absorbs light at 610–620 mμ, and oxidative changes in the fat. These studies provide a basis for further work on the relation of these changes and the compounds produced to the undesirable flavors, odors and discolorations associated with irradiating meat with sterilization dosages.

The major spoilage microorganisms present in fresh beef *(Pseudomonas geniculata)* are relatively radiation sensitive. Their radiation sensitivity is dependent upon population level. Also, some substance is present in meat juices which partially protects this microorganism against gamma radiation. Similar partial protection was afforded by ferrous ion when autoclaved with glucose or tryptone, and citrate. Because of the sensitivity of these microorganisms to irradiation, it is suggested that low dosage irradiation (<100,000 rep) might be used to prolong the shelf life of beef kept under refrigeration. Meats treated with these low levels of radiation show no evidence of damage with respect to odor, flavor, or color. The same low level of irradiation treatment would not be effective in prolonging the shelf life of cured meats because the common spoilage microorganisms for cured meats are much more radiation resistant.

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Research in the United States in the Radiation Sterilization of Foods

By R. G. H. Siu, R. G. Tischer and B. Morgan,* USA

Historically, the stream of civilization has followed the availability of food. After the recession of the glacial period, around 6000 B.C., the ensuing climate favored rich vegetable and animal life in certain parts of the world. Neolithic man began crude farming operations. He cultivated plants and bred animals. As man progressively relieved himself of the anxieties and uncertainties of the life of the hunter, he had time to devote himself to the advancement of culture and the accumulation of inventions, which continually raised his standard of living. He learned to use polished stone tools with sharpened edges, to carve out boats for water transport, to plow and to use the sled. He mastered the art of masonry to improve his shelter and he developed wool clothing and leather goods. He had houses of wood, clay and stone. He had pottery. Coon pointed out in his interesting story of man[3] that "despite the growth of cities and the rise of empires and leagues of nations, most of the people of the world still live in villages and perform tasks invented by Neolithic man."

Once man began to farm, however, he was confronted with the uncertainties of the weather. Crops and meats had to be stored for the lean years. It was not by chance that during those early times the plants cultivated, such as wheat, barley, flax and beans, were capable of easy storage and ready distribution. Thus, already 6000 years ago man was confronted with three minimum prerequisites for the foundation of advancing civilization: the growing, the storing and the distributing of food. To the degree that man controlled these three functions, he was able to devote the excess time and energy to the development of the sciences, the arts, and his spiritual and cultural qualities. As these latter activities became emphasized, there was a compensating demand for more efficient means of food production, storage and distribution. Through the reciprocal stimulation of these two groups of pursuits the progressive advancement of man reached its present peak.

While the food problem has been solved in many geographical areas, from a world point of view we must confess a concern which needs be faced squarely. Today, over half of the world's population is not receiving an optimum diet, even though at the same time a food surplus exists in other parts of the world. Furthermore, the population is increasing at the rate of twenty million per year. This growth is outstripping the increase in *per capita* food production. The solution of food production, storage and distribution problems on a world wide basis, therefore, is one of the most important challenges confronting modern man.

Methods of food preservation have been sought since the time of early man. Drying, smoking, pickling, salting and curing of meats, fruits and vegetables have been in use for thousands of years. A great step forward was the development of a canning process by Nicholas Appert in 1809. In all of these food preservation processes, however, losses occur in the appearance, flavor, odor, texture and nutritive qualities of foods, which rob man of much of nature's gifts. With the introduction of large scale refrigeration late in the last century, it became possible to preserve and ship foods at low temperatures with good retention of quality. Unfortunately, only a limited segment of the world is blessed today with the benefits of continuous refrigerating facilities.

As a result of these considerations, two important contributions to the world food problem may be stated as follows: (*a*) with the limited supply of food and the availability of refrigeration facilities can a means be found to extend the shelf life of refrigerated foods and, (*b*) in those areas where refrigeration is not available, can a process be developed which will enable food to retain most of its original qualities long enough to permit world wide shipping, storage and consumption.

The radiation processing of foods offers just these potentialities. For this reason, many laboratories in the United States, as well as the Government itself, have sought to push this new technique over its technological hump for the benefit of man. This paper will survey the activities going on at the present time in the United States and give a summary of the technical state of the art.

INSTITUTIONS ACTIVE IN THE UNITED STATES

American universities, industry and Governmental agencies have been vigorously pursuing this program since 1949. We should mention some of the leading institutions. In the academic world we find the pioneering studies of Massachusetts Institute of Technology and the extensive work of the University of Michigan. Other laboratories that have been active

* The Quartermaster Corps.

for several years in this field include the Stanford Research Institute, Columbia University, Food Research Institute and the American Meat Institute Foundation. In industry, Swift and Company has been a leader from the food standpoint, and General Electric Company and the High Voltage Engineering Corporation have devoted intensive effort in the development of beta-emitting generators as a source of radiation. At the present time the United States Government subsidizes about three-fourths of the national effort, which is being conducted in about forty organizations, scattered throughout the country.

Within the Government, the Atomic Energy Commission spearheaded the governmental effort in sponsoring much of the earlier work. Two years ago, the governmental program was passed over to the Defense Department because of the extensive facilities for food research and development vested in the Army's Quartermaster Corps. This program is currently coordinated by the Quartermaster Corps, assisted by an advisory committee of the National Academy of Sciences.

These laboratories represent a great diversity of interests and ability. They are not limited to those groups with main interest restricted to food. Rather they represent laboratories having excellent records of accomplishment in biology, chemistry, physics, engineering and adjacent scientific, industrial and technological fields. A list of the principal laboratories carrying out investigations related to food irradiation is given in Table I.

NATURE OF IRRADIATION PROCESS

The process consists of subjecting foods to ionizing radiations instead of heat. There is only a few degrees rise in temperature in the food itself, which is exposed in the order of seconds or minutes. This is contrasted to the canning technique in which the product may be kept for as long as an hour or more at 240°F. The irradiated products thus retain their fresh appearance, instead of the overcooked quality available from conventional canning.

Once the microorganisms have been destroyed the food, of course, must be protected from recontamination. For this reason, the food is usually sealed hermetically in metal, plastic or other containers before exposure to the radiations. It is also possible to envision a process of radiation coupled with subsequent aseptic canning.

APPLICATIONS OF RADIATION PROCESS

The use of ionizing radiation can be adjusted to produce varying degrees and types of preservation, determined largely by the amount of radiation to which the food is exposed.

If the food is exposed to doses of radiation so that it receives between two to two and a half million roentgens equivalent physical (rep), total sterility may be achieved. This type of treatment prevents microbial spoilage and the resulting food can be stored without refrigeration without fear of bacterial breakdown.

Table I. Major Laboratories in the United States Active in Research Related to Food Irradiation

Academic

- Alabama Polytechnic Institute
- Columbia University
- Cornell University
- Florida State College
- Iowa State College
- Massachusetts Institute of Technology
- Michigan State College
- Ohio State University
- Oregon State College
- Pennsylvania State University
- Texas A&M College
- Union College
- University of California
- University of Chicago
- University of Colorado
- University of Illinois
- University of Massachusetts
- University of Michigan
- University of Minnesota
- University of Rochester
- University of Utah
- University of Wisconsin

Government

- Atomic Energy Commission
  - Argonne National Laboratory
  - Brookhaven National Laboratory
  - Materials Testing Reactor Station
  - Oakridge National Laboratory
  - Washington Headquarters
- Department of Agriculture
  - Western Utilization Research Branch
- Department of Defense
  - Air Force Aero-medical Laboratory
  - Army Chemical Corps
  - Army Medical Service
  - Army Quartermaster Corps
  - Naval Bureau of Supplies and Accounts
  - Naval Research Laboratories
- Department of Health, Education & Welfare
  - Food & Drug Administration
- National Academy of Sciences (quasi-governmental)

Industry

- American Can Company
- Applied Radiation Corporation
- Electronized Chemical Corporation
- General Electric Company
- High Voltage Engineering Corporation
- Laboratory of Vitamin Technology
- National Canners Association
- Phillips Petroleum Company
- Pillsbury Mills
- Swift and Company

Non-profit

- American Meat Institute Foundation
- Armour Research Corporation
- Food Research Institute
- Midwest Research Institute
- Southern Research Institute
- Southwest Research Institute
- Stanford Research Institute
- Wisconsin Alumni Research Foundation

Using only one tenth of this dose the great majority of the microorganisms are killed. By using normal refrigeration the few survivors can be prevented from reproducing and spoiling the food. Such a process has been shown to extend the useful storage life for fresh and cured meats by a factor of five or more. This process may be equally applicable to other fresh foods.

Another application is the eradication of insects infesting grains, flour and other foods.[14] Radiation in the order of one to five per cent of the sterilizing dose can achieve these results. In the same range lies the destruction of trichina worms in pork.[6]

When approximately one per cent of the sterilizing dose is employed, other applications of radiation have been reported. One of the most interesting is the effect on the sprouting of potatoes and onions.[1, 15] The sprouting was inhibited up to as much as three times the normal storage. Preliminary evidence was also obtained[1] that the bitterness which develops in the juice of certain oranges upon standing is decreased with irradiation.

SOURCES OF RADIATION

Several methods are available and several others are being considered to furnish the beta and gamma radiations currently used.

Machines capable of accelerating electrons (beta radiation) from 1 to 10 million electron volts are available. Four types are being involved in the food radiation program. These are:

(*a*) General Electric Company's resonant transformer.[10] This is a modification of the conventional X-ray therapy machine. The metal target is eliminated. In its stead is placed a metal window, permitting a direct passage of electrons.

(*b*) High Voltage Engineering Corporation's Van de Graaff Accelerator.[5] Instead of the pulsed characteristics of the resonant transformer, this is a continuous discharge machine.

(*c*) Electronized Chemical Corporation's Capacitron.[9] This is characterized by an extremely high intensity burst in the order of micro-seconds.

(*d*) Applied Radiation Corporation's Linear Accelerator. This is an indirect type of accelerator, which does not require a source of high speed electrons to begin with.

The direct electron generators available at the present time range from one to three Mev with power output in the order of 0.5 to 12 kw. This is sufficient for sterilizing 50 to 3000 pounds of food per hour. They are very satisfactory for research purposes. In order to scale up to production levels, however, the power output will have to be in the order of 40 to 60 kw.

Gamma radiations can also be produced by accelerators. But the method is inefficient. Decaying atoms or radioisotopes provide a richer source for the purpose. There are several,[4, 8] the principal ones being:

(*a*) Spent fuel assemblies from a reactor emit both gammas and betas. Sources of these assemblies providing as high as 4×10^7 rep/hr are being used. The decay curve is rather steep during the first 20 days, however.

(*b*) Fission products from radioactive wastes from reactors comprise a source of gammas. The United States Atomic Energy Commission has planned for the construction of a separation plant to obtain the cesium-137 isotope, a gamma emitter with a 33-year half-life. The plant should be in operation in September 1956, producing about 200,000 curies of cesium per year.

(*c*) Specially produced isotopes such as radioactive cobalt-60, emitting 1.17 and 1.33 Mev gammas with a half-life of 5.3 years, have been used in much of the earlier work on food radiation.

(*d*) Nuclear reactors show promise of being technically and economically feasible. There are several ways in which reactors may be used. An external fuel circuit may be installed in a homogeneous fluid fuel reactor. A second possibility involves the passage of materials, which may be activated by neutrons to produce gamma rays, through or near the reactor core and subsequently circulated to an outside radiation chamber. Finally, the short-lived gamma-emitting radioactive fission gases may be pumped from the reactor core.

At the present moment the American industry is improving the design of electron accelerators as a source of beta rays. The Atomic Energy Commission is jointly evaluating with the Quartermaster Corps the various reactor designs for gamma rays. Of particular interest is the question of possible coupling of a food-radiating with a power-producing facility.

CURRENT STATE OF THE ART

As far as wholesomeness of foods is concerned, there is no evidence from the many experiments conducted on animals to suggest toxicity from radiated foods. In matters pertaining to the health of man, we must always be conservative. The more extensively a food is to be used, such as would be the case if our optimism holds out in the radiation of foods, the less risk we should take. There is no reason for us to suspect any toxicity from the radiation of foods with beta rays below 10–15 Mev. So far, the toxicity tests in the United States have been a procession of negative results. However, we must continue to push this phase of the work to the point near certainty, so that all peoples throughout the world can subsist on radiated diets with absolute confidence. To date, a series of tests utilizing upwards of four thousand test animals for periods in excess of two years have shown no need for concern in eating foods processed in this new way. Controlled experiments using human subjects have been started in May.[8]

Before discussing the specific promise of different foods in the radiation process, it may be well to mention the destructive reactions that still occur in irradiated foods.

While microorganisms are destroyed by 2,000,000

reps, some enzymes require over 10,000,000. This means that in some foods other techniques must be coupled with the radiation process to inactivate the enzymes, which in themselves are capable of decomposing the food. Perhaps blanching in the cases of vegetables, short dielectric heat pulse for meats or enzyme inhibitors may accomplish the task. But these still need to be studied.

Irradiation induces biochemical changes in the foods themselves. This phenomenon is not unexpected, inasmuch as all means of food preservation induce changes of one sort or another. An example of this change is a decrease in vitamin content. There also appears to be a change in the plant cement, pectin, bringing about a limpness in certain radiated fresh fruits and vegetables. It is not clear whether this degradation of pectin is similar to that brought about by heat. Other chemical changes that may be induced in food by irradiation[2, 11, 12, 13] include: the production of amines and ammonia, oxidation of the double bonds in lipids, oxidation of alcohols to carbonyl groups, selective oxidation of terminal groups of hexoses, or of the alpha methylenic carbon atom. These changes can be decreased by irradiation in the frozen state, in the absence of oxygen or in the presence of anti-oxidants or free radical acceptors. Much work remains to be done on this score before definite statements can be made regarding their effectiveness.

As far as irradiated foods are concerned there is considerable variation in their susceptibility to the development of off-flavor, off-odor and texture breakdown. A summary is provided in Table II. In the first column are listed foods, which do not undergo significant changes in flavor, odor and texture during irradiation. Those in the second column undergo some change, although not too objectionable. The third column includes foods, which are unacceptable taste-wise or texture-wise. In this connection, there is much conflict in the results from different laboratories on the behavior of many foods. The table gives an average opinion.

As far as extension of refrigerated shelf life by means of lower dosages of radiation is concerned, Table III lists the items which show current promise.

Table II. Present Estimates of Promise for Storage of Perishables Without Refrigeration; Dose: 2,000,000 rep

Good	*Fair*	*Poor*
Bacon	Apple juice	Banana
Beans, green	Apple sauce	Beans, lima
Beef liver	Asparagus	Cantaloupe
Broccoli	Beef steak	Celery
Brussels sprouts	Bread	Cheese
Carrots	Cabbage	Lemon juice
Chicken	Cherries	Lettuce
Cod fish cakes	Corn	Milk
Pork	Frankfurters	Oranges
Pork sausage	Halibut	Orange juice
Waffles	Ham	Squash
	Hamburger	Strawberry
	Lamb chops	Syrup
	Peas	Tomato juice
	Spinach	

Table III. Extension of Refrigerated Shelf Life; Dose: 100,000–500,000 rep

Beef steak	Hamburger
Cabbage	Lamb
Cherries	Luncheon meat
Cole slaw	Peaches
Endive	Sausage
Fish	Salami
Frankfurters	Scallops
Ham	Tomatoes

In any new commercial process the ability to perfect a new process or a new product is, in itself, not enough to insure wide acceptance of success. After the technical process has been developed, the method must be shown to be feasible and competitive in the economic market. If we were to project today's technical knowledge into the future, it would appear that this process can become competitive in America. Estimates of the cost of irradiating food range from a fraction of a cent to seven cents per pound for total sterilization.

Treatment of food with lower doses would be reflected in lower costs per pound figures. There are not, however, enough hard facts available to give definite answers in this area. The type and dose of irradiation are still indefinite variables as are the most efficient means of providing these radiations. It is toward the end of securing these answers, as well as those in the area of food technology, that we are currently carrying on an economic feasibility study.

From an analysis of the findings to date it appears that the earliest applications of radiation to foods would be the deinfestation of insects and the inhibition of sprouting of potato. The extension of shelf life be baked products should find early adoption. The extension of the refrigerated shelf life of formulated foods, meats, fruits and vegetables should follow suit soon thereafter. So should the destruction of trichina in pork. Sterile formulated foods for storage without refrigeration appear the next in line. Finally there are the sterile meats and vegetables for storage without refrigeration. Of course, these are rankings of classes of items and there will be many individual exceptions.

SUMMARY

In summary, we in the United States are keenly aware of the importance of radiation of foods as a means of contributing to the improvement of the nutrition of peoples all over the world. There are many difficult problems to be solved before the process can be realized. But we are optimistic over the eventual success of the process.

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Feeding Studies in the Appraisal of the Wholesomeness of Radiation Sterilized Foods

By T. E. Huber and H. F. Kraybill,* USA

Within the past decade considerable interest has been shown in the possibility of sterilizing foods by use of irradiation, particularly with the beta (electron) and gamma types. Foods sterilized by radiation may be superior to foods sterilized by the conventional procedures of heat or freezing. Although significant improvement has been made in the quality of foods processed by heat and freezing there are recognized disadvantages. When such techniques are used, inferior texture, flavor and nutrient losses result when compared to fresh food products. Sterilization of foods by ionizing radiation accompanied by only a few degrees rise in the temperature of the food product, the so-called "cold sterilization method," may provide a processing technique superior to the food preserving procedures currently employed.

Initial investigations were concerned with the technology and the chemistry of ionizing radiation on biological materials. Feeding investigations have recently been undertaken in order to determine the nutritive properties or the wholesomeness of irradiated foods.

Rather extensive investigations have been undertaken on the changes in nutritive value of foods exposed to high energy radiation. Kung, Gaden, and King[1] working with milk products demonstrated that Vitamin A, tocopherols and ascorbic acid were sensitive to sterilizing doses of gamma radiation. Carotenoids and riboflavin were moderately sensitive at the radiation sterilization dose but the enzyme phosphatase, sensitive to heat treatment, was only slightly altered. These same investigators noted significant losses in other micronutrients in certain food products such as cream cheese and cheddar cheese which were irradiated at 80,000 roentgens per hour until sterilization was effected.

Vitamin destruction by ionizing radiation has been reported by several investigators. Proctor and coworkers[2] have shown that 74 per cent of ascorbic acid in aqueous solution was destroyed when irradiated at 75,000 roentgens. Essential fatty acids present in high concentrations have been reported by Polister and Mead[3] to have an accelerative effect on the autoxidation of essential metabolites.[4] Although Vitamin C is quite radiosensitive, niacin and riboflavin are more radioresistant. Other micronutrients such as methionine or cysteine exhibit some sparing action or act as inhibitors curtailing, to some extent, the destruction of vitamins. Thus, it is evident that the destruction of labile vitamins may occur in pure solution. However, the destruction of vitamins in a complex system such as a food product may not be apparent due to the presence of naturally occurring radioresistant compounds.

During irradiation some degradative changes may occur in the macronutrients. Fats are susceptible to oxidation, yielding peroxides and carbonyls; while proteins with sulfur-containing dipeptides may rupture, yielding mercaptans and hydrogen sulfide. These subtle and rather obscure changes detected in flavor and odor variation are extremely difficult to determine by chemical procedures and the extent of these degradative changes on nutritive quality remain to be properly assessed. There are indications that the biological value of some proteins may be decreased by irradiation sterilization of a protein mixture.

Studies initiated in 1948 by DaCosta, *et al.*[5] relating to the nutritional aspects of feeding irradiated rations to test animals showed that there was an impairment in the fertility of the male and an increased mortality in litters suggesting the destruction of Vitamin E (Table I). Subsequent investigations at Swift and Company Research Laboratories, Chicago, Illinois,[6] indicated no gross toxicity, but similar findings with regard to vitamin loss. Supplementation of the diet with alpha tocopherol appeared to correct the reproductive difficulties observed in these rat feeding experiments. Thus, these observations supported the hypothesis that the irradiation process is oxidative in nature and facilitates the destruction of anti-oxidants such as Vitamin E. It is equally well known that other forms of food processing currently in use also destroy vitamins.

From the experimental feeding data now available, it is evident that if radiation induced toxicity changes are present, they are of an obscure nature. Accordingly, in an appraisal of the wholesomeness of irradiated foods it is essential to test for radiation induced toxicity which might be rather obscure by appropriate feeding experiments and to determine also the effect of ionizing radiations on the nutritive value of the irradiated product. To test for substances that may result in induced toxicity from

* Washington, D. C. and Denver, Colorado.

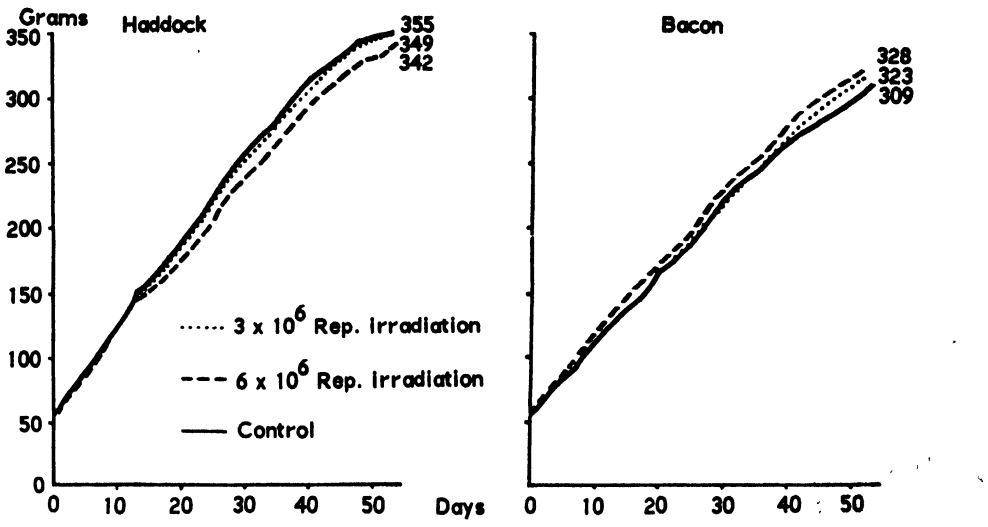

Figure 1. Growth rate of rats on diets containing irradiated foods

irradiation it is common practice to conduct short-term feeding trials for an eight-week period as well as long-term feeding experiments for two years or continued through four or more successive generations of the test animal. In feeding experiments, one attempts to obtain evidence of toxicity by feeding a large amount of irradiated food in the diet such as feeding a mixture of 65 per cent unirradiated basal ration containing all the known nutrients, plus 35 per cent by dry weight of the irradiated food to be tested. In the short-term experiments food consumption and rate of growth of the animals are the principal criteria utilized in comparing the results of feeding the irradiated diet with the non-irradiated diet. In addition, any gross abnormalities in the animals are investigated by histopathological examination of the tissues.

Long-term feeding trials with rats and other animal species are designed to obtain not only data on food consumption and growth but also information on reproduction, lactation, size of litters, viability of young and longevity. In addition, observations are made on the effect of feeding irradiated foods, injecting extracts of such foods into the animal or painting extracts of the food on the skin in order that the presence of radiation induced carcinogens might be detected.

A broad research program has been established at a number of universities and research institutions for studies relating to toxicity and nutritive value or wholesomeness of irradiated foods (Table II). It is apparent that the scope of these investigations is comprehensive enough to provide extensive data on the nutritional and physiological effects of irradiated foods on a broad spectrum of test species such as mouse, rat, chicken, duckling, dog, monkey and man. In any appraisal of the nutritive quality of irradiated foods it is desirable to determine the biological value of protein, the metabolizable energy of macronutrients, and the concentration of tissue enzymes in both the control and irradiated food groups. Such indices permit an objective evaluation to be made of the capability of a particular food to maintain normal metabolic processes in the test animal.

The literature pertaining to the destruction or loss of vitamins or macronutrients by conventional methods of processing is quite voluminous. Complete data is not yet available on the extent of nutrient loss occurring during the radiation sterilization of foods; however, there is no significant difference in the

Table I. Historical Development of Toxicity Studies of Irradiated Foods

Institution	*Year started*	*Types of irradiated food*
1. Medical Nutrition Lab.	March 1948	Laboratory basal ration
2. Swift & Company	September 1950	Raw ground beef
3. Columbia University	May 1952	Milk products
4. University of Michigan	March 1953	Canned ground beef
5. Various Universities	March 1954	50 representative foods

Table II

Contractor	*Areas of research (all feeding experiments)*
1. Alabama Polytechnic Institute	Vitamin studies and longevity (rats and chickens)
2. University of Illinois	Metabolizable energy—Biological value of protein
3. University of Colorado Medical Nutritional Laboratory	Subacute and chronic toxicity—Human feeding
4. Columbia University	Vitamin E and fatty acids
5. Oregon State College	Reproduction, growth, subacute and chronic toxicity
6. University of California	Fats and fatty acids
7. Texas A. & M. College	Longevity, reprod. (Rats & chickens)
8. Cornell University	Growth, reprod., lactation (dogs)
9. University of Michigan	Growth, reprod., egg prod. (chickens)
10. University of Rochester	Digestibility studies (dogs)
11. Wisconsin Alumni Research Foundation	Carcinogenicity (rats and mice) subacute toxicity
12. Armour Research Foundation	Subacute toxicity testing

Table III. Daily Food Consumption in Grams Dry Weight (Short-Term Feeding Experiments*)

	Irradiation Level		
Food	*3 × 10⁶ rep*	*6 × 10⁶ rep*	*Unirradiated control*
Haddock	12.8	12.1	12.3
Bacon	11.5	10.9	10.6
Peaches	15.3	15.6	16.7
Fresh ham	13.0	13.3	12.6

* Number of weanling rats; 10 per group; diet: 35% dry weight irradiated food; duration: 8 weeks.

growth of male weanling rats fed non-irradiated and irradiated foods for eight weeks (Fig. 1). No significant differences have been noted in the food consumption of these test animals for the same period of time (Table III).

Toxicity testing of a representative group of 50 irradiated foods using male weanling rats as the test animal is now in progress. There is no evidence to suggest any toxicity from the feeding experiments on twelve of the irradiated foods tested thus far. These negative findings have provided the basis for testing the twelve irradiated foods on human volunteers.

It is believed that these investigations on the technology and wholesomeness of irradiated foods will provide sufficient data to enable one to make an objective and intelligent evaluation of the feasibility of feeding foods sterilized by radiation.

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Industrial Utilization of Fission Products; Radiation-Sterilization of Foods

By Masanori Nakaidzumi,* Japan

Materials used for the study were kneaded sea products such as Kamaboko and Narutomaki and raw meat of tuna fish. These materials were put in a polyethylene sack from which air was taken out and which was closed very tightly. As the radiation sources; Co^{60} of 20 curies and 40 curies were used. Irradiation conditions were as follows: In the case of Narutomaki, we keep the distance between the radiation source (Co^{60}, 20 curies) and the material at 16 cm and irradiate it for 120 hours continuously at room temperature. In the case of Kamaboko, we keep the distance between the radiation source (Co^{60}, 40 curies) and the material at 1–3 cm and irradiate it for 1–40 hours. For tuna meat the same conditions as in the case of Kamaboko were used.

Results of the experiment are as follows:

Narutomaki: After the irradiation, cultured for seven days at 37°C and then kept for 12 days at room temperature, was not spoiled but in a fresh condition.

Kamaboko: After one hour irradiation, bacteria decreased to 1/10 of the pre-irradiation level. In case of four hours' irradiation, bacteria either completely died or very few of them survived. In the case of irradiation of eight hours or over, no bacteria were found.

Raw meat of tuna fish: The same results were obtained as in the case of Kamaboko.

In conclusion, it may be said that (*a*) for the prevention of putrefaction of kneaded sea product or foodstuff like raw fish, a minimum of 400,000–500,000 r is necessary, (*b*) continuous irradiation for the shortest period possible can produce the desired result of sterilization. It has also become clear by the sensitivity test that as a result of short distance irradiation Kamaboko and raw fish meat like tuna fish bore radiation odor and the clear reddish color of tuna fish became rather brown.

* Professor of Radiology Dept., Medical Faculty of Tokyo University.

Studies on the Properties of an Electrolytic Cell Consisting of an Electrode System in a Chloroform-Alcohol Solution under γ-Irradiation

By C. G. Österlundh and E. Haeffner,* Sweden

With the aim of studying the effects of radiation on mixtures of chloroform and alcohol, the electrical conductivity of such solutions was measured before and after irradiation with γ-rays. As the radiation effect was found to be appreciable, a chloroform-alcohol solution was then used as electrolyte in a cell which produces an electric current on irradiation. It produces also a current after the end of the irradiation, i.e., the energy absorbed during the irradiation can be recovered as electrical energy and can be measured.

INCREASE OF CONDUCTIVITY IN CHLOROFORM ALCOHOL MIXTURES

The formation of hydrogen halides during the irradiation of hydrocarbon halides dissolved in water, alcohol and acetone has been studied by Minder *et al.*[1-6] The acid formed was determined by extracting with water and measuring the conductivity of the water solution. It was found that the amount of hydrogen halide is proportional to the irradiation dose at all concentrations.

In this investigation mixtures of chloroform and ethyl alcohol were irradiated and the change of the conductivity of the solution itself was measured. Mixtures containing 50–100 per cent by weight of chloroform and doses up to 1000 r were used. The conductivity was measured 15 minutes and 48 hours after the end of the irradiation. The stability of solutions which have not been irradiated was also studied.

Experimental

Chloroform (p.a. Riedel-de Haen, Hanover) and ethyl alcohol (99.5%, Vin- & Spritcentralen, Stockholm) were mixed to the desired composition and 15 ml samples were pipetted into black-painted pyrex tubes with ground stoppers.

The conductivity of the solution was measured at 15°C with a special sond which was connected to a conductivity meter (Brüel & Kjaer, Copenhagen, Type 5402). The sond, which is shown in Fig. 1, was calibrated with 0.1 M potassium chloride solution.

