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Modern Instruments in Chemical Analysis

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FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK TORONTO LONDON
1956

MODERN INSTRUMENTS IN CHEMICAL ANALYSIS

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Library of Congress Catalog Card Number 56-8857

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THE MAPLE PRESS COMPANY, YORK, PA.

Preface

There are several categories of scientists and technicians who are interested in instruments which are of actual or potential value in analytical chemistry. The instrumentalist is interested in instruments per se. The analytical chemical specialist works with one instrument, or relatively few special instruments, to carry out chemical analyses. He may confine his work , for example, to microscopes of various types, or to spectroscopes, or to the infrared spectrophotometer in particular, or to X-ray equipment, or to any one, or a combination, of a limited number of instruments. The specialists in both these categories must have, each in his own way, a detailed knowledge of the basic principles of the instruments with which they are concerned and of the functions of the most minute parts involved in their operation. For such this book is not intended. Each group of instruments would require a book or more of its own to be written by a specialist in that group of instruments.

This book is intended rather for the general analytical chemist and the many other chemists interested in these techniques. Their main interest is in finding the most direct and most economical methods for the qualitative or quantitative analysis of the materials and systems with which they are confronted. They have, furthermore, no overriding preference for one instrument or another and will use any which promise to give better or cheaper analytical information.

Any one chemist obviously cannot become an expert in all instruments. He must of necessity lean on the instrumentalist or the analytical specialist for much detail regarding specific instruments. He must, however, know enough about many instruments and methods to be able to pick and choose wisely among them when making selections for his special needs. The analytical chemist would be unwise to allow either the instrumentalist or the analytical specialist to make this choice for him. He himself should be in a better position than they to understand the proper place of the instrumental measurement in the whole scheme of an analysis, of which the instrumental measurement may be only a part.

The aim of this book is to present to such readers information concerning a number of instrumental techniques and equipment which in

our judgment will aid the analytical chemist in making the indicated choices. To do this in the compass of a book of moderate length has called for many decisions on what to include and what to exclude, as well as on what to emphasize and what to subordinate. Clearly not all the numerous instrumental methods could be included without either, on the one hand, unduly extending the size of the book or, on the other hand, treating the included material in too sketchy a fashion. Those methods have been included which in some important aspects are recent enough so that one could not assume that the average practicing analytical chemist or any other interested chemist would have learned all that should be known about them in school. On the other hand, some methods, which are currently in the research or development stage, have not been included because they are not yet sufficiently well advanced to be considered as a practical part of the analytical chemist's tool chest. For the methods which have been included, it was necessary to strike a reasonable balance between theory and practice. Our approach has been to introduce just sufficient theory to provide the reader (in our judgment) with the bare minimum necessary for him to follow intelligently the subsequent exposition of the workings of the apparatus in question and its application to analysis. As for details of apparatus and analyses, again we have tried to present what was felt would enable the reader to grasp the implications of the particular technique for analytical chemistry and to get started in the use of the technique. By means of the references to the analytical literature and to specialized books we believe that the reader who wishes to go more deeply into any given technique or apparatus will be aided in doing so.

The authors are indebted to many publications to which reference has been made and to those whose names follow who criticized parts of the manuscript and made many helpful suggestions: W. Allen, S. M. Davis, C. M. Judson, J. P. Leineweber, J. B. Lombardo, J. S. Parsons, C. G. Whinfrey, S. R. Wiley, and J. T. Woods.

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CHAPTER ONE

Introduction

The rapid growth in the use of instruments in analytical chemistry is due to several factors. A basic reason for this growth is the fact that radiation of wavelengths in the visible range can be read and their intensities measured far more precisely with instruments than with the human eye. Radiation of wavelengths that are in the invisible regions, e.g., ultraviolet, infrared, and X rays, can likewise be measured. Also, with instruments, electrical measurements are made which cannot readily be obtained in any other manner.

The rapid advance of these methods has kept pace with the manufacturers' ability to produce equipment that is reliable, at what can be considered economical prices. It is true that many such instruments are complicated and expensive. These are bought because they do what could not otherwise be done and generally perform what can be done by other means in a much more rapid and precise manner, thus eventually saving much time and cost of labor.

In recent years instrumentation as applied to chemical analysis, chemical structure, and chemical and physical research has advanced to a stage where it has become a really necessary part of a forward-looking organization. In many cases the sample need not be altered, or only a minute amount may be necessary for analysis. For repetitive work enormous savings of time may be achieved. For research work such instruments lead the way to newer methods and often to basic discoveries.

It is, of course, obvious that instruments have always been used in chemical analysis. Balances, pipettes, viscosimeters, colorimeters, to name only a few, have been employed for many decades. The present usage of the term "instrumental" analysis does not have a strong basis and, in some ways, is a somewhat unfortunate choice. This is because the instrument is, shall it be said, just another piece of apparatus to obtain data which will be interpreted using a chemical viewpoint and after, in many cases, a preparation of the sample or solution in a form suitable for use in the instrument employed. In other words the reading so obtained is but a link—albeit a most important one—in the main

chemical procedure. The fact that the chemical analysis, usually starting by a chemical preparation and ending in a chemical deduction, is the all-important factor is sometimes forgotten.

On the other hand, it is true that many of these chemical deductions cannot be made without the use of such equipment, which is then all-important. The point that is being stressed is that, important as their use is and it can be most important, otherwise this book would not have been written—from the point of view of a chemical analysis, the analysis itself is of greater importance, and the measurement is a part of this analysis.

Because it is now general practice to call such methods "instrumental methods," the title of this book emphasizes such methods.

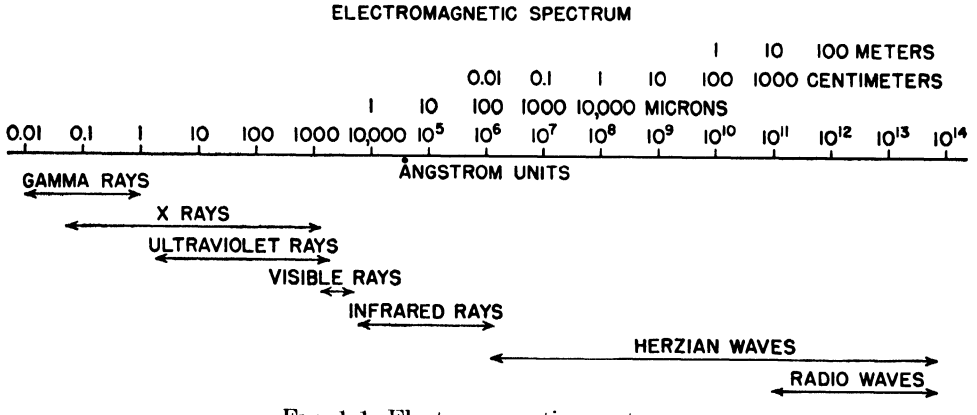


FIG. 1-1. Electromagnetic spectrum.

Electromagnetic Radiations. As has already been indicated, much of the advance in instrumental methods has been in areas involving measurement of electromagnetic radiations. Electromagnetic radiations are known which range from extremely minute wavelengths to some miles in length. The complete range is called the electromagnetic spectrum. An abbreviated diagrammatic representation is shown in Fig. 1-1. This is of interest in that several ranges of these waves are employed to characterize some feature of the chemical sample being analyzed by some of the instrumental methods discussed in the following chapters. In general, the shorter the rays, the more penetrating, or "hard," they are. Conversely, the longer they get, the less penetrating, or the "softer," they are. The properties of the rays therefore vary with their wavelength, and different methods of detection and measurement of intensity are necessary. In order of increasing wavelength, gamma rays, which are hard; X rays, relatively hard; ultraviolet rays, visible rays, and infrared rays, which are relatively soft, are all employed in the methods given in this book.

The following are the generally accepted approximate wavelength ranges of these five types of rays useful in analytical work:

Gamma rays	0.01 or lower to 1.4 angstrom units
X rays	0.06 to 1,000 angstrom units
Ultraviolet rays	200 to 4,000 angstrom units
Visible rays	4,000 to 8,000 angstrom units
Infrared rays	8,000 to 4×10^6 angstrom units

Angstrom units can be conveniently converted to other units by using the following equation:

$$1 \text{ meter} = 10^2 \text{ centimeters} = 10^6 \text{ microns } (\mu) = 10^9 \text{ millimicrons } (\text{m}\mu) = 10^{10} \text{ angstrom units}$$

Gamma rays are emitted when atomic nuclei disintegrate. They are detected by the same means as X rays. X rays are produced by the sudden stoppage or deceleration of fast-moving electrons. They can be detected by photography, diffraction effects, chemical action, phosphorescent effects, ionization of gases, photoelectric effects, and penetration effects. Ultraviolet rays are radiated from very hot bodies and emitted by ionized gases. They can be detected by photographic, phosphorescent, ionization, and chemical effects. Visible rays are also radiated from very hot bodies and emitted by ionized gases. Detection depends upon sensation of light, photography, photoelectric effects, chemical action, and reflection, diffraction, and refraction effects. Infrared rays are the heat radiations from hot bodies. Detection depends upon the rise in temperature of a body receiving the rays, upon the heating produced in bolometers and thermocouples, and upon photographic, reflection, and refraction effects.

Choice of Method. It is possible to use a wrong or at least an inappropriate method and so to obtain valueless data or results that could have been far more informative had a more suitable method been employed. The choice of method is thus critical and is usually decided upon after a careful consideration of the chemistry involved in the analysis.

For instance, should a quick appraisal of the metallic elements in a material be desired, the use of an emission spectrograph is indicated. With this, almost all the chemical elements present, and in a rough quantitative measure, can be found within a relatively short time, a matter of minutes.

Should an insoluble inorganic substance be the subject of investigation, it is clear that methods involving solutions, such as many spectrophotometric methods, cannot be employed without much preliminary preparation. Such preparation may be necessary and advisable, and this is often

the heart of the analysis. For a quick analysis, emission spectrography may again be best, or X-ray analysis, using diffraction or fluorescence methods, may be most useful.

If the nature of the compound itself is required, X-ray diffraction analysis may well be used to give a quick answer.

Since many organic compounds are soluble, either in water or in organic solvents, methods that employ such solutions are useful. Thus spectrophotometry—visible, ultraviolet, infrared, and Raman—is of great use for such materials.

Soluble acids, bases, or salts, either organic or inorganic, which undergo dissociation into ions, in aqueous or nonaqueous media, may frequently be determined advantageously by methods which are based upon the electrical charges of the ions. Such methods, which are treated in later chapters, include potentiometry, conductometry, high-frequency oscillometry, coulometry, polarography, and amperometry. The four last-mentioned methods may also be used for many nonionizable substances.

These are but a few suggestions and possibilities. Obviously, a good chemical knowledge of the material to be analyzed is necessary before a correct decision as to the method can be made. The possibilities of analysis are dependent upon the form or, in many cases, the forms which the subject of analysis can be made to assume.

For example, a well-crystallized material, and this includes many crystals below microscopic size, will normally give an excellent X-ray photograph or spectrometer diagram; poorly crystallized material usually will not. On the other hand, this poorly crystallized material may be soluble in water, or dissolve in acid, or can be made to dissolve by using a fusion method. Once it is in solution a number of other methods may be applied, e.g., spectrophotometry or polarography. Appropriate heating and subsequent cooling may sometimes change the crystalline character of a sample.

Mass spectrometry depends upon the magnetic separation of ions in an attenuated gas stream. Some solids can be advantageously vaporized and then analyzed by this method.

Sample Required. The actual method of analysis may be dependent upon the amount of sample available. Should there be only a few milligrams, a nondestructive method such as X-ray analysis may be indicated. If the substance is soluble, it may be possible to make useful spectrophotometric readings on a fraction of a milliliter of solution. The sample could, in some cases, be recovered from solution.

When a few milligrams are expendable, particularly with inorganic insoluble substances, much information can often be obtained by burning the sample in an electric arc and recording the spectrum with a spectrograph. In some cases, a very small sample indeed will suffice when a

mass spectrometer is available. This applies particularly to gases where the difficulty of obtaining a representative sample is not usually present.

Larger, and indeed all, samples require adequate sampling. This simple fact cannot be stressed too much, since results obtained are at the best only as good as is the sampling. It may be advisable in some cases to separate the material into two or more fractions, obtain their relative amounts, and analyze each.

Preparation of Sample. Very often, the actual preparation of a sample is the most tedious and important part of the analysis. In a simple case, the sample may be employed as is. Direct solution may be all that is necessary. A reaction with a reagent could give a colored compound the color intensity of which is quantitatively measured. In many cases considerably more complex means must be employed. For example, it is possible to analyze completely insoluble silicate materials by means of spectrophotometric and flame-photometric methods at a considerable saving of time over conventional classical methods. Before this can be done, various means of bringing the substance into solution must be employed, e.g., fusion with alkali and treatment with sulfuric and hydrofluoric acids. Then various interferences must be prevented, proper dilutions made, and separations effected.

It is not infrequently necessary to employ special techniques. For example, in infrared analysis thin specimens are required and much care may be employed to prepare them. By their very nature, radiochemical methods require special handling.

All this further indicates that a thorough knowledge of the chemistry of many substances is necessary as well as a good understanding of the potentialities of the instrumental methods available.