The irradiations were made with γ-rays from a 0.36 c Co^{60} source placed at a distance of 3 cm from the samples. A dosage rate of 5.4± 1 r/min was determined by measuring the rate of oxidation of a 1.5×10^{-4} M ferrous sulphate solution in 0.4 M sulphuric acid. The ferric iron concentration was determined by adding 2 ml 1.5 M potassium thiocyanate solution to a 10 ml sample, extracting the

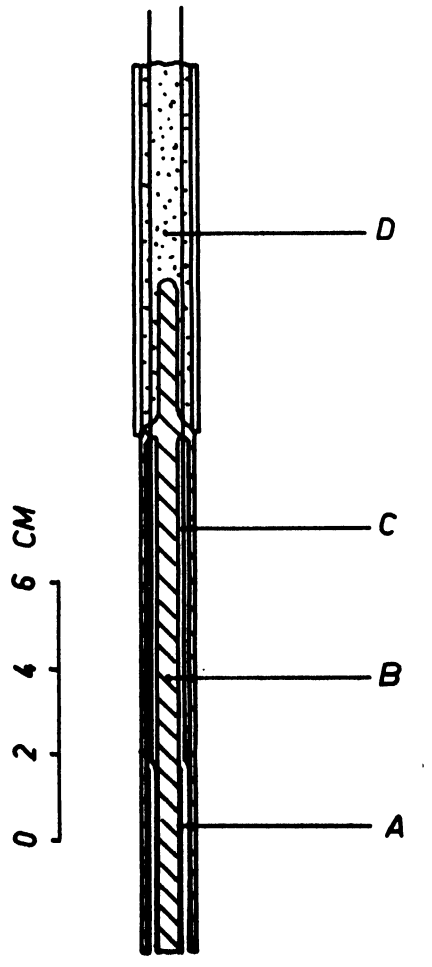

Figure 1. The conductivity sond designed for dipping into the sample containers. The electrodes consist of two platinum tubes 2 mm apart. All surfaces in contact with the liquid are of glass except the two platinum ones facing each other. (A) platinum electrodes; (B) glass tube and rod; (C) glassed platinum wire; and (D) polythene holder

* Aktiebolaget Atomenergi, Department of Physics, Stockholm, Sweden.

thiocyanate complex with 1.5 ml of a 1:1 mixture of ethyl ether and amyl alcohol and measuring the extinction of the organic phase with a Fisher electrophotometer. The G-value of the oxidation of Fe^{2+} to Fe^{3+} was assumed to be 15.6.[7]

Every value in the diagrams is the mean of three measurements carried out in the same manner.

Results

The increase of the conductivity with the irradiation dose is shown in Fig. 2. As can be seen from curve 4 there is a small increase after the irradiation which must depend on a slow secondary reaction. Experiments indicate that this reaction decreases if the chloroform concentration increases.

The dependence of the conductivity on the composition of the solution is shown in Fig. 3. There is a maximum increase at about 70 per cent chloroform. This maximum is still more pronounced if the ratio between the conductivity after and before the irradiation is considered.

Stability measurements were carried out with 50 per cent solutions. For samples stored at 40°C, the conductivity doubled in 2–3 weeks, but at 15°C no increase was observed in 4 months.

THE ELECTROLYTIC CELL

It is shown that a cell with electrodes of graphite and lead and with a chloroform alcohol electrolyte yields an electric current on irradiation.

Experimental

The cell is shown in Fig. 4. The lead electrode was covered by a thin oxide layer at the start of the experiment. The cell contained 180 ml electrolyte consisting of 70 per cent chloroform (p.a. Merck, Darmstadt) and 30 per cent ethyl alcohol. The temperature was kept constant at 15°C. Daylight was almost completely shut out by the surrounding radiation shield.

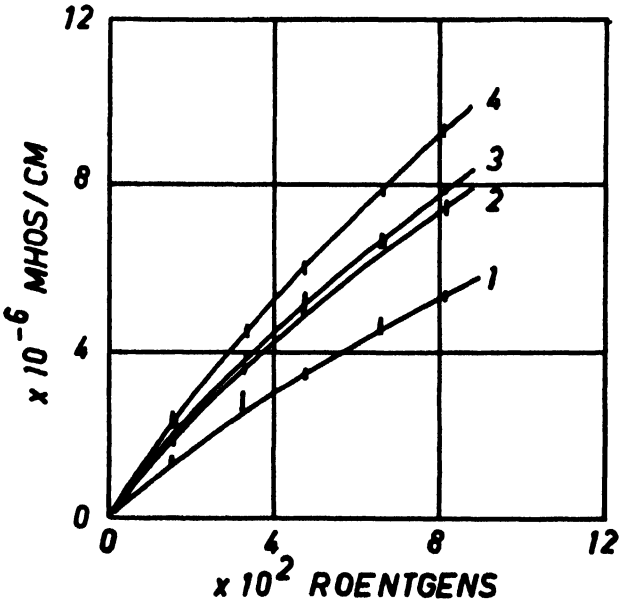

Figure 2. The increase of conductivity of chloroform alcohol solutions with irradiation. Curves 1, 2 and 3; 80, 60 and 70 per cent chloroform solutions measured 15 min after the irradiation; curve 4, 70 per cent solutions measured after 48 hours

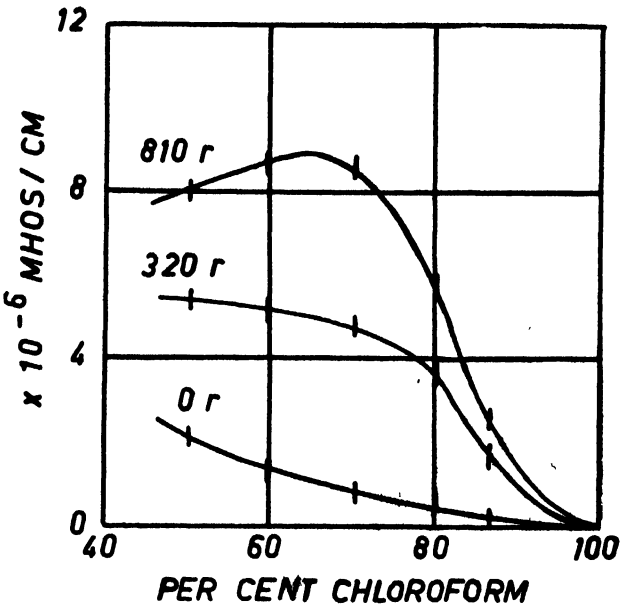

Figure 3. The conductivity of irradiated chloroform alcohol solutions

The irradiations were made with a 0.40 c Co^{60} source which was inserted in a well defined position in the middle tube. The dosage rate was determined by the ferrous sulphate method and was found to be 9.6 ± 1 r/min.

The strength of the current from the cell and the electromotive force were measured with an accuracy of 1 per cent.

Measurements and Results

Without irradiation, the electromotive force of the cell was 0.47 volts at 15°C. The graphite formed the positive pole.

When the cell was short-circuited through an ammeter of negligible resistance, a small current was observed which reached a constant value of 1.3 μa after a few days. The γ-source was now inserted and the current strength was found to increase rapidly to a limited value as shown in Fig. 5. When the source was removed, the current slowly assumed the initial value. The source was inserted again and the current became stable at 10.4 μa.

Resistances of different magnitudes were now inserted in the external circuit and the current was recorded. In Fig. 6 the current is plotted versus the voltage between the electrodes. The voltage on open circuit, i.e., the emf of the cell under irradiation, is 0.97 volts. The internal resistance of the cell was calculated to be 1.0×10^5 ohms by using the formula $E = I\,(R_i + R_e)$ where E is the emf, I the current, R_i the internal resistance and R_e the external resistance. This was verified by the fact that the maximum power of 2.5×10^{-6} watts was obtained in the external resistance when this was about 1.4×10^5 ohms.

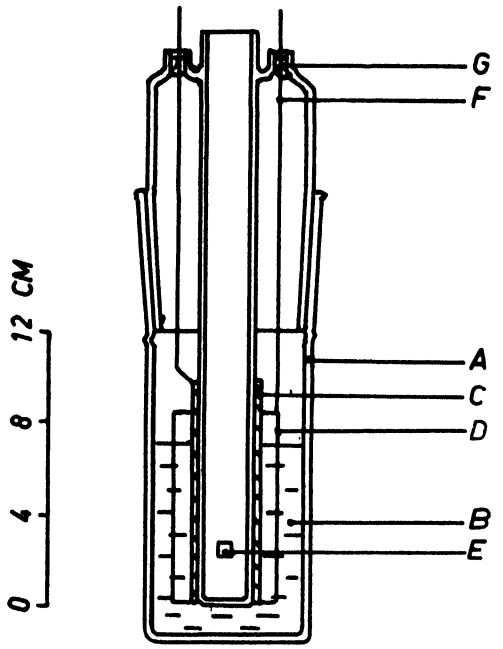

Figure 4. The electrolytic cell. The cell consists of a Pyrex vessel (A) which holds the electrolyte (B). A graphite electrode (C) is fastened to the middle glass tube and surrounded by a perforated lead electrode (D). (E) γ-source; (F) copper wire; and (G) polythene plug

When the cell was short-circuited again 70 days after the start of the experiment, a constant current of 13 μa was obtained. This was probably due to changes of the composition of the lead electrode which became covered by a white layer of lead chloride. The decrease of the current before the stable value is reached in Fig. 5 may also be connected with such chemical changes of the electrode surface.

THE ACCUMULATING EFFECT

An electric current is also obtained after the end of the irradiation. The dependence of the current strength on the design of the cell and on the circumstances for irradiation and discharge has been studied.

Experimental

The cells were contained in small Pyrex tubes with electrodes dipping into the organic solution. A few different types were used containing 12–17 ml liquid. A cell for 17 ml which could be sealed off under vacuum is shown in Fig. 7.

A mixture with 70 per cent chloroform was used

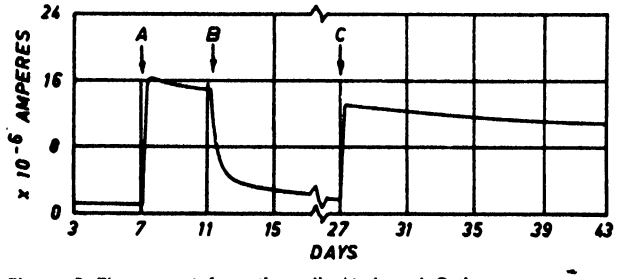

Figure 5. The current from the cell. At A and C the γ-source was inserted and at B it was removed

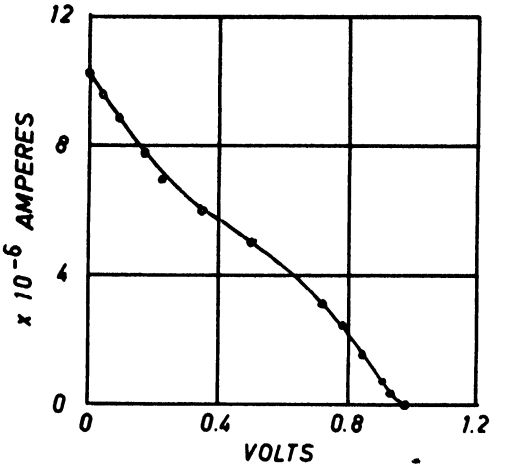

Figure 6. The relation between the current and the voltage between the electrodes

in all experiments when not otherwise stated here.

To irradiate the cells they were placed at 4 cm from a 4 c Co^{60} source which gave a dosage rate in the cells of 45 ± 5 r/min. The temperature was 20°C.

After the irradiation, the cells were put into a thermostat at 15°C and connected with the measuring device for the determination of the emf and were then short-circuited through the ammeter for current measurement.

As daylight seems to have a slight effect, the irradiations and measurements were carried out in a manner which excluded most of the daylight.

Measurements and Results

Two series of experiments were made with varying dosage. The electrodes consisted of graphite and lead. In one series, the liquid volume was 17 ml and the current measurements started 20 min after the end of the irradiation, and in the other series the corresponding figures were 12 ml and 15 min.

The emf of the cells before irradiation is 0.46 ± 0.04 volts. When a cell is irradiated, the emf increases to a value which depends on the irradiation dose in the way shown in Fig. 8. The limiting value of the emf for the two series is 1.12 volts and 1.07 volts respectively.

The current received from the cells decreases rapidly at the beginning of the discharge. A few results are quoted in Table I.

The relation between the current strength two

Table I. The Discharge of 12-ml Cells through an Ammeter of Negligible Resistance

Dose × 10^3 r	Current strength: 2 min after shortcircuit, × 10^{-6} amp	Current strength: 24 hours after shortcircuit, × 10^{-6} amp
0	2	0.9
28	25	1.1
51	36	1.6
186	66	3.3
320	83	6.8

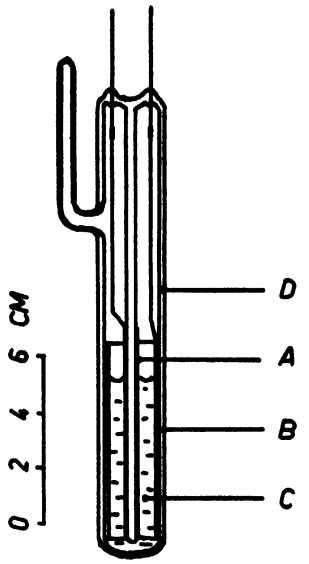

Figure 7. The 17 ml electrolytic cell: (A) lead electrode; (B) graphite electrode; (C) electrolyte; and (D) Pyrex tube

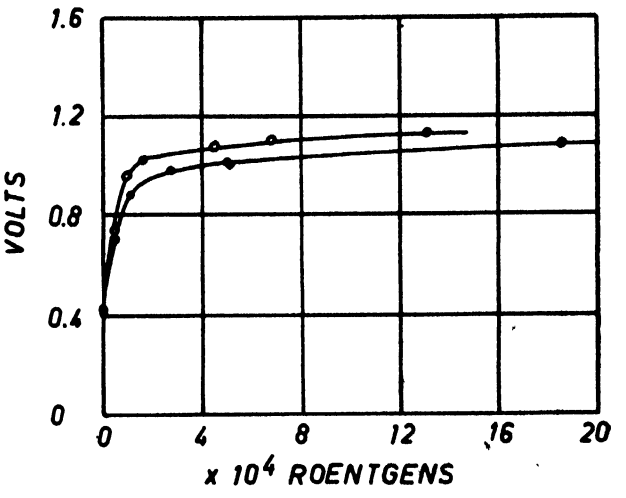

Figure 8. The emf as a function of the irradiation dose: circles, 17 ml cells; points, 12 ml cells

minutes after the cells have been short-circuited and the irradiation dose is shown in Fig. 9. The equations of the two lines are: $i = 16\ d^{0.49}$ and $i = 23d^{0.56}$, where i stands for the current in μa and d for the dose in units of 10^4 r. The current obtained from cells which have not been irradiated varies between 2 and 4 μa.

By integrating the discharge curves it is easily seen that the charge obtained from the cells also increases with the irradiation dose.

In another series of experiments the time between the irradiation and the discharge was varied. For 1 hour the emf and the current do not change from the values measured after 5 min, but after 24 hours the emf has decreased by 13 per cent and the current by 37 per cent.

The electrode materials have a fundamental influence on the properties of the cell. Graphite and platinum function well as positive electrodes and lead, silver and copper as negative ones. Platinum, gold and tantalum are not suitable as negative electrodes. Aluminium cannot be used as it reacts spontaneously with the electrolyte. The results are summarized in Table II.

To study the influence of the oxygen content in the solution, all oxygen was removed from the electrolyte by subliming the chloroform-alcohol mixture into the cell tubes in vacuum. This results in a current after irradiation five times as big as that in an air-saturated cell. The emf, on the other hand, is increased very little by the irradiation.

A few experiments were made with pure alcohol as electrolyte. In this case, also, a current is observed, but it is much smaller than in the presence of chloroform.

DISCUSSION

Under the influence of γ-radiation a number of decomposition products, e.g., hydrogen chloride, are formed in the solution. In a suitable cell, these products react with the electrodes so that an electric current is obtained through an external connection between the electrodes. A reaction between the electrodes and the decomposition products seems to be necessary for the cell to function. It is evident that the yield depends on two processes each incompletely known, i.e., on the initial radiation chemistry reaction and on the following electrochemical reaction.

If the electrode reaction in the cell at the passage of n faradays is represented by

$$\nu_1 A_1 + \nu_2 A_2 + \ldots = \nu_1' A_1' + \nu_2' A_2' + \ldots$$

and if a_i is the activity of a substance A_1 which takes part in the reaction, the electromotive force E may be written

$$E = E_0 - \frac{RT}{nF}\left(\Sigma \nu_i' \ln a_i' - \Sigma \nu_i \ln a_i\right)$$

Some of the substances taking part in the reac-

Table II. The Effect of Different Electrode Materials; the Liquid Volume Was 12 ml and the Discharge Started 15 Minutes after the Irradiation

Exp. no.	Electrodes pos.	Electrodes neg.	Dose, $\times 10^3$ r	Before irrad., volts	After irrad., volts	Current 2 min after shortc., $\times 10^{-6}$ amp	Current 24 hrs after shortc., $\times 10^{-6}$ amp
23	C	Pb	51	0.41	1.00	36	1.6
31	C	Ag	51	0.02	0.59	36	1.5
35	C	Cu	51	0 22	0.41	19	1.4
30	C	Pt	51	0.11	0.07	0.2	—
32	C	Au	51	0.08	0.04	0.1	—
38	C	Ta	51	0.45	0.35	0.2	—
56	Pt	Pb	46	0.45	0.93	31	1.6

tion are formed by the irradiation and the activities of these substances are changed. This results in a change of the emf. The experiments show that the emf is increased with the irradiation dose and reaches a limit value.

The electrical energy generated in the cell originates partly from the radiation energy absorbed and partly from the energy evolved in the chemical reaction. It is, however, interesting to compare the radiation energy and the electrical energy evolved in the battery. The energy absorbed in 1 gram of water is 93 ergs/r. In the first cell the weight of the liquid was 211 grams and the dosage rate 9.6 r/min. With correction for the electron density the rate of energy absorption in the cell is calculated to be 2.9×10^{-4} watt. The greatest power received in the external resistance was 2.5×10^{-6} watt, which corresponds to 0.9 per cent of the absorbed radiation energy.

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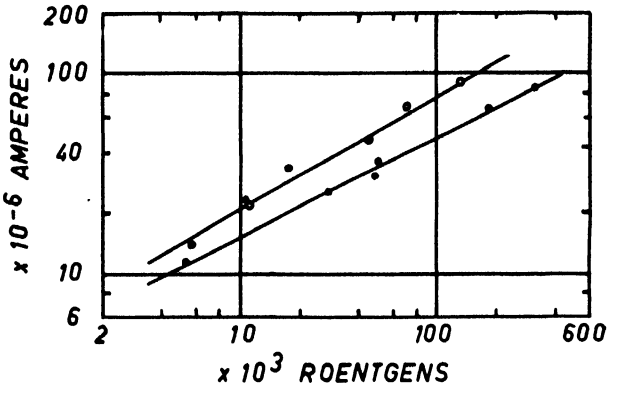

Figure 9. The current 2 min after shortcircuiting the cells: circles, 17 ml cells; points, 12 ml cells

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The Direct Conversion of Radiation into Electrical Energy

By E. G. Linder, P. Rappaport and J. J. Loferski,* USA

The direct conversion of nuclear radiation into electricity has recently attracted considerable attention, particularly during the past year with the increasing interest in peaceful uses of atomic energy. At the present time, judging from available publications and reports, about a dozen research organizations in the United States have active projects in this field. It appears that the immediate interest lies in the possible application of such a process to produce simple, compact and long-life power sources. However, as will be clear from later discussion, only very small amounts of power are feasible at the present time.

It is intended to present a general survey of the various methods of direct conversion, by which is meant a one-step process of converting the radiation (from radioactive isotopes in the present case) into electrical energy. Some of the more interesting and promising methods will be given specific attention, and the methods which have been studied especially at the Radio Corporation of America Laboratories will be described in greater detail. The future prospects of the various methods will be evaluated. In general, the aim will be to give an up-to-date picture of the direct conversion situation.

The grand total of power available from radioisotopes is limited by the supply of fission products produced mainly as by-products of nuclear reactors. It has been estimated that if all the present electrical power consumed in the United States were produced by nuclear reactors the annual output of radioactive waste would be sufficient for the production of power at the rate of 400,000,000 watts, which represents only a few hundredths of 1% of the energy consumed in the country.[1] This figure is further reduced because the radioactive energy could not be converted into electrical energy with more than a few per cent efficiency. In spite of these factors, the power which might be available is still a substantial amount especially when it is compared to the total power supplied in the US from the annual production of batteries which is approximately 2,000,000 watts. It is also estimated that by 1965 the US output of fission products should be 6.1×10^6 grams. This would correspond to 3×10^9 curies, which would have a heat power level of 6.1×10^6 watts at age of one year.[2] However only a small fraction of this would be convertible to electricity by direct processes. It is evident from these estimates that fission products cannot be considered as a possible principal source of power, in fact their availability in large quantities is contingent upon the use of reactors as the principal source of commercial electric power. They should be considered rather as a possible auxiliary source of considerable magnitude, with a possible maximum roughly equivalent to that produced by batteries at the present time.

TYPES OF RADIATION

The types of radiation which are being worked on may be classified into two categories: (1) charged radiation; and (2) uncharged radiation. Examples of charged radiation are: electrons or beta rays, alpha particles, ions, and fission particles. Examples of uncharged radiation are: X-rays, gamma rays, neutrons, and light also may be included if it is produced by some nuclear process.

The most important source of charged radiation at the present time is radioactive material, which is available in the form of fission products, as mentioned above.[3] The most suitable type is beta radiation. As examples, two of the better known beta-emitting materials, strontium-yttrium-90 and tritium, or hydrogen-3, may be cited. The former comprises about 5 per cent of the bulk radioactive material, the latter is produced in undisclosed quantity. The properties of these which are of interest to us, in relation to their use as sources of electrical energy, are shown in Table I.

Figure 1 shows the beta-ray spectrum of $Sr\text{-}Y^{90}$, after the radiation has passed through 0.0075 cm of aluminum, as measured by L. N. Russell.[4] There are two peaks: one for strontium-90 at about 0.3 Mev and one for its daughter product, yttrium-90 at about 0.8 Mev. Significant characteristics of this type of radiation are the high average energy of the particles or the quantum energy, and the spectrum extending from zero to a high upper limit.

No suitable fission product sources of other types of charged radiation are available at present, except perhaps polonium-210, which is an alpha emitter. However, alpha particles possess the disadvantage of causing serious radiation damage due to their comparatively large mass.

We turn now to the second category of radiation, namely the uncharged type. The most important source of this is the sun; however, radioactive material is becoming a source of increasing importance

* Radio Corporation of America, RCA Laboratories, Princeton, N.J., USA.

Table I. Electrical Properties of One Curie of Beta Emitter

Property	Sr^{90}–Y^{90}	H^3
Disintegration rate, dps	3.7×10^{10}	3.7×10^{10}
Current, amp	6×10^{-9}	6×10^{-9}
Avg. voltage, volts	5×10^{5}	6×10^{3}
Power, watts	3×10^{-3}	3.5×10^{-5}
Half-life, years	20	12.4
Weight, gm	5×10^{-3} (100% pure)	

although of a somewhat different radiation type within the same category. Radioactive materials may produce X-rays and gamma rays. By use of indirect processes or auxiliary materials, for example phosphors, light also may be produced.

The most available radioactive source in this class is the gamma emitter cobalt-60. Its quantum energy is 1.33 Mev and its half-life 5.3 years. This is too penetrating to be well-suited for power applications. A softer radiation and a longer life is desirable, but not available now in practical amounts and at suitable prices. Americium-241 may eventually be available, since it is of interest also for medical radiography.[5]

Uncharged nuclear radiation has not been investigated as extensively as the charged type in regard to direct conversion processes. This may be due to the fact that the latter, by virtue of its charge, is less far removed from energy in electrical form, and is compatible with a larger variety of conversion processes. Another influential factor is probably the lower specific ionization of the uncharged type. However, the conversion of uncharged radiation, in particular soft gamma rays, is worth further study. This view is supported by the promising results obtained in the conversion of solar light by semiconductor junction devices.

A further important consideration related to radiation types is the power available from a radiation source. This can be computed by considering the amount of radiation emitted from a surface (such as an electrode) coated with a layer of radioisotopes. The emitted radiation is limited by the self-absorption of the isotope layer. Increasing the thickness does not increase the radiation output indefinitely. Little increase is obtained for a layer exceeding about one beta or gamma range in thickness. Taking the Sr-Y^{90} mixture as an example, it has been computed that the maximum power available is approximately 0.4 watt/cm^2. This would correspond to a layer about 2.5 mm thick. For Co^{60} the available power is about 1000 times greater, because of the greater density, the shorter half-life and, most important, the smaller absorption coefficient. However, this would require a layer about 12 cm thick. The cost of a limiting layer of either Sr-Y^{90} or Co^{60} would be prohibitive at the present time.

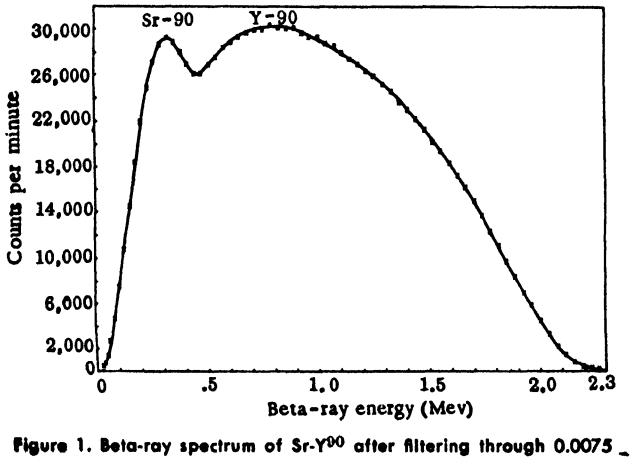

Figure 1. Beta-ray spectrum of Sr-Y^{90} after filtering through 0.0075 cm of aluminum

Another topic connected with type of radiation is that of shielding. With any converter it is important that the radiation level it produces in its vicinity does not exceed the tolerance value for health protection of personnel, or for radiation damage to any other organisms or materials. The shielding requirements, therefore, depend upon the nature of the radiation. For alpha or beta radiation the solution is not as difficult as with gamma rays. The former may be absorbed by a few millimeters thickness of almost any common solid. There is however some production of bremsstrahlung (about 1 per cent of the energy), and frequently some gamma radiation due to impurities, and additional shielding is necessary because of these. However, for low-energy radiation such as probably eventually will be used, the problem is not serious.

In the case of gamma radiation the difficulties are more serious because of the greater penetration. The absorption is exponential, and thus there is no maximum range as with beta particles. As an example, 2 Mev gamma radiation will be reduced in intensity by a factor of 10 for each 5 cm of lead shielding. Thus for intense sources the shielding required is prohibitive except possibly for large, stationary devices, which might eventually be developed. It is only the soft gamma rays that appear to be of possible practical interest now for example, below 0.1 Mev, a thickness of only 0.025 cm is required to yield a tenfold reduction in intensity.

METHODS OF CONVERSION

The processes of direct conversion may be classified into four categories:

(1) Direct charging methods. These are usable only with charged radiation and involve the simple collection of charged carriers by an electrode to create a voltage.

(2) Contact potential methods. These may utilize both types of radiation, and operate by using contact potential fields to separate charges and produce currents.

(3) Thermocouple methods. Either type of radiation is used to generate heat by simple absorption. The heat is used to activate thermojunctions.

(4) Semiconductor junction methods. Carriers are formed within the semiconductor by either type

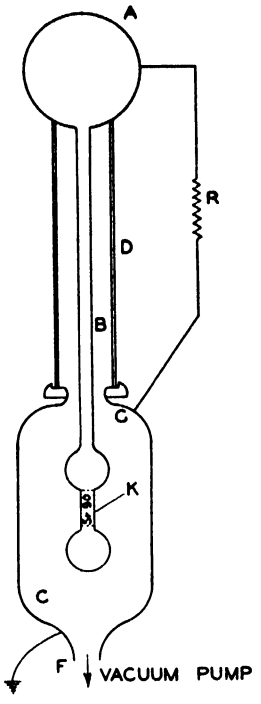

Figure 2. Schematic diagram of high-voltage direct-charging device

of radiation, and separated by the internal junction field.

This classification is not exclusive and other methods are possible but it does include most of the methods which have been explored up to the present time.

Some of the principles involved in the direct charging method go back to the early days of radioactivity. The Curies[6] appear to have been the first to have detected a voltage by a direct charging method. This work was done in 1900. However, the Curie device was not a power generator which supplied useful energy to a load circuit. Their interest was in studying properties of radioactive materials and radiation, and in particular in demonstrating that one of the components of radium radiation carried a negative charge. In 1903, R. J. Strutt[7] in England performed a direct charging experiment, in which he enclosed radium in a thin-walled glass container and was thus able to charge a gold leaf electroscope. In 1913, a more ambitious attempt was made in England by H. G. J. Moseley.[8] His apparatus was basically similar to Strutt's. Using 20 millicuries of radon he reported potentials near 150,000 volts. The voltage was limited by insulation breakdown. None of these workers, however, were interested in power generation nor were their devices suitable for that purpose.

The first RCA work in this field with which the authors were associated was started immediately after World War II, and was aimed specifically at power generation. This early research was done by Linder and Christian[9] and was published in several papers in 1947 and 1948. A sketch of the apparatus is shown in Fig. 2. The radioactive material which was Sr-Y^{90} was contained in electrode K. This was connected by a supporting shaft B to the high-voltage terminal A K was surrounded by a collector C. The high-voltage insulator D, separated and insulated the two terminals A and C. The collector C was evacuated so that negatively charged beta rays or electrons passed from K to C leaving a positive charge on K and charging C negatively. This type of device is essentially a self-charging condenser. Using one-fourth of a curie of radioactive material, a voltage of about 365,000 volts was generated. The power produced was 0.2 milliwatts at an efficiency of 20%.

This is a comparatively high efficiency, but unfortunately the characteristics of this particular device did not lie in a range practical for wide application. The available current was only about 10^{-9} amperes, and the impedance was about 10^{14} ohms. However, it is possible for the current to be increased and the impedance decreased by using larger amounts of radioactive material. The limitations on this are largely economic at the present time.