CHAPTER TWO

Emission Spectroscopy

The region of the electromagnetic spectrum dealt with in this chapter is roughly from about 2,000 to 10,000 angstrom units. It includes the visible region and parts of the ultraviolet and infrared regions. The means of excitation are usually electric arcs or sparks. The radiation is dispersed by means of a prism or grating and the spectra photographed on films or plates; or, as in the latest type of instrument, specific radiations are measured and recorded electronically.

Emission spectroscopy is probably the oldest method in which dispersion of refracted rays is used to detect and measure the presence of elements. The science has now grown so that modern electronic-computation emission spectrographic instruments are very complex. In its earliest form, e.g., the discovery by Newton of the heterogeneous character of sunlight, a spectrum was produced on the wall of a room by allowing a ray of sunlight to pass first through a hole of small diameter and then through a glass prism.

Later (1814) Fraunhofer observed spectral lines by using a slit light source and a diffraction grating in place of a prism. Each image of a narrow slit contained light of one color. Kirchhoff and Bunsen (1859) built the first practical spectroscope. By means of this they were able to demonstrate the presence of many elements in the sun and to discover a number of previously unknown elements. The use of emission spectroscopy as a means of analysis had been sporadic until about 20 to 30 years ago when instrument makers commenced to build suitable equipment. The early instruments nearly always used prisms, first glass and then quartz, which will pass and refract ultraviolet rays. Prisms are still used, especially in Europe, but in the United States the majority of instruments incorporate ruled gratings.

USES OF EMISSION SPECTROSCOPY

The spectra obtained are chiefly from atoms and identify very specifically the elements present in the material examined. Simple molecular

formations produce band spectra consisting of very numerous lines which are relatively weak. Consequently, a spectrum is a fingerprint of elements present. By observing where lines are placed relative to others, positive identifications of metallic elements, and also a few nonmetallic elements such as carbon and the halogens, may be obtained. Spectra of common and rare gases may be obtained when they are excited in Geissler tubes at high voltages.

In chemistry a major use is to identify rapidly the constituent cations in a sample. Very minor traces of elements register on the spectra, and positive identification can be made where chemical analysis might miss such small amounts. Much quantitative work is done, more particularly in amounts of about 10 per cent down to parts per million. Techniques are rapidly being devised for accurate estimation of much larger percentages.

Much knowledge has been obtained of the configuration and energy states of the atom by this means. Much more help to physics can be expected in the future. Astronomy was one of the first sciences to use this potent means of identification. Not only the composition of the celestial objects but also the relative speed of stellar motion as given by the shift in the infrared region (the Doppler effect) can be obtained.

Almost all branches of science owe much to the emission spectrograph, e.g., mineralogy, metallurgy, medicine, and biology. In many cases it is unrivaled for speed and detection of trace quantities.

ATOMIC AND MOLECULAR SPECTRA

The motion of electrons around a positively charged nucleus gives rise to atomic spectra. The motion of electrons in a molecule is associated with two or more positively charged nuclei. These nuclei not only move in a straight line as in atomic motion but also vibrate and rotate about their center of gravity in a periodic manner. The latter motions exhibit spectroscopic activity and also affect the electronic spectrum of the molecule. A very complicated fine structure results.

The atom of an element consists of a compact nucleus comprising positively charged protons and neutral neutrons. The atomic number of an element Z is the same as the total number of protons and is characteristic of that element. Electrons, negatively charged particles of equal though opposite charge to that of protons, and equal in number to the protons in a neutral atom, surround the compact nucleus in a more or less diffuse but orderly manner. They may be thought of as located in orbits with which discrete energies are associated. Each orbit is spoken of as an *energy level* in the atom.

According to the quantum theory, radiant energy is discontinuously

emitted as quanta. The energy e of each quantum is related to the frequency of the radiant energy according to the equation

$$e = h\nu$$

where h is Planck's constant (6.62×10^{-27} erg sec) and ν is the frequency of the radiation in vibrations per second.

When an atom is excited by an electric arc, spark, or even by a flame, particles collide. From a normal *ground state* the outer valence electrons are removed to other outer orbits of higher energy levels. This is an unstable condition and the electrons return to lower energy states either in one jump or in a series of jumps via intermediate energy levels. One spectral line or several are emitted depending upon which return path is taken. Theoretical calculations based on the quantum theory agree very closely with the measured wave numbers of groups of lines of an element. A number of these so-called *series* of lines have been measured and have been named after those who studied them:

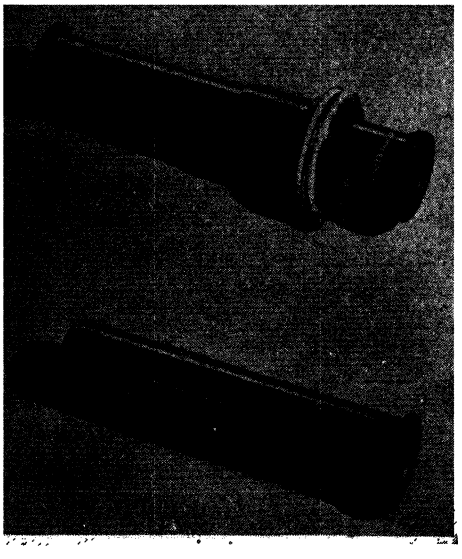


FIG. 2-1. Bausch and Lomb hand spectroscope.

Lyman series in the ultraviolet region

Balmer series in the visible region

Paschen series in the infrared region

Brackett series in the extreme infrared region

Pfund series in the very extreme infrared region

INSTRUMENTATION

Since emission spectroscopy has been in use for many more years than most of the other spectroscopic methods dealt with in this book, a larger number of instruments is available. These range from a hand spectroscope (Fig. 2-1), through which is viewed a small but often useful spectrum of a flame, to very expensive equipment.

For qualitative and semiquantitative work the recently introduced Spectranal (Fig. 2-2) employs a specific phenomenon. When a platinum electrode and a suitable excitation electrode are immersed in approximately 10 per cent nitric acid solution, and when a suitable voltage is applied to these electrodes, a large number of small fluctuating arcs are formed on the surface of the immersed portion of the excitation electrode.

This light when viewed through a spectroscope is seen to be composed of the spectral lines of the metallic elements in the excitation electrode. If the material is dissolved in the nitric acid, the spectral lines of the dissolved elements will be seen.

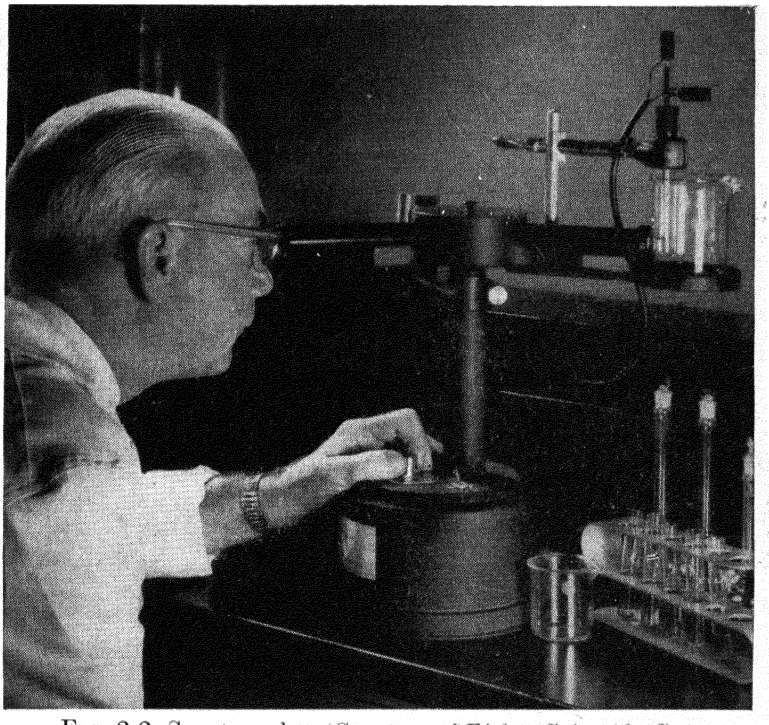


FIG. 2-2. Spectranal. (*Courtesy of Fisher Scientific Co.*)

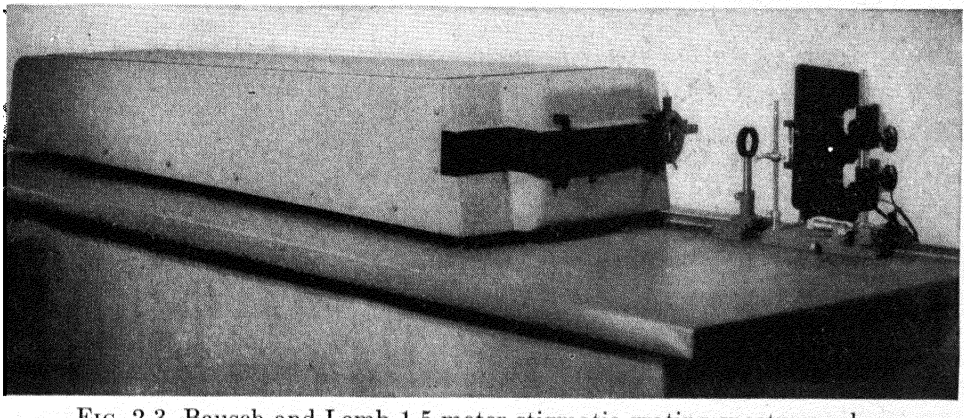


FIG. 2-3. Bausch and Lomb 1.5-meter stigmatic grating spectrograph.

Of most use are spectroscopes that photograph the diffracted spectra. These are referred to as spectrographs. There are too many on the market to present them individually. Figs. 2-3 to 2-5 show some of the instruments, which vary in cost according to accessories and elaboration

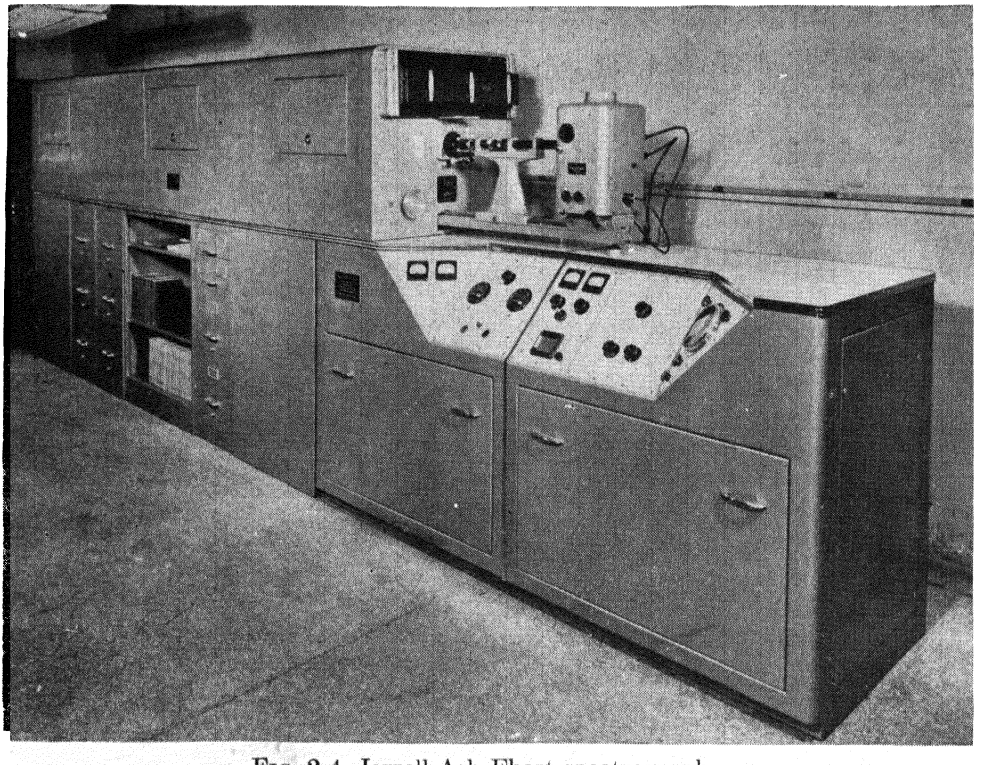


FIG. 2-4. Jarrell-Ash Ebert spectrograph.

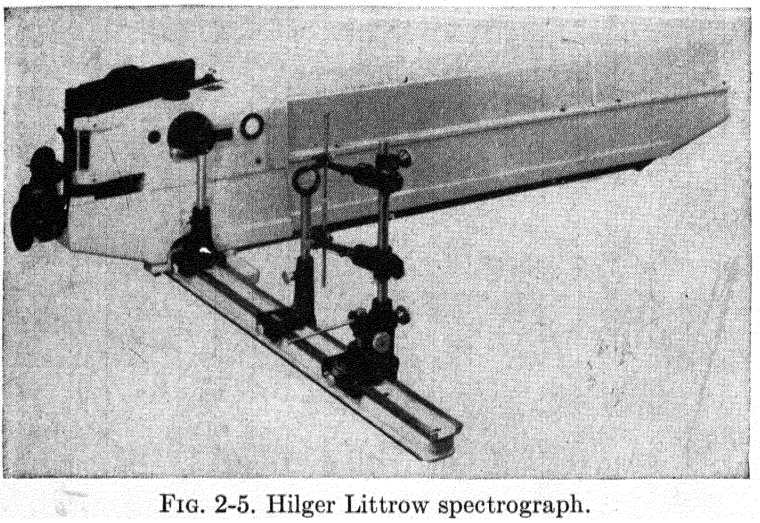


FIG. 2-5. Hilger Littrow spectrograph.

of design. In essence they all consist of (1) a light source, (2) collimating lenses to focus the light beam upon (3) a slit through which a narrow and comparatively long beam of light is impinged directly, or by means of mirrors, through a prism or onto a diffraction grating. The resulting spectrum of diffracted rays is directed upon a photographic plate

or film. By hand or mechanical arrangements the plate may be moved so that successive spectra may be photographed—one immediately below the other, thus facilitating comparison.

Of quite recent design are the direct-reading instruments (Fig. 2-6). Instead of photographic film to receive the spectra, single or individual phototubes are placed to catch desired wavelengths. By electronic amplification, intensities of these selected lines are almost immediately obtained, and by direct comparison under known stabilized conditions, percentages of the elements corresponding to these selected lines are obtained. Naturally such instruments are expensive, but for routine purposes involving many thousands of determinations, such high prices are soon justified by considerable savings in time and cost.

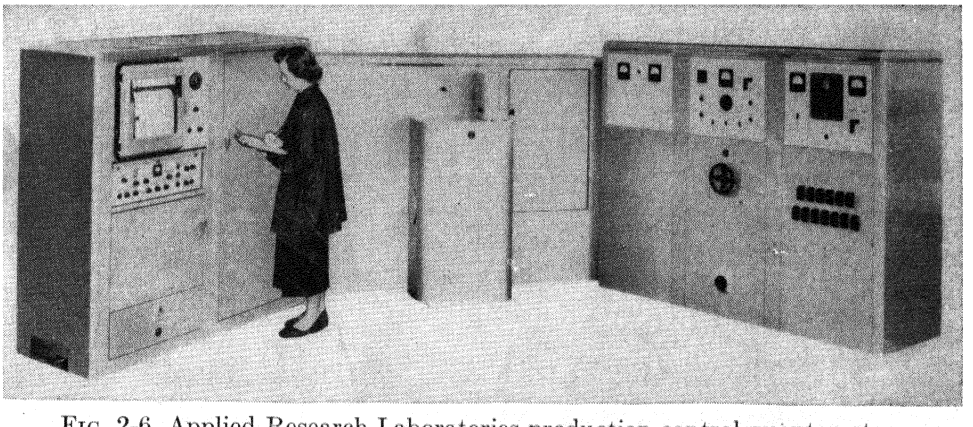


FIG. 2-6. Applied Research Laboratories production-control quantometer.

Power Source. In most cases the light source is electrical. Of greatest use are d-c arc units and a-c high-voltage spark equipment, with a-c arc units a poor third. Instruments comprising all three sources are available. Figure 2-7 shows one of these at present on the market.

It is of utmost importance that a unit giving excellent service and results be used. Even the best spectrograph will give inferior results with a poor light source. Trite as this remark may appear, it is surprising how little it is observed in practice. Of course, it is as important in reference to other accessories used, e.g., spark stand, lenses, slit, microphotometer, etc. A balanced complete unit of good quality is far preferable to one with a more expensive spectrograph and inferior accessories.

Arc-spark Stand. This is the housing for the electrodes in which the sample is excited. It generally varies with individual makers (Fig. 2-8). Sturdy construction with clean lines and accessibility and freedom from corners to collect debris are preferable to mere mechanical conveniences. The stand should be provided with proper protection from harmful radiation and fumes, be easily cleaned, and contain a tinted window for the

observation of the arc or spark operation. Both electrodes should be smoothly adjustable vertically and at right angles and should have a device to lock them in any position. Water cooling is advantageous. A safety switch is normally incorporated to shut off current when electrode holders are exposed for handling. Proper insulation should be provided, particularly for use with high-voltage sparks.

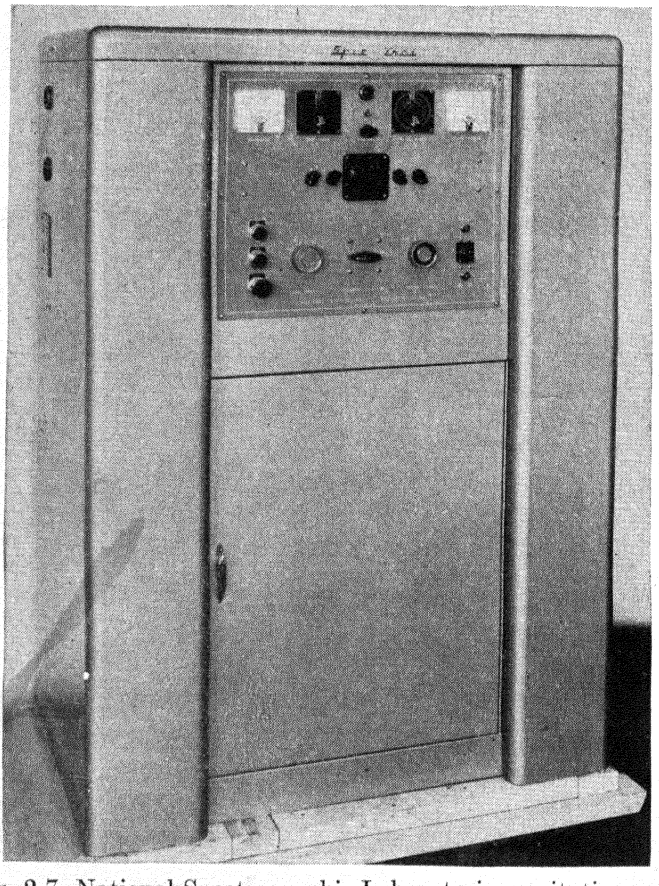


FIG. 2-7. National Spectrographic Laboratories excitation unit.

Photometers and Microphotometers. In quantitative and semiquantitative work it is desired to obtain measurements of the amount of the elements present. Under known and controlled conditions the density of the photographic line is proportional to the amount of substance that produces the line. These densities may be measured roughly by eye using an illuminated glass-topped box or accurately by means of a microphotometer (Figs. 2-9 and 2-10). The density of the enlarged projected image of the required line is measured by a photocell or phototube. These instruments may accommodate 35-mm film up to 30 in. in length and 4- by 10- and 2- by 10-in. plates. Reference plates or films are pro-

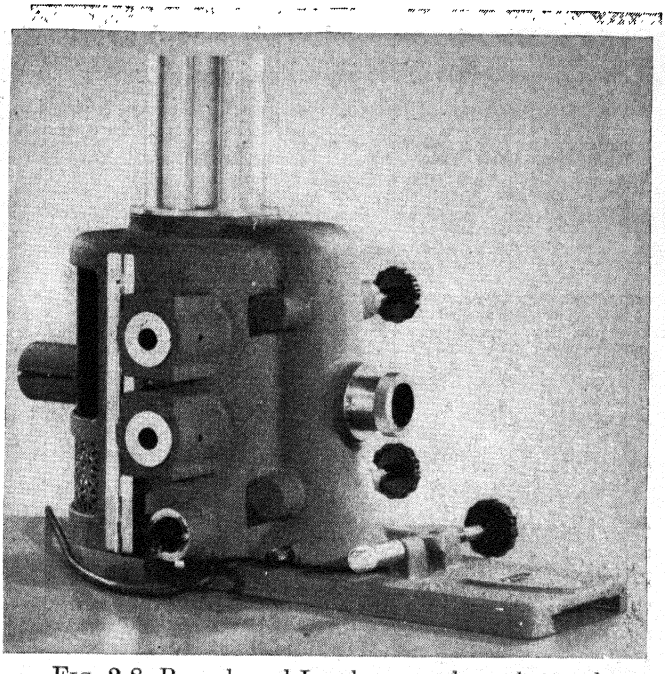


FIG. 2-8. Bausch and Lomb arc and spark stand.

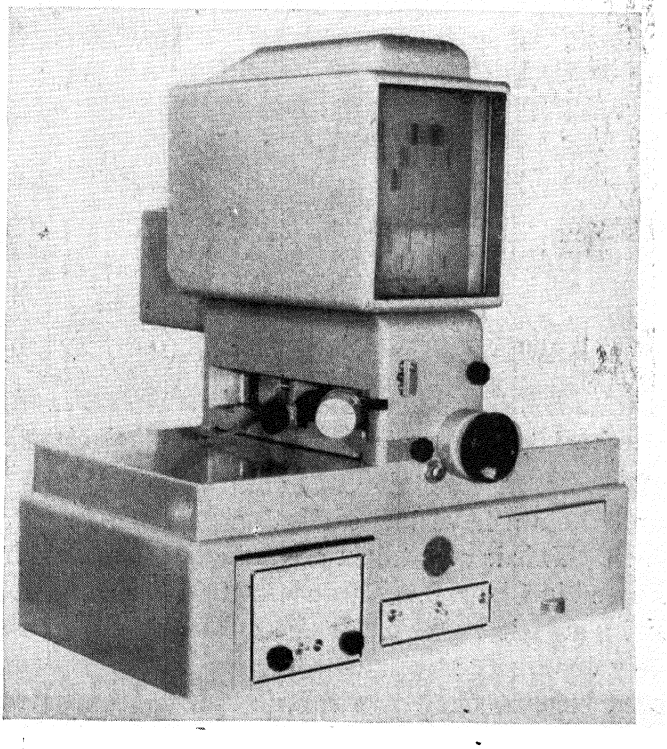


FIG. 2-9. Applied Research Laboratories projection comparator densitometer (microphotometer).

vided which have spectra to cover all regions and orders of spectra produced on the spectrograph which the densitometer supplements. They also have both d-c arc and a-c spark spectra of iron with truly representative line densities. The positions of several of the strongest lines of each element are indicated with their symbols and also the positions of several lines of various degrees of sensitivity which are suitable for the quantitative analyses of most common elements.

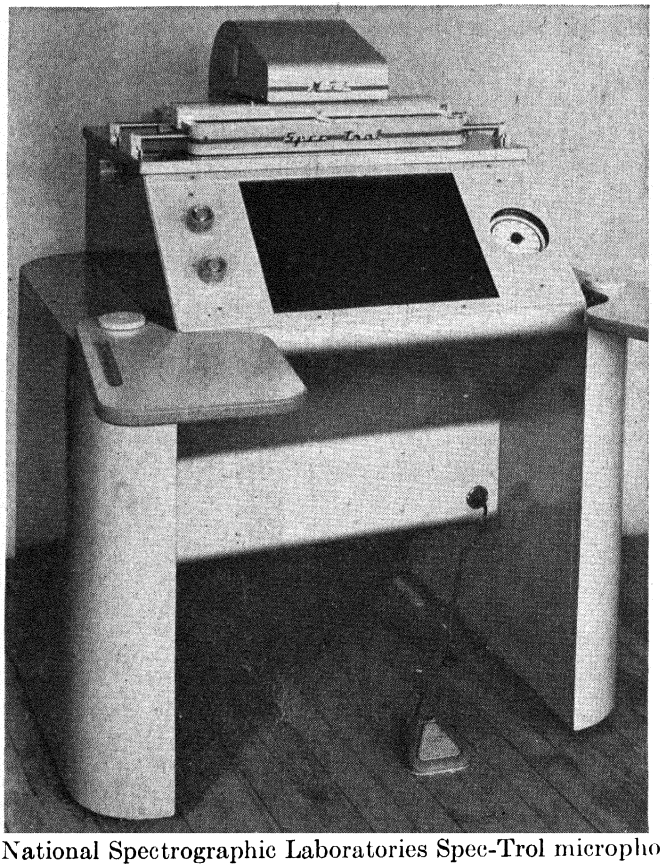


FIG. 2-10. National Spectrographic Laboratories Spec-Trol microphotometer.

Common Sources of Excitation. Some elements such as sodium, potassium, and lithium have low excitation potentials and can be volatilized in flames. This is now taken advantage of and the photometry of flames is discussed in Chap. 3. Furnaces attain higher temperatures but are not used in practice. The *electric-arc discharge* between two electrodes is widely used. Purified carbon or graphite in the form of rods is very often used because they give a radiation relatively free from continuous (background) radiation. Under certain frequent conditions cyanogen, formed by interaction of the carbon and nitrogen from the air, gives strong bands around 3,500 to 4,200 A. Both d-c and a-c arcs are employed at voltages varying between 115 and 5,000 volts. The most

widely used is the d-c 220-volt arc. The temperature attained varies with the current density and the distance between the electrodes and runs as high as 8000°C, around 5000°C being about normal. Figure 2-11 shows a simple d-c arc circuit. The inductance irons out surges and inequalities of the current, which is limited by the variable resistor.