Figure 3 shows a second type of direct charging device. RCA work on this began about in 1950 and was first published in 1953. These papers were by P. Rappaport and E. G. Linder.[10] Recently further work on this method has been published by J. H. Coleman.[11] The device consists of three principle parts: a radioactive source S, a dielectric film F, and a metal collector P. A unidirectional flow of current takes place through F which is thin enough to pass beta particles but acts as an insulator for other forms of current. This is perhaps the simplest type of direct charging device but it is subject to the same limitations as the first type. It can produce several thousand volts but the current and the impedance depend upon the amount of radioactive material used, in fact all direct charging methods suffer this same limitation. They should become more feasible commercially as fission products become cheaper and more plentiful.

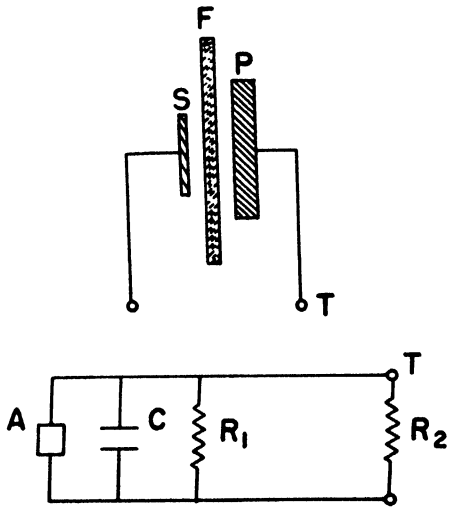

Figure 3. Dielectric type direct-charging device and equivalent circuit

The second conversion method to be discussed is the contact potential method. The principle involved here goes back to 1897, when Lord Kelvin,[12] only a year after the discovery of radioactivity by Becquerel, used the radiation from uranium to ionize the air between two plates of dissimilar metals and reported that he had observed a potential between them of up to 1.9 volts. However, there is no indication that he considered his device to be a power generator. He was interested in the properties of uranium and his paper was entitled "Experiments on the Electrical Properties of Uranium." More recently work in this field has been done by J. V. Kramer,[13] who published in 1924, and still more recently by P. F. Ohmart,[14] and also by A. Thomas and J. Petrocchi,[15] who are carrying on investigations of this method at the present time.

The basic principle is illustrated in Fig. 4. Here are shown two electrodes of dissimilar metals between which there is enclosed an atmosphere of gas, for example argon. Radiation of any type having sufficient energy to ionize the gas will produce carrier pairs. These will be acted upon by the field due to the contact potential difference of the metal surfaces, the positive ions flowing in one direction and the negative electrons in the opposite. This produces an electric current which may pass through an external load R, and thereby do useful work. This particular device has an especially low efficiency due mainly to the low absorption coefficient of gases for radioactive radiation, and the high ionization energy for gases (about 30 ev) as compared to semiconductors (about 1 ev) to be discussed later. However, the efficiency may be somewhat improved by using low-energy radiation or gas under pressure.

The third or thermocouple method converts radiant energy directly to heat and this in turn to electricity by means of the thermoelectric effect. If the absorption of the radiation is complete, and in practice it could be made nearly so, the efficiency of the method would be that of the thermojunction. Since the efficiency increases with junction temperature difference it will in general be low for low power inputs. A thermocouple device of this type using polonium-210 has been studied by K. C. Jordan and J. H. Birden.[16] With 57 and 146 curies the electrical power delivered to a load was respectively 0.1 and 0.2 per cent of the power developed as heat. The maximum power delivered was 1.8 and 9.4 milliwatts respectively. Using solar radiation efficiencies of about 1.0 per cent have been attained, and by using concentrating reflectors or lenses it is estimated that an efficiency of about 5 per cent would be possible.[17]

The thermocouple method is clearly a simple, rugged and long-life process. Furthermore, the application of modern solid state theory and experience towards the improvement of thermocouples would likely prove to be profitable. It appears that this method is worthy of further study.

The fourth or semiconductor method is one in which there has been much recent interest. The first work in this field was reported by P. Rappaport in 1954.[18] This method employs a p-n junction of materials such as silicon, or germanium. The device may be energized by radiation of either the charged or uncharged type. By a simple process utilizing the internal electric field of the junction the radiation energy is converted directly into electrical energy. When electromagnetic radiation is used the process is called the photovoltaic effect, and when electrons are used it is termed the electron voltaic effect.

The details of a typical device are shown schematically in Fig. 5. The junction, itself, may consist of, for example silicon, with p-type on the left and n-type on the right. A lead is connected to each of these regions by means of an ohmic contact. These leads in turn are connected to a load resistance R.

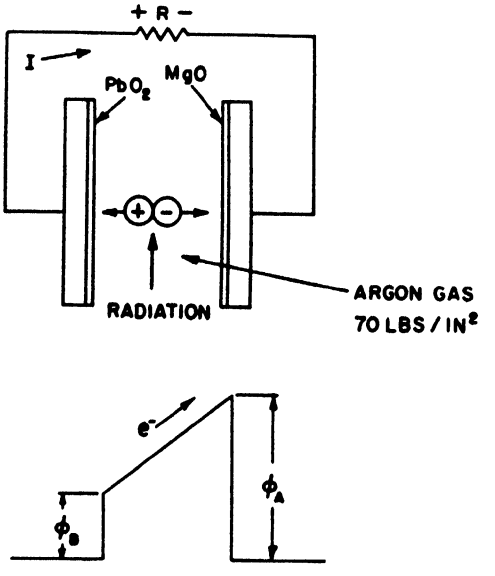

Figure 4. Contact potential device

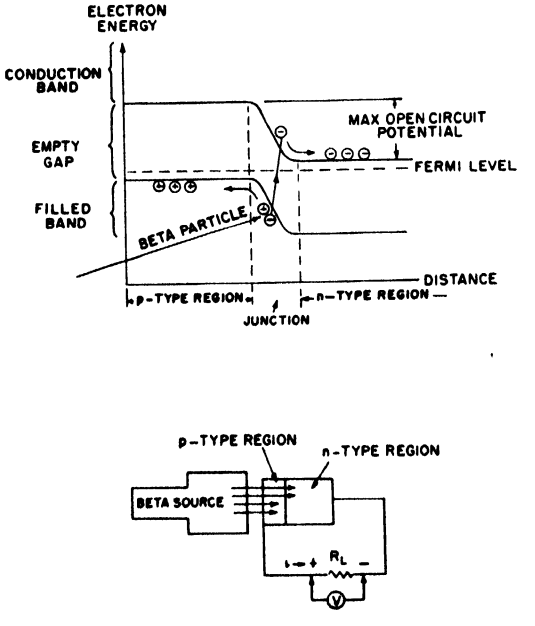

Figure 5. Energy level diagram for a p-n junction (above); schematic arrangement (below)

To the left of the junction is shown a source of any type of ionizing radiation.

At the top of the figure the internal conversion process is illustrated. Here are shown the energy levels in the p-region, and n-region, and in the intermediate region, in which the junction occurs. Each of these regions contains a filled band, a forbidden band or empty gap and a conduction band. As shown, there is an internal electric field in the region of the junction. Incident ionizing radiation creates free carrier pairs, the electrons being raised into the conduction band, and the holes remaining in the filled band. These carrier pairs diffuse to the junction region where they are acted upon by the electric field in the junction, so that the electrons move to the right and the positively charged holes to the left. Thus an electric current is created due to the motion of these charged particles. This current then may flow into an external circuit and do useful work.

Figure 6 shows an equivalent circuit for this type of device. The short circuit current I_s produced by the bombarding radiation is shown as generated by the current generator on the left. This current divides into two parts; the first of which I_j flows back through the junction as shown, and the second I flows through the load to do useful work.

The total current I_s produced by the absorbed radiation, that is, the saturation current, is given by

$$I_s = eGL \tag{1}$$

where e is the electronic charge, G is the rate of generation in carriers per second, and L is the diffusion length.

The expression for the current I_j which flows back through the junction is one well-known in rectifier theory,[19] and may be written

$$I_j = I_0(\epsilon^{\frac{Ve}{kT}} - 1) \tag{2}$$

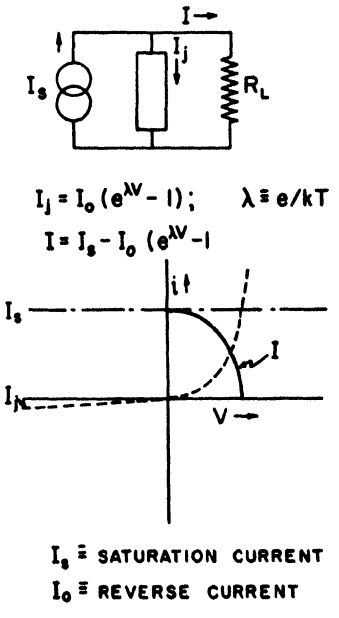

Figure 6. Equivalent circuit and current-voltage curve for semiconductor converter

The net current through the external load is therefore

$$I = I_s - I_j = eGL - I_0(\epsilon^{\frac{Ve}{kT}} - 1) \tag{3}$$

From these equations a formula for efficiency can be derived, and it can be reduced to the approximate expression:

$$\eta \approx \frac{kT}{e}\frac{m}{V_1} \ln \frac{I_s}{I_0} \tag{4}$$

where $m = I_s/I_1$, V_1 is the average incoming particle voltage, and I_1 is the bombarding current. The approximation is valid only for

$$\ln \frac{I_s}{I_0} \geq 10$$

The current-voltage characteristic as represented by these equations is shown at the bottom of Fig. 6. Since this is not a straight line as in an ohmic device it can be seen that the internal resistance of such a generator is a function of the current drawn from it. Experimental current-voltage curves are shown in Fig. 7. The output current is plotted horizontally and the voltage generated vertically. The different curves are for three different silicon units.

The geometry of such devices is important to the efficient use of the emitted radiation. This is true of course in the case of any device utilizing such radiation. Radiation from radioactive material is emitted in all directions. It cannot be reflected or refracted, and thus focussed, beamed or concentrated, by any known practical method. Hence, for the sake of efficiency, energy converting devices must be designed to intercept as nearly as possible through a solid angle of 4π steradians. Furthermore, in the case of the p-n junction type of device it is important that the radiation be as intense as possible since the efficiency increases with increasing radiation intensity. This may be seen from Equation 4, since I_s is proportional to radiation density. A practical type of design incorporating these features is shown in Fig. 8, where a layer of radioactive material is sandwiched between two p-n junctions as shown.

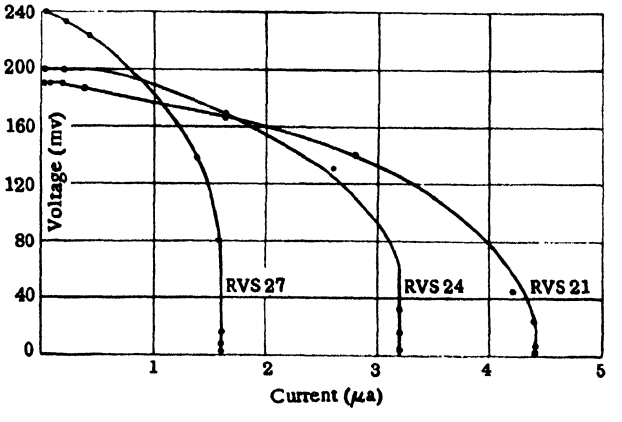

Figure 7. Experimental current-voltage curves for silicon p-n junction converters

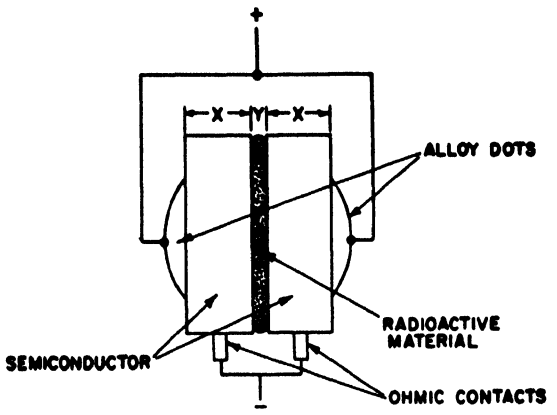

Figure 8. Double junction arrangement for the efficient use of radioactive emission

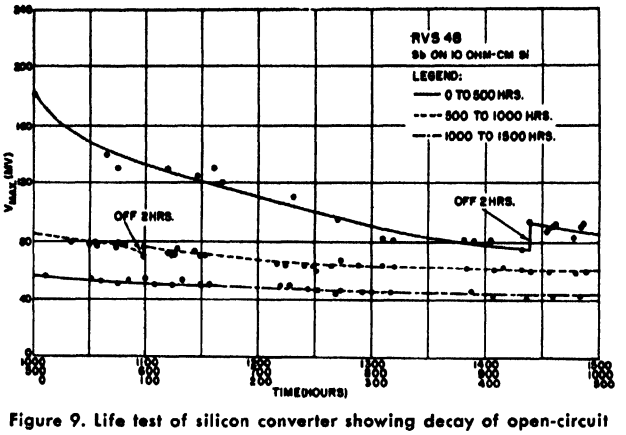

Figure 9. Life test of silicon converter showing decay of open-circuit voltage with operating time

A further geometrical requirement for good efficiency is that the diffusion length of the carriers in the semiconductor, the thickness of the semiconductor, and the depth of penetration of the radiation all be of the same magnitude. This insures that the radiation will be completely absorbed and that the maximum number of produced carriers will reach the junction. This requirement becomes impractical for high-energy uncharged radiation, and is one of the reasons why this method is best suited to charged types or soft electromagnetic radiation.

The semiconductor type of device has an important characteristic which enables it to overcome two disadvantages associated with the direct charging types of devices, namely small current and high internal impedance, as was pointed out previously. These disadvantages are overcome by high current multiplication in the semiconductor. In other words, each Sr-Y^{90} beta particle that penetrates silicon, for example, will produce on the average about 200,000 new electrons. This high electron multiplication increases the output current by a similar factor and reduces the internal impedance by the same factor. Because of these changes in current and impedance this type of device has characteristics which are in a practical range for the operation of electronic equipment, especially transistorized equipment. With practical amounts of radioactive material it is possible to design small power units, with sufficient current and a suitable impedance for operating equipment of this type.

On the other hand, this semiconductor type of converter is subject to a significant amount of semiconductor radiation damage, when it is used with radioactive material of certain types. If the incident radiation is sufficiently energetic it may damage the structure of the crystal by knocking atoms out of their equilibrium lattice positions, that is, by the production of Frenkel defects. This results in a deterioration of the device so that there is a decrease in efficiency and output. An example of this is shown in Fig. 9 which shows the results of a 1500-hour test of a unit using beta rays from strontium-yttrium-90. It is seen that the voltage drops rapidly at the beginning but more slowly later so that it is almost stabilized at the end of 1500 hours. However, during that interval, the output voltage has dropped from 180 millivolts to about 50.

Fortunately there appear to be remedies for this type of damage. As has been said the damage is a function of the particle or quantum energy of the radiation. The radiation from strontium-yttrium-90 which was used in the experiment described above has an average quantum energy of about 1 Mev. It has been found that if the quantum energy of the radiation is decreased, the damage decreases rapidly and a threshold energy can be found below which damage does not seem to exist. This effect is illustrated in Fig. 10. Here a function related to the probability of atomic displacement is plotted on the vertical scale vs quantum energy of the radiation on the horizontal scale. These results were obtained with

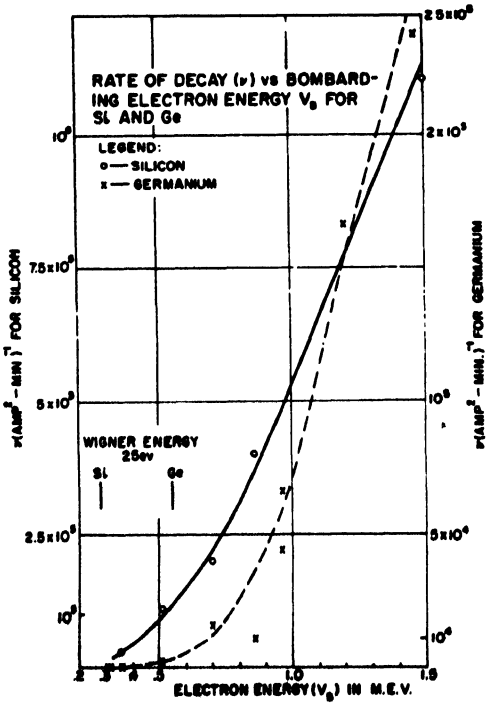

Figure 10. A function of the probability of atomic displacement vs bombarding electron energy for Si and Ge

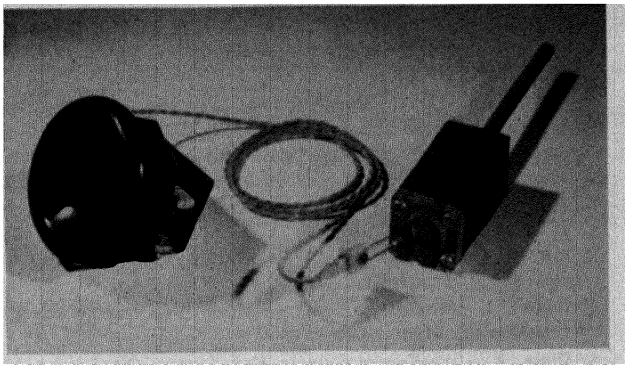

Figure 11. Experimental transistorized audio oscillator (left) powered by radioactive battery (right)

mono-energetic electron radiation from a Van de Graaff generator. It is seen that the probability drops very rapidly and in this case approaches zero at about 0.3 Mev for Si and 0.5 for Ge. These threshold data will be published in detail in the near future.[20] Thus the indications are that by using radioactive materials whose quantum energy of radiation does not exceed the threshold value, it should be possible to construct converters of this type whose life is not limited by radiation damage.

Experimental applications of these devices have included powering a 1000 cycle/sec oscillator shown in Figure 11. The oscillator used one transistor and was driven by a single silicon junction 0.5 cm in diameter in conjunction with 0.050 curies of Sr-Y^{90}. In another application a simple radio broadcast receiver, having a crystal diode detector and three transistor audio amplifier stages, which required 10 microwatts of power, was operated by eight silicon units of the type described above.

CONCLUSIONS AND PROSPECTS

In this final section the principal characteristics of the various methods will be discussed with a view towards evaluating them for practical uses present and future.

Turning first to the direct charging methods, it has been seen that this is restricted to the conversion of the charged type of radiation only. It can produce high voltages readily (several thousand volts and up), and is capable of the highest efficiency of all methods discussed. However, it possesses the disadvantages of low current and high internal impedance which can be overcome only by the use of large amounts of radioactive material. At the present time, the cost of such material is far too great to permit its use in practical devices in the amounts that would be required for this purpose. There seem to be a few special applications, particularly in the instrumentation field, (such as dosimeters and radiation meters) where the power requirements are in the sub-microwatt region. In these applications direct charging devices especially of the dielectric film type (see Fig. 3) may come into use in the immediate future. Except for such as these it does not seem likely that this type of device will be of great practical interest until radioactive material becomes cheaper by several orders of magnitude than it is at the present time.

The second method, namely the contact potential one, uses both types of radiation provided that the quantum energy exceeds that required to produce ion pairs in gases, which is about 30 ev in general. Devices of this type produce a fraction of a volt per cell, and about 10^{-9} to 10^{-10} amperes (in models currently being investigated). Hence the current and impedance are not in a very practical range. The cells appear to be quite sensitive to the surface condition of the electrodes. No data appear to have been published regarding possible radiation damage to these surfaces. The power conversion efficiency of this method is severely limited by the high energy cost per carrier pair produced. Possible present applications are the same as those mentioned for the direct charging method.

The third or thermocouple method, depends upon the development of heat and therefore is able to use all types of radiation. The devices are rugged, compact and of long life. Their only disadvantage appears to be their low power conversion efficiency. If further research could multiply this by a factor of ten or more, the thermocouple method would likely move into the practical realm.

The semiconductor method has attracted more attention than any of the others. It can be used to convert the energy of both types of radiation, including visible light, and is the basis of the so-called "atomic batteries" and "solar batteries." With silicon, which is the best material found thus far, outputs of about one-half a volt are obtainable. The current is about 10 microamperes for a 0.3 cm^2 unit when 50 millicuries of Sr-Y^{90} are used. The best observed efficiency is 3 per cent. However, the current should increase linearly and the efficiency logarithmically with power input according to Equations 1 and 4. For example, if 7.5 curies of 100% radioactive Sr-Y^{90} were used, the power input would be 0.1 watts/cm^2 and equivalent to that obtained from sunlight. The computed values are $I_s = 5$ milliamperes and $\eta = 6.6$ per cent. No experiments have been made with this high a level of radioactive input power, but the comparable experimental figures for solar energy are $I_s = 8$ milliamperes and $\eta = 5.95$ per cent.[21] It should be remembered however, that operation at this elevel using silicon and Sr-Y^{90} would result in a very high rate of radiation damage. It would be feasible only if this difficulty were circumvented.

Finally, in regard to all types of power sources using radioactive material, there are several problems yet to be solved before such devices can be considered practical. These are related to: (1) the high cost of radioactive material, (2) radiation shielding, (3) radiation damage, and (4) low efficiency.

In regard to the cost, the more abundant and cheaper beta materials include Sr-Y^{90} which is

$500.00 per curie, and H^3 which is $100.00 per curie. The most abundant and cheapest gamma material is Co^{60}, which costs $50.00 per curie. US Atomic Energy Commission facilities for the production of these materials are being enlarged, but vast reductions in cost will be necessary before practical applications will be possible for any power range greater than a few microwatts.

As pointed out above, the shielding requirements for $Sr\text{-}Y^{90}$ are such that small-sized sources are not possible if the external radiation is to be held below the tolerance level. Low-quantum energy radiation seems to be the logical answer.

The solution of the radiation damage problem seems to lie also in the use of low-quantum-energy radiation, so that the damage threshold is not exceeded. Unfortunately, there is not available at the present time an abundant, cheap, long-life material of this sort. In regard to the damage in the case of the semiconductor process, another solution would be the use of a semiconductor material of high atomic weight so that the threshold would be raised.

Although efficiencies of only a few per cent have been achieved thus far (except for the direct-charging, high-voltage device) higher efficiencies are theoretically obtainable by the use of larger quantities of radioactive material, as has been indicated above. And here again the problem of cost and availability arises.

Thus it appears that all the obstacles to a practical larger power source could be solved by the appearance of a radioactive material which was of low cost, had low quantum energy, and a suitable half-life. Among available isotopes nickel-63 meets all these requirements except that of cost. It emits 0.063 Mev beta radiation, and has a half-life of 85 years; however the present AEC price is $45.00 per millicurie. It is to be hoped that attention will be given to this and other materials in the same category.

Until this ideal radioactive material is available it appears that commercial radioactive power sources can be considered only for microwatt applications. These might include radiation meters, dosimeters, condenser chargers and leakage compensators, timing circuits, current and voltage reference sources, biasing units, simple transistorized equipment, etc. It is to be expected that the practical energy level for commercial applications will gradually rise as the atomic energy industry develops and radioactive material becomes more plentiful. What the ultimate possibilities are for commercial applications at higher power levels can be clarified only by future developments.

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Beta-Ray-Excited X-Ray Sources

By L. Reiffel and R. F. Humphreys,* USA

It has long been recognized that there is a lack of convenient radio-nuclides emitting gamma rays in the energy region below 400 kev. This situation has prompted a considerable search among known isotopes and has led to the use of materials such as thulium-170[1] and iron-55. As a possible alternative to finding isotopes with a suitable gamma-ray spectrum for operation in the classical X-ray region and with adequately long half-life, an investigation has been conducted in our laboratory over the past several years designed to assess the potentialities of beta-ray excited X-ray sources. Such sources are constructed using beta-ray emitters to bombard target nuclei in the same manner that electrons in an X-ray tube bombard the anode. The basic physics involved in beta-ray excited X-ray sources has long been well-known and thoroughly studied. It is of interest, however, to determine to what extent such sources yield useful radiation in practical applications. It is apparent at the outset that these sources cannot compete with electronic X-ray sources in any situation where very high intensity is required. Conversely, their zero power consumption, small size and portability, long-time stability, and economy might be of value in many applications.

Fortunately, there is a rather wide choice of beta-ray emitters suitable for use in providing low energy X-rays. In all there are perhaps ten pure beta emitters ranging from Sr^{90}-Y^{90} with a 2.2 Mev beta and an effective half-life of 20 years, down to substances such as P-32 with a 1.7 Mev beta and a 14-day half-life or Pm^{147} with a 0.22 Mev beta and a 2.7-year half-life. In addition to these pure beta emitters, it is possible to tolerate, under certain circumstances, an inherent gamma-ray component, provided the energy of the gamma rays is appropriate to the problem. This is the case, for example, with europium-155 which, in addition to beta rays, emits 80 and 90 kev gammas.

Two mechanisms are active in producing X-radiation when beta rays are allowed to interact with target nuclei. The first is the result of simple acceleration of charge during the beta absorption process and gives rise to bremsstrahlung radiation. The second mechanism involves radiation arising principally as a result of ionization in the K shell of target atoms with subsequent emission of characteristic or K radiation. K radiation may be excited directly in an interaction between a beta particle and a target atom or indirectly when bremsstrahlung radiation, formed elsewhere in the target material, is absorbed photoelectrically by a target atom.

For thin targets, the efficiency of bremsstrahlung production is proportional to the square of the atomic number and directly proportional to the beta-ray energy. A number of studies of the efficiency of the process for particular beta emitters has been reported in the literature. Goodrich, *et al.*[2] reported a quantum efficiency of five per cent for bremsstrahlung formation by P^{32} betas on brass. In this laboratory Sr^{90}-Y^{90} betas on lead have yielded efficiencies in excess of ten per cent considering only X-rays in excess of 30 kev. Studies on this point which are directly applicable to the design of beta-ray excited X-ray sources have been made by Linden and Starfelt.[3] One may conclude that the effectiveness of beta-ray excitation compares quite well with the branching ratio for emission of useful X-rays in materials such as thulium-170 (which has a branching ratio of eight per cent).

Various geometric configurations can be used by beta-ray excited X-ray sources. Liquids may be mixed with the beta emitter material or solid powders can be intermixed to achieve good excitation geometry, or a core of beta ray emitter can be surrounded by a casing of target nuclei. In some instances the source may be designed with a reflection target wherein the beta emitter is separated from the target surface, in almost direct analogy to an X-ray tube. A typical source using a transmission or casing target is shown in Fig. 1 and a typical reflection target configuration is shown in Fig. 2. The X-ray spectra obtainable from sources of various design have been examined using a sweep-type scintillation spectrometer and a thallium-activated sodium iodide phosphor. The observed pulse height spectrum is, of course, smeared by the finite resolution of the detector but serves as a qualitative indication of the spectral shapes obtainable. Figure 3 shows the spectrum obtained from strontium-90-yttrium-90 betas bombarding a lead target and illustrates the difference in the spectra obtained with transmission and reflection targets. The effect of the characteristic absorption edge of the target is particularly evident for the transmission target source.

* Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois.

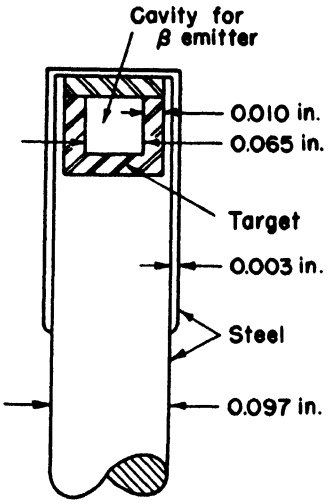

Figure 1. Typical transmission-target source

Since the intensity of the bremsstrahlung continuum decreases rapidly as the beta energy is decreased it is evident that low energy emitters should be used if relatively monochromatic X-rays are required. The ratio of the target K-line intensity to the continuum will increase appreciably with decreasing beta-ray energy; also the integrated intensity is markedly reduced at low beta-ray energies. Figure 4 illustrates the spectrum obtainable from a composite lead and barium target with strontium-90-yttrium-90 betas filtered through 0.2 cm of plastic. The spectrum is relatively free of continuum. Figure 5 illustrates the almost completely monoenergetic spectrum obtainable by using a source such as shown in Fig. 1 to excite fluorescent X-rays in an auxiliary target material. The actual intensity spectrum in Fig. 5 would exhibit very sharp spikes in the vicinity of 74 kev—the K_α and K_β lines of lead.

The wide variations possible in both energy spectra and half-life available from the several source designs may be used in a number of applications. Such

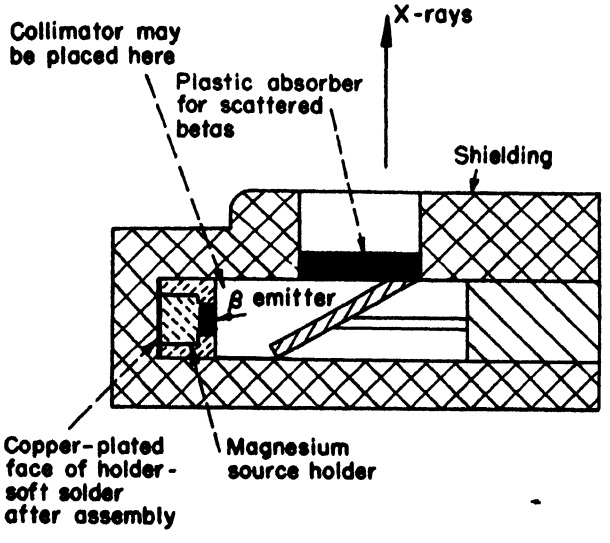

Figure 2. Reflection-target source

sources may be used in radiography[4] of thin sections or light materials. To establish the feasibility of radiography, a 10 mc strontium-90-yttrium-90 source using a lead target and type K film was employed to radiograph electronic components and an aluminum step wedge with 0.125 cm steps. A typical radiograph which results is shown in Fig. 6. From the performance of such model sources it appears feasible to obtain carrier-free activity such that one curie of strontium can be incorporated in a 1.5 mm focal spot. For emitters of shorter half-life, the specific activities could be correspondingly higher.