Figure 2-12 shows the approximate temperatures present in a d-c arc carrying 10 amp current. The *rate of volatilization* of a sample depends

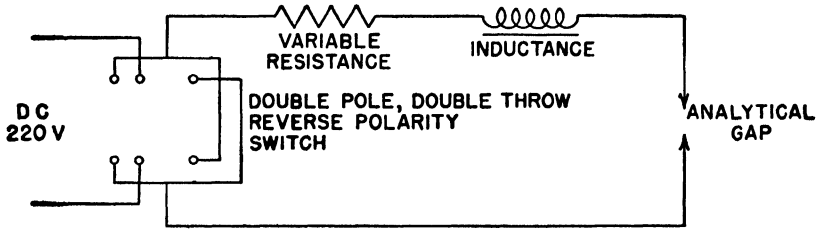


FIG. 2-11. Simple d-c arc circuit.

upon its condition in the arc as a salt, metal, main constituent, or minor constituent. In quantitative work it is essential to volatilize the elements completely or, if incompletely, in a reproducible manner. If the volatilization characteristics of a desired element are known, it is possible to concentrate its effect upon the photographic plate by burning off the more volatile elements before exposing the plate. To determine the volatile elements, the exposure may be stopped before the less volatile elements start to come off. The d-c arc is used perhaps more than any other type of excitation. The *a-c arc* is difficult to maintain if the electrodes are more than 2 mm apart. It is not used to any extent with low voltages. The current builds up, goes out, and reverses continuously. The arc area is only a fraction of a square millimeter, much smaller than with the d-c arc. The localized temperature is quite high. The a-c arc has one decided advantage in that it constantly picks out a new surface area, the whole of which is arced. This is not always so with the d-c arc. Consequently the a-c arc may at times be better for quantitative work. The d-c arc is often used, but it is necessary to choose the exact area and height necessary to attain constant temperatures. Thermal and electron energy are both present in the a-c arc while largely thermal energy is present in the d-c arc. Figure 2-13 shows a simple a-c arc layout.

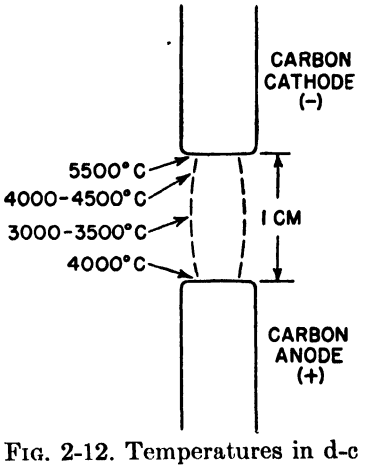


FIG. 2-12. Temperatures in d-c arc.

Sparks are obtained by means of induction coils, mechanical interrupters, and condensers. They are of high voltage and produce high temperatures, around 10,000°C, of very short duration (microseconds). The area covered is small but moves all over the electrodes. Because of the short duration and small area of the spark the total heat energy present is considerably smaller than with arc discharges. The voltage breakdown depends entirely upon the resistance of the analytical gap

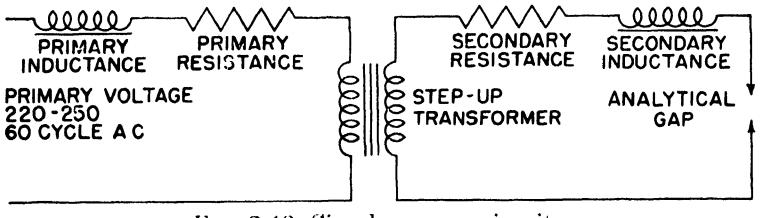


FIG. 2-13. Simple a-c arc circuit.

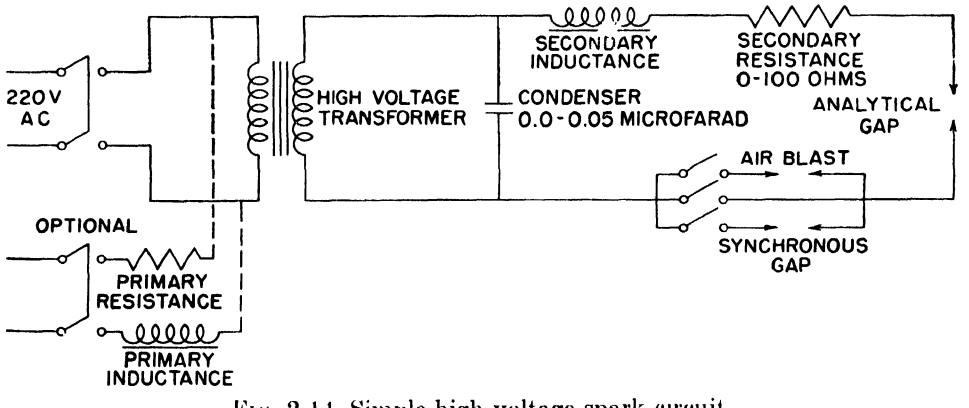


FIG. 2-14. Simple high-voltage spark circuit.

(the distance between the electrodes). A number of modifications are employed, e.g., with and without a synchronous (rotating-spark) gap. Lines of ionized atoms predominate in spark spectra. High-voltage sparks attain 10,000 to 40,000 volts while low-voltage sparks, around 1,000 volts, are dense and of high capacity. An over-all increase in line intensity occurs when the inductance is increased. Sparks in general are also less stable. Increased current causes corresponding decrease in ionized-atom lines. Resistance has little other effect than to control the amount of energy. The arc source is much more intense than the spark source. The latter is almost imperative for high excitation potential elements.

Figure 2-14 shows a simple high-voltage spark circuit. This type of excitation is largely used for quantitative purposes in metal analysis and also with solutions. Briefly it may be said that the d-c arc gives high sensitivity and low precision or reproducibility. The a-c high-voltage

spark gives low sensitivity and high precision or reproducibility. The a-c arc is midway between these two in both these characteristics.

General arrangement of a spectrograph is shown in barest detail in Fig. 2-15. The *lens* may be of glass which will transmit visible and very near infrared radiation or of quartz which, in addition, transmits ultraviolet radiation. *Gratings* generally vary in length from 1 to 8 in. and in number of lines per inch from 5,000 to nearly 40,000.

The *angular dispersion* of a grating or prism depends on the dispersing element used and is given by the formula $d\theta/d\lambda$. It measures the variation with wavelength λ of the angle of deviation θ of the emergent light beam. Of more frequent use is the *linear dispersion* $dl/d\lambda$ which is the actual distance dl of separation in the spectrum of two close lines differing

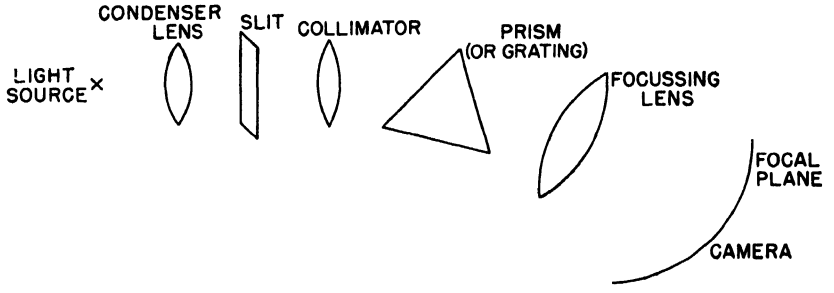


FIG. 2-15. Simple general arrangement of a spectrograph.

in wavelength by $d\lambda$. The reciprocal of this is in common use and is called the *reciprocal dispersion* or the *plate factor*. It is clear that good dispersion is necessary to separate lines. For many commercial instruments the normal dispersion is around 2.5 to 7 A per millimeter. Other instruments have from around 15 A per millimeter to 0.27 A per millimeter. The latter is attained by use of the newer echelle attachment. With prisms the dispersion varies with the wavelength; e.g., a Littrow spectrograph has a dispersion at 2,000 A of 2.0, and at 8,000 A of 59.0. Diffraction gratings give almost uniform dispersion throughout the spectrum.

Even if the dispersion is small, it will be of little use unless the spectrograph has good *resolving power*. This is defined as $\lambda/d\lambda$ where $d\lambda$ is the wavelength interval between two close lines of similar intensity that can just be resolved with the instrument at wavelength λ. Rayleigh's criterion states that two spectrum lines of equal intensity are considered as being just resolved when the diffraction maximum of one falls on the first minimum of the other. This is shown in Fig. 2-16. Dispersion determines the approximate position in the spectrum at which light of a given wavelength will fall; resolving power determines how well that light can be separated from light of other wavelengths falling nearby. The resolving power of most spectroscopes lies between 5,000 and 200,000.

Diffraction gratings have recently been used more than prisms as the difficulties of manufacturing them have been overcome. A good grating —and it is still quite difficult to produce them consistently—has a number of advantages over a prism. Two advantages are even dispersion and diffraction of all wavelengths. Theoretically, the greater the number of lines in the grating, the greater its resolving power. The greater the number of lines per unit length, the greater the dispersion of the grating. Successive maxima occur, corresponding to different *orders* of a diffraction grating. Most gratings are so cut that only two orders are of sufficient strength to affect the photographic emulsion. The dispersion of the second order is twice that of the first order. Carefully made replicas of good gratings can be as good as the originals.

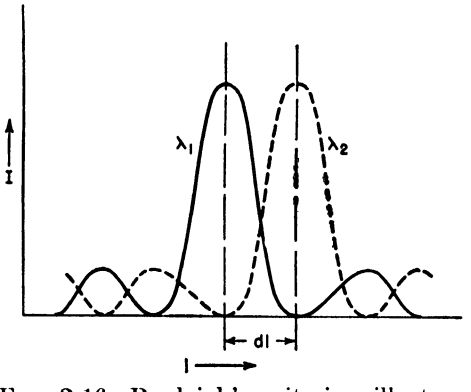


FIG. 2-16. Rayleigh's criterion illustration.

Echelles are gratings with rulings of several hundred lines per millimeter. They are used in at least one modern spectrograph. Echelles diffract the dispersed rays still further so that very high dispersion is obtained and very fine and close lines can be separated. The spectrum is spread out horizontally by a prism or grating and is then further dispersed (at right angles to this) by an echelle. Such an instrument is of great use in devising new techniques and in analyses where line interference affects the analysis, e.g., in the determination of boron in steel. The optical system of an echelle spectrograph is shown in Fig. 2-17.

Mountings for Gratings. A concave grating ruled with parallel lines equally spaced along the chord of its arc will give spectrum lines in sharp focus on a circle (*Rowland circle*) the diameter of which is equal to the radius of curvature of the grating. Placed in a *Rowland mounting* this grating gives a spectrum of nearly uniform dispersion. This mounting is less used than formerly since only a limited region of the spectrum can be photographed at one time. The system has a high degree of astigmatism which leads to a loss in intensity. It is also somewhat cumbersome.

With the *Eagle mounting*, astigmatism is less and higher orders can be reached than with the Rowland mounting. This mounting occupies a long narrow space.

The *Abney mounting* is similar to the Rowland, only both the grating and plateholder are kept stationary while the slit is movable. Small gratings (2 in.) and two slits are used. Since the curvature of its Rowland circle is high, film is used instead of plates.

The *Paschen-Runge mounting* has grating, slit, and plateholder all fixed. Thus all parts of the spectrum are always in focus and the entire spectrum can be photographed at one time, using a sufficient number of plates or film.

A stigmatic (lack of astigmatism) image at the normal to the grating is obtained over any desired short region of the spectrum when a grating is illuminated by a beam of parallel light. In such an instrument the dispersion is cut in half since at the normal the new focal curve lies halfway out of the Rowland circle. A concave mirror may be used to increase the angular aperture and eliminate astigmatism. This is called a *Wadsworth mounting*.

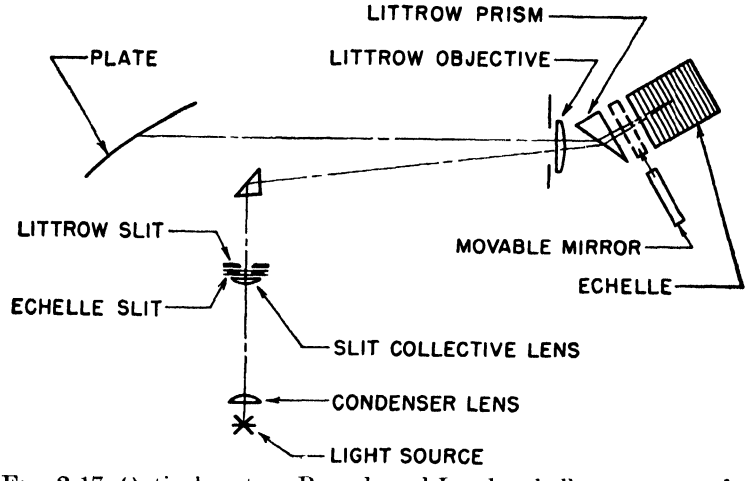


FIG. 2-17. Optical system Bausch and Lomb echelle spectrograph.

The *Littrow mounting* is frequently used in both prism and plane grating spectrographs. It is designed to give high linear dispersion using a long-focus camera lens. In the case of a prism the radiation made parallel by a collimating lens enters a 30° prism mirror coated on its back face. It then passes back through the same prism and collimator, bringing the spectrum to a focus. This mounting is most advantageous when used with a quartz prism (and lens) because the reverse passage through the prism compensates for any optical rotation produced by the initial passage.

PHOTOGRAPHIC PHOTOMETRY

Photography is much used in emission spectroscopy for the following reasons: (1) light intensity is integrated on the emulsion, which (2) is highly sensitive; (3) the intensities of a large number of spectral lines can be recorded at one time; and (4) a permanent record is obtained. These advantages outweigh disadvantages such as the necessity of very careful control of the whole process, nonlinearity of response, great vari-

ation of sensitivity with wavelength, and the time required in processing. All wavelengths below 13,000 A can be photographed, though not all on the same emulsion.

The density of a photographic line d on a negative is obtained by measuring with a densitometer the fraction of a beam of light passed through the line that emerges on the opposite side. The ratio of the transmitted light I_t to the incident light I_0 is called the transmission T of the line. The density is the logarithm of the reciprocal of the transmission; thus

$$d = \log_{10} \frac{I_0}{I_t} = \log_{10} \frac{1}{T}$$

The so-called "H&D" (Hurter and Driffield) curve of a photographic emulsion (Fig. 2-18) shows how the density of the image alters with light intensity, while exposure time and development conditions are constant. The *contrast* of an emulsion, usually called *gamma* (γ), is defined as the tangent of the angle θ between the straight-line portion of this characteristic curve and the intensity axis. The gamma value ranges from 0.6 for low-contrast to 6 or 7 for high-contrast emulsions. In the latter the grain-size variation is small. For most purposes emulsions of intermediate contrast are used. Contrast changes rapidly at normal development times (e.g., 5 min) and is a function of the temperature. Hence the development temperature should be accurate to around 0.5°C and the time to within a few seconds. The *speed* of an emulsion relates to its response to exposure and so is an approximate indication of the least amount of light necessary to produce a useful line.

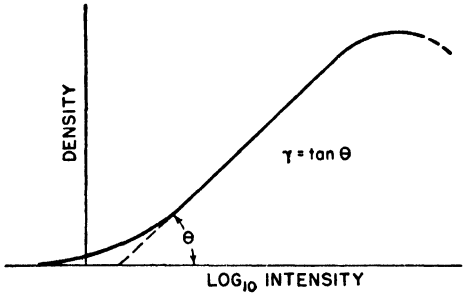


FIG. 2-18. Photographic-emulsion curve.

A number of photographic emulsions are available, most of which can be had in a whole series of color sensitivity (spectral range). The best emulsions should possess good color range, good contrast, high speed, and uniform contrast γ.

The following are suggested emulsions from the different types available:

2,000–4,000 A.....	Type I-O (UV sensitized)
2,300–4,000 A.....	Spectrum analysis No. 1 or No. 2
2,350–4,500 A.....	Type III-O, or 33
3,500–7,000 A....	W&W Panchromatic, or type IV-F
6,700–8,500 A....	Type I or II-N
8,500–10,000 A ...	Type I-M
10,000–12,000 A	Type I-Z

QUALITATIVE ANALYSIS

Under normal conditions of excitation semimetals and nonmetals, such as selenium, sulfur, carbon, the halogens, and the common gases, are not detectable. By the use of special conditions some of these can be detected. At least 55 elements can be identified. The remarkable thing about emission spectroscopy is that, if all these 55 elements happen to be present in detectable quantities in one material, all of them, under proper conditions of excitation, will leave their impress on a photographic emulsion and can be qualitatively identified. It is this fact which makes this method of such use in chemical analysis. A few minutes may suffice to show all the metallic elements in a substance and, roughly, the relative amounts present. Chemical analysis would take much longer, and even so, small amounts of elements would be likely to be overlooked. With this quick and reliable information, the analysis can be properly planned to give maximum accuracy in a minimum of time.

The elements can be detected by wavelength measurement. This normally involves determining the location of a line relative to known lines It is thus necessary to have tables of elements with the wavelengths and the relative intensities produced by them under standard conditions. The first *wavelength tables* were published by Kayser and contain about 10,000 lines. The present most complete set of tables in English, by Harrison of MIT, has 100,000 lines. In this the lines are given only in order of wavelength. However, the specific intensities are only approximate. These tables, or condensations thereof, are invaluable. A useful set of lines, in which the most sensitive lines and those likely to cause interference are specially noted, is given in Ahrens, "Spectrochemical Analysis." Others appear in Brode, "Chemical Spectroscopy" and in chemical handbooks (Chemical Rubber, Lange, etc.).

In general, spectra are interpreted by comparison with the spectra of *reference standards.* These are produced on the same emulsion as used for the analyzed sample and under exactly the same conditions of exposure and processing. The latter requirements are most essential. The *iron spectrum* has numerous lines well scattered through the whole spectrum and is usually employed as a comparison standard to identify wavelengths. Indeed, most microphotometers—and also visual comparators—use a standard photographic spectrum of iron with the angstrom measurements accurately inscribed thereon. This spectrum must be taken on a spectrograph with exactly the same characteristics as the one used for the sample.

The taking of a useful spectrum is not simple. The excitation conditions are most important because the more volatile elements may show up more than the less volatile. For this reason a small thoroughly mixed

sample must be taken and all of it vaporized in the arc or spark. The high intensity of the d-c arc is well suited to this purpose. A knowledge of the type of material to be examined is useful so that the conditions of excitation can be better regulated. For most metals it is possible to detect 0.001 per cent in 10 mg of sample. Silver, copper, beryllium, sodium, and calcium can be detected to 0.0001 per cent; arsenic, antimony, tellurium, and bismuth to 0.005 per cent; phosphorus to 0.10 per cent; and selenium, the excitation potential of which is very high, to 10 per cent. These values are for normal excitation conditions. Special sources and conditions may produce even higher detectability.

QUANTITATIVE ANALYSIS

In essence, the conditions used for quantitative work are the same as for qualitative, except that every procedure must be scrupulously exact; standard materials must be employed and must be photographed with the samples one after the other on the same plate. Because of the large number of possible variations, standard procedures have not yet been fully developed. The American Society for Testing Materials has published a series of tentative methods for certain metals and materials. Small amounts, from say 10 per cent down to parts per million, can be as accurately and in many cases more accurately determined by these means than by wet-chemical-analysis methods. Larger percentages, which necessarily require a higher percentage of accuracy based on the element determined, are not so readily obtained. Rapid steps are, however, being made to obtain accuracies comparable with those of wet-chemical methods on elements which are present to the extent of over 90 per cent.

In specification work, by means of several standards that vary slightly, it is possible to tell at a glance if the sample complies with the specification.

A number of *standard samples* are available from the National Bureau of Standards. Alloys and ores are properly melted to prevent segregation, or well mixed, and subjected to the most careful chemical analysis. Rocks, minerals, glasses, and clays with exact composition can be obtained. These are all nationally recognized standards. Others are issued by other well-known sources. Many can be prepared for routine use in any chemical laboratory.

In much quantitative work the *internal-standard* method, or a modification of it, is used. Instead of computing actual intensities, intensity ratios are obtained of the line of the element in question to that of a line of an element usually present in constant amount. A variable internal standard is also sometimes employed. By this method the effects of many variables are canceled out since both sample and standard receive identical treatment. However, several factors must be considered. The

internal standard must be free from all but negligible amounts of the element to be determined. Both comparison lines should have similar excitation potentials. Self-absorption must be absent. Both sample and standard should volatilize at similar rates (this is tied in with their excitation potentials). Finally the comparison lines should be approximately at the same wavelength so that the photographic-emulsion characteristics will be practically identical. To a somewhat lesser degree it is important that the atomic weight of the internal-standard element should be near that of the sample element when this is low; and the internal-standard element should be usable over a fairly wide variation of composition.

A series of *standard samples* must be available which are essentially similar in composition to the unknown. The concentration of the element in the various standards must be known and should cover the complete range of concentrations expected. At least five standards are usually preferred to set up analytical working curves which are later used to complete the analysis of the various elements in the unknown. The transmittance values of suitable spectral lines are measured. These should be free of interference and appear on the negative within measurable photographic densities. These transmittance values are converted to ratios corresponding to the intensities of the radiations produced by the elements to be analyzed, divided by the intensities of the radiation produced by the standard reference element. For each element there is a specific intensity ratio corresponding to a certain concentration. The intensity ratios are plotted against concentration, usually on a log-log graph. In most cases a straight-line *analytical curve* is produced known as the *working curve.* There may be several working curves for each element. The number depends upon the concentration and the available spectral lines. The spectra of the unknown materials are obtained by precisely the same procedure used with the standards and the same spectral lines for each element are measured and their intensity ratios computed. Application of these intensity ratios to the working curve produces the concentrations of these elements in the unknown. It is common practice to run a few standards at the same time with the unknowns as a control on the validity of the established working curve, unless it is found that such a practice is not necessary.

The simple internal-standard method applies when the reference standard occurs in approximately equal concentration in all standards and unknowns. This is an abridged form of a procedure of computation which can be applied in a general case. In this general procedure, the *concentration-ratio method* or the *mutual-standard method*, the working curve consists of a plot of concentration ratios vs. intensity ratios in which the concentration ratios are the concentrations of the analytical elements divided by the concentration of the reference element. This general

method is not limited to the use of a reference element which has equal concentration in all samples and standards. However, the reference element is usually the major constituent in the material.

SPECIFIC METHODS

As examples of the procedures involved, two methods are given substantially as they appear in the ASTM book "Methods of Emission Spectrochemical Analysis." These are typical of many procedures, one using spark and the other d-c arc techniques.

Spectrochemical Analysis of Magnesium-base Alloys by the Cast Pin–Spark Technique. The following alloying and impurity elements are determined by this procedure in the ranges of concentration shown.

	Concentration Range, Per Cent
Measured photometrically:	
Aluminum	4.0 –10.0
Zinc	0 30 – 4.0
Manganese	0.10 – 0.40
Silicon	0.05 – 0 25
Copper	0.01 – 0 07
Measured visually:	
Lead	0 01 – 0.05
Tin	0 01 – 0.05
Iron	0 005– 0.01
Nickel	0 001– 0.005
Beryllium	0.001– 0.005

Method. A controlled-spark excitation of a metal-pin sample is used for all elements. A metal pin is obtained by drawing molten metal into a 6-mm OD Pyrex-glass tube. After removal from the tube, the pin is machined so that the end has a slightly rounded tip. The pin is used as the lower electrode and a ¼-in. graphite rod as the upper electrode. For visual estimation machined metal pins are used for both lower and upper electrodes. Electrodes are separated by a 3-mm gap in either case.

A spectrograph with good resolving power and dispersion and with a high-voltage spark source is employed. The spectral lines are obtained on an Eastman spectrum analysis No. 1 film and are measured with a microphotometer. The films are developed, washed, and dried under controlled conditions. To convert microphotometer readings to log-intensity ratios and then to per cent concentrations a calculating board is used.

Standard samples for use in this work are available as listed in "Report on Standard Samples for Spectrochemical Analysis," ASTM 1950 publication STP No. 58B.

For the elements measured photometrically the excitation characteristics are input voltage 110 volts, primary voltage 40 volts, capacitance 0.007 microfarad, inductance 1.4 millihenry. The same conditions are used for the visually measured elements except that all added inductance is removed. For all elements the exposure conditions are, using the spectral region 2,130 to 4,250 A and with the image focused on the grating, slit width 0.050 mm, slit length 1.5 mm, and spark preburn period 10 sec. The visually estimated elements require 30 sec exposure, while the photometrically measured elements require 10 sec exposure.

The emulsion-calibration spectrum is obtained from a spark between two aluminum pins using a five-step rotating sector.

To process the films, develop for 3 min at 70°F in Eastman D-19 solution, use an acetic acid stop bath for 15 sec, fix for 1½ min in Eastman rapid hypo solution, wash thoroughly (1 min in a special washer), and blow dry using an infrared heater.

TABLE 2-1

Element	Analytical line, angstroms	Internal-standard line, angstroms	Concentration range, per cent	Concentration index, per cent
Aluminum	Al 2,652 49	Mg 3,073 99	4 0–10.0	6 30
Zinc	Zn 3,282 33	Mg 3,073 99	1 0–4 0	2 30
	Zn 3,345 02	Mg 3,073 99	0 30–1 30	0 60
Manganese	Mn 4,033 07	Mg 3,073 99	0 10–0 40	0 18
Silicon	Si 2,881 58	Mg 3,073 99	0 05–0 25	0 10
Copper	Cu 3,273 96	Mg 3,073 99	0 01–0 07	0 025
Lead	Pb 2,833 07		0 01–0 05	
Tin	Sn 3,175 02		0 01–0 05	
Iron	Fe 2,599 40		0 005–0 01	
Nickel	Ni 3,414 76		0 001–0 005	
Beryllium	Be 3,130 42		0.001–0 005	

Visual estimations are made for lead, tin, iron, nickel, and beryllium.

Transmittance measurements for the analytical line pairs and lines of the calibration spectrum are made on a projection-type microphotometer. The emulsion-calibration curve established from previous films is assumed to remain constant. A standard-alloy sample is run on each film and serves to check any major shift in the analytical curve and also indirectly in the emulsion-calibration curve. The line pairs shown in Table 2-1 have been selected so that the analytical lines have transmittance readings between 20 and 80 per cent when the transmittance of the internal-standard line is about 30 per cent. The transmittances of the analytical line and of the internal-standard line are converted to log-intensity ratios

by means of the calculating board. The latter is a mechanical convenience for the plotting and reading of logarithmic intensities and logarithmic concentrations for plate calibrations and for analytical working curves. This procedure when used for several samples serves to establish the analytical curves relating log-intensity ratios to per cent concentration. For routine work, log-intensity ratios are converted to per cent concentrations by reference to the appropriate analytical curve. The average of duplicate determinations, corrected by a control standard in duplicate on the same film, is reported for each alloying element. The visual estimations are made by comparison with a standard run on the same film.