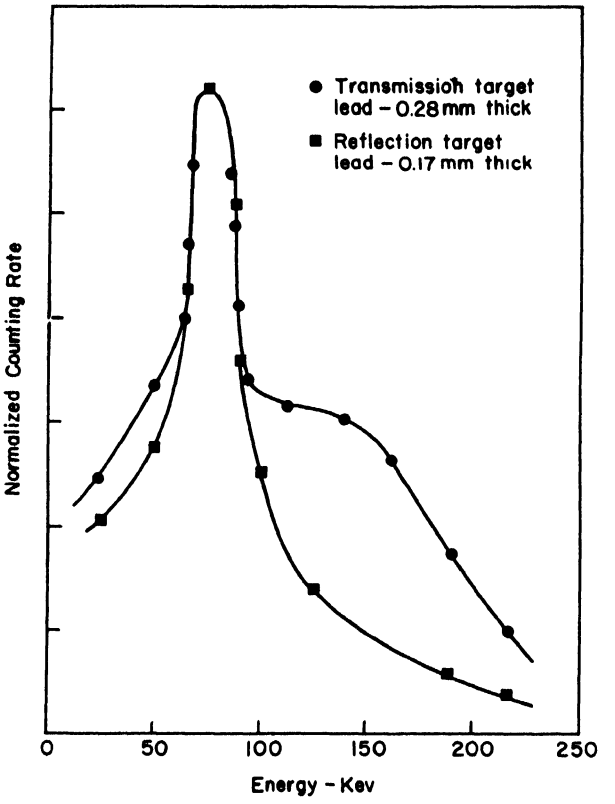

Figure 3. Beta-ray excited X-ray spectra: Sr^{90}-Y^{90} betas (0.2 cm plastic filter)

With a full-scale strontium-90 source now under construction radiographs of full density should be obtainable through 1 cm of aluminum with 4 minutes of exposure on type K film and a source-to-film distance of approximately one foot. Intensification screens in combination with faster films would reduce appreciably the required exposure, and it thus appears likely that such sources will be useful in industrial radiography. Their utility in this area will be greatly increased as new radiochemical separation plants come into operation which can isolate large quantities of beta-emitting fission-product material. The availability of such materials is probably essential before the sources can compete with alternative methods on an economic basis. It is likely that the sources alone will not be sufficiently intense for medical radiography, but it appears probable that image intensification systems using either electronic

or solid state devices will soon be available. Intensifiers operating in combination with such sources may well result in overall increase in portability of medical radiographic equipment. It is also possible that freedom to place the source of X-rays within the object to be radiographed will prove to be advantageous in medical as well as in technical applications. Although there has been no investigation made, it appears that the sources may be useful for therapeutic purposes because of the wide range of half-lives and spectra obtainable.

Either the continuous spectrum from a source emitting primarily bremsstrahlung or a line-spectrum of known properties may be used in thickness gauging and in density determinations. In its simplest form, a device for this purpose would consist of a suitable source and an appropriate detector with provision for inserting the sample to be measured between source and detector. Because of the high efficiency of many detectors in the low energy X-ray region, relatively small sources may be used with excellent results. A continuously balanced system used for density or thickness measurements is shown in block diagram form in Fig. 7. The use of a servo-driven absorption wedge to compensate for changes in thickness, or in density, results in an indication which is linear rather than exponential in these parameters. Furthermore, problems associated with detector stability are minimized, and the over-all accuracy of the indication is improved. Such a system has been used, for example, to determine the density of liquids flowing at high velocity to an accuracy of better than one per cent and with a response time of less than two seconds. Sr^{90}-Y^{90} beta sources with lead targets and europium-155 have been successfully used in this application. The primary advantage to the former occurs from the extremely good time stability of the source intensity.

The line spectra obtainable from beta-ray excited sources are admirably suited to absorptiometry, particularly for the control of coatings or additives as well as in chemical analysis. One specific application of this technique centers around the use of antimony characteristic radiation to probe the silver content of photographic emulsions and thereby control the thickness of the sensitive layer. This may be accomplished without appreciable fogging of the film because of the extreme sensitivity of the detectors used to determine the radiation level. Using such techniques, it appears that adequate control can be achieved while delivering a dose of less than 25 microroentgens to the film. The sampling area under such circumstances would be approximately 20 square centimeters. This application is illustrative of the possibility of setting the incoming radiation at the critical absorption edge of an element of interest and thus rendering the control system preferentially sensitive to variations in this element.

In certain simple chemical systems, the X-rays from such sources can be used in the manner of con-

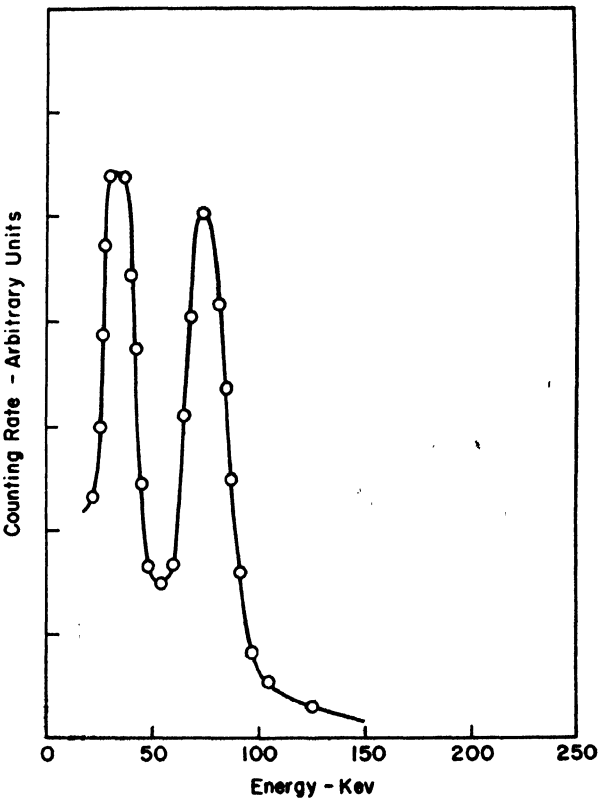

Figure 4. Spectrum from composite Ba-Pb target: reflection target source, Sr^{90}-Y^{90} betas

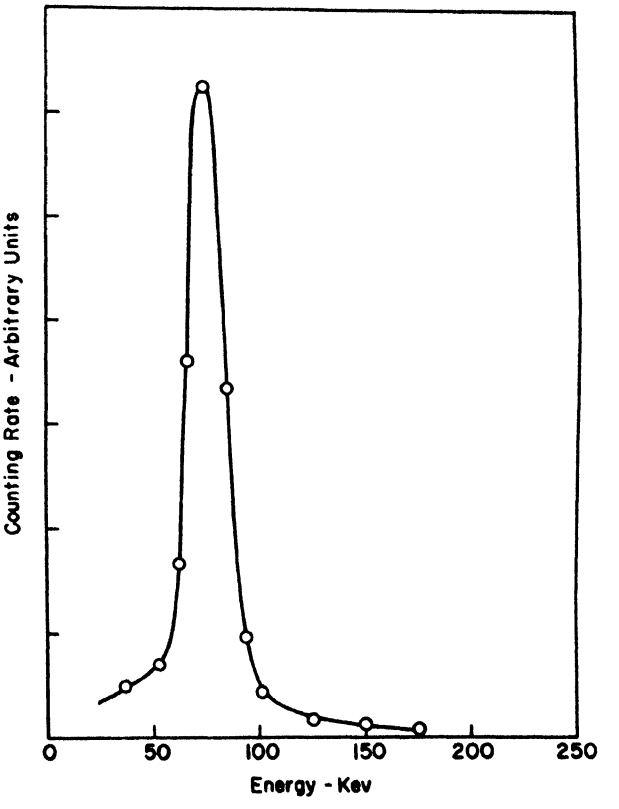

Figure 5. Lead fluorescence spectrum: excited by transmission target source, Sr^{90}-Y^{90} betas, uranium primary target

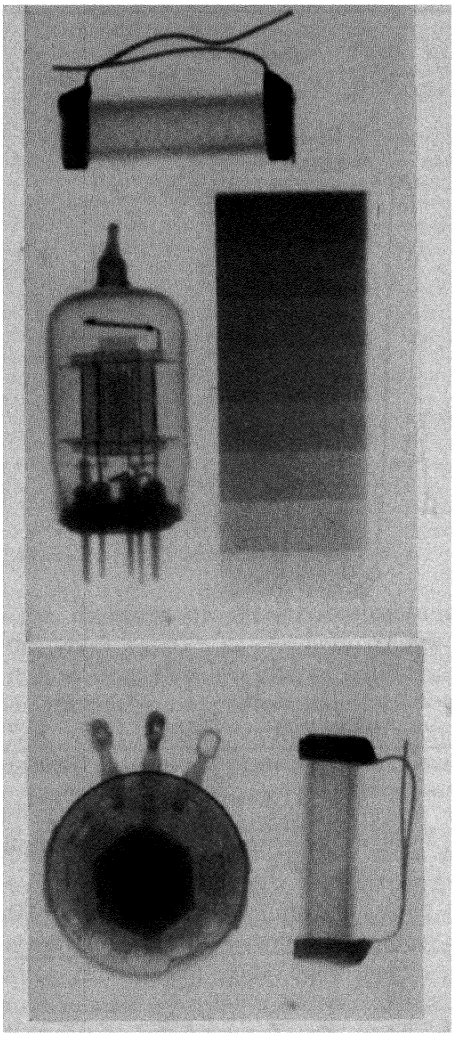

Figure 6. Typical radiographs taken with bremsstrahlung source: 10 mc, 11 inches, 34 hours

ventional fluorescence analysis. Here the low intensity of the sources may be at least partly compensated for by the use of large aperture detectors such as proportional counters or scintillation counters preceded by Ross filters. Such a method may be used to monitor the lead content of the atmosphere in an industrial plant by collecting filter paper air samples and searching for the presence of lead characteristic radiation when the sample is exposed to a suitable source.

In most of the applications examined, with the exception of radiography, the sources have employed

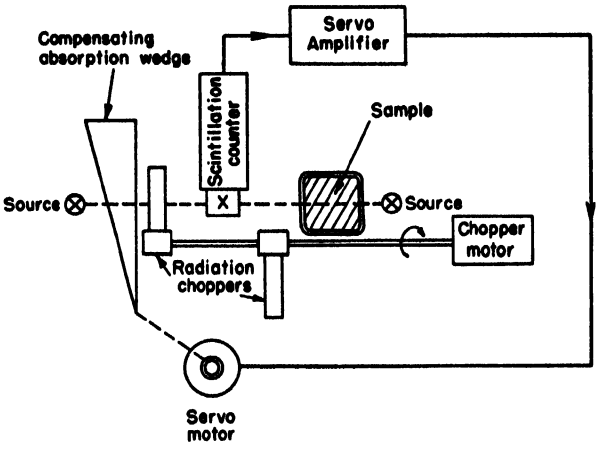

Figure 7. Thickness or density measurement system

millicurie amounts of beta emitter to achieve adequate counting rates in the detectors. Indeed, the practicality of beta-ray excited X-ray sources, which, in essence, rely on a secondary effect for their operation, depends primarily upon the existence of high efficiency detectors such as scintillation or proportional counters. The yield of X-rays per millicurie of beta emitter will of course vary with the details of the source but for purposes of qualitative design may be taken as one-tenth millicurie of X-rays per millicurie of energetic beta particles in a transmission target design. Sources with reflection targets would require reduction of this figure by about one order of magnitude. In spite of the relatively low yield obtainable, these sources appear to be practical solutions to a number of problems. In certain areas, notably in radiography, they are probably competitive with materials such as thulium-170 but may well be superceded by the development of newer radionuclides such as europium-155 and americum-241. On the other hand, beta-ray excited sources are extremely flexible in their properties and should retain a certain degree of utility for some time to come.

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Technology and Economics of High-Intensity Ionizing Radiations

By Michael Michaelis,* USA

Since shortly after the discovery of X-rays by Roentgen in 1895 and of radioactivity by Becquerel in 1896, scientists have attempted to utilize the bactericidal properties of ionizing radiations. However, it has only been in very recent years, with the development of atomic particle accelerators and nuclear reactors, that the practical possibilities have become intriguing. Potentially valuable means of preserving food, of sterilizing medical drugs and of producing chemicals and plastics now seem a real possibility.

These "nonpower" uses of atomic radiation are frequently overshadowed in popular interest by the possibilities of atomically-propelled ships and aircraft, and by the promise of plentiful electricity from nuclear fuels in a power-hungry world. However, the primary hunger of mankind as a whole, increasing in numbers at the rate of 200,000,000 every 10 years, is still for food. The greatest possible increase in food production will not for decades be enough to meet the minimum adequate diet for all the peoples of the world. It may well be, therefore, that among the potential benefits of atomic energy, radiation-preservation of food will rank high in its impact on world economy.

This paper is presented in an attempt to summarize the present status and expected trends of some of these promising applications of high-intensity ionizing radiations. The subject matter covered is confined to research and engineering projects in the United States of America and all technological, cost and market data are quoted in relation to this country only. Even so, the wealth of information is such that only general principles and a few examples can be discussed here. It is hoped, however, that they may serve as criteria for assessing potential benefits of ionizing radiations in different parts of the world. Wherever possible, both technology and economics of a particular process are treated in such a way as to show their interdependence and their respective influence on future trends. In many instances, numerical data is as yet only tentative, because of the early stage of certain lines of investigation. Nevertheless, such data is included provided it is sufficient to help in evaluating projected processes.

* Arthur D. Little, Inc., Cambridge, Mass. Including work by L. E. Brownell, University of Michigan; S. A. Goldblith, Massachusetts Institute of Technology; R. L. Loftness, North American Aviation, Inc.; B. Manowitz, Brookhaven National Laboratories; M. Michaelis, Arthur D. Little, Inc.

IONIZING RADIATIONS

Energy can take many forms, several of which are easily converted into one another and all of which can be used, at least in principle, to perform some kind of work. Radiant energy, or radiation, is the form in which energy can be transferred from one point to another through space.

Physical science has discovered many useful forms of work which radiation can perform. We are concerned here with its ionizing properties in interaction with matter, resulting in significant chemical or biological reactions. Primary absorption by matter of radiation, whether it be wave or corpuscular, results in liberation of electrons. The number released depends on the intensity of radiation and their velocity is a function of the energy level of the incident radiation. The liberated electrons lose their energy by exciting or ionizing molecules along their paths. These ionized molecules react with other molecules to produce the over-all reaction. These "secondary" effects are believed to account for the great majority of the chemical reactions with which we are concerned, whereas direct hits of the incident radiation quanta on sensitive areas of bacteria, molds or yeasts are the primary agents responsible for the sterilizing effects noted.

Table I shows sources and types of radiation which can promote chemical and biological reactions. The scope of the present survey is concerned only with effects of radiation on materials in bulk. We shall, therefore, be discussing mainly beta (electron) and gamma radiations, i.e., radiations of sufficient energy to penetrate matter and available at high enough intensities to produce significant effects. In so doing, let us recognize though that other forms of radiation, such as ultra-violet for instance or alpha, also have important chemical effects which have found many practical uses, e.g., in surface sterilization and gaseous electric discharges.

To a first approximation, the relative ionizing power as well as the relative biological effects may be considered as roughly equal for both beta and gamma radiations.

Nomenclature used in conjunction with ionizing radiations is frequently confusing to industry and our present purpose is best served by using units of measurement to which industry is accustomed. Such

Table I. Sources of Radiation for Promotion of Chemical and Biological Reactions

Source	*Radiation*
Radioactive elements	
Natural such as Ra, Th, Po	Alpha, beta and gamma
Artificial such as Co, Ta, Po	Mainly beta and gamma, some alpha
Uranium fission	Neutron, beta and gamma
Uranium fission products such as Cs, Sr, Xe	Beta and gamma
Electrical apparatus	
Incandescent or fluorescent solids and gases	Ultraviolet to infrared spectrum
Cathode rays	Electrons
Accelerators such as Van de Graaff, linear accelerators, resonant transformer, and capacitron	Electron, proton, deuteron, alpha
Targets of accelerators	X-ray or gamma

a unit is the watt, as a measure of power. The standardization of the power output from different radiation sources in terms of watts, would serve to remove the physicist's terms "rep" (roentgen equivalent physical which is the quantity of ionizing radiation causing an energy gain of 93 ergs per gram of tissue absorbing this radiation) and "curie" (equivalent to 3.7×10^{10} disintegrations per second of radioactive material), together with their associated ambiguities, from the language of industry. The following conversion data is, therefore, presented.

Figure 1 is a chart for converting to watts the number of curies of radioactive material emitting ionizing radiation of different energy levels, derived from the energy equivalence of 1 curie-Mev and 5.9×10^{-3} watts.

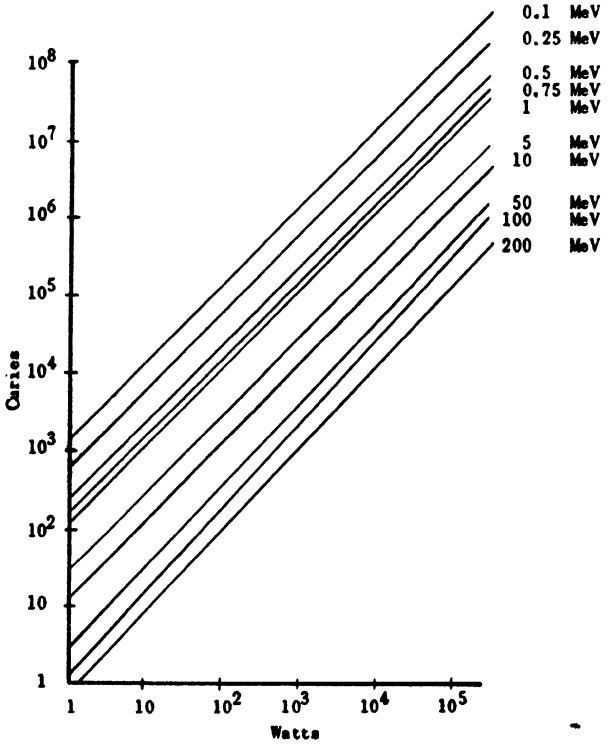


Figure 1. Conversion of "curies" to "watts"

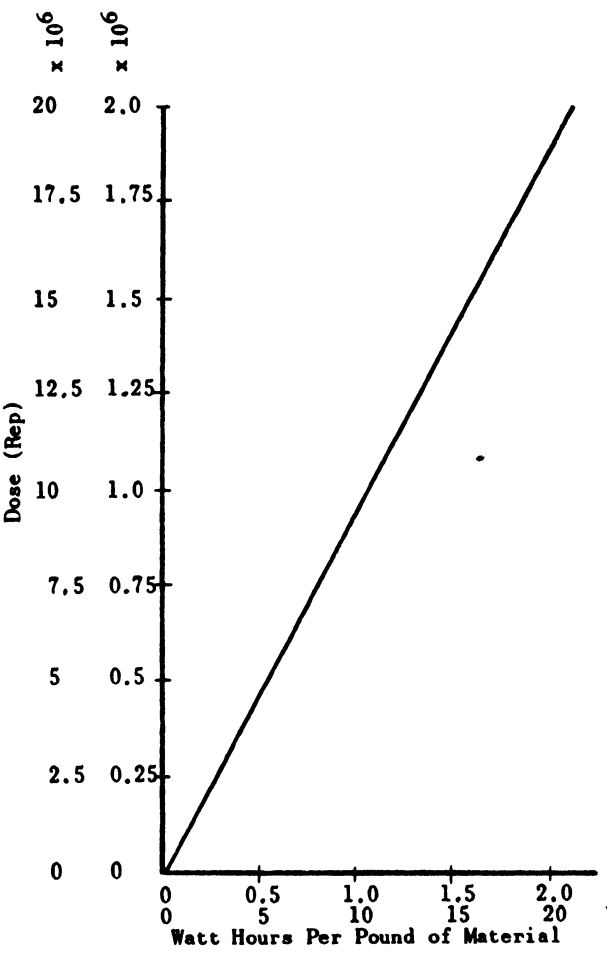


Figure 2. Conversion of "rep" to "watt-hours per pound" of material

To convert rep to watt-hours per pound, we note that one pound of material, in order to receive a dose of 2×10^6 rep must absorb 2.1 watt-hours of energy from the incident ionizing radiation. This conversion-rate is shown graphically in Fig. 2.

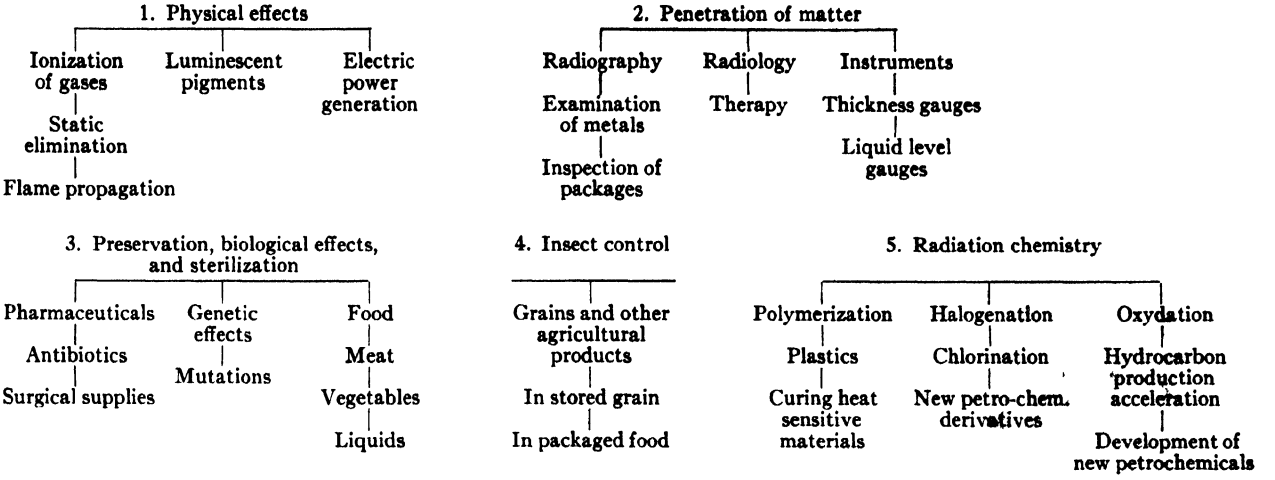
Finally, information on the radiation energy absorbed in matter, available from standard text books and expressed in terms of centimeters of water penetrated, (since most chemical and biological reactions occur in materials of nearly unit density) together with a utilization factor (denoting radiation absorbed by material as a percentage of radiation emitted by source) presents to the industrial engineer, in his own terminology, the processing potential of various sources and associated irradiation geometry.

Figures 1 and 2, together with radiation data for typical uses discussed in the next section and the energy potentials and utilization factors of alternative radiation sources presented later, may thus be used as a convenient means to analyze experimental radiation data available, in order to choose the optimum arrangements for new applications.

USES OF HIGH INTENSITY IONIZING RADIATION

A selected list of potential uses is shown in Table II, assembled into major groups. Groups 1 and 2

Table II. Selected List of Potential Uses of High Intensity Ionizing Radiation



are included in this survey for sake of completeness but are only briefly commented on as follows:

Physical Effects

Ionization of gases, e.g., air, for elimination of *static electricity* has been found to be highly effective using radioactive sources. Radium and polonium in foil form are some of the sources chiefly used in competition with electrostatic generators, humidity devices and direct electrical grounding. The equipment or radiation source market, estimated to require only a few 10,000 curies of radioisotopes per year, is not readily definable or amenable to analysis.

The effect of beta radiation on the spark ignition, i.e., flame propagation, of a mixture of combustible gases has been studied. First experiments found the results to be relatively insignificant and without benefit: a small but definite depression of the explosion limit resulted.[19]

Luminescent pigments are now available, activated by artificial radioisotopes such as strontium-90. This form of activation, requirements for which are estimated at well over 10,000 curies per year, will be used in competition with radium or ultra-violet.

Electric *power* generation from massive radioisotope sources such as fission products has been suggested. However, reference to Fig. 1 shows that even if a 100% effective method (current experimental efficiencies are only in the order of 1 per cent of converting beta fission product energy into electrical energy were achieved, the quantity of fission products to supply a typical home with 6 kw of electrical energy would amount to one million curies. Rough calculations, therefore, show that this means of domestic power production is prohibitive in cost, regardless even of the potential health hazard of the required radioactivity.

Penetration of Matter

Radiography of materials is receiving considerable stimulus from the use of packaged high intensity sources of artificial radioisotopes. Cobalt-60, iridium-192, tantalum-182, and cesium-137, for instance, are being used with considerable savings compared with radium sources, while retaining the obvious advantages of portability and size over X-ray machines or electron accelerators. Exposures with the latter generally take only a fraction of the time necessary for radioactive sources. In many cases, however, this disadvantage can be overcome by suitable production scheduling.

Thulium-170 promises to be a useful low-energy gamma ray source, equivalent to about 80 kv X-rays.[1]

The potential market for radiographic sources, such as cesium-137, may be quite large ranging up to 10^6 curies. Competitive isotope price levels are currently dominated by the price for cobalt-60, available at \$3–\$14 per curie depending upon specific activity.

The recent development of a scintillation crystal-television camera detector suggests that a sensitive means of instantaneous observation of radiographs is becoming practical. If sufficient contrast is obtained at the cobalt-60 energy level of 1.25 Mev, radiographs through 33 cm of steel, or more than 1 meter of concrete would be possible. Radiation intensities as low as 2×10^{-5} milliwatts per square centimeter are detectable by this means, although definition remains a problem because of radiation scattering.

Therapeutic applications of radiology and other direct *medical uses* are likely to require only a small fraction of the total quantity of radiation available from fission products, and electrical machines, out of all proportion to the untold benefits obtained. The amounts required may be gauged from the following.

The radiation effects of 21 microwatt-hours per pound of tissue (20 rep) are detectable in the blood of human beings, 500 microwatt-hours per pound (475 rep), if administered to the whole body, is considered to be a lethal dose for half the population (LD-50) and doses of 5.25 to 10.5 milliwatt-hours per pound (5000 to 10,000 rep) are required locally in treatment of malignant diseases.

Pure beta emitters are desirable for surface treatments. Phosphorus-32 and strontium-90 are being used increasingly for this purpose. Up to 500-curie amounts may be needed at any one time. Interstitial irradiation with gamma emitters, such as cobalt-60 or radium may require about 10 to 100 curies for every 100 patients. Sources of 10,000-curie strength are required for teletherapy purposes, but not more than about 100 of these are likely to be required in the foreseeable future.

Thulium-170 and xenon-133 are likely to be useful for portable medical radiographic apparatus. High specific activity is necessary to achieve the required point source size for good definition. Sources of 1-curie strength with dimensions less than 1–2 mm are being developed for this purpose.

Finally, medical uses are not subject to economic considerations to the extent that competitive industrial practices require. Advantages in technology are, therefore, of decisive importance without primary regards to cost.

Control *instrumentation* using sources of radiation can improve certain industrial manufacturing processes. Beta ray thickness gauges are an example of this. Such uses, however, will not provide a large market for radiation sources regardless of the millions of dollars currently saved by users through improved process control.

The radiation applications with which this survey is primarily concerned fall within preservation and sterilization of foods and drugs, biological effects, insect control, and radiation chemistry.

Table III shows a selected list of applications, typical of each of these groups, together with types of radiation and energy requirements to produce the stated results. Processing rates and cost depend upon radiation source design and will be discussed later. For the present, let us identify and describe

Table III. Radiation and Processing Requirements for Selected Applications

Application		*Type and energy of alternative radiation*		*Appropriate energy absorption required in material treated*			
Preservation, sterilization, and biological effects	*Package size (cm) and weight*	*Electron*	*Gamma*	*Rep*	*Watt-hours per pound*	*Results achieved*	*General remarks*
Meat (fresh cuts)	60 × 45 × 20 112 pounds	5 Mev	0.75–1.2 Mev	80,000	0.085	Partial sterilization in bulk	No undesirable flavor and color changes
Meat and vegetable (canned)	No. 2 can, 1 1/3 pounds 8.5 dia × 11.5 long	10 Mev	0.75–1.2 Mev	2×10^6	2.1	Complete sterilization in bulk	Flexible containers possible
Meat specialties (e.g., sausages)	Cellophane wrap 1.9 × 15.2 × 10	0.5 to 1.0 Mev	—	0.5×10^6	0.5	Surface sterilization only	Radiation penetrates only 0.2 cm.
Liquids (canned soup)	No. 1 can, 1 pound 6.8 dia × 10 long	8.5 Mev	0.75–1.2 Mev	2×10^6	2.1	Complete sterilization in bulk	Flexible containers possible
Vegetables							
Fresh potatoes	Conveyor belt (continuous) or bulk 100 pound lots	2–4 Mev	0.75–1.2 Mev	20,000	0.021	Sprouting suppressed	No undesirable taste
				5000	0.005	Sprouting inhibited	Stored satisfactorily up to 18 months
Fresh onions	Conveyor belt (continuous) or bulk 100 pound lots	2–4 Mev	0.75–1.2 Mev	8000	0.008	Sprouting suppressed	Stored satisfactorily up to 5 months
				4000	0.004	Sprouting inhibited	
Mutations of plant species		—	0.75–1.2 Mev	1000	0.001	Disease-resistant and higher-yield plant species produced	
Drugs							
Antibiotics	Multi-dose vials 40 cm^3	6 Mev	0.75–1.2 Mev	2×10^6	2.1	Complete sterilization in bulk	High process rate, sterilization time in order of seconds, required
Surgical supplies (Sutures)	Vials 1.2 dia × 10 long 10 grams	3 Mev	0.75–1.2 Mev	2×10^6	2.1	Complete sterilization in bulk	High process rate, sterilization time in order of seconds, required
Insect control							
In stored grain	Continuous flow	6–10 Mev	0.75–1.2 Mev	50,000	0.05	Complete disinfestation in bulk	Reinfestation questioned
Radiation chemistry							
Polymerization		2–10 Mev	0.75–1.2 Mev	Up to 10^7	10.5	*See Text*	
Cross linkage		2–10 Mev	0.75–1.2 Mev	2×10^7	21	*See Text*	

some of the more important features of specific radiation applications.