The *precision* of the method is given by the repeatability of determinations over a period of several weeks on different films (by different operators) under routine conditions. The results of the spark determinations shown in Table 2-2 were so obtained.

TABLE 2-2. DATA ON PRECISION OF METHOD
(All results on same sample)

	Average concentration	Coefficient of variation	No. of determinations
Aluminum	6.30	2 6	30
Zinc	3.10	3 6	30
Copper	0.026	6.9	30
Silicon	0 14	9.2	30
Manganese	0.30	6.1	30

The coefficient of variation ν is calculated as follows:

$$\nu = \frac{100}{C}\sqrt{\frac{\Sigma d^2}{n}}$$

where C = average per cent concentration
d = difference of the determination from the mean
n = number of determinations

Since copper is reported to the nearest whole value (either 0.02, 0.025, 0.03, 0.035, etc.) the coefficient of variation is increased. Similarly, silicon and manganese are reported to two significant figures, and thus the larger coefficient of variation is largely accounted for.

Compared with chemical results, the spectrochemical figures were just within 5 per cent of the amount so found. The remaining elements were well within 5 per cent of the amounts determined by chemical means.

The visually determined impurity elements were within routine chemical accuracy, and consequently quantitative photometric methods are not necessary.

It is of interest to note that the analytical curve set up for aluminum was found to undergo small parallel shifts almost daily. This necessitated the use of a standard sample on each film. No reason for the displacements has been found.

Spectrochemical Analysis of Ceramics and Other Nonmetallic Materials by the Powder–D-C Arc Technique. This method, which can be used for ceramics, ores, slags, paints, ashes, and other nonmetallic materials, requires much less time and less material than do chemical methods. Even major constituents have been successfully determined in a number of cases, e.g., copper-base alloys;[1] ceramics, solders, Alnico and ashes;[2] silicon, iron, and aluminum in mineral powders;[3] and miscellaneous materials.[4] The reduction of the densities of the principal lines of the major components, usually too high for accurate densitometry, and the elimination of self-absorption at high concentrations are accomplished by the addition of a buffer material. By this means the reduction of the complexity of the spectrograms is also accomplished by eliminating many of the less sensitive lines. The influence of component elements upon each other is also lessened.

The buffer may be added in the form of powder, solution, or low-melting-point alloys. Insoluble materials are best handled as powders, the finely powdered sample and buffer being thoroughly mixed. Lead oxide (PbO), bismuth oxide (Bi_2O_3), cupric oxide (CuO), nickel oxide (NiO), and barium nitrate [$Ba(NO_3)_2$] have all been used as buffers and internal standards. This method uses CuO, generally in a mixture of 1 part of sample to 49 parts of CuO and 100 parts of pure graphite powder. Such a mixture has been found satisfactory for the determination of most elements in the range of 0.30 to 35 per cent. The proportion 1:9:20 is occasionally used when the concentration of the element sought is less than 1 per cent. Because large amounts of buffer are used, it must be very pure. The buffer should not be used if it contains more than 0.001 per cent of the element sought in the sample.

Method. A *spectrograph* is employed having sufficient resolving power and linear dispersion to separate the lines clearly in the spectrum of the sample in the region of 2,300 to 5,000 A. Most commercial instruments having a reciprocal linear dispersion of 10 or fewer A per millimeter at 2,800 A are suitable. A d-c arc source is employed with an open-circuit voltage of 250 volts, and a maximum arc-current output of 15 amp. Eastman Process or equivalent plates or films are used to record the spectra, and a densitometer, having a precision of ± 1.5 per cent for optical densities between 0.2 and 1.5, is used to measure the transmittance of

the spectra. Open-tray development at 68°F may be used. Calculating boards are helpful though not essential.

National Bureau of Standards certified samples or others of known reliability are used as spectrochemical standards. Dry at 110° to 120°C for 1 hr and mix thoroughly in a smooth agate mortar the following: 1 part standard base, 49 parts cupric oxide (CuO), and 100 parts of pure graphite powder by weight.

Single sets of standards can be made to contain a number of elements, but it is best that not more than four elements or compounds be included. Values of standards should be chosen to comprise the expected amount of the element or compound in the sample.

The sample is prepared similarly to the standard, 1 part of sample (100 mg), 49 parts of CuO, and 100 parts of graphite powder. Thoroughly mix the dried ingredients in a smooth mortar. Other ratios may be used, depending upon the amounts of the required elements present.

The anode of the *electrode system* consists of a high-purity graphite rod ¼ in. in diameter and 1 in. long with a cup cut into the end with a No. 15 (0.180-in.) drill to a depth of ⅛ in. The upper electrode (cathode) consists of a high-purity graphite rod $\frac{3}{16}$ in. in diameter and 1⅛ in. long, with a flat end. The gap width is maintained at ¼ in. Arc the samples, in triplicate, with a series of standards, in the d-c arc at an initial current of 13 amp limited by a resistance in series. Make no further adjustments after the initial setting. The *exposure* conditions are as follows: spectral region 2,400 to 6,000 (or as required) A; slit width and length, depending upon the specific spectrograph and densitometer, 0.02 to 0.08 mm and 1.0 to 3.0 mm, respectively; a neutral three-step filter or an equivalent sector wheel or step sector transmitting 100, 20, and 4 per cent approximately of the incident light; no arc preburn period; and 60 sec arc exposure.

The spectrograph is illuminated in such a manner that the resulting spectral lines represent radiant energy from the entire arc column except for about $\frac{1}{64}$ in. from the tip of each electrode which is to be screened out.

Process the plates or films in Eastman Dektol developer for 4 min at 68°F. As stop bath use running water for 15 sec. Fix for 3 min in Eastman acid fixing bath with hardener, wash for 5 min in running water, and blow dry.

Where the *emulsion calibration* is required in terms of relative intensities calibrate by means of a step-sector method, a step-filter method, or by the two-line method of Churchill.[5] Where the spectra of the standards are placed on the same emulsion, the calibration is made directly in terms of percentage concentration of the element required vs. the ratio of the densities or transmittancies of the line pairs employed (Table 2-3).

Determine the *optical density* or transmittance of the analytical line pairs listed in Table 2-3 and convert to relative intensities using the

emulsion-calibration curve previously obtained. From these data plot an analytical curve for log-concentration vs. log-intensity ratios from the spectra of the standards for each element for which an internal-standard line is listed in Table 2-3. For the elements for which no internal line is listed in Table 2-3 plot intensity vs. log concentration. Determine the concentration of the element sought in the samples by reference to the appropriate analytical curve. Report the average of triplicate determinations.

TABLE 2-3. ANALYTICAL LINE PAIRS

Element	Analytical line, angstroms	Internal-standard line, angstroms	Element	Analytical line, angstroms	Internal-standard line, angstroms
Aluminum	Al 3,082.16	Cu 2,768 88	Magnesium	Mg 2,776.69	Cu 2,768 88
	Al 3,092.71	Cu 2,768 88		Mg 2,782 97	Cu 2,768 88
				Mg 2,798.06	Cu 2,768.88
Boron	B 2,496 78	Cu 2,768 88	Manganese	Mn 2,576 10	Cu 2,768 88
	B 2,497.73	Cu 2,768 88		Mn 2,798 27	Cu 2,768 88
Beryllium	Be 3,130 42	Cu 2,768 88	Sodium	Na 3,302.32	Cu 3,208 23
	Be 3,131 07	Cu 2,768 88		Na 3,302.99	Cu 3,208.23
	Be 3,321 34	Cu 2,768 88		Na 5,889 95	None
				Na 5,895.92	None
Barium	Ba 3,071 59	Cu 3,126 11	Lead	Pb 2,833 07	Cu 2,768 88
	Ba 4,554 04	Cu 4,248 96		Pb 2,873.32	Cu 2,768.88
	Ba 4,934.09	Cu 4,248 96			
Calcium	Ca 3,158 87	Cu 3,126 11	Silicon	Si 2,506.90	Cu 2,768.88
	Ca 4,226.73	Cu 4,248 96		Si 2,514.33	Cu 2,768 88
				Si 2,516.12	Cu 2,768 88
				Si 2,524.12	Cu 2,768 88
Chromium	Cr 4,254.35	Cu 4,248.96	Titanium	Ti 3,349.41	Cu 3,126.11
	Cr 4,274.80	Cu 4,248 96		Ti 3,361.26	Cu 3,126.11
	Cr 4,289.72	Cu 4,248.96			
Iron	Fe 2,599.40	Cu 2,768.88	Zinc	Zn 3,345.57	Cu 2,768.88
				Zn 3,345.57	Cu 3,126.11
				Zn 4,810.53	Cu 4,248.96
Lithium	Li 3,232 61	Cu 3,126.11	Zirconium	Zr 2,571.39	Cu 2,768.88
	Li 4,602 86	Cu 4,248.96			

Where the emulsion is not calibrated, determine the optical density of transmittance of the analytical and internal-standard line pairs listed in Table 2-3. Plot an analytical curve relating log-concentration vs. density (or log-transmittance) ratios from the data obtained on the standards for each element for which an internal-standard line is listed in Table 2-3. For the elements for which no internal-standard line is listed in Table 2-3 plot optical density vs. log concentration. Determine the concentration

of the element sought by reference to the appropriate analytical curves. Report the average of triplicate determinations. This procedure is permissible if the spectra of the standards are photographed on the same emulsion as the spectra of the samples and if the lines used have optical densities between 0.20 and 1.5.

The *precision and accuracy* of this method are indicated in Table 2-4. Compared with chemical determinations, 19 out of 22 are in good agreement. Three are omitted from the average. These data cover some of the elements and compounds embraced by this procedure. Experience with miscellaneous applications indicates the general precision to be better than ± 10 parts per 100.

TABLE 2-4

Sample	Compound	Percentage by spectrochemical method	Percentage by chemical method	Difference	Difference, per cent
F-66	Al_2O_3	7.61	7.58	+0 03	+0.4
S-7	Al_2O_3	1.04	1.0	+0.04	+4.0
Sierramic talc	Al_2O_3	1.07	1.15	−0.08	−7.4
NBS No. 76	Al_2O_3	36.2	37.7	−1.5	−4.0
F-66	BaO	16.4	15.74	+0.66	+4.2
S-7	BaO	4.13	4.17	−0.04	−1.0
F-66	CaO	0.94	0.54	+0.40	74.1*
S-7	CaO	0.64	None		
Sierramic talc	CaO	0.42	0.43	−0.01	−2.3
NBS No. 76	CaO	0.265	0.27	−0.005	−1.8
F-66	Fe_2O_3	1.15	0.91	+0 24	+26.0*
S-7	Fe_2O_3	0.71	0.66	+0.05	+7.6
Sierramic talc	Fe_2O_3	1.37	1 39	−0.02	−1.4
NBS No. 76	Fe_2O_3	2.30	2.37	−0.07	−3 0
F-66	MgO	23.7	24.6	−0.9	−3.7
S-7	MgO	50.2	50.9	−0.7	−1.4
Sierramic talc	MgO	31.6	31.2	+0.4	+1.3
F-66	SiO_2	47.1	50.12	−3 02	−6.0
S-7	SiO_2	44.5	42.99	+1.51	+3 5
Sierramic talc	SiO_2	57.2	58.8	−1.6	−2.7
NBS No. 76	SiO_2	56.0	54.7	+1.3	+2.4
Ash tar	ZnO	0.53	0.55	−0.02	−3.6
			Avg. difference		3.3

* = values omitted from average.

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CHAPTER THREE

Flame Photometry

Emission spectroscopy, broadly speaking, deals with the examination of the energy emitted from a substance when suitably excited. This energy can be analyzed for intensity and for its wave components. It is obvious that materials may be excited in various ways. The excitation caused by flames comes under the heading of Flame Photometry and is actually a part of the broader sphere of emission spectroscopy. Since flames, even very hot ones, are sources of considerably less intense energy than are electric arcs or sparks, it follows that the higher states of excitation are not normally attained, and all the elements may not be heated sufficiently strongly to give their characteristic spectra. With present-day sensitive spectrophotometers and amplifying devices over forty elements may be determined. For reasons to be given later, only a few of these are at present advantageously estimated by these means. The success of this method has, to date, depended largely upon its great usefulness in determining the alkali metals.

Flame photometers are very simple to use. They consist of a burner and an atomizer (for the substances to be determined must be in solution) followed by a dispersing system. This may comprise a small prism or grating, a monochromator to pick out the desired wavelength, or simply a wavelength filter. A barrier-layer cell or electronic amplifier then picks up and amplifies the energy of the separated wavelength, or band of wavelengths. The amplified energy is measured, usually not in terms of absolute units but in units which are related to a standard.

The basic principle underlying this means of analysis was made use of in 1859 by Bunsen and Kirchhoff.[1] More recently, Lundegardh[2] revived the method. In the early 1940's Barnes and coworkers devised a practical instrument for determining sodium and potassium. These two elements are rather readily excited by flames, producing spectra of which certain intense lines under appropriate conditions can be measured photometrically. The readings are recorded by a milliammeter or sensitive galvanometer. The difficulties previously encountered in applying this rather obvious method were mainly due to inability to obtain a steady

flame, to apply a constant amount of sample, and to measure the effect.

At present, the elements that are most advantageously determined by flame-photometric means are sodium, potassium, and lithium. This is so because most elements are not nearly so readily excited as are the alkali metals and therefore do not give very strong signals, and also because of

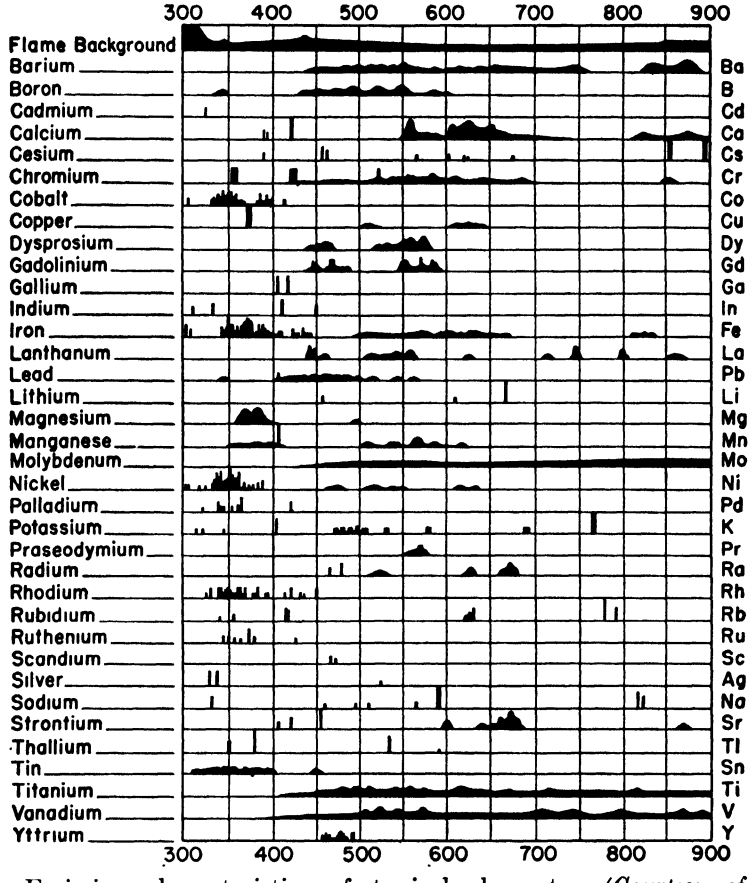


FIG. 3-1. Emission characteristics of typical elements. (*Courtesy of Beckman Instruments, Inc.*)

conflicting wavelengths. Another reason is that the chemical determination of these elements is long and tedious, much more so than that of other commonly analyzed elements.

Calcium, barium, and magnesium are also commonly determined. Many other elements, e.g., boron, cesium, chromium, copper, gold, iron, lead, manganese, mercury, nickel, palladium, rubidium, ruthenium, silver, strontium, thallium, tin, and a number of others, may be estimated by the use of more sensitive spectrometers and amplifiers. Very few methods for these elements have been published. Table 3-1 gives a number of lines of different elements that can be used. Strong lines which

TABLE 3-1. WAVELENGTHS AND DETECTION LIMITS OF VARIOUS ELEMENTS WITH THE FLAME PHOTOMETER*

Element	Wavelength	D	Element	Wavelength	D	Element	Wavelength	D
Aluminum	484.2*b*	2	Gold....	267.6*a*	20	Rhodium . .	369.2*a*	0.1
	467.2*b*	3	Indium	451.1*a*	0.1		343 5*a*	0.1
	396.2*a*	4		410.2*a*	0.1		350.3*a*	0.1
Barium.	553.6*a*	0.3		325.6*a*	1	Rubidium. .	780.0*a*	0.01
	873 *b*	0.3	Iron ..	372.0*a*	0.2		794.8*a*	0.03
	493.4*s*	0.4		386.0*a*	0.2		420.2*a*	5
Beryllium	471 *b*	25		373.6*a*	0.3	Ruthenium	372.8*a*	1
	510 *b*	100	Lanthanum....	442 *b*	0.5		378.6*a*	2
Bismuth	472.3*a*	30		438 *b*	0.5		349.9*a*	10
	306.8*a*	70		560 *b*	0 6	Samarium ..	651 *b*	10
Boron..... ..	548 *b*	1	Lead..... ..	405.8*a*	2	Silver .	338.3*a*	0.05
	521 *b*	2		368.3*a*	2		328 1*a*	0 1
	495 *b*	3		364.0*a*	3	Sodium .	589.3*a*	0.0002
Cadmium. .	326.1*a*	2	Lithium....	670.8*a*	0.002		330.3*a*	1
	228.8*a*	40	Magnesium. ..	371 *b*	0.1		819.5*a*	10
Calcium . .	422.7*a*	0.003		383 *b*	0.1	Strontium .	460.7*a*	0 02
	622 *b*	0.004		285 2*a*	0.2		681 *b*	0.01
	554 *b*	0.01	Manganese	403.3*a*	0.01		407.8*s*	0 5
Cerium ..	481 *b*	2		279.8*a*	1	Tellurium	363 6*b*	10
	493 *b*	2		561 *b*	2		372 *b*	10
Cesium	852.1*a*	0.1	Mercury .	235 7*a*	10	Thallium	377.6*a*	0 1
	894.4*a*	0.2	Molybdenum .	600 *c*	3		351 9*a*	2
	455.5*a*	50	Neodymium .	659 *b*	5		535.0*a*	5
Chromium.	425.4*a*	0.1		462 *b*	10	Tin..	317 5*a*	1
	360.5*a*	0.1		430.4*a*	10		349 *b*	1
	520.6*a*	0.1	Nickel .	352.5*a*	1		303.4*a*	1
Cobalt... .	353.0*a*	1		341 5*a*	1	Titanium	518 *b*	0.2
	341.2*a*	1		351 5*a*	2		497 *b*	0.3
	350.2*a*	2	Niobium. .	450 *c*	2		715 *b*	1
Copper. .	324.8*a*	0.01	Palladium	363.5*a*	0 1	Uranium	550 *c*	1
	327.4*a*	0.01		340.5*a*	0 1	Vanadium	576 *b*	0 2
Dysprosium. .	552 *b*	1		361 0*a*	0.2		550 *b*	0.3
	570 *b*	1	Potassium.. ..	766 5*a*	0.001		528 *b*	0.3
Gadolinium	462 *b*	1		404.6*a*	0.2	Yttrium .	444 *b*	5
	570 *b*	10		344.7*a*	3		483 *b*	5
	450 *b*	10	Praseodymium	562 *b*	10	Zinc ..	213.9*a*	500
Gallium..... .	417.2*a*	0.1		571 *b*	10		500 *c*	200
	403.3*a*	0.1						

The type of emission is indicated following the wavelength (in millimicrons): *a* denotes an arc line (emitted by the neutral atom), *i* an arc line emitted in the inner cone of the flame, *s* a spark line (singly ionized atom), *b* the maximum of a molecular band (usually emitted by an oxide of the type MO), and *c* a convenient wavelength in a continuous emission (when lines and bands are absent). The exact wavelength of a band (*b*) usually depends upon the resolving power of the instrument, because these bands are normally asymmetric and complex. Therefore, they are usually quoted only to the nearest millimicron.

Detection limits (*D*, in ppm) are in most cases quoted for the most sensitive commercially available flame photometers; specifically this refers here to a Beckman model DU quartz spectrophotometer with oxyhydrogen flame attachment, multiplier phototube for 200 to 620 mμ and red-sensitive phototube for longer wavelengths.

* Beckman Instruments, Inc.

are not included are in most cases near lines of other metals, and interference would result if they were used. Consideration must be given to other elements present before a specific line is chosen. In Figure 3-1 are given emission characteristics of typical elements determinable by flame photometry. This chart is useful in considering possible interferences and should help in choosing the best lines for use under specific conditions.

ADVANTAGES OF THE METHOD

The flame photometer is extremely useful in determining small amounts of sodium, potassium, and lithium when present in solution. Less than 0.1 ppm can be measured under optimum conditions. This is far less than can be determined with any degree of accuracy by usual chemical methods. Higher concentrations can readily be determined by dilution, with accuracies equal to or above those obtained by classical chemical methods.[3] A number of different elements can theoretically be determined on the same solution in the presence of one another and of most other common elements. Relatively small samples are necessary. The time needed to make such determinations, when the sample is in proper solution, is often a fraction of that required by the usual chemical methods. Even when appreciable preparatory work is involved, much time may be saved when large numbers of samples are to be analyzed.

The classical J. Lawrence Smith method for determining sodium and potassium in refractory materials, while admirable in many respects, is well-known to be quite tedious, and, unless extremely careful work is done, liable to several rather grave errors. Much work can be saved and accuracy enhanced by applying the flame photometer.[3,4,5]

In biological work where interfering elements and substances are often present in great amount, this instrument is much used since considerable time is saved, especially on multiple samples.

LIMITATIONS OF THE METHOD

When certain lines of an element other than that being measured lie near those lines of the element which are in use, interference may result. In many cases, this interference is sufficient to vitiate the result. Anions also may cause serious error if in excess of the amount necessary to combine with the metal being measured, especially for metals other than those in group I. The anions may be present as salts of other elements or as free acid. Differences in air and gas pressure and in solution viscosity, and the presence of organic molecules are known to cause appreciable errors. It is fortunate that, in many cases, such interferences can be eliminated by various means. The original articles of Barnes and

element lithium to pass. The photoelectric system performs a dual function. It will measure the light intensity produced by a single element being determined, or it will measure the ratio of a light intensity produced by the element being determined to that of the added internal-standard element, normally lithium. The outputs from the two phototubes are amplified separately.

When used as a direct-reading photometer, the internal-standard dial is set at zero. As a ratio-comparison photometer the internal-standard dial is adjusted until its signal exactly balances that of the unknown.

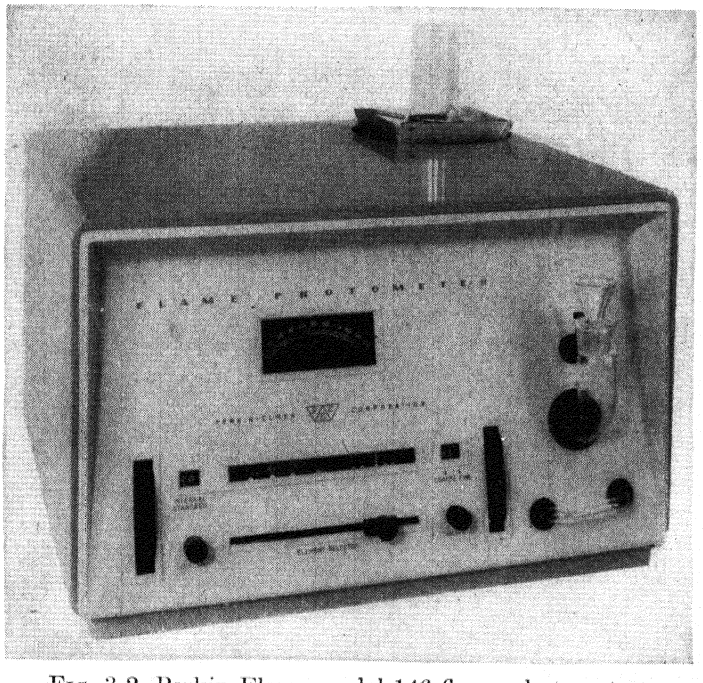


FIG. 3-2. Perkin-Elmer model 146 flame photometer.

The instrument has a double-scanning phototube unit containing both a red- and a blue-sensitive phototube. This enables the complete range of the instrument to be scanned, when using acetylene, without the necessity of changing phototubes.

This is an excellent instrument for determining sodium and potassium. With special care, calcium and other elements may be determined. Since the spectral bandwidth employed is not very narrow despite the use of a monochromator, less sensitivity must be expected for elements the lines of which are either weak or broad or consist of bands.

Beckman Flame Photometer. This differs from the previous instrument in that it is an attachment specially designed to be used with the Beckman quartz spectrophotometer and the Beckman model B spectrophotometer (Fig. 3-3). This arrangement ensures high resolution for the

spectral lines, especially with the DU (quartz) instrument. Interference due to overlapping lines and bands is hence considerably reduced. The photometer consists of an atomizer-burner unit in a metal housing, sample-positioning mechanism, focusing mirror and adjustments, and a separate pressure-control panel. The atomizer-burner is made of Pyrex with a straight noble-metal atomizing tube that discharges directly into the flame. The gases used are hydrogen or acetylene, and oxygen. These give a very hot flame.