Preservation, Sterilization, and Biological Effects

Today there are four basic methods of food preservation, namely, heat processing, dehydration, refrigeration and the use of chemicals. Radiation sterilization offers the first promising new principle of food sterilization since Nicholas Appert in France discovered the art of canning in 1809. While 100 years elapsed before heat-processed canning was introduced on a scientific basis around 1905, we find that radiation sterilization has made relatively faster progress, in step with modern technology and needs. In 1948 there were only 3 laboratories in the USA undertaking research in this field. Today there are some 40 institutions in this country actively pursuing research projects, aided by a $6 million grant administered by the US Quartermaster Corps.[2]

The use of ionizing radiations in sterilizing foods (and drugs) is unique in that micro-organisms are killed with only a small rise in temperature. This is important in preserving certain nutritive values of food and essential for such heat-sensitive drugs as antibiotics. Even though about 50 times more energy is required for sterilization by heat than by ionizing radiations, the thermal energy is uniformly distributed. The small amount of energy absorbed per molecule is generally not sufficient to break chemical bonds. Ionizing radiation, on the other hand, gives up its energy in discrete amounts and raises a few molecules to energy levels far in excess of those required to rupture chemical bonds, thereby freeing a significant number of oxidizing and reducing radicals which produce most of the desirable effects as well as some of the undesirable chemical and physical effects noted below.

On an experimental basis, sterilization of foods and drugs has been accomplished by destroying bacteria, yeast or molds with radiation doses of 1 to 4 million rep (1 to 4.2 watt-hours per pound of food). However, problems remain to be solved. Some of these are economic ones and they will be discussed later in this paper. A minor engineering problem relates to the safety of personnel operating these radiation installations. In illustration of this, it suffices to recall that the ratio of lethal doses for humans and micro-organisms is about 1 to 2500. However, a great deal has been learned in the last 10 years about the safe handling of intense radiations so that this problem is not insurmountable.

Major problems to be faced in radiation sterilization of foods are certain undesirable color, flavor and texture changes that occur with radiation sterilization. These changes vary from product to product and are, for instance, more noticeable in animal products such as meat and milk than in vegetables. Considerable progress has already been made to prevent these undesirable effects but the problem has not yet been solved completely.[3]

The search also continues for subtle changes, not necessarily detectable by conventional physical and chemical tests, that may possibly have a physiological effect upon the consumer. Conclusive evidence of the absence of acute or chronic toxicity must be established. Animal feeding studies have shown no toxic effects and human feeding and clinical tests were begun early this year.

Negative results obtained with irradiated samples of 24 trace elements, ranging from aluminum to zinc and occurring in food, indicate that induced radioactivity does not appear to be a problem, at least for food irradiated with cobalt-60 (1.2 Mev) gamma rays.[4] On a theoretical basis the expected energy level for possible induced radioactivity is somewhere above 8 Mev. It is dependent on such factors as relative isotope abundance and cross-section of the particular elements under treatment, as well as the type of radiation used—gamma or electron.

Similarly, the effect of radiation on food nutrients requires further study. Some sacrifices in this respect are made in all types of food preservation and the same would appear to be true of radiation sterilization. Finally, if radiation preservation of foods becomes a reality container requirements may change considerably, from rigid to non-rigid types.

With these remarks in mind let us discuss some specific examples.

Meat (Fresh, Packaged Cuts)

Large-scale wholesaling and retailing of fresh meat may be improved by preparing packaged standard cuts of fresh meat in retail-size portions at the packing house rather than at the retail market.[6] Loss of spoilage of cut meat (currently avoided by freezing), may be prevented by radiation partial-sterilization which extends about 5 times the shelf-life of fresh cut meat, at ordinary refrigerator temperatures. No undesirable flavors or discoloration of meat have yet been found with such partial-sterilization radiation doses. There may, however, be a danger of such low-dose treatment removing aerobic radiation-sensitive bacteria and leaving a better anaerobic environment for pathogenic botulinum organisms to grow.

Advantages of this proposed process to the consumer would include lower costs of meat and extended refrigerator shelf-life. For the retailer, shipping costs would be reduced, butchering and packaging requirements would be lessened and freezer storage space would be eliminated. The processing and packing house would benefit from greater economy due to mass-handling of cutting and packaging and from reduced shipping and handling costs (70 pounds of cut meat is equivalent to 100 pounds of carcass meat).

From Table III it is seen that 112 pound lots of packaged, cut meat may be partially sterilized with 0.085 watt-hour per pound of meat (80,000

rep) of 0.75 Mev gamma rays or 5 Mev electrons.

Other Packaged Meat, Vegetable and Liquid Foods

Table III shows radiation sterilization data for some other typical products.

Canned meat and vegetables may be completely sterilized by an energy absorption of approximately 2.1 watt-hours per pound (2×10^6 rep) from 10 Mev electron or 0.75 Mev gamma radiation. Packaged sausages are surface sterilized (sealed hermetically in cellophane) by absorbing 0.5 watt-hours per pound (0.5×10^6 rep) from 0.5 to 1 Mev beta (electron) radiation. The purpose of such treatment is to extend shelf-life in refrigerator. Canned soups receive complete sterilization by absorbing approximately 2.1 watt-hours per pound (2×10^6 rep) from 8.5 Mev electron or 0.75 Mev gamma radiation.

Fresh Potatoes and Onions (Fresh Vegetables)

On a weight basis the potato remains the most important single vegetable in the domestic diet. Annual production in the USA is about 14 thousand million pounds valued at 526 million dollars. About 75% of this crop is harvested in the fall and cannot be held in storage for more than about 4 months without sprouting or softening. Experiments have shown that potatoes could be kept satisfactorily for up to 18 months at common storage temperaures of about 10°C, after absorption of 0.023 watt-hours per pound (20,000 rep) or 0.009 watt-hours per pound (5000 rep) of 1.3 Mev gamma radiation. At these different radiation dose levels sprouting was respectively suppressed or inhibited.[7]

Similar experiments showed that sprouting of onions, stored for 5 months, was inhibited or suppressed by 1.3 Mev gamma ray absorption of 0.005 watt-hours per pound (4000 rep) and 0.009 watt-hours per pound (8000 rep) respectively.[8]

There are, however, cheap and reasonably effective methods of achieving the same effects by chemical means and the economics of radiation processing are, therefore, crucial.

Mutations of Plant Species

It is well-known that hereditary changes and disturbances in the chromosomes are caused by ionizing radiations. There now is experimental evidence that some radiation-induced mutations in plants are desirable changes. As a result of fundamental studies the solution of some specific agricultural problems is being attempted.

These studies are still in their early stages but promising results have already been obtained.[13] A rust-resistant variety of oats was produced within a period of 18 months and at very small cost. Conventional plant breeding methods would have taken at least 10 years and considerable expense to achieve the same result.

Plant diseases cause an estimated annual agricultural loss of 3 thousand million dollars in the USA. Radiation induced mutation of species would seem to be a method which promises to produce crops immune to these diseases. A project to produce corn resistant to leaf blight is now being undertaken.

Radiation doses of the order of 0.001 watt-hours per pound (1000 rep) are commonly used for plant mutation experiments.

Aside from disease resistance, other desirable characteristics can be induced by irradiation. Among the most striking ones is a new variety of peanut, so developed, which has about a 30 per cent higher yield per acre. Radiation-induced mutations have also produced strains of microbes, producing greatly increased yields in antibiotic drug manufacture.

Drugs—Antibiotics and Other Medical Supplies

Antibiotics, in general, are heat sensitive, and therefore, cannot be sterilized by conventional thermal processes. Since they are the product of microbial synthesis, the problems in obtaining sterile pharmaceutical material are obvious. Aseptic manipulation is the current method used. It is costly and it involves intricate processing and testing operations. On the face of it, radiation sterilization promises a better and safer product. The added cost, however, may prove to be a drawback, bearing in mind the relatively low price of, say, penicillin today. Also, more and more oral preparations of antibiotics are being used (not requiring sterility) and less parenterally administered products (sterilized) are needed.

A relatively small number of plants provide the required output of penicillin so that it is obvious that any radiation treatment must be rapid and continuous. Assuming a multi-dose (1,500,000 oxford units) vial end product, production rates of about 6000 vials per hour must be handled for 20 hours a day. The sterilization time should, therefore, be of the order of one second. The radiation dose to achieve complete sterility for penicillin is 2.1 watt-hour per pound (2×10^6 rep) from 6 Mev electron radiation.[9]

Similar principles apply to other medical supplies such as vitamins, plasma and other blood fractions, surgical grafts and sutures. The last-named has been included in Table III.

Insect Control

Estimated yearly damage done by insects to stored grain in the United States runs into many millions of dollars. Fumigation is one of the methods frequently employed for disinfestation. Experimental data shows that radiation doses of less than 0.1 watt-hour per pound (100,000 rep) produce rapid lethal effects in most of the insects concerned. It is suggested, therefore, that radiation processing of stored grain might prove profitable in view of the heavy losses incurred with present practices.[10]

Three Mev beta or 0.75 Mev gamma radiation absorbed at doses of 0.06 watt-hour per pound

(50,000 rep) are sufficient to kill the majority of insect pests and prevent the reproduction of all types. Re-infestation, however, is a problem. It might be prevented by packaging the cereal but this again raises other practical processing problems.

Polymerization and Cross-Linkage

Radiation-initiated polymerization of the addition type has been demonstrated.[11, 12] This form of reaction-initiation has basic industrial advantages:

Polymerization can be accomplished at low temperatures where adverse thermal effects can be avoided. Formation of certain isomers, only formed at low temperatures, can be realized. No foreign substances such as catalysts or promoters are added, so that the polymer formed is essentially pure. Polymerization in the solid state is possible. Molecular weight control by temperature can be achieved over a wide range since the initiation step is temperature independent. Finally, the polymer formed may have superior physical properties since radiation can attack polymer molecules in a polymerizing system causing branching and cross-linkage and altered molecular weight distribution.

Besides improving many existing chemical processes, radiation initiation of chemical reactions may lead to a range of new materials, including tougher plastics. An example, already in commercial production is irradiated polyethylene, able to withstand continuous use of 125°C as against 70°C for unirradiated material. Recent experimental results have shown that high molecular weight polyethylene cross-links readily under radiation. Such irradiated material has shown no deterioration at 200°C.[19] Direct chemical means, however, have also been found which produce high temperature polyethylene and the radiation method must compete with them.

Chemical reactions of this kind are initiated by energy absorption in excess of 10.5 watt-hours per pound (10^7 rep) from 2–10 Mev electron or 0.75 Mev gamma radiation.

SOURCES OF HIGH-INTENSITY IONIZING RADIATIONS

Practical sources of high-intensity ionizing radiations may be listed in the following groups:

(1) Particle accelerators: Van de Graaff machine, microwave linear accelerator, resonant transformer, and Capacitron. (X-ray machines are generally uneconomic for radiation processing. Even though 2 Mev X-rays have an energy spectrum equivalent [for industrial purposes] to that of cobalt-60, the conversion efficiency is only about 6 per cent, and this is further reduced in practice by poor irradiation geometries.)

(2) Nuclear reactors: special-purpose, to provide radiation facilities only; and dual-purpose, to provide heat power plus radiation facilities.

(3) Reactor by-products: fission products and packaged, high specific-activity radioisotopes.

In the remarks that follow, each of these sources is briefly described and estimated cost figures are quoted. In regard to these costs, it should be emphasized that, in many cases, they are tentative only. Much of this uncertainty is due to the fact that radiation processing on a commercial scale has so far only been carried out in a few isolated instances. Actual operating and comparative data is, therefore, lacking. It is believed, however, that even the tentative cost data presented will serve to illustrate current thinking and planning in this field.

Particle Accelerators

Among the three groups of radiation sources enumerated, particle accelerators are unique in that some of them have been commercially available for several years. Actual industrial processing has been carried out with them and relevant cost data is, therefore, factual rather than estimated.

During recent years, particle accelerators have made advances in two major directions. On the one hand, some types have been fully engineered for commercial production, and their operating reliability under industrial conditions is being improved. Secondly, the electron energy output level has been raised, thereby overcoming their previous limitation through lack of pentration. The microwave linear accelerator is of particular note in this respect.

Of the various types of accelerators, the ones most readily available for large-scale commercial use are Van de Graaff machines, traveling-wave linear accelerators and resonant transformers. The Capacitron should also be included here although it has not yet been used to the extent of the former types.

Van de Graaff Accelerators[14]

This machine produces intense beams of high energy electrons within a sealed pressurized chamber. Electric charge is sprayed on to a high speed insulating belt and thus passed to a high voltage terminal, which is insulated from the accelerator shell by compressed gas. Electrons are accelerated at high velocities through an evacuated tube in which a potential difference is maintained between the high voltage terminal and the lower end of the accelerator. Near the tube exit, the electron beam is generally scanned by use of a magnetic field, so as to irradiate uniformly a product on a moving conveyor belt.

This scanning is a particular advantage possessed by electron radiation as against gamma rays. It results in higher utilization efficiencies, about 50–85 per cent for scanned electrons as against 20 per cent or less for a typical gamma irradiation arrangement. Cross-firing from multiple machine installations can potentially increase this efficiency even further.

Van de Graaff machines are made in a number of models ranging from 1–3 Mev electron energy

with power outputs from 250 to 12,000 watts. Capital costs of such installations range from $40,000 to about $450,000, increasing with power output.

As a typical example of operating costs let us consider the 0.085 watt-hour per pound (80,000 rep) dose required for partial sterilization of meat. On the basis of a throughput from 10,000 to 30,000 pounds per hour (typical of a good-sized meat processing plant) and assuming a 50 per cent utilization factor, we find that radiation processing costs work out to about 0.1 cent per pound. These operating costs include 10-year amortization of the capital costs of the complete installations, maintenance and labor.

Traveling-Wave Linear Accelerators[15]

Unlike the electrostatic accelerator which produces a constant current electron beam of uniform energy, the linear accelerator generates a series of current pulses, of a few microseconds duration, at repetition rates up to and even in excess of 500 pulses per second. The beam energy is substantially constant with a small percentage spread. Scanning techniques are equally applicable giving utilization efficiencies of 50–85 per cent. Some care has to be taken in the proper selection of scanning frequency, pulse repetition frequency and speed of product under the beam, but the end performance of the pulsed linear accelerator is quite similar to that of the Van de Graaff machine.

Linear accelerators are now being made with electron energies from 5–13.5 Mev. Powers up to about 1000 watts have been achieved in practice and higher outputs, up to 5000 watts, are being developed. Capital costs of these installations range from $125,000 to $225,000 increasing with power output. Operating costs are dependent upon reliability, not yet proven in practice, but are believed ultimately to be roughly the same as for the Van de Graaff machines.

Resonant Transformers[16]

Continuing development in the high voltage X-ray field over the last decade has made available this type of equipment for the production of high-energy electron beams. In this case a secondary or high-voltage circuit is tuned to resonance, thereby eliminating the need for an iron core. This results in numerous advantages over conventional transformers, including reduction in size and weight and ability to incorporate a continuously-evacuated multisection cathode-ray tube as an integral part of the high voltage assembly.

Electron generators, built on this principle, are now available with energies of 1 and 2 Mev and power outputs from 1000 to 3000 watts. Capital costs of the generator range from $45,000 to about $86,000. Such equipment can be bought or leased at rental charges ranging from $7 to $40 per hour.

Capacitron

The Capacitron produces high electron accelerating voltages and great electron intensities during microsecond time periods. A number of capacitors is charged in parallel through resistors from a rectifier unit. The capacitors are discharged in series by means of gaps which spark over at predetermined voltages.

A prototype Capacitron has been designed to generate 5 Mev electrons with power output pulses up to 12 kw at repetition frequencies of 1 pulse every two seconds. Capital and operating costs are estimated to be of the same order as some of the previously described accelerators of like electron energy and power output.

Nuclear Reactors

Nuclear fission produces sources of ionization in the form of neutrons, radioactive fission products and instantaneous fission gamma rays, as shown by the distribution of fission energy in Table IV.

Direct neutron irradiation may be disregarded for food processing purposes, because of the danger of inducing radioactivity in the material processed.

From the distribution of fission products shown in Table IV, it is noted that the gaseous products alone account for over 30 per cent of the total radiation energy. This energy represents about 1 per cent of the total reactor heat energy. In order to utilize it, a homogeneous, liquid-type reactor is indicated, because among the many types of reactors, it seems most adaptable to removal of these gaseous products.

Table IV. Distribution of Fission Energy

Kinetic energy of fission fragments	162 Mev
Fission neutron energy	6
Instantaneous gamma energy	6
Neutrino	11
Radioactive fission products:	
Delayed gamma energy	5
Delayed beta energy	5
	195 Mev

Principal radioactive fission products (10 sec after fission):

Product families	*Per cent of total*
Rubidium and cesium	20
Strontium and barium	2.6
Yttrium and lanthanum and cerium	4.5
Antimony	4.8
Molybdenum and tellurium	5.2
Bromine and iodine and tantalum	27.7
Xenon and krypton (gaseous)	32.4

Instantaneous gammas are available only directly adjacent to the reactor core, are accompanied by neutrons, and may, therefore, be disregarded for radiation food-processing. Even circulating fuel, away from the reactor core, emits sufficient delayed neutrons to make it unsuitable for this purpose.

On first sight, therefore, the fission gas products appear as the major source of radiation available for material processing purposes. Additional gamma

energy, however, may possibly be obtained by placing a "fertile" material such as $MnSO_4$ in the reflector solution.[17] Through neutron activation, this material emits high-energy gamma rays with a half life of 2.6 hours. It may, then, be possible to circulate this gamma-active reflector solution to a radiation facility outside the reactor.

Although neutron radiation has been disregarded in the above, it should be noted that such radiation may in fact be of interest for chemical as distinct from food processing. No specific data on this possibility, however, is being presented here.

Confining ourselves, therefore, to the gamma facilities, we have further to distinguish between special purpose reactors, installed as part of, say, a food processing plant, and central electricity station power reactors having irradiation facilities. The latter clearly introduce shipping problems for the material to be processed, since nuclear power stations are not often likely to be in close vicinity to food manufacturing plants.

With these general remarks in mind, let us briefly examine the potential of reactors for radiation processing.

Special Purpose Reactor

Tentative specifications have been proposed for a 3-million-watt-reactor with only gamma rays from extracted fission gases used.[17]

About 30,000 watts of fission gas gamma energy (3×10^6 curies at 0.75 Mev) would be available for processing purposes from such an installation. Capital costs are estimated at 2 million dollars and 10 year amortization is assumed. Total operating costs are calculated to be about $900,000 per year. This plant would be capable of processing about 27,000 lb of meat per hour, with a partial-sterilization dose of 0.085 watt-hours per pound (80,000 rep), assuming a utilization factor of about 10–20 per cent. The cost of radiation processing then works out at about ½ cent per pound of meat.

Installations of this type have not yet been built and proven out in practice. The above data should, therefore, be considered only as an approximate estimate of the trends in special purpose "radiation processing reactors."

Dual Purpose Reactors

In discussing power-reactors, one frequently hears of the "dual-purpose" machine. It seems, therefore, justifiable to ask if a power reactor can be used for a dual purpose in another sense, that is not for the purpose of making plutonium as a by-product but for the purpose of producing radiation as a by-product.

One example would be a liquid sodium-cooled reactor that is designed for 200 million watts of heat generation. The circulating sodium may produce in the heat exchanger room a gamma radiation level approaching 10 watt-hours per pound of material processed per minute (10,000 rep per minute). This large quantity of radiation is essentially free of cost *per se*, with the exception of conveyor and other irradiation facilities that need to be built specially for processing purposes. Assuming a utilization factor of 10 per cent and a treatment dose of 0.085 watt-hour per pound (80,000 rep), this facility would be capable of processing some 250,000 pounds per hour.[18]

This rate of throughput is clearly more than a single food manufacturer is likely to require. One reactor of this kind could, therefore, serve several of them simultaneously. Cost figures for the transshipment of materials to the reactor site cannot be quoted in general terms, nor can the acceptability to manufacturers of having such an essential treatment undertaken outside their plant, be readily assessed.

An intriguing argument, however, arises from the following thought: i.e., should manufactors be willing to pay ⅕ cent per pound treated, this would represent a gross income to this hypothetical power station equivalent to one cent per kilowatt hour of electricity generated. This figure would reduce to a rather lower net income figure, taking into account the operating and other costs involved in such a radiation facility. Even so, it is argued that the economy of nuclear power stations may be significantly affected, in favor of their over-all competitiveness with conventional stations, by the provision of irradiation services.

Although the above remarks relate here to sodium-cooled reactors only, similar reasoning may be applied to the utilization of gamma energy from "cooling" fuel elements at the site of other type reactors. More is said of this in the following.

Reactor By-products

Fission Products

In order to appreciate the over-all radiation potential of fission products in a nuclear reactor economy the following facts are of interest.

The fission of 1 per cent of one pound of uranium (colloquially called "one per cent burnup") produces about 90-million watt-hours of energy, distributed as shown in Table IV. The beta and gamma radiations from the fission products each account for about half of the total time-integrated energy of 5-million watt-hours.

Fission products decay approximately as shown in Table V. One-half their energy is delivered within the first minute after fission. It may take up to one day after removal from a reactor to make the fission product-bearing fuel elements available for processing. On this assumption, it is found that the fission product energy remaining, after one day has elapsed, is only 0.61 million watt-hour. About half of this is gamma energy. Assuming a typical utilization factor of about 15 per cent, a full sterilization gamma ray dose of 2.1 watt-hours per pound could, therefore, be given to 22,000 pounds, from the fission

Table V. Delayed Beta and Gamma Power and Time-Integrated Energy from Fission Products Produced by 1 Per Cent Burnup of 1 Pound of Uranium[21]

Time after fission	*Beta and gamma power (watts)*	*Beta and gamma energy integrated over the time periods as shown (watt hours × 10^6)*
0	Indeterminate	2.5
1 minute	3.1×10^7	0.77
6 minutes	3.6×10^6	0.66
1 hour	2.3×10^5	0.53
1 day	5.0×10^3	0.42
1 year	4.2	0.07
10 years	0.26	0.12
Infinity	0	—
		5 00

products of 1 per cent burnup of 1 pound of uranium.

If estimates of about 175-million kilowatts of nuclear power generated per annum in the USA in 1980 prove to be correct, it can be calculated that this would involve the replacement of about 8500 tons of uranium annually at 1 per cent burnup. Fissioning of this amount of uranium could thus make available a sterilizing gamma ray dose for 38×10^{10} pounds of material processed or about 2000 pounds per head of population of the US. The potentially available radiation energy from fission products, in a growing nuclear power complex is, therefore, considerably in excess of foreseeable requirements for food processing or other purposes. (In explanation of the words "growing nuclear power complex," it should be said that the nuclear power estimate for 1980 given above represents only 10 per cent of the total electric power demand predicted for that year.)

Looking at it another way, one might say that one half of the food consumed annually *per capita* in the US could potentially be sterilized by residual fission product radiation, available from a nuclear power station complex supplying only about 1–2 per cent of the country's electricity requirements.

The forms in which fission products may be utilized are either spent fuel elements in which the fission products are mixed with uranium and other elements, mixed fission products where uranium has been extracted and the fission products concentrated, or refined products where individual isotopes such as cesium-137 have been isolated and concentrated to high specific activity.

Depending on their shape, spent fuel elements are more or less limited in their use by the shielding effect of the heavy element uranium. On the other hand, separation and concentration costs are not incurred and much "hotter" sources can be utilized.

Mixed fission products do not suffer from self-shielding limitations, but spent fuel elements must generally be allowed to "cool" for about 6 months before the fission products can be extracted. Much of their useful activity is thereby wasted.

Separated and concentrated fission products are generally restricted to those with a long half-life such as the gamma emitter cesium-137 or the beta emitter strontium-90.

Little is known about the actual cost of either spent fuel elements, mixed or concentrated fission products. In the main, this is due to the fact that no large-scale reactor or fuel element-reprocessing installations have yet been operated commercially. One way in which estimates have been prepared is to work from the known price of some separated products, such as cesium-137, now available in small quantities, and then to extrapolate prices on the basis of a 0.6 scaling factor commonly employed by chemical plant designers, and assumed to be applicable in the present case. From this estimated value for megacurie cesium sources, estimates for mixed fission products have been prepared taking into account their relative value in terms of half life of the radiation produced. Finally, costs for a spent fuel element irradiation facility are estimated on the assumption that construction and operation of the facility will be the major costs incurred, since the cooling fuel elements themselves will be available at a nominal rental charge at the reactor site. On this basis, the following tentative estimates have been published:[19]

Spent Fuel Elements

Capital cost of the irradiation facility was estimated at about $50,000. Total annual operating costs, including 10-year amortization of capital costs, come to about $65,000 assuming an average of 260 days per year (16 hours per day). Cost of the fuel elements is believed to be insignificant at the reactor site where spent elements are usually "cooled." A nominal rental charge may be made on a 2-month replacement basis, this being a suggested rotation schedule.

Based on a minimum dose of 0.01 watt-hour per pound (10,000 rep) for potato irradiation, and an annual capacity of 35 million pounds, the irradiation costs are estimated at 0.18 cent per pound.[19] The potatoes must be shipped to the reactor site and this involves additional costs.

During each 2-month period of use of one charge of fuel elements, frequent adjustments will have to be made in the speed of the conveyor moving potatoes through the irradiation rooms to compensate for decay of the fission products.

Mixed Fission Products

Capital cost of the irradiation facility is estimated at $66,000. Using 2 years' old mixed fission products, with an output of about 1000 watts (150,000 curies) of gamma energy, the cost of this source is estimated as about $38,000 plus about $5000 for shipping. Total installed cost is, therefore, about $110,000.

One-sixth of the source will require replacement every four months to compensate for decay. Assuming a 10-year useful life for the installation, the estimated annual operating costs are about $95,000.

Based on a minimum dose of 0.01 watt-hour per pound (10,000 rep) for potato irradiation and a work schedule of 260 days a year (16 hours per day) the annual irradiation capacity is calculated to be 37 million pounds per year. The irradiation costs are, therefore, estimated as 0.25 cent per pound.[19]

Separated and Concentrated Fission Products

Cesium-137 (0.66 Mev, half-life 37 years) has been proposed as a source, concentrated to a specific activity of ½ curie per gram. The cost of such a 150,000 curie (900 watts) source is estimated at $120,000. The total installed cost, including shipping and irradiation facilities is then about $190,000. Assuming a 10-year useful life, the estimated annual operating costs are about $75,000.

Based on a minimum dose of 0.01 watt-hour per pound (10,000 rep) for potato irradiation, and an annual capacity of 37 million pounds per year (working at the rate of 16 hours per day for 260 days a year), the irradiation costs are estimated at 0.2 cents per pound.[19]

High Specific Activity Isotopes

Packaged isotopes, such as cesium-137, may be obtained from fission products as discussed in the previous section. Prices of $6 per curie for 1000 curie amounts of Cs^{137} are quoted for capital costs of the source alone and a 0.6 cost scaling factor is applied in estimates for larger sources.

Alternatively, sources such as cobalt-60 may be produced by neutron irradiation in reactors. The current price of cobalt-60 ranges from about $3 to $14 per curie, corresponding to specific activities from a few curies per gram to about 70 curies.

It has been suggested that substantial amounts of high specific activity cobalt-60 may be obtained by irradiation in large production or power reactors. Cost estimates suggest that the price of high specific activity cobalt-60 may then come down to $1 per curie or less.[20]

These plans are too tentative as yet to go any further in an examination of irradiation costs based upon them. It would seem possible that high specific activity sources if widely used are another factor which may affect the nuclear power economy by providing by-product revenue to reactor operators.

GENERAL COMMENTS AND FUTURE TRENDS

In view of the sparseness of available and factually substantiated data, it seems premature to make any searching economic comparisons between all the different sources potentially available for radiation processing. Each proposed use requires careful study, and even then we may find only temporary conclusions in view of the rapidly advancing technology.

However, it appears that particle accelerators, as of today, have advantages as far as the economic picture is concerned. Their commercial availability and proven use make this belief easier to substantiate. Their technical advantages include greater inherent safety, (since power shut-off means radiation shut-off) and easily controlled flexibility of radiation, both in energy level and power output. Their constancy of output means that throughput of material can be kept constant, resulting in simpler production scheduling. Scanning of the electron beam results in considerably higher utilization efficiencies than are now believed possible for gamma sources. Shielding required for adequate protection of personnel is generally speaking less costly for these high energy electron sources than for gamma emitters. On the other hand, reliability of accelerator operation, when in continuous use, must still be proven. Stand-by generators are required in case of power failure. Limitation of radiation penetration from currently available models is still a handicap.

On the assumption that costs for material conveyor arrangements and other operating and overhead costs are roughly comparable for all the sources discussed, it would appear that their comparative economics is largely a matter of capital costs and processing rates required. In this respect, the present capital costs of accelerators is characterized by the relatively high costs involved in custom-building each apparatus. Future requirements for greater numbers of them is likely to result in cutting present capital costs, perhaps by as much as one-half. Output energy levels can potentially be increased as required, and thus make electron penetration entirely comparable to gamma rays. On the other hand, a growing nuclear fission power industry, as we have seen, is going to produce vast amounts of potentially available gamma-emitting fission products. Widespread use of these "waste products" may significantly improve the over-all economy of nuclear power production. There is, therefore, every justification for continued development in this field in order to achieve economic utilization of fission products. Reasonably accurate cost estimates, however, will depend upon actual rather than estimated data for reactor operation and fuel-reprocessing plants.

However, even the few tentative estimates presented in this paper make it apparent that costs for irradiation of certain materials from fission products are now believed to be approaching the right order of magnitude to invite consideration of pilot plant facilities. The same may be said of special nuclear reactors for radiation treatment, provided that processing requirements can be found where their large radiation potential can be adequately used. Such requirements are likely to be confined to a relatively few manufacturing plants having a very high throughput of processed materials, at least until capital costs of such special reactors can be appreciably lowered.