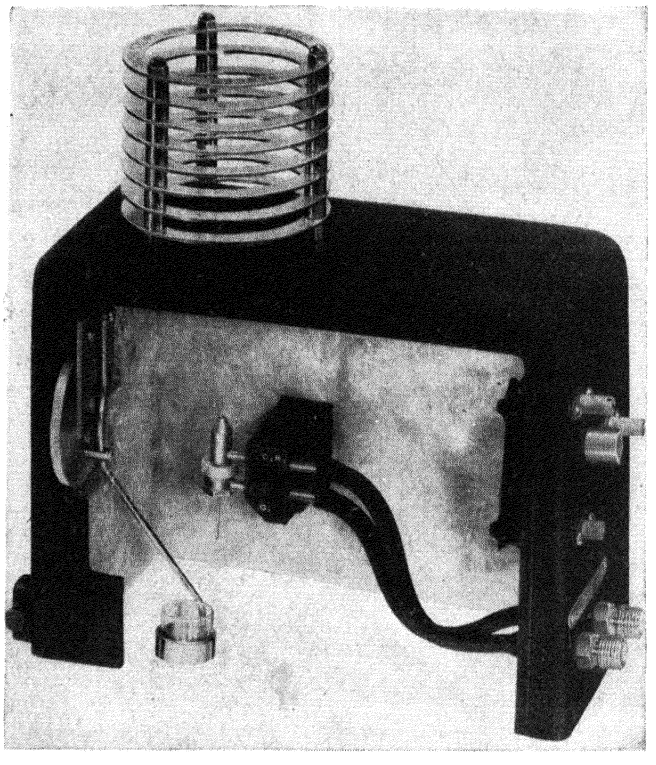


FIG. 3-3. Beckman flame-photometer attachment for model DU spectrophotometer.

The spectral lines from the element in the flame are used as the light source of a regular Beckman model DU spectrophotometer which will isolate the lines and measure their intensities in the usual manner (page 72). A photomultiplier attachment is also available. This increases the flame signal manyfold so that very small amounts of elements, and those with weak flame emission, may be measured. It is possible to use a recorder and obtain a complete spectrum of the contents of the solution.

Since this is a single-beam instrument, the internal-standard method is not readily employed. To use this method, it would be necessary to make successive settings of the wavelength of the element being determined followed by that of the standard. Reproducibility should be checked for each analysis. Lithium could be added to each sample and the intensity

of the lithium and of the sodium measured individually. This would compensate for chemical effects of foreign ions but not for the effect of air or of viscosity. These effects may be reduced by alternately measuring the lithium and the sodium intensities several times on each sample and obtaining the average ratio value. This whole procedure is, obviously, too tedious for normal use.

The sensitive dispersing system enables many rather weak lines to be separated and measured so that a number of elements can be determined.

Other Flame Photometers. Among these are the Baird, Barclay, Coleman, Fox, and Weichselbaum-Varney instruments, each of which has its particular advantage. All operate on the same general principle. The Baird model uses filters and stresses simplicity with accuracy. The Barclay flame photometer combines operating simplicity with variable sensitivity and a high order of accuracy over a wide range of concentrations. The Coleman instrument may be operated with any of the Coleman photometers, or with a separate galvanometer. The three last-mentioned instruments are limited in the number of elements determinable. The Weichselbaum-Varney universal spectrophotometer uses a high-temperature flame and an efficient photometer system. It gives rapid results with at least 14 elements. The Fox photometer is quite simple, uses filters, and is readily serviceable. A comparison of some instruments is given by Fox.[10]

ELEMENTS DETERMINABLE

Sodium, potassium, lithium, calcium, barium, and magnesium and perhaps also chromium, strontium, and manganese are at present about the only elements for which special techniques have been published. Many other elements have been determined with more or less accuracy. Table

TABLE 3-2

Element	Concentration range, ppm	Minimum detectable, ppm
Sodium	3–1,000	0.01
Lithium	10–1,000	0.05
Potassium	10–1,000	0.05
Magnesium	500–1,000	25
Calcium	200–1,000	2
Strontium	200–1,000	2
Barium	500–1,000	20
Chromium	200–1,000	20
Manganese	500–1,000	20

3-2 gives a list of approximate concentration ranges and minimum detectable amounts of element that can be expected with a typical instrument.

USE OF BAND SPECTRA

Spectral emission normally consists of atomic lines and also lines due to the presence of diatomic molecular bands. The former generally give more reliable measures of concentration than do the bands. The hotter the flame the more intense are the atomic lines and the less intense the molecular bands. The latter are more dependent on general sample composition and are therefore more subject to interference.

It may be useful to use bands when they are more intense than the main atomic lines of the element. It may then be practical to make calibration standards with compositions similar to the samples and thus compensate for most of the errors. Calcium can be determined by this method as it has a strong emission band around 5,550 A.

INTERFERENCES

Apart from the preparation of the original sample by chemical means, and, it should be warned, this may involve considerable work, the greatest amount of work and thought in the use of the flame photometer is in connection with interference by other ions. Air and gas pressure must be and can be regulated rather readily. Solution viscosity is not normally important but may have to be considered.[7] Organic solvents can be used where the substance is insoluble in water. Clearly, calibration curves used with one solvent cannot be used for another solvent. All foreign ions in solution will, if not compensated for, throw off results very appreciably. In 1946, Berry, Chappel, and Barnes introduced the internal-standard method to reduce the effects of gas- and air-pressure fluctuations, foreign ions and molecules, and viscosity differences.[8,11,12,13] Figure 3-4, reproduced from the paper by Berry, Chappel, and Barnes, shows the effect of a number of interferences and refers to an earlier flame photometer. It is important to realize that, as is found by studying published results, different instruments give different interference effects. There is, at present, no clear explanation of this.[14] Of course, when properly calibrated, each instrument should give good reproducible results.

Tables 3-3 and 3-4 show the interferences obtained with acetylene and propane flames as given by the Perkin-Elmer Company in their Model 52C Manual. These figures may be taken as indicative and approximate, and vary somewhat with the instrument and the technique employed.

The tables and figures given serve only as a guide and must not be used to correct results. They do show, however, that effects are serious and

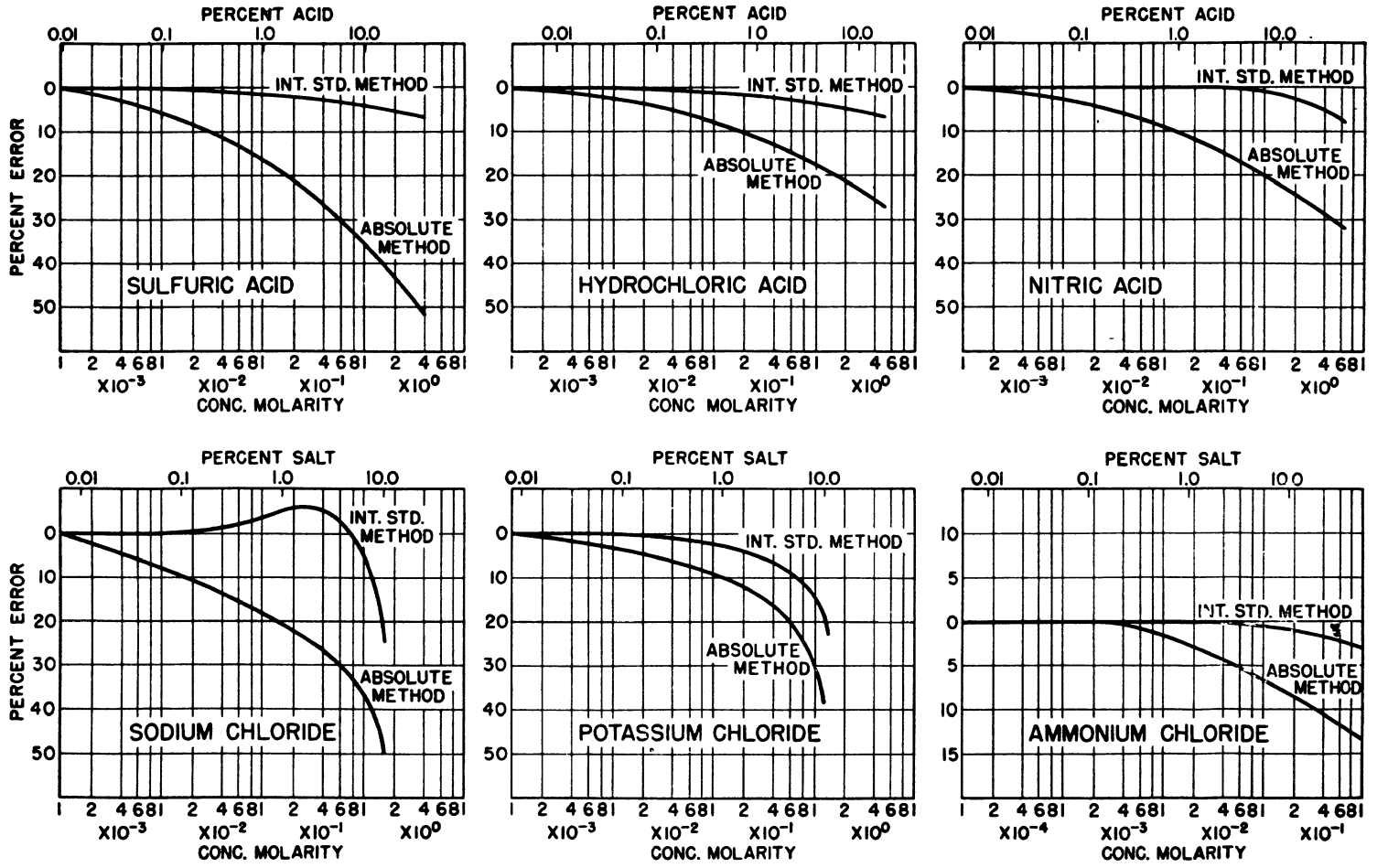


FIG. 3-4. Effects of certain interferences.

TABLE 3-3. INTERFERENCE WITH AN ACETYLENE FLAME (TEMP. 1275°C)
(Interference as concentration of unknown element equivalent to 1,000 ppm of interfering element)

Unknown element \ Interfering element	K	Li	Na	Ba	Sr	Mn	Ca	Cr	Mg
K	1,000	2	1	8	2	5	3	3	6
Li	1	1,000	0	1	70	0	4	1	0
Na	1	3	1,000	2	4	1	8	2	6
Ba	60	200	500	1,000	200	300	25,000	700	100
Sr	5	3	8	10	1,000	2	4	20	1
Mn	200	10	30	0	0	1,000	0	20	10
Ca	0	6	10	3	5	6	1,000	50	6
Cr	30	20	60	0	0	0	2,000	1,000	0
Mg	60	60	200	. .	80	60	200	40	1,000

TABLE 3-4. INTERFERENCE WITH A PROPANE FLAME (TEMP. 1050°C)
(Interference as concentration of unknown element equivalent to 1,000 ppm of interfering element)

Unknown element \ Interfering element	K	Li	Na	Ba	Sr	Mn	Ca	Cr	Mg
K	1,000	1	0 5	4	0 5	1	2	1	1
Li	2	1,000	1	2	100	0	2	2	0
Na	1	3	1,000	1	3	0	5	1	5
Ba	200	20	500	1,000	100	200	300	500	100
Sr	80	20	100	40	1,000	10	0	100	10
Mn	200	10	80	0	0	1,000	0	30	40
Ca	20	60	200	20	0	40	1,000	300	60
Cr	.	.	.	.	.	.	500	1,000	
Mg	100	50	300	0	50	30	0	0	1,000

must be counteracted. Rubidium interferes greatly with the determination of potassium. Large amounts of sodium tend to enhance the intensity of the calcium and potassium emission. Aluminum interferes in calcium determinations and may be removed with a comparatively weak base such as pyridine, or other organic precipitating agent. Hence it is essential to study carefully the effects produced by the other elements or substances present, when a procedure is being set up for the determi-

nation of a specific element. Often synthetic solutions containing the chemical equivalents of all the major components of an unknown can be made up and the effect of the components determined. In other cases, the results obtained can be compared with carefully analyzed samples in which the component has been determined chemically and interferences discovered by this means. The cause having been determined, the interference must be eliminated by getting rid of the substance causing the trouble or by adding the interfering substances to the standardizing solutions. As has already been mentioned, a second means of counteracting interference is to use an internal standard. Much work remains to be done both on the cause and on the elimination of interferences.

STANDARDS

Elements Alone. Comparison standard solutions must be available. How many and what range will depend largely upon the amount of alkali metals in the sample solution. It is best not to use more than 200 ppm of sodium or potassium as the strongest solution to give maximum deflection. The larger the number of standards between this maximum and the lowest-strength solution, the better in order to obtain a smooth curve. The following are given as possible useful groups of standards:

200, 150, 100, 75, 50, 25	ppm
100, 80, 60, 40, 20, 10	ppm
75, 60, 45, 30, 15, 7.5	ppm
50, 40, 30, 20, 10, 5	ppm
25, 20, 15, 10, 5, 2.5	ppm
10, 8, 6, 4, 2, 1	ppm
5, 4, 3, 2, 1, 0.5, 0.2	ppm

For samples in which both sodium and potassium are present, it may be advantageous to make up standards containing both of them in known and varying amounts. For biological samples another group of standards close together is essential.

Use sodium chloride and potassium chloride of ACS or even greater purity, dry at 105°C and weigh 2.5413 grams of the former or 1.9066 grams of the latter. Dissolve in distilled water in a 1,000-ml Pyrex flask and make up to volume at the temperature marked on the flask. These will give solutions containing 1,000 ppm of sodium or of potassium as the respective elements. Store these concentrated stock solutions in special No-Solvit glass bottles or well-stoppered polyethylene plastic bottles. Prepare the desired more dilute standards from these, using carefully calibrated burettes or pipettes.

Should the internal-standard method be used, add the requisite amount of concentrated lithium nitrate solution to give 100 ppm lithium as the element, in the final solution. Exactly similar amounts of this internal standard must also be added to the sample solutions