It goes without saying that, all else being equal, many manufacturers will prefer to carry out radiation processing in their own plants. Costs of radiation processing at the site of central power station reactors must, therefore, become so low as to overcome the reluctance and costs involved in trans-

shipment of materials. Conversely, the handling and shipping costs of fission products and isotopes as well as their waste-disposal, must be sufficiently cheap and trouble-free to compete with particle accelerators installed at the preferred site of use. Replacement of decaying fission products may involve relatively frequent handling in order to maintain required throughput rates for processed materials.

The foregoing remarks are based on our present knowledge of required radiation dosage levels as presented above. Changes may occur here, too. In food preservation, for instance, it is possible that dosages required for comparable effects may be lowered if current experiments lead to practical methods of making bacteria more sensitive to radiation damage. Some researchers also believe that the survival of bacteria is not dose-rate dependent, whereas side effects are. Should this be so, and it is a very controversial subject, it would appear to be a factor in favor of scanned or pulsed electrons as against broad beam gamma rays.

It seems certain that other significant applications of radiation processing will be found as the technology of this field develops. There are, however, some indications that a few of these processes, notably in the chemical field, may revert to strictly chemical techniques, albeit novel ones resulting from our newfound knowledge of radiation reactions. Radiation chemistry may, therefore, come to be regarded as a research tool in addition to its processing potentials.

Finally, although it is hardly within the scope of this paper, attention should be drawn to the real need for greater standardization of dosage measuring techniques in the high energy, high intensity radiation field with which we are concerned. The problems of dosage measurement are frequently severe, and appropriate techniques must be agreed upon in order that proper experimentation and treatment may be carried out.

SUMMARY

The technical feasibility of radiation processing in order to achieve desirable chemical or bactericidal effects has been demonstrated. Further careful tests are being undertaken to establish non-toxicity and consumer acceptance of such processed materials, particularly foodstuffs.

The comparative economics of radiation processing, both as between different radiation sources and as compared with present conventional means to achieve similar effects, cannot yet be thoroughly examined in view of lack of quantitative data. Both fission products and particle accelerators are expected to find appropriate uses for radiation treatment. Processing costs, with the latter now range from less than 1/10 cent per pound for high volume, low dosage irradiation to 6 cents per pound for low volume, high dosage irradiation. They are likely to decrease as further development of accelerators takes place. Continued effort in developing the economic use of fission products appears desirable, particularly to owners of reactors, in order to derive benefits from the very large amount of "waste" fission products potentially available from a nuclear power economy. Even special nuclear reactors may prove economic for some processing applications.

Relatively high capital costs are involved with all the different radiation sources available. To realize low processing costs, any one installation must be utilized at its highest rate of efficiency commensurate with plant and process capacities.

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Use of Radioisotopes in the Production of Self-Luminous Compounds

By C. W. Wallhausen,* USA

Radioactive self-luminous compounds, consisting of a radioactive salt such as radium bromide or sulfate mixed with a phosphorescent material, represent one of the original commercial applications of radium. The phosphor most generally used is zinc sulfide but radioactive materials other than radium, such as mesothorium or polonium, have at times been substituted as activators. Alpha particle emission is a characteristic common to all these activators and light emission of self-luminous compounds using these radioactive materials is essentially an alpha particle effect. Beta particles contribute to the effect but the contribution is minor and difficult to determine quantitatively. Relative efficiencies of alpha and beta can be rather crudely demonstrated by depositing a radium salt on a glass plate and superimposing a second glass plate which has a phosphor coating on the under side. Such an arrangement will demonstrate combined alpha and beta effect and beta effect can be isolated by interposing a thin alpha absorber. Experiments of this nature, performed before artificially produced beta emitters were available, led to the erroneous conclusion that since the alpha to beta ratio of efficiency as an activator was from 100:1 to 1000:1, beta activation would never be practical. The widespread acceptance of this conclusion acted as a deterrent to the initiation of research in this field but at the present time developments are keeping abreast of the educational program which must accompany the beta activated phosphor utilization program.

It has been mentioned that the phosphor most widely used in self-luminous compounds is zinc sulfide or one of its modifications. From the standpoint of efficient energy conversion or maximum visible light output, no other phosphor has yet been found that will compare favorably. Zinc silicate, calcium sulfide, calcium tungstate, cadmium tungstate, strontium sulfide, cadmium sulfide and various phosphates have sometimes been found useful substitutes where characteristics other than maximum visible light output are important.

The pronounced difference in characteristics between alpha and beta activated self-luminous compounds must be understood in order to appreciate the advantages of the latter and to visualize the new fields which their availability has opened.

Alpha activation appears to be a mechanical effect similar to triboluminescence. Each alpha particle, in striking a phosphor crystal, produces an individual flash of light which can be readily observed under magnification. The effect of millions of such scintillations occurring simultaneously is to produce what, to the eye, appears to be a uniformly luminous surface. A similar process may occur with beta activation; however, no scintillations have been observed even at low levels of activation. No effort has been made to study the mechanics of beta activation but the difference in the characteristics of the two types of compounds indicates that alpha effect may be purely mechanical while beta effect may be electrical or electro-magnetic.

Alpha activation results in a pronounced deterioration of the phosphor crystal with resultant decrease in brightness level of the compound. This deterioration is proportional to amount of alpha present and limits the maximum practical brightness levels which can be obtained. A luminous compound having an initial brightness of 100 microlamberts or 1 lux will have one half or less of this brightness after six months. One hundred microlamberts therefore represents the approximate maximum brightness from a practical, commercial standpoint. At this level, choice of phosphor is limited to the green or yellow zinc sulfide, in the range 5200 to 5700 Ångstroms, since those of other color are much less responsive to activation, and therefore exhibit much greater rate of deterioration.

When a beta emitting isotope is utilized, the problem of phosphor deterioration appears to have been eliminated. Self-luminous compounds, incorporating various pure beta emitters, have been produced at brightness levels as high as 1000 microlamberts or 10 lux in the green or yellow range and 100 microlamberts in other colors. At these levels, no decrease in brightness due to phosphor deterioration has been observed on materials which have been under test for five years or more. A brightness decrease, which is directly related to the decay of the activator, does occur, and can be accurately predicted from the half-life of the isotope. Recent experiments in the field of electroluminescence indicate that phosphor deterioration does occur at brightness levels ten to one hundred times higher than those mentioned above. It is possible that similar results will be obtained

* United States Radium Corporation.

with beta activated compounds as the amount of activator is increased and this problem is now under investigation.

Increase in the useful life, and the possibility of higher light intensities are thus two outstanding advantages of beta activated compounds. Other advantages include: (1) greater availability of a wide selection of beta emitting radioactive elements; (2) freedom from gamma radiation, making it possible to shield all primary radiation; (3) ability to produce a greater range of colors at practical brightness levels; (4) absence of radioactive gaseous decomposition products; and (5) relative cost.

Isotopes which have been successfully used include tritium (hydrogen-3) carbon-14, sulfur-35, cobalt-60, krypton-85, strontium-90, cesium-137, promethium-147, thallium-204. Two of these do emit gamma radiation in addition to beta and usefulness is limited. Reference to the tables of available fission and irradiation products will suggest other suitable isotopes. Choice, however, is governed by life of the isotope, availability, chemical form, purity, cost and chemical inactivity in the presence of phosphor crystals.

Preparation of isotope activated compounds is, aside from precautionary measures which must be observed in handling radioactive materials, very simple. The isotope in water soluble form, is intimately mixed with the phosphor suspended in water, and precipitated as a water insoluble salt. The gaseous isotopes are somewhat more difficult to process. Utilization in the gaseous form is effective but creates the problem of adequate gas tight sealing and some difficulties are encountered with absorbtion of the isotope on container walls. Reactive gases such as tritium can be utilized in the form of tritiated organic compounds and mixed with or deposited upon the phosphor crystals.

Attempts have been made to establish a definite relationship between energy of the emitted radiation and efficiency of the isotope as an activator. Results have not been conclusive and at this time it can only be stated that with increasing beta energy a decrease in the amount of activator in millicuries is required to produce a given brightness level. Quantitative results are difficult to obtain because effectiveness of the beta particles is obscured by a number of factors which cannot at this time be controlled. Specific activities of various isotopes differ and internal shielding within the activators therefore varies. Chemical processing differs and variations in the degree of intimacy of the mixture occur which also creates internal shielding. Some activators react with the phosphor, change the responsive properties or cause discoloration of the crystals resulting in light absorbtion. This latter effect is particularly critical in the case of the heavy metal isotopes which in general form dark sulfides.

The ratio of efficiency of alpha to beta radiation has been shown to vary widely with the method of processing of luminous compound. The previously accepted ratio of 1:100 to 1:1000 applies only in specific instances. In the case of low energy tritium beta particles (0.0189 Mev), the ratio appears to be of the order of 1:5000 to 1:7000. The corresponding ratios for promethium-147 (0.223 Mev), thallium-204 (0.78 Mev) and strontium-90-yttrium-90 (0.54 and 2.18 Mev) are approximately 1:40, 1:12 and 1:14.

Sensitivity to beta radiation of phosphors of even the same color varies widely because of differences in method of preparation and resultant differences in physical and chemical characteristics. The ratios mentioned above, therefore, are approximate only. To produce 100 microlamberts or 0.1 lux in a particular green phosphor required 70 microcuries per gram of radium in equilibrium with its decay products, 1.3 curies of tritium, 10 millicuries of promethium-147, 3 millicuries of thallium-204 and 1.4 millicuries of strontium-90. These ratios do not correspond to the ratios of energies and it is apparent that other factors such as depth of penetration into the crystal, completeness of absorption of radiation and scattering influence the results. In colors other than green greater divergence from the energy ratios is apparent and no explanation is as yet available to explain the variation. The above ratios were determined by using currently available isotopes and do not take into account differences in internal shielding caused by different chemical forms or specific activities.

Unshielded beta activated luminous compounds naturally exhibit a much higher surface radiation level than alpha activated materials of comparable brightness level. Shielding, which can be accomplished quite easily, is therefore essential. With certain limitations, both plastic and glass are excellent shielding materials. Either material is satisfactory with luminous compounds of low isotope content. At intermediate levels cerium glass or plastics such as methacrylate or polystyrene are required, while at high levels only cerium glass has so far been found satisfactory. Further investigation will doubtless reveal other useful transparent shielding materials but the problem of degradation and discoloration of plastic and glass poses certain limitations. The problem of decomposition of plastic under beta bombardment has frequently been mentioned as a serious obstacle. Fortunately, this has not been the case with the plastics currently being used. Beta particles, to be effective in producing luminosity, must be absorbed in the phosphor crystals. Even though the isotope content is high in the brighter luminous compounds, the effective radiation reaching the plastic shield is low due to this absorption in the phosphor. This is particularly true with the low energy beta emitters. Since most useful phosphors are somewhat transparent, light is transmitted from a reasonable depth and thick layers can therefore be used both to increase efficiency and also provide an absorbing medium for the beta radiation.

The thickness of a plastic, such as methacrylate,

required to eliminate all primary beta radiation, ranges from approximately 0.18 cm for carbon-14 and promethium-147, to 1.0 cm for strontium-90-yttrium-90. Radiation due to bremsstrahlung, the result of the action of beta particles on the luminous source container components, can be detected at the surface of the sealed and shielded units. The energy of this secondary radiation varies with the energy of the primary beta radiation and the materials of construction of the source container. Complete shielding of bremsstrahlung can be accomplished by increasing thickness of the container walls. Approximately 12 to 15 centimeters of methacrylate are required to absorb bremsstrahlung produced in plastic by 2 Mev beta particles. Proper selection of window material is therefore of prime importance both from the standpoint of the best life characteristics as well as protection against radiation.

In practice, the luminous compounds are usually utilized as a powder distributed in a resin binder, encased in a sealed unit consisting entirely of plastic or glass or, a metal support in combination with plastic or glass. No attempt will be made to point out in detail the precautions which must be observed in assembling such units, since many variables are involved. Selection of a binder for the powdered compound and a sealing material for the window requires the same consideration as selection of the window material. Choice of metal components is important since bremsstrahlung production is directly related to density. To overcome the problems it has been found necessary to employ various techniques such as placing low density absorbers between the luminous element and metal parts, heat sealing, double chemical sealing and combining chemical and mechanical sealing.

Research on beta activated luminous compounds has now been in progress for more than eight years and during this period several hundred special sources have been prepared for a variety of potential commercial applications. Only a few have so far been adopted as production items primarily because widespread use must also be accompanied by an educational program on the characteristics of radioactive materials and their safe use. Typical of the applications in which these compounds have been found useful are the following:

1. Safety markings in commercial aircraft, mines, photographic dark rooms and many other areas where electrical failure may occur, or where other sources of illumination are not available or may not be desirable.
2. Ship channel markers or buoys.
3. Calibration sources for photometric equipment.
4. Instrument dial and panel illumination.
5. Comparison sources in light meters.
6. Illumination of cross hairs in optical equipment.
7. Color identification of equipment used in darkness.
8. Low level general illumination.
9. Signalling equipment for use in life rafts.
10. Activation of photocells.

Efforts so far have been concentrated on the solution of simple problems which could not be solved satisfactorily by the use of alpha activated compounds. A review of some of the improvements in the characteristics of self-luminous compounds brought about by the use of beta activation will suggest many new applications and provide a measure for determining the potential of these materials.

Internally activated luminous compounds can now be prepared in a color range to cover the entire visible spectrum and extending into the long ultraviolet and short infrared.

The range of brightness level considered practical has been extended by a factor of from ten to twenty times and further extension is possible.

Useful life at high brightness levels has been extended from a matter of weeks or months to years. Selection of a desired useful life is possible by choosing an isotope with the proper characteristics.

Hazard from penetrating radiation can be minimized or entirely eliminated by shielding.

Hazard from possible ingestion can be minimized by selection of less toxic isotopes.

Although great strides have been made in developing these compounds, much basic research and development remains to be done. Some of the problems which are being or should be investigated include:

1. A study of the basic mechanism of phosphor activation by beta particles.
2. A study of phosphors to determine variables that influence efficiency.
3. Improved temperature sensitivity of phosphors.
4. Further work on ultra-violet and infrared emitting luminous compounds.
5. Investigation of additional transparent shielding materials.
6. Improved techniques for using the beta activators most efficiently.

The development of isotope activated luminous compounds is in its infancy and offers attractive possibilities from both a research and also commercial standpoint. How rapidly it can or will develop depends upon the effort put into it, the effectiveness of the required educational program regarding the use of radioactive materials, and the cooperation of potential suppliers of these radioactive products in making every effort to supply only the safest possible units to the public. The products, if properly encapsulated, present no greater hazard to the public than other well-known toxic materials. The hazard is not so well understood, however, and it is the responsibility of the supplier to furnish properly designed, shielded and sealed sources and to provide all information necessary to make certain that the source will be maintained in a safe condition. Serious consideration should be given to the universal adoption of uniform rules governing the distribution of these and other radioactive sources.

Nuclear Batteries—A Survey

By W. Shorr,* USA

The conversion of nuclear energy into useful electrical power has aroused not only keen interest but also poses one of the major challenges of our time. The nuclear reactor, with its potentially limitless source of power, utilizes the heat energy derived as a result of nuclear fission. This heat is then harnessed to the conventional steam engine or generator. Such a process is an indirect use of nuclear energy. The only process known today by which nuclear energy may be converted directly into electrical power is that used in the nuclear battery.

The nuclear battery generates but a very minute amount of power and it is not believed that it will ever seriously challenge the ubiquitous chemical battery, except perhaps in such instances where a minute and continuous power output is desired for a very long period of time. The unique properties of the nuclear battery will, however, stimulate the invention of new or the redesign of existing devices and gadgets. These will advantageously make use of the following significant characteristics:

1. A source of continual voltage and current in a compact and portable size.
2. Very long life, generally considered equivalent to the half-life of the radioisotope employed.
3. Operation inherently insensitive to extreme temperature conditions, pressure variations or strong electric or magnetic fields.

The concept of the nuclear battery is not new; as early as 1913 H. J. G. Moseley[1] described a nuclear charger with which he achieved voltages of over 150 kv. The significance of the nuclear battery, as a practical device, had to await the development of the nuclear reactor and the subsequent availability of large quantities of fission-products and pile-activated radioactive isotopes at relatively low cost.

GENERAL CONSIDERATIONS

The source of energy in the nuclear battery is the radioactive isotope. As the isotope undergoes spontaneous disintegration, the strength of the source is reduced accordingly, the rate of change being characteristic of the isotope. Thus the useful life of the nuclear battery is limited only by the half-life of the isotope and the specified electric power output. The half-lives of the known isotopes vary from fractions of a second to about 10^{12} years. Although the number of these isotopes is large, practical considerations dictate the choice of isotopes having (1) high ratio of activity to mass, (2) half-lives ranging from one to twenty-five years, and (3) pure beta or alpha radiation. The absorption of these charged particles by matter gives rise to bremsstrahlung, a weak electromagnetic radiation, but these may be easily shielded and reduced to a safe radiological level. Gamma rays, on the other hand, are attenuated by matter, though difficult to absorb completely. Their energy, therefore, would not be dissipated within the narrow confines of the nuclear battery and external radiation thus produced would be dangerous and difficult to shield.

The isotopes finding most use in nuclear batteries are strontium-90–yttrium-90 and tritium; polonium-210 has also found some application as a heat source and as a secondary electron initiator. Pertinent physical properties of these three isotopes are listed in Table I.

The energy theoretically available from one curie of a pure beta emitter, such as Sr^{90}-Y^{90}, may be readily calculated. The primary current (I_p) is the product of the number of disintegrations and the charge of the beta particle (of which there are two in Sr^{90}-Y^{90}):

$$I_p = 2 \times 3.7 \times 10^{10} \times 1.6 \times 10^{-19} = 11.8 \times 10^{-9} \text{ amp}$$

From the power relation where P_p is primary power:

$$P_p = I_p V$$

and where V is the average beta energy, the available power is:

$$P_p = 11.8 \times 10^{-9} \times 5 \times 10^{5} = 59 \times 10^{-4} \text{ watts/curie.}$$

The isotopes Sr^{90}-Y^{90} and tritium are products of the nuclear reactor and thus available in large quantities. Polonium-210 is obtained through the irradiation of bismuth and is relatively rare. The prices currently quoted for the three isotopes are: tritium, \$100/curie; strontium-90, \$500/curie; and polonium-210, \$2500/curie.

The picture of technological development in nuclear power and isotope demand is rapidly changing and it may be expected that the cost of isotopes will reach a competitive price level and, therefore, a more receptive market.[2]

The direct conversion of nuclear energy into electrical energy has been accomplished in a number of ways. These may be classified under one of four basic processes: (1) Constant current charger type:

* Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.

Table I. Properties of Some Isotopes

Isotope	Particle	Half-life	Maximum energy	Average energy*
Sr^{90}-Y^{90} Sr^{90}	β^-	25 yr	0.65 Mev	0.22 } 0.5 Mev
Y^{90}	β^-	60 hr	2.2 Mev	0.73 }
H^3	β^-	12 yr	18 kev	5.5 kev
Po^{210}	α	138.4 d	5.4 Mev	——

(*a*) primary current collector with vacuum insulation, (*b*) primary current collector with solid dielectric, and (*c*) secondary current collector; (2) contact potential difference, gas ionization type; (3) current multiplication with *p–n* junction type; and (4) thermopile type. These will be discussed in terms of mechanism of operation, construction and current and voltage characteristics.

DISCUSSION

Constant Current Charger Type

Moseley's nuclear charger may be considered the prototype battery of this type. His device consisted of a radium source suspended from an insulated support inclosed in an evacuated metal sphere. The alpha particles, emitted from the radium, were collected by the metal sphere, charging it positively, thus producing a potential difference exceeding 150 kv between the two electrodes. As more radioactive isotopes became available, interest in the conversion of radioactive energy increased. Miller,[3] Linder[4] and Christian and Linder[5] conducted investigations on a basically similar vacuum type charger. In one form of generator, employing improved design and vacuum techniques, Christian and Linder attained a voltage of 365 kv with a 25-mc Sr^{90}-Y^{90} source. Though a higher voltage was theoretically possible, internal spark-over tended to limit the voltage to this maximum value. The work of these investigators demonstrated the feasibility of producing high potentials by the use of radioactive materials.

Coleman[6, 10] and Rappaport and Linder[7] showed that the vacuum may be replaced by a solid dielectric and thereby achieve greater compactness and potentially a higher degree of reliability. The primary beta current was attenuated by absorption in the solid dielectric and the voltage obtained was about 10 kv, considerably less than that obtainable with the vacuum dielectric type.

The energy conversion process in the constant current charging generator is essentially the same for both the vacuum and solid dielectric types. Coleman's device (cross section shown in Fig. 1) consists of a thin polystyrene capsule (the dielectric) into which a precipitated compound of Sr^{90}-Y^{90} is placed and then sealed off, a monel wire making contact with the source through the seal. The collector electrode is an aluminum cylinder into which the polystyrene capsule is inserted, with a lead shield finally inclosing the assembly. Primary beta particles are emitted from the source, the majority of which penetrate the dielectric and impinge on the collector electrode. The insulator effectively prevents the return of backscattered primaries and lower energy secondaries, and thus a high potential difference is built up between the two electrodes. The equivalent circuit for such a battery may be depicted as in Fig. 2.

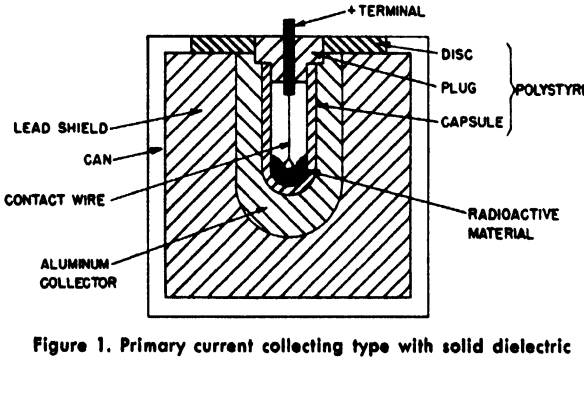

Figure 1. Primary current collecting type with solid dielectric

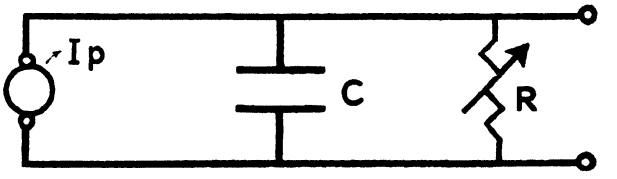

Figure 2. Equivalent circuit of constant current type battery

The circuit is typically that of a capacitor, with a built-in power source, where the collector electrode constitutes a continuously recharging negative plate. I_p is the essentially constant primary beta current (decreasing to one-half its original value after 25 years for a Sr^{90}-Y^{90} source), C is the capacitance of the device and R is the insulation resistance. Figure 3 is a photograph of a nuclear battery of the solid dielectric type, showing its relative size.

The build-up of the no-load voltage of a battery of this type is shown in Fig. 4. The voltage attained by the battery is defined by the equation:

$$V = RI_p(1 - e^{-\frac{t}{RC}})$$

and is similar to that given by Christian and Linder for their vacuum dielectric device. In the conditions where $t << RC$

$$V = \frac{I_p t}{C}$$

and where $t >> RC$

$$V = I_p R$$

Under controlled humidity conditions, a voltage exceeding 17 kv was attained within 5 hours. The voltage varies with respect to the external load; Fig. 5 shows rate of the charging voltage of a solid dielectric type battery as a function of capacitive load.[8]

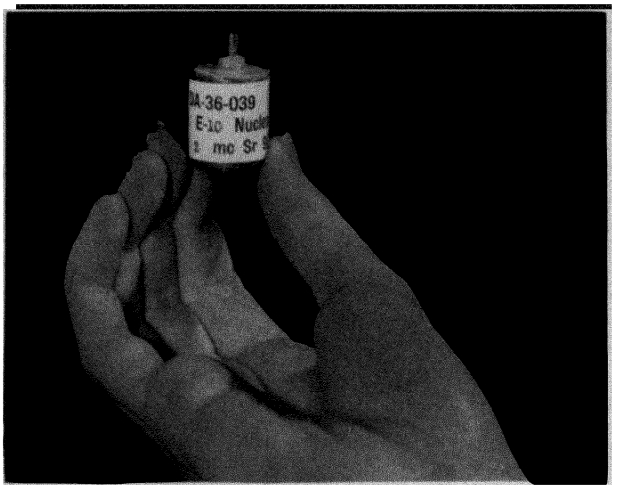

Figure 3. Primary current type battery with solid dielectric

The effect of constant beta radiation on the plastic insulator was of practical significance, since ionizing radiation generally was known to cause lowering of electrical resistance and physical degradation in insulators. Such a condition would seriously limit the life of the nuclear battery and render it impractical. Coleman and Bohm[9] were first to observe that insulators, while still under beta radiation, showed a decrease in specific volume resistivity for a period of time, reached a minimum and then showed a definite increase until physically degraded. The induced conductivity depended upon the beta current density and the temperature. Under high beta current density, all plastic insulators, other than polystyrene, failed in a few weeks as a result of physical degradation. Polystyrene increased in resistance for almost two years under a beta source of 250 mc of Sr^{90} (100 $\mu\mu a/cm^2$), corresponding to about a 40-year extrapolated life in a battery using 10 mc of Sr^{90}. Their results definitely indicated that high insulation resistance for some insulators can be maintained under ionizing radiation.

It has been stated that temperature has no observable effect upon the nuclear disintegration process. However, certain structural elements composing the nuclear battery do introduce temperature dependency of voltage. The resistance value of the polystyrene insulation changes with variations in temperature, as does the external insulation separating the emitter and collector electrodes. High humidity and dust also tend to decrease the output voltage as a result of surface conduction across the external insulation.

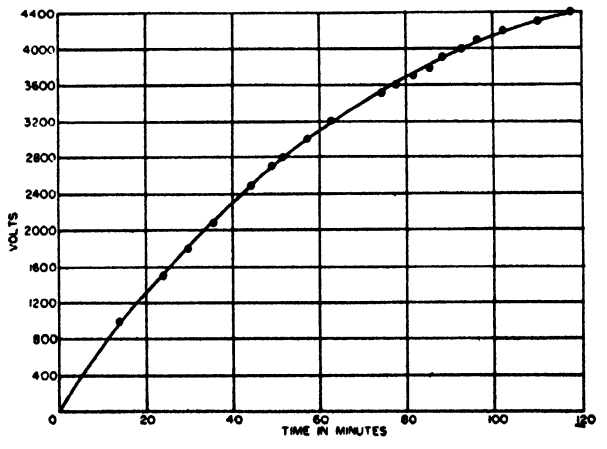

Figure 4. No-load charging voltage as a function of time

The current output at zero voltage, of a battery with a 10 mc Sr^{90}-Y^{90} source, was found to be 50×10^{-12} amperes. The maximum available current from 10 mc of Sr^{90}-Y^{90} is:

$$10 \times 2(3.7 \times 10^{7}) \times 1.6 \times 10^{-19} = 120 \times 10^{-12} \text{ amp}$$

The current collection efficiency is thus about 40%, the remainder of the current being mostly absorbed by the insulator wall. The power efficiency of the device is the ratio of $P_p = I_p V$ for both the theoretical and measured values:

$$\text{Power efficiency} = \frac{50 \times 10^{-12} \times 10^{4}}{120 \times 10^{-12} \times 5 \times 10^{5}} \times 100 = 0.83\%$$

The use of tritium in the solid dielectric device in lieu of Sr^{90} was investigated by Coleman, Gibson and Cohen.[6] They were unable to obtain any useful voltage since the weak beta particles were almost entirely absorbed by the insulating dielectric. A simple cell structure was designed which consisted of a solid tritiated zirconium source (the maximum ratio of H^3/Zr is about two, but only one was attained here), a high vacuum, as the dielectric, and a carbon collector electrode. Although the vacuum eliminated current loss due to ionization, backscattering of primary electrons tended to lower the current yield.

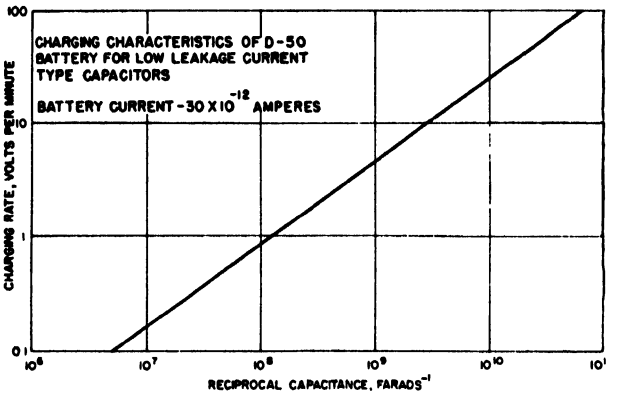

Figure 5. Charging characteristics of D-50 battery for low leakage current type capacitors: battery current, 30×10^{-12} amperes

The tritium device had a maximum no-load voltage of about 1500 volts; at 300 volts the current output was 0.55 $\mu\mu a/mc$, or a current density of about 21 $\mu\mu a/cm^2$. The over-all efficiency was approximately 0.1 per cent. Further improvement in power output may be expected by increasing the H^3/Zr ratio and by minimizing backscattering and secondary electron production through the choice of a more suitable collector electrode. The investigation of solid dielectric films is complicated by the fact

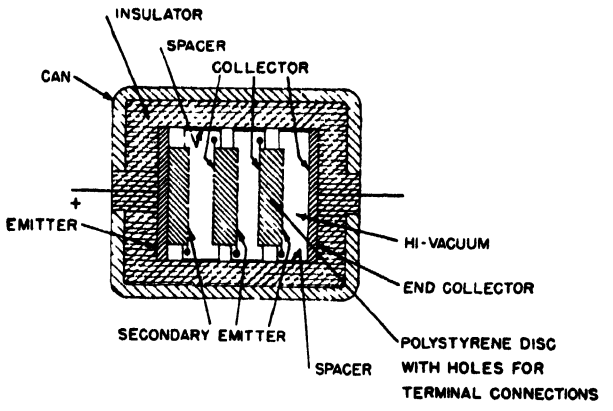

Figure 6. Secondary current collector type battery

that a film thickness in excess of one micron shows excessive beta absorption, and that such thin films must have high resistivity under radiation.

The use of secondary electron emission, as a means of enhancing current generation in the constant current type battery, was investigated by E. Schwarz[11] from purely theoretical considerations. A design proposed for such a device is given in Fig. 6. The component parts consist of a primary source of betas, a moderator to slow down the primaries, a secondary emitter having a high secondary emission factor (such as magnesium oxide) and a collector electrode, preferably graphite coated aluminum to minimize backscattering and bremsstrahlung production. A high vacuum (about 10^{-5} mm Hg) is maintained between the emitter and collector electrodes.

In the secondary current collector battery, both the primaries and secondaries contribute to the current. However, the secondary electrons would be repulsed as the collector electrode becomes increasingly negative, and the battery then would behave like a primary current charger type, with current and voltage considerably reduced as a result of the deliberate absorption of the primary beta particles.

The collector voltage, under no-load conditions, may approximate 200 volts. As a greater current drain is imposed, this voltage would drop to about 20 volts, a value corresponding to that of the fastest secondary electrons reaching the collector electrode.

The power output was analyzed for a practical case of a tritium source device in which it was assumed that the collector voltage (V_c) was 20 volts, the secondary emission ratio (δ) was 10, and in which second order effects, such as internal current leakage and backscattering, were neglected. The power per curie was given as:

$$P = K \times E_a \times \delta$$

where K = a constant for the source (for tritium $K = 2.1 \times 10^{-11}$ watts/ev/curie), and E_a = attenuated average energy of the primaries.
Substituting:

$$P = 2.1 \times 10^{-11} \times 2.5 \times 10^{3} \times 10 = 5.25 \times 10^{-7} \text{ watts/curie}$$

The ratio P/P_p, the calculated power of attenuated tritium beta current and its unattenuated primary power, yielded the calculated efficiency of the secondary emission battery:

$$\text{Power efficiency} = \frac{P}{P_p} \times 100$$

$$= \frac{5.25 \times 10^{-7} \times 10^{2}}{3.5 \times 10^{-5}} = 1.5\%$$

Contact Potential Difference (CPD), Gas Ionization Type

When a gas is irradiated by beta particles, ionization results. If this occurs in an electric field, such as produced by the contact potential difference of two dissimilar metallic electrodes, which are electrically connected through an external conductor, the ions will migrate to the electrode of opposite charge and conduction through the gas takes place. The electrical energy delivered to any external load is the resultant of the ionizing energy of the beta particles. The *CPD* enables the neutralization of ions and the transfer of their charge to the circuit to take place.

The contact potential difference in metals equals the difference in their work functions:

$$CPD = \phi_A - \phi_B$$

The work function is defined as being that minimum energy required to remove one electron from inside the metal to infinity. The work function of metals varies from 1 to 8 electron volts. Accurate determination of the work function is difficult, due to the marked influence of surface conditions and, to a lesser extent, to temperature.[12, 13]

Kelvin,[14] investigating the contact potential difference of metal electrodes, developed a method for determining the *CPD* by measuring the deflection of an electrometer, connecting the two metals, when the gas in the intervening gap is ionized by a radioactive source. The method essentially fulfilled the basic requirements of the *CPD*-gas ionization battery.

Kramer[15] first described and exhibited a battery in which the gap between the zinc and carbon electrodes was irradiated by a radioactive substance spread over the surface of the carbon. The voltage was given as approximately 1 volt and the current, obtained with a small area cell, as about 3×10^{-4} amperes. This exceedingly large current can only be explained on the basis of a superimposed electrochemical current, several orders of magnitude greater than the radiation current.

Ohmart and others[16, 17, 18] investigated the dynamic conditions producing current flow in the *CPD* cell. The output current was shown to be a complex function of type and intensity of the ionizing radiation, type and pressure of the separating gas, the contact potential difference, cell geometry, and external load.

Thomas and co-workers[17] investigated the theoretical and practical design aspects of the energy conversion process in the *CPD* device, and analyzed the competing processes of ion collection and recombination as functions of ion mobility, recombination

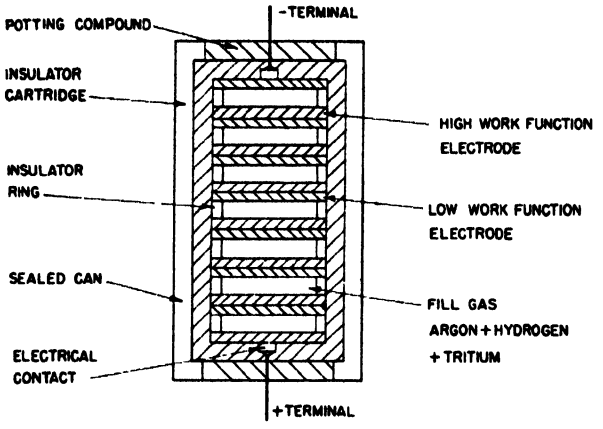

Figure 7. Contact potential-gas ionization type

rate, gas pressure and applied field. Two conditions must be fulfilled for proper battery operation: First, the ionization potential of the gas must be higher than the larger work function ϕ_A of one electrode. This will allow electrons to escape from the electrode surface and neutralize the positive ions. Secondly, in the presence of negative ions, the work function of the low work function electrode must be higher than the electron-affinity of the negative ion. This will permit the transfer of the negative charge to the electrode. The first condition normally exists; the second would fail in the presence of strong electro-negative gases, such as oxygen and chlorine.

A schematic drawing of a multi-cell structure designed by Thomas, *et al.*, is shown in Fig. 7, and in Fig. 8 a photograph of several 100-volt batteries indicates the relative size of the structure.

A stable electrode couple was found to be magnesium and lead dioxide, with a *CPD* of 1.6 volts. The magnesium is evaporated onto a stainless steel disc, one surface of which was anodized in a lead nitrate solution. Units of these cells, the number determined by the desired voltage, are spaced by an insulating ring and the whole encased in a gastight container. The fill gas is a mixture of argon, hydrogen and tritium, the activity per cell being approximately 1 millicurie.

A curve relating current and voltage for a recent model battery is given in Fig. 9. The rate of the voltage buildup of another battery across a 25 mfd capacitive load is shown in Fig. 10.

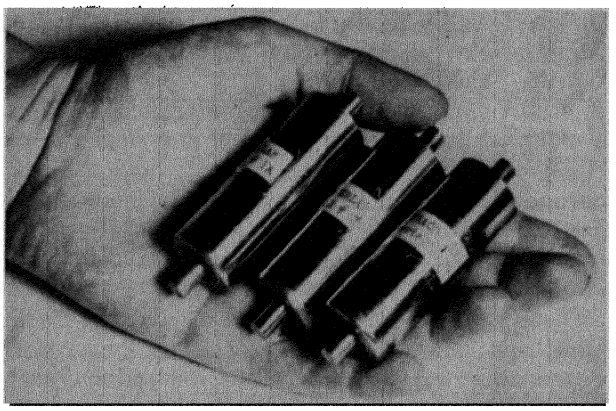

Figure 8. Experimental models of CPD-gas ionization type battery

Some current multiplication takes place in the *CPD* battery, since the energy for producing one ion-pair in argon is 28 electron volts and the average primary beta energy from tritium is 5500 ev. The current is thus enhanced by a factor of:

$$\frac{5500}{28} = 200$$

However, current losses due to recombination and wall absorption effects, and the limitation of the voltage per cell to the *CPD*, result in an over-all efficiency of approximately 1 per cent.

Current Multiplication with p-n Junction Type

The effects of radiation on semi-conductors have been studied by numerous investigators.[20] The high resistivity of semi-conductors enables the ionization effects of radiation to be readily detectable in these materials. The irradiation of germanium with betas of less than 0.7 Mev has been reported as causing a decrease in resistivity by a factor of about 10. Junction barriers exposed to electron bombardment have been used as crystal counters.

Rappaport[21] described alloy-type *p-n* junction devices fabricated either from germanium or silicon and measured the current and voltage resulting from the irradiation of the junction with high energy beta particles. He defined the maximum, or open circuit, voltage of the device by the approximate expression:

$$V = \frac{KT}{e} \ln \left(\frac{I_s}{I_0} + 1\right)$$

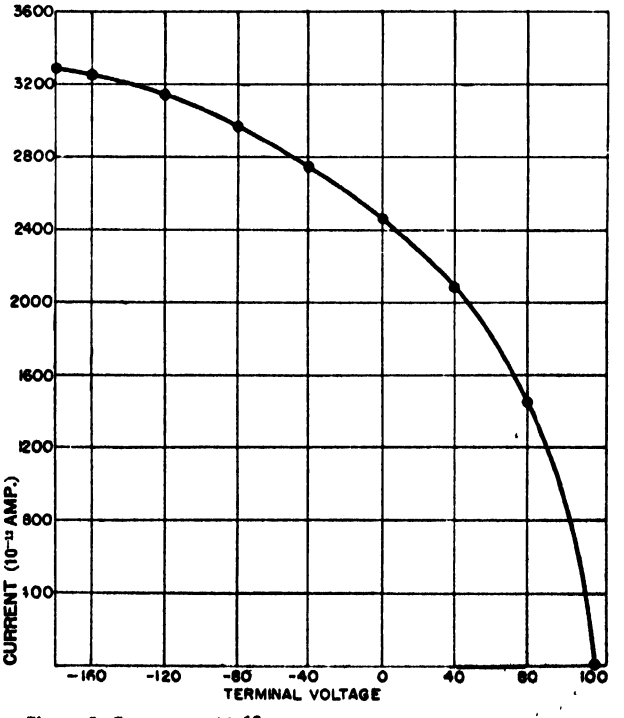

Figure 9. Current ($\times 10^{-12}$) vs voltage for Tracerlab model 14A

Table II. Physical and Electrical Characteristics of Two Experimental Units

	Battery No. 1	*Battery No. 2*
Radioactivity	57 curies Po^{210}	146 curies Po^{210}
Thermocouple	Silver-soldered chromel-constantan	Welded chromel-constantan
Number of junctions	7	40
Internal resistance	0.25 ohm	15 ohms
Maximum voltage	0.042 volt	0.750 volt
Current at maximum power	0.085 amp	0.025 amp
Temp. grad. between junctions	78°C	224°C
Maximum power delivered	1.8×10^{-3} watt	9.4×10^{-3} watt
Activity of Po^{210} in watts	1.8 watt	4.65 watt
Efficiency	0.10%	0.20%

where: K = Boltzmann's constant, T = absolute temperature, e = electronic charge, I_0 = reverse saturation current, and I_s = short circuit current.

His measurements were made on silicon and germanium p-n junctions, about ¼ cm^2 in area; the radioactive source was 50 millicuries of Sr^{90}-Y^{90}. The silicon device generated a maximum voltage of 0.25 volts and a short circuit current of 10^{-5} ampere, whereas the germanium device yielded 0.030 volts and 2.5×10^{-5} ampere. The multiplication factor was computed as 1.5×10^5 and 1.9×10^5, respectively, after correcting for wafer thickness as compared to depth of beta penetration and for surface recombination. The over-all efficiency for both devices was given as 0.4 per cent: with a device of optimum design, this may be increased to about 2 per cent. Figure 11 shows one type of battery.

Characteristic voltage versus current curves are shown in Fig. 12. The useful life of the device is considered to be comparable to the 25-year half-life of the Sr^{90} source. It was observed, however, that radiation damage to the junction seriously limited this life. The use of lower energy betas may materially reduce the extent of the radiation damage and thereby improve the life of the junction.

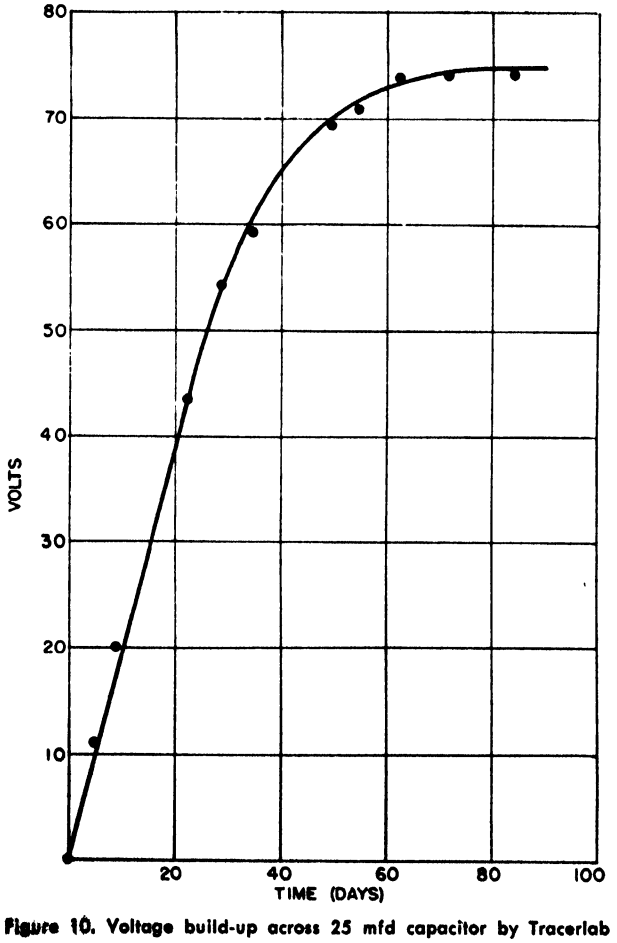

Figure 10. Voltage build-up across 25 mfd capacitor by Tracerlab model 5A

Thermopile Type

A current flow will be produced when two dissimilar metal conductors are joined together to form a closed circuit and the junctions, thus formed, are kept at different temperatures. This phenomenon is the well-known Seebeck effect. The thermoelectric power (volts/degree) of any thermocouple is the change in electromotive force for each degree change in temperature of the hot junction:

$$\frac{de}{dt} = B + Ct$$

where B and C are constants determined from the change in E of the hot junction for any two temperatures.[22]

Jordan and Birden[23] described a generator, using the thermoelectric principle, in which the heat source was a radioactive material. They analyzed the theory as applied to the thermopile device and described the fabrication and performance of two units, one powered by 57 curies and the other by 146 curies of polonium-210. Figure 13 gives some details of the construction of the battery. Table II shows pertinent characteristics of the two experimental units.

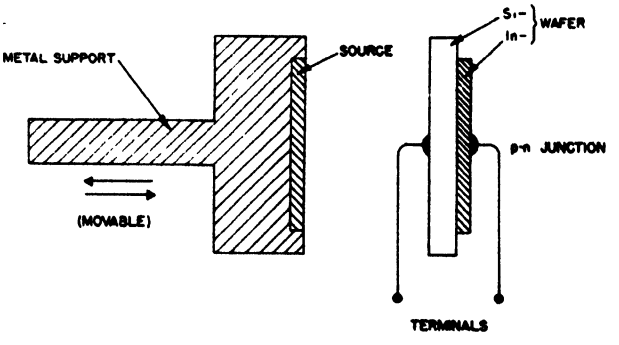

Figure 11. Electron voltaic type

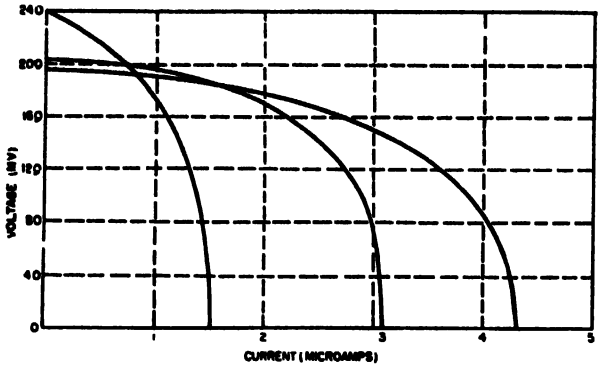

Figure 12. Current vs voltage for various silicon *p-n* junction devices

The maximum, or open circuit, voltage is seen to be dependent upon the number of thermocouple junctions and the quantity of radioactivity or temperature gradient between the hot and cold junctions; it is inherently independent of ambient temperature. The open circuit voltage decreases with time, the rate being determined chiefly by the half-life of the radioactive source and only partly by the structural design.[24] For a polonium-210 source (half-life 138 days) the rate was given as 0.5 per cent per day. Sr^{90}, with a half-life of 25 years, may be used as a source other than Po^{210}. The rate of voltage decrease, using a Sr^{90} source, would be less than 0.01 per cent per day and the useful life of a strontium battery approximately 70 times that of the Po^{210} device. The amount of strontium-90 required to produce an equivalent power output would be proportionately greater.

CONCLUSION

It should be evident that the technology of nuclear batteries is still in its very beginnings. The physical and electrical characteristics, briefly reviewed for the different radiation energy conversion devices, should be accepted merely as trends in a transient phase of nuclear battery development.

ACKNOWLEDGEMENT

We wish to acknowledge with appreciation the discussions and assistance of Dr. Erich Schwarz; Mr. John H. Coleman of Radiation Research Corporation, West Palm Beach, Florida; and Mr. Alexander Thomas of Tracerlab, Inc., Boston, Massachusetts.

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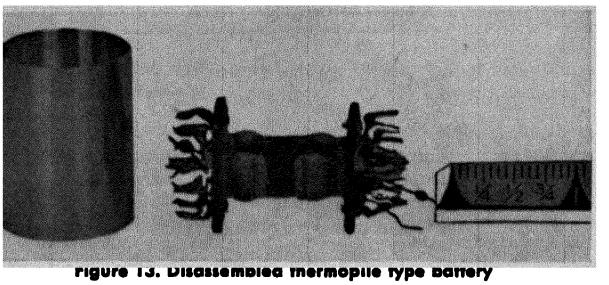

Figure 13. Disassembled thermopile type battery

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† Thermoelectric generator.

The Direct Transformation of Nuclear Energy into Mechanical Power and its Application to Very Low Power Devices

By R. Keller, A. Krassoievitch and J. M. Favey,* Switzerland

From the days of Moseley, back in 1913, through Rappaport, Linder and Christian, in 1951–1954, many authors have worked on the direct utilization of radioactive sources in high-voltage, low-current, generators. The early papers aroused but little interest, in spite of the originality of the process, and long remained but isolated laboratory achievements, mainly due to the fact that the *natural* radioactive sources were scarce and costly. Now, for the last few years, with the development of the industrial techniques of nuclear physics, a great many fission products or artificial sources of radioactivity have become available, if not cheaply, at least readily and in substantial amounts, their main sources of supply being, as is well known, in the countries which operate atomic reactors.

Thus it is that the ideas of the early workers recently were picked up again, giving rise to interesting generator designs (often called "piles" in the popular periodicals) developing high voltages but low powers with isotopes, for instance, such as strontium-90 and tritium. The latest papers even mention the possibility of achieving larger currents, under lower voltage, by bombarding p-n junctions with β-particles coming from an artificial source of radioactivity.†

Thus, it now seems possible to make use of the radioactive energy developed by the nuclear process in order to make low power generators, the "life" of which would be 20 to 30 years on an average, and which would be simple, sturdy, and relatively cheap.

Even now, the following question is in order: how can these generators be adapted to very low power mechanical or electromechanical devices, the prime function of which would be, in the last analysis, to transform this radioactive (or electrical) energy into mechanical energy?

As the matter now stands, it would seem to us that the question admits of two answers, on which we will endeavor, in this paper, to expatiate at some length:

1. By using the generators "as are," through "motors" which transform the electrical energy into mechanical power.

2. By transforming the radioactive energy as directly as possible (without going through the stage of a fixed generator), into mechanical energy.

We shall concentrate our attention on the second solution, and show that it is possible, along those lines, to make a device which will be of some interest for very low power applications, particularly in the watchmaking industry.

Before going into the matter, let us review the practical solutions already found, particularly in the form of high-voltage generators.

NUCLEAR GENERATORS

The principle on which they operate is very simple: a certain amount of radioactive material (a beta emitter for instance) is deposited on an insulated electrode, located in a vessel full of gas under low pressure. Another electrode (the "target") gathers the particles emitted, and thus becomes negatively charged with respect to the former. In fact, it can be stated that this amounts to the charging of a capacitor by means of electrons which are caused to pass from one electrode to the other. In this fashion, it becomes possible to store energy under high voltages, which may reach, under certain conditions, several hundreds of kilovolts, in other words, to carry out the direct transformation of nuclear energy into electrical power. Naturally, the current which such a generator is capable of delivering remains very low, as well as its power.

In fact, it can readily be shown that the maximum power which can be achieved is of some 4 to 5 microwatts per millicurie, for a β-emitter for instance. Figure 1 shows a simple diagram of such a generator.

The source most commonly used, in the current models, is strontium-90, which emits β-particles, the half-life of which is about 30 years, for an energy of about 0.7 Mev.‡ Sr^{90} is transmuted, by that emission, into yttrium-90 which, in turn, by 2.2 Mev emissions, is turned into a stable isotope, zirconium-90, with a half-life of some 60 hours.

The advantages of the use of Sr^{90} are many: it is fairly readily available, its price is not prohibitive, its half-life is relatively long, it does not emit gamma rays§ (if free from impurities) and its chemical preparation is easy. In addition, the energy of the electrons it releases is high, and there are no gaseous byproducts.

* Laboratoire de Recherche, Patek, Philippe & Co., S.A., Geneva.

† Beta particle = high-energy electron.

‡ 1 Mev = 10^6 electron-volts, namely the energy acquired by an electron accelerated through a potential drop of one million volts.

§ Gamma rays are very energetic (very hard) X-rays.

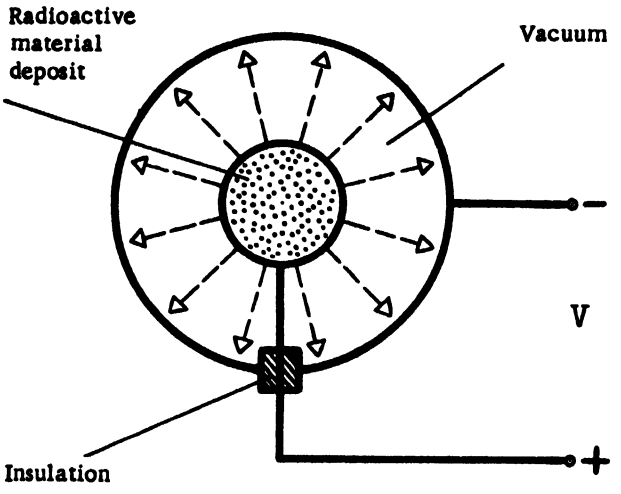

Figure 1

The main difficulties which arise, in making such a generator, are insulation problems, since the current used for charging is very weak and the behavior of a dielectric under very low pressure and radioactive bombardment poorly known.

Linder and Christian made a generator having a maximum voltage of 365 kv, using 250 millicuries[¶] of Sr^{90}, under a pressure of 10^{-3} mm of mercury. Zero voltage current was 1.05×10^{-9} amperes.

Naturally, it is possible to make lower voltage generators, which simplifies the insulation problems, but one can expect less power from these generators for the relatively low voltages.

Other prototypes were made, in the USA as well, by Rappaport and Linder, in which the "vacuum" was replaced by a dielectric, such as polystyrene or mica (Fig. 2).

This device offered some advantages: the vacuum installations were eliminated, the voltage obtained high, the $S \rightarrow C$ distance could be covered by high energy particles and, when traveling in the opposite direction, low energy particles were stopped by the dielectric. On the other hand, several interesting studies could be made, particularly on the behavior of the irradiated dielectric, the secondary emission and the absorption of β-particles by matter.

With sources of some 50 mc of Sr^{90}, the authors reached voltages of some 7 kv by using polystyrene as the dielectric. In addition, they were enabled to study the effects of the bombardment on the material used, as well as that of the thickness of the dielectric on the speed at which the device was being charged. They came to the conclusion that the dielectric could be substituted for the vacuum to good purpose.

Finally, a third type of generator was recently mentioned by Rappaport: namely a very low voltage generator. This was a p-n junction (germanium or silicon) bombarded by a 50 mc source of Sr^{90}. The current was much stronger than in the generators described above, reaching 10^{-5} amp (short circuit) while the open circuit voltage did not exceed 250 mv. The multiplication factor of the current was of some 1.5×10^{-5} for silicon.

The electrical power of such a generator was some 0.8 microwatt (transformation efficiency, about 0.4%). The author believes he will reach 2 μw by making a closer study of the device.

Such a generator was used for feeding a transistor oscillator operating in the audio range. Nevertheless, some parasitic effects of the bombardment on the junction crystals appear to limit its useful life.

To these three generator types, some of which now already are in production, let us add those which work on the same principle, but in which tritium is the radioactive material, and which are also mass produced. They operate under a voltage of approximately 400 v and can deliver a power of 0.01 to 1 μw.

We thus have rapidly reviewed the principal achievements of the day and can now deal with the principal subject of this article, namely the use of this radioactive energy in very low power devices, more specifically its transformation into mechanical energy.

UTILIZATION OF HIGH-VOLTAGE NUCLEAR GENERATORS

The first idea which comes to mind, when dealing with high-voltage nuclear generators delivering a low current, is the use of electrostatic devices for the transformation of electrical energy into mechanical power. It should be made clear that the other type of generator, that which delivers a low voltage, could be used with conventional electromagnetic devices, but this possibility will not be explored here, since our work has not progressed enough in the direction of an industrial embodiment.

Limiting ourselves, for the time being, to the field of watchmaking in which the powers which come into play happen to be very small, it will at once be apparent that there are two possible applications for

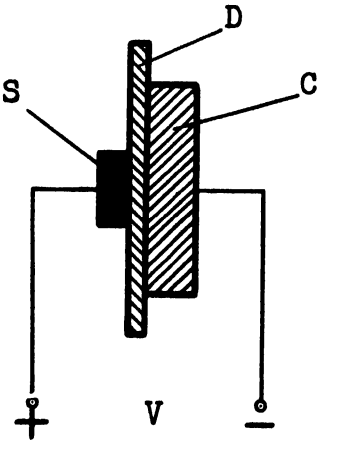

Figure 2. Principle of operation of the dielectric type of nuclear generator: (S) radioactive source; (D) dielectric; (C) collector or "target"; and (V) voltage obtained at terminals

¶ 1 millicurie = 1 mc, the quantity of a radioactive material which emits the same number of particles as one milligram of radium.

such an electrostatic device: (*a*) as an oscillator (regulating device); (*b*) as a winding-up engine (driving a spring or microspring) coupled with a conventional regulating device, through a reduction gear train giving a more or less important ratio.

It should be remembered that, as an oscillator, the period of this device will be relatively large, by reason of the charging time of the generator. In addition, adequate precision is hard to achieve, since the duration of the impulse, from the very nature of things, is rather long.

Let us remember that a particularly simple prototype of an oscillator (torsion wire for instance) was made by one of the authors at the Geneva Institute of Physics, and that it operated perfectly. Naturally, the only source of energy it used was a radioactive isotope, in this case some Sr^{90}.

In addition, long before the first nuclear generators appeared, the Patek Philippe laboratory studied, for other purposes, an entirely electrostatic regulating device (oscillator) which operated on the basis of a very simple principle, and now can be adapted to high-voltage supply from a nuclear source.

The oscillations were perfectly kept up and, but for a few points of detail, the operation was perfect when the device was tested with a common or conventional type generator. Its adaptation to a radioactive type generator raises several problems which are new, but not essentially different from those encountered before.

As regards the winding engine, it can readily be visualized, either as an electro-motor in the true sense, which places a spring under load, or again as a mechanism which transmits its torque to a moving part located relatively close to the conventional adjusting device through the storage of a small amount of power (microbarrel). In this last case, as it were, one would have a "loose" coupling. Rotary motion of the engine can take place, either continuously or by relaxation (this point will be taken up again with regard to the direct transformation of radioactive energy into mechanical energy).

Thus, the devices which have just been very briefly described above play the part of actual electrical engines, which transform electrical energy into mechanical power. Accordingly, consideration has been given to the entirely conventional system shown in Fig. 3.

We shall now see how it is possible to do without such a system and study, in greater detail, the main purpose of this article.

DIRECT TRANSFORMATION OF NUCLEAR ENERGY INTO MECHANICAL ENERGY

The principle is extremely simple: a radioactive deposit is to be made *directly* on the moving assembly of the engine, which is always of the electrostatic type. This rules out the need for a cumbersome outside fixed generator having a complicated set of connections, at times involving friction contact

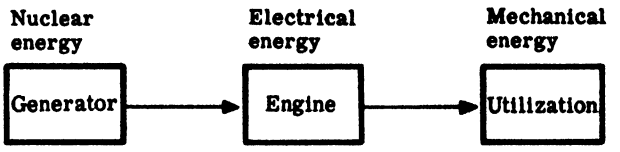

Figure 3

(Patek Philippe patent). Figure 4 shows a schematic diagram of such a device.

The rotor is electrically insulated from the stator, and we are again dealing with the process of charging a capacitor, hence with the creation of electrostatic attraction forces, and finally with the displacement of a rotor plate which can move with respect to the stator.

It will readily be seen that we have a torque, thus mechanical energy, usable on the rotor shaft.

Naturally, for continuous operation, the capacity must be discharged, which immediately leads to the following two possibilities of operation: (*a*) continuous rotation, and (*b*) relaxation.

The prototypes made and studied at the Patek Philippe laboratory were of the two types described above. Nevertheless, the relaxation type system was the only one considered, for being much more advantageous from a mechanical standpoint, particularly as regards losses by dry friction.

It can readily be shown that the usable work, in a mechanism of that type is

$$\tau u = i \int_0^T v(t)dt - W_c \qquad (1)$$

in which: i = radioactive current; T = period (time elapsed between two discharges); $v(t)$ = voltage variation during the cycle, as a function of time; W_c = energy stored in the capacitor.

On the other hand, since the torque is given by:

$$M = \frac{V}{2}\frac{\partial C}{\partial \theta} \qquad (2)$$

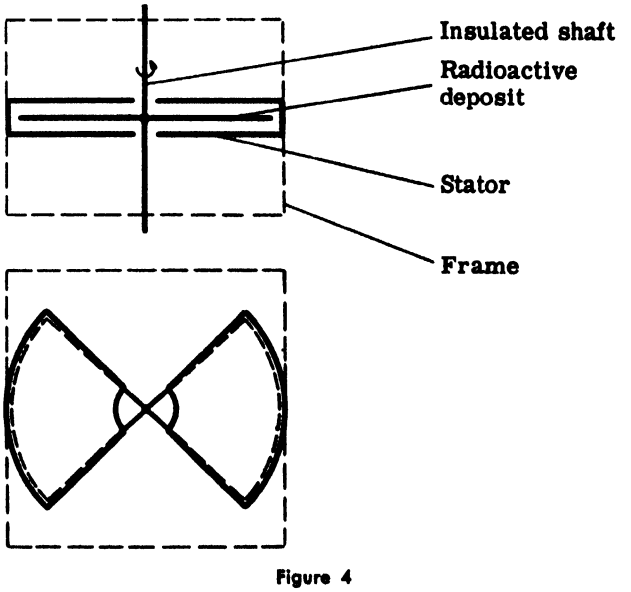

Figure 4

and if provisions are made for $\delta c/\delta\theta$ to remain constant, as well as the angular speed (w) of the rotor, one gets:

$$\frac{\partial C}{\partial \theta} = \frac{1}{\omega}\frac{dC}{dt} \tag{3}$$

from which dC/dt = constant. Or again:

$$V = \frac{it}{C} = \frac{it}{\frac{dC}{dt}\cdot t} = \text{const.}$$

Thus, from Equation 2, M = constant. It can be shown, by rearranging Equation 1, that with $\tau u = M\omega T$:

$$M\omega T = i\int_0^T v(t)dt - \frac{1}{2}C_t V^2 \tag{4}$$

$$MT = iVT - \frac{1}{2}C_t V^2$$

in which C_t is the maximum capacity, just prior to discharge. Thus, Equation 3 can be written:

$$\frac{\partial C}{\partial \theta} = \frac{1}{\omega}\frac{C}{T}$$

and with Equation 2, one will get:

$$\underbrace{M\omega}_{\text{useful } P} = \underbrace{iV}_{\text{generator } P} - \underbrace{M\omega}_{\text{power lost in the discharge}}$$

Thus, useful $P = (\frac{1}{2})$ P gen.

Thus, when disposing of 50 mc of Sr^{90}, half of the electrons of which are lost by absorption, and working under 10,000 volts: $i = 300 \times 10^{-12}$ amp; P gen. $= iV = 3 \times 10^{-6}$ watts $= 3$ microwatts, and useful $P = 1.5$ μw which is sufficient to operate the works of a clock.

Figure 5 shows a schematic diagram of one of the devices made by the Patek Philippe laboratory. This was a nuclear engine of the direct transformation type, relaxation operated, and coupled to the middle-sized gear of a clockwork through a very weak spring.

The overlap angle was about 90 degrees, and discharge took place at maximum overlap (maximum capacity).

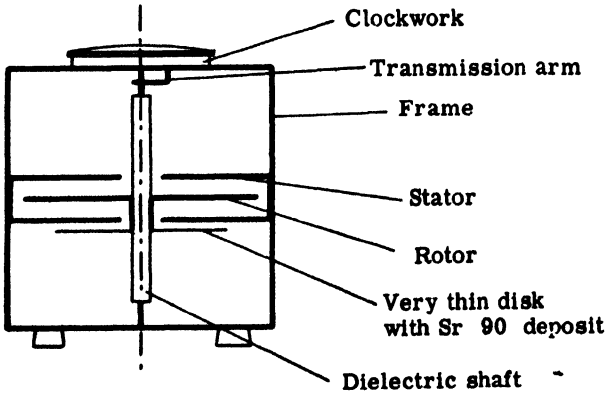

Figure 5

Since half of the generator power was lost during discharge, it was thought that a part could be recovered by modifying the manner in which the plate overlap varies (sudden change in capacity) in such a way as to come to the end of the stroke with very little voltage.

This mechanism operated under the following conditions at the end of the year 1954, as follows: vacuum, about 10^{-4} mm Hg; voltage, 6 to 7000 volts; period, 10 minutes approximately; and amplitude of balance motion, 200 degrees.

The main difficulties encountered in the design and manufacture of such an engine are due to several factors, namely:

Insulation Difficulties

The dielectric must meet very exacting specifications. It must not change under radioactive bombardment and, similarly, it must not release gas under a high vacuum. Polystyrene and Teflon had to be abandoned in favor of glass and porcelain. In addition, the dielectric-vacuum interface often was the seat of microdischarges, as well, in fact, as the space between the electrodes. The true mechanism of these discharges still is poorly known, particularly in the presence of a nuclear bombardment. It is believed that it bears a strong correlation with gases absorbed by the material (metallic or other) such, for instance, as hydrogen.

Degassing

All materials, even the stablest of them, release a small amount of gas under such high vacuum and preliminary degassing, therefore, is necessary. This, however, is not very serious where the vacuum is maintained. In a sealed vacuum, the presence of "getters" is known, even now, to be most useful, and could be applied, for instance, to future devices.

Radioactive Material Deposit

It is rather difficult to achieve this deposit in a stable fashion without any risks of absorption and substantial self-absorption by the carrier, if the yield is to be satisfactory. This is one of the points on which the researchers now concentrate their efforts.

Choice of the Material for the Fixed and Movable Electrodes

This choice must be made with the objective in mind of avoiding a new emission of electrons, where it is bad, and favor it where useful. Since this depends a great deal on the atomic number of the element under consideration, a light material is chosen for the fixed parts (Al, for instance), while a heavy element is used for the rotor. Let it be specified that this re-emission is all the greater as the bombarded element has a larger atomic number.

Finally, it is necessary, in order to operate with the most favorable solid angle, that the part of the engine which "gathers" the electrons, should sur-

round that which contains the isotope as much as possible.

Sharp angles also are to be avoided, in order to rule out any effects due to field edges, which would be particularly bad in this type of equipment.

Needless to say that very special care must be given to the making of the mechanical parts of the device, for very obvious reasons.

It will be seen, from all the above, that we now have a real possibility of making use of nuclear energy in very low power mechanisms and, particularly, in the field of clockmaking. The fact remains that the road which still has to be traveled before an industrial version can be made is fairly long. The change, in particular, from a compensated vacuum to a sealed vacuum, the transmission of motion (by a magnetic device for instance) outside the capsule, and the delicate degassing problems come to the forefront.

It may not be out of order to feel that all these difficulties will be overcome in a short time, and that one of the peaceful applications of nuclear energy, its direct transformation into mechanical energy, soon will be an industrial reality.

We propose, in a paper to be published at a later date, to come back in greater detail, scientifically speaking, on this problem, the multiple aspects of which we have now merely touched upon.

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Record of Proceedings of Session 23C

SATURDAY MORNING, 20 AUGUST 1955

Chairman: Mr. J. Guéron (France)

Vice-Chairman: Mr. H. Wei (China)

Scientific Secretaries: Messrs. A. Milojević and A. Finkelstein

PROGRAMME

23C.1. Polymerisation induced by radiation

P/168 The effect of gamma-radiation on some chemical reactions of possible industrial importance..... L. C. Anderson *et al.*

P/465 Recent developments in the irradiation of long-chain polymers ..... A. Charlesby

DISCUSSION

23C.2. Food sterilization

P/172 Progress and problems in the development of cold sterilization of foods..... B. E. Proctor and S. A. Goldblith

P/225 Prevention of human helminthic diseases by gamma radiation of food, with particular reference to trichinosis..... H. J. Gomberg and S. E. Gould

P/175 Sterilization of medical supplies with gamma radiation ..... L. E. Brownell and J. J. Bulmer

DISCUSSION

23C.3. Conversion of radiation into electricity

P/794 Studies on the properties of an electrolytic cell consisting of an electrode system in a chloroform-alcohol solution under γ-irradiation ..... C. G. Österlundh and E. Haeffner

P/169 The direct conversion of radiation into electric energy.... E. G. Linder *et al.*

DISCUSSION

The CHAIRMAN: This session is devoted to the applications of fission products.

There is no need to dwell on the importance fission products are destined to assume in the near future. In his extremely well-balanced statement yesterday evening on the future of atomic energy, Sir John Cockroft gave those products the prominence they deserve (Volume 16, these Proceedings).

None of the papers to be presented today is specifically concerned with fission products, but all of them presage an extensive use of these sources of radiation in the future.

The first two papers deal with the chemical reactions induced by radiation.

Mr. J. J. MARTIN (USA) presented paper P/168.

Mr. A. CHARLESBY (UK) presented paper P/465.

DISCUSSION OF PAPERS P/168, P/465

The CHAIRMAN: The two papers we have just heard are now open to discussion. I should first like to point out that the papers relating to this session which it was not possible to read include one by Mr. Michaelis dealing with the same type of work as the papers just presented.

I will begin by giving the floor to Mr. Magat, who has a question for Mr. Martin.

Mr. MAGAT (France): I think it is clear to anyone who has done a little radiation chemistry that ionizing radiation is an excellent means of producing free radicals, and that it will therefore probably be used in industry as an initiator for chain reactions—for halogenation, polymerisation and oxidation. But I think that if we are to achieve rapid success in using fission products, it is first necessary to make reliable and reproducible experiments which will enable us to determine, say, whether, for a given reaction, very intense and highly localized sources should be used or whether, on the contrary, since the speed of the reaction increases only with the square root of the intensity, [and the length of the chains—whether of the polymers or halogenation chains—decreases] it may be preferable to use a complex of relatively weak sources giving an irradiation field of average intensity but uniform in space.

I feel that this is a problem which we have to solve fairly quickly, as it is essential to know, for

industrial radiochemistry, whether sources with high specific activity have to be prepared or whether, on the other hand, those of low specific activity can be used. Both the cost of the sources and of the installations will, in fact, be very different in the two cases.

To give you an example based on the results obtained by the Manowitz and Ballantine group, in the United States, and our own group, in Paris, the efficiency of polymerising methyl methacrylate can be determined fairly accurately. If we use seven sources of 15 curies—i.e., a hundred or so curies in all, these sources having a height of 20 cm and a diameter of 5 mm—and if we arrange them suitably in a receptacle 50 cm in diameter and 20 cm in height, something between 20 and 25 tons of polymethacrylate will be obtained a year, working at 60°. If the intensity of these sources is quadrupled, a factor under 2 would be obtained for efficiency, for with very intense fields the speed of reaction increases more slowly than the square root of the intensity.

In conclusion, I would stress that there is not much point in indicating the *G* value for chain reactions as the number of molecules converted per 100 ev, as this number depends to a very large extent on the speed with which the dose is given. Reference should be made, rather, to the number of primary radicals formed, for it is by adopting that basis that the efficiency of the reaction can be calculated for any field, intensity or pressure.

Mr. MARTIN (USA): I certainly think that the comments were well made concerning the effects of the intensity of the source of the reaction. In our calculations at the University of Michigan, we assumed that the rate of chemical reaction varies approximately as the intensity, rather than as the square root of the intensity, because, in the particular case that we quoted in our paper, this gave a more conservative estimate of the cost. In other words, it required a larger source.

We have made some experiments in which we varied the intensity and we found that the usual reciprocity law holds in that the radiation yield depends approximately only upon the total dose and is more or less independent of the rate at which the dose is delivered. I certainly think, however, that there is much more to be done in this respect, especially with high-intensity sources.

Mr. LÉVÊQUE (France): Can Mr. Martin explain the differences in radiation yields given for the polymerisation of ethylene? Looking over the table he has drawn up, I note, in fact, that the first two tests were made at the same temperature (217° and 220°C) and absolute pressure (1100 and 1175 psi), and that the yields recorded differ almost in the ratio of 3 to 1 (4030 to 1400). It is important, I think, to have an exact knowledge of this yield in order to assess the economic possibilities of this method.

Mr. MARTIN (USA): The question is very good. We have found a considerable variation in the radiation yield of polyethylene. In other words, in one run the yield might be several-fold greater than in another run. In attempting to find out what is the cause of this, we have made a number of studies in which we deliberately added inhibitors of various types, particularly oxygen. Also, in a very recent experiment—performed within the last month, as a matter of fact—we used some very pure ethylene. It had been especially refined by the Dow Chemical Company, and we obtained radiation yields about four times greater than anything reported in this paper. We are strongly of the opinion that, if we can obtain the very pure chemicals, we can obtain much larger yields in most of our chemical reactions. Furthermore, this is not limited to the production of polyethylene. We have found precisely the same thing in the chlorination of some of the aromatic hydrocarbons, and we now have a very special technique of purifying an aromatic hydrocarbon by chlorinating it first in the presence of a small amount of ultraviolet and then carrying out the rest of the reaction in the presence of gamma radiation. Undoubtedly, this purification step could also be carried out in the presence of gamma radiation; we simply use ultraviolet in the laboratory for convenience. This means that we chlorinate the hydrocarbon for just a short time in the presence of radiation, distill off the aromatic hydrocarbon which has not been chlorinated, and use the distillate in our experiments.

Mr. BRIMUS (Romania): In Romania we have tried several industrial methods for the manufacture of hexachlorocyclohexane; for example, photo-chemical chlorination by sunlight or ultraviolet rays, chlorination without light with reaction initiation by free radicals (nitro-iso-butiro-nitril) and chlorination without light with ice and liquid chlorination without any catalyst.

All these methods give a yield of 12 per cent active isomers. In Romania we have adopted the industrial method without light and without catalyst. We consider that the method of chlorination in the presence of rays cannot compete with this process.

I should be glad to hear if Mr. Martin could give us some further information on this problem.

The CHAIRMAN: Before I ask Mr. Martin to reply to this question, I wonder if Mr. Brimus could give us his opinion, since he has carried out experiments with these various methods of inducing polymerisation reactions.

Mr. BRIMUS (Romania): We believe that the gamma radiation method may be superior to the method without light, as it may give a higher yield than we obtain.

Mr. MARTIN (USA): It happens that we are currently working on this very problem of trying to determine how to increase the percentage of the active gamma isomer in benzene hexachloride. Our results to date indicate that this percentage, which is approximately 12 in the industrial process, is dependent mostly upon the temperature and not upon the inten-

sity of the radiation. In our most recent experiments, we are endeavouring to chlorinate benzene at temperatures of zero Centigrade and lower. The information presented in our paper today is based largely upon reactions in the neighborhood of 20° to 25°C, which is considerably higher. We have great hopes and, on the basis of preliminary experiments, we believe that the percentage of gamma isomer will be increased by making runs at a much lower temperature than the 20° to 25°C runs reported here.

The CHAIRMAN: I also would like to put a question to Mr. Martin and to Mr. Charlesby as well: are they in a position to compare the polyethylenes obtained by radiation or modified by radiation, with the product obtained by polymerisation at low pressure and low temperature which we have recently been told has been obtained in Germany with extremely interesting properties.

Mr. MARTIN (USA): Although we have measured the physical properties of the solid polyethylenes that we have made, we have not yet been able to obtain any of the commercial products being manufactured through the new, low-pressure Ziegler process. Therefore, we do not at this time have any direct comparison. We feel that, probably, our polyethylenes are more highly cross-linked than those produced by the low-pressure Ziegler process, but this question will certainly require further study.

Mr. CHARLESBY (UK): I feel that a considerable amount of information comparing the irradiation-produced polyethylene with the polyethylene produced by the Ziegler process may be deduced from a study of such things as density. The density figures of both the Ziegler-process polyethylene and the irradiation produced polyethylenes—these figures were given this morning—indicate that both are much more highly crystalline than the more conventional polyethylene. The Ziegler polyethylene is almost certainly of a much higher molecular weight than the irradiation polyethylene. The two, however, have the common property of being almost entirely linear as compared with the conventional polyethylene which is commercially used at the moment.

Mr. MAGAT (France): I do not wish to ask a question, but to offer some comments or additional information.

In his very interesting paper on the effects of radiation on long-chain polymers in the form of solids or in solution, Mr. Charlesby made brief reference to an extremely important factor—the presence or absence of oxygen during irradiation. With my colleagues, Mr. Wall and Mr. Durup, I have succeeded in establishing that oxygen plays a very important role in the degradation of long-chain polymers in solution. The very fine research carried out by Karpov and his colleagues in the Soviet Union and by Chapiro in France has also shown that oxygen plays an important role in the cross-linking of solid polymers, particularly polyethylene. Soviet investigators have demonstrated with the infrared spectroscope the existence of intermolecular bridges consisting of oxygen and corresponding to ether bridges. In studying cross-linking in the free atmosphere at low pressure, Chapiro, however, demonstrated that some of the bridges formed were unstable and fractured between 80° and 150°C. He advanced the hypothesis that these were peroxide bridges. In order to determine whether the variations in mechanical properties observed were in fact due to a break in the chemical link, we added acrylonitrile monomer to pre-irradiated polyethylene and heated the mixture to 120°. Under these conditions, the polyethylene is swollen by the acrylonitrile and a very rapid polymerisation of the latter was observed. The polyacrylonitrile formed is completely bound chemically to the polyethylene chains; in other words, grafted polymers are obtained.

This therefore provides a second radiochemical method of preparing this type of co-polymers, which are difficult to produce by conventional chemical methods.

I would remind you that at session 12B, I gave a more detailed description of another procedure for preparing polymers consisting simply of irradiating a polymer swollen by a monomer of a different type. It is extremely remarkable that the object retains its form during the process of grafting, even if its volume is increased thirty times. For example, from a film of polyethylene weighing 0.12 gm we obtained a film of polyethylene grafted with acrylonitrile weighing almost 3 gm, i.e., a film containing only 3 per cent of the original polyethylene and 97 per cent of acrylonitrile. It nevertheless was still a film.

The preparation of graft polymers constitutes a possible application of ionising radiations and hence a possible use of fission products in the very near future, since the amounts required are moderate and the procedure is very much simpler than the conventional procedures otherwise employed.

Mr. B. E. PROCTOR (USA) presented paper P/172.

Mr. H. J. GOMBERG (USA) presented paper P/225.

Mr. L. E. BROWNELL (USA) presented paper P/175.

DISCUSSION OF PAPERS P/172, P/225, P/175

The CHAIRMAN: Before opening the discussion, I should like to draw your attention to the fact that five papers were submitted in connection with this second part of the meeting which were not selected for presentation. One of these, a short memorandum from Japan, deals with attempts to preserve fish in a de-oxygenized atmosphere.

I have received a number of questions for one or another of the three authors who have just presented their papers. The first question is from Mr. Comar.

Mr. COMAR (USA): I should first like to ask Mr. Proctor what intervals of time and effort are needed to determine by laboratory tests whether food

subject to radiation sterilization may be undesirable from a health standpoint.

Mr. PROCTOR (USA): In this respect, I must refer to the regulations of our Food and Drug Administration in the United States. They require that feeding be carried out on small laboratory animals such as rats through several successive generations in order to determine the effect both on development, on growth and from the standpoint of reproductivity. Beyond that, they require that a considerable number of larger animals such as dogs be fed. The complete time interval required for this type of experimentation is at least two years. The food and the care involved make it a very expensive procedure.

Mr. COMAR (USA): My next question is directed to Mr. Gomberg. Are there any specific tests being made on diseases other than trichinosis at this time?

Mr. GOMBERG (USA): We have just started tests on *ascariasis lumbar cortis* and we are planning to start tests very shortly on *taenia* in our laboratory. We are also hoping to interest other laboratories in following a similar line. If I can speak for a moment, I have four slides which I wish to show concerning the effect of radiation on inhibiting the development of *ascaris* eggs.

Slide 1 shows a group of *Ascaris* eggs which have just been removed from the female. The albumin coating on the outside of the egg can still be seen. In the subsequent slides, this will have been washed away.

Slide 2 is after seven days. You can see that there is advanced cleavage. The egg has started to develop.

Slide 3 is after thirty-four days. You can see the completed larvae formed, in fact, one has broken out of the egg. This is the truly infective stage when the larvae emerges in the intestine.

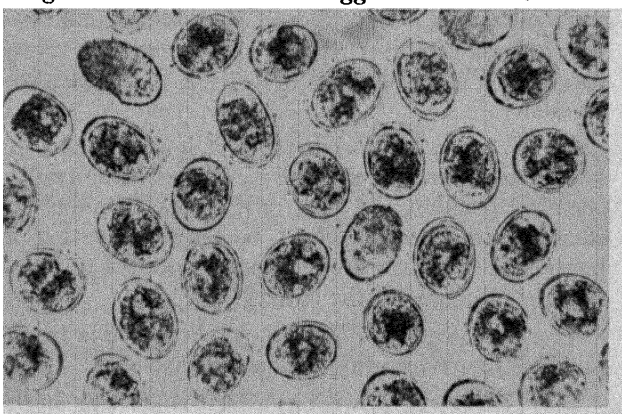
On Slide 4 is a group of eggs 34 days after having been irradiated at 100,000 roentgens. You see that there are no complete larvae forms present. The ova divided to some extent, but then, development was completely arrested. We are now testing to see whether we can find particularly sensitive points in the life cycle so as to reduce the amount of radiation. As I have indicated, we plan several tests with other parasites.

Mr. KOWALSKI (Poland): Have any attempts been made to use ionizing radiation for destroying the virus of hepatitis in lyophilized human plasma.

Mr. GOMBERG (USA): I have no information on that. I am sorry.

Mr. LEBORGNE (Uruguay): I want to know if Mr. Gomberg has any experience or project with ionization radiation in hydatid cyst disease. That is really a very important problem in our country.

Mr. GOMBERG (USA): We have selected the hydatid disease as an example of one in which we



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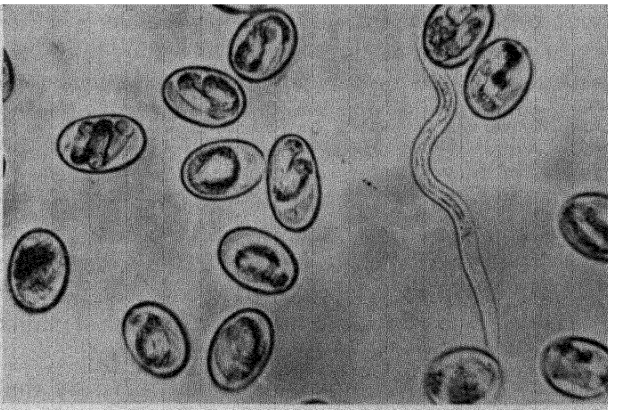

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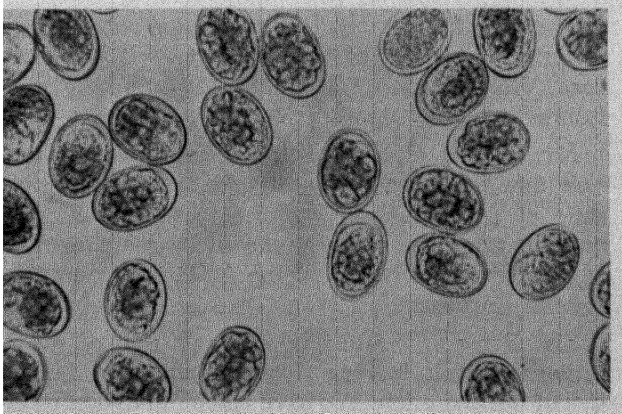
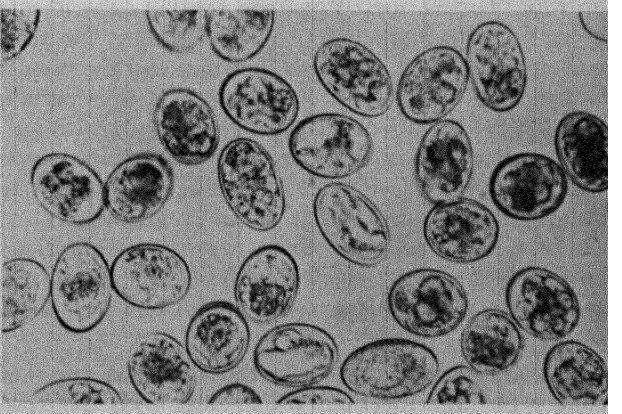


Slide 2



Slide 4

feel important research can be done. We have not as yet started. As I have indicated, this field has just opened. As far as we are concerned, all I can say is that we would be happy to co-operate with any group. This disease is more native to South America, particularly Argentina. We feel that it would be most logical for the work to be done there. We would offer any co-operation that we could to help the research work get started.

The CHAIRMAN: We also have some comments from Mr. Magat.

Mr. MAGAT (France): As a physico-chemist, I am extremely concerned at the use of huge doses of ionizing radiations for the sterilization of food. We know that radiations always have two different effects; on the one hand, they produce free radicals and on the other, if oxygen is present, they produce peroxides.

Where we are dealing with a viscous medium and particularly with a viscous medium divided into small cells, as is the case with biological tissues, radicals can only be eliminated by extremely slow recombination and can survive for months at least and probably for years. If peroxides are produced, they will be decomposed into radicals either by heat or by processes of oxydo-reduction during the preparation or ingestion of food. While we still have no precise information about the role of free radicals in the biological process, we know from the experiments of Latarjet that peroxides have a very specific biological action, at least on viruses. I therefore wonder whether experiments carried out on relatively short-lived animals are capable of providing us with information on the results of the ingestion of products containing large quantities of peroxides or free radicals over a period of fifty years.

That does not mean that the use of radiations for sterilization will always be excluded because even if this danger exists, some means of eliminating these radicals or peroxides before ingestion will possibly be found. But this is a matter to which I think attention should be paid from the very outset.

Mr. PROCTOR (USA): This comment is very well taken. I think Mr. Magat will be interested to know that in our country, besides many experiments going on with animals, there are some feeding experiments going on with humans as well. Of course, the tests will necessarily be of longer duration and the results will not be known for a long time. But it is certain that the investigations that are being made with animals are pertinent to those which are being made with foods, and I think that each can be helpful to the other in the work that is being conducted.

The CHAIRMAN: Are there any further questions on the three papers which have been submitted or in connection with the discussion which has just taken place?

We will now pass on to the third and last group of papers for this meeting, which deal with the conversion of radiation into electricity.

Mr. E. HAEFFNER (Sweden) presented paper P/794.

Mr. E. G. LINDER (USA) presented paper P/169.

DISCUSSION OF PAPERS P/794, P/169

The CHAIRMAN: The two papers which have just been presented are now open for discussion.

I should first like to point out that the papers which were not selected for presentation include a study by Mr. Shorr on nuclear batteries. If Mr. Shorr is present, I should be glad to give him the floor.

As he is not, I will read out a question by Mr. Turkevich of the United States addressed to Mr. Haeffner. The text of the question is as follows:

The efficiency of the pile described by Mr. Haeffner is approximately 0.9 per cent. Is there any hope of increasing this efficiency, and if so how?

Mr. HAEFFNER (Sweden): As we have reported in our paper, one method of increasing the power efficiency is by the exclusion of oxygen in the solution. That gives a current about five times as large as when oxygen is present. We do not know if there are any other means of doing this, and I think more extensive experiments need to be carried out in order to get an answer to that question.

The CHAIRMAN: I also would like to ask Mr. Haeffner whether this efficiency is a total efficiency, comparing the electrical energy obtained with the radiation energy introduced. He himself indicates that a part of this energy comes from a chemical reaction. What proportion of it is due to the chemical reaction?

Mr. HAEFFNER (Sweden): It is impossible to answer what part of the energy comes from radiochemical reaction and what part comes from electrochemical reaction. It would be very interesting to know this. Such an investigation is needed to know the real efficiency of the battery.

The CHAIRMAN: Would it not be possible to obtain this figure by using marked electrodes?

Mr. HAEFFNER (Sweden): That is perhaps an interesting solution of the problem. We have not tried it.

The CHAIRMAN: Mr. Linder pointed out the need for larger quantities of radioactive materials at lower cost. What is the probability of this in the near future?

Mr. LINDER (USA): I do not have a very extensive knowledge of the present state or future possible state of production of radioisotopes. I think that question might be better answered by some member of the Isotopes Division of the AEC if anyone happens to be present.

Mr. RUPP (USA): The price or cost of radioactive materials is very strongly influenced by the size of the operation. We have taken the fission products, for example, to the small-laboratory millicurie

stage and through the large-scale laboratory stage of curie operations and then through the semi-work stage at the 100 to 1000-curie level at the present time. At the Oak Ridge National Laboratory we are building a large pilot plant which will have a capacity of 200,000 curies of cesium per year and possibly a like quantity of strontium-90. We have found very large factors in the decrease of the cost in the early stages so that I should think that in proceeding further from the present semi-work stage factors of a reduction of 100 are not unreasonable.

Mr. EPREMIAN (USA): There appear to be certain similarities between the atomic battery, using semi-conductors, and devices for the conversion of solar energy to electricity. I should like to ask Mr. Linder to discuss the similarities and differences between the two types of devices.

Mr. LINDER (USA): In reply to that question, since this Conference is concerned with atomic energy I mentioned the use of solar energy only very briefly. However, it brings up a very interesting point, I think, because as a matter of fact the semi-conductor type of atomic battery which I described is somewhat analogous in its operation to the so-called solar battery. They are similar in that they both use semi-conductor *p-n* junctions, and at the present time they also both use silicon as the semi-conductor material. A present difference is, of course, the type of radiation used by the two devices, one using solar radiation and the other using nuclear radiation. However, this is not a basic difference theoretically since it is merely a question of the part of the spectrum in which you are operating. If we consider the electromagnetic spectrum, solar batteries operate in the region of visible light, whereas semi-conductor devices operate in the gamma ray region. Actually devices of this type will operate over the entire electro-magnetic spectrum, the only requirement being that the quantum energy of radiation be sufficiently high to produce free carriers, pairs within the semi-conductor material. Of course, the atomic battery will operate also on charged particle radiation, such as alpha and beta radiation—and that is another difference. There is also a geometric difference; visible light radiations will penetrate only a few thousandths of an inch. The junction must therefore be very close to the surface in order to utilize the carriers formed by the radiation. On the other hand, beta radiation will penetrate one or two millimeters, depending upon its energy, and therefore the junction can be formed much deeper in the material, so that the fabrication process is different and the geometry is different.

Another important difference at the present time is that solar batteries have efficiencies of from 6 to about 10 per cent whereas with atomic batteries the highest efficiency we have got is about 3 per cent. This difference is probably due to the amount of input energy which we are able to use. From the sun the input energy is about one-tenth of a watt per square centimeter but to get that much energy from radioactive material at the present time would be entirely out of the question because of excessive cost; but computations show that if the input energy were the same for an atomic battery and for a solar battery the efficiencies would be substantially the same.

PEACEFUL USES OF ATOMIC ENERGY:

Proceedings of the International Conference in Geneva, August 1955.

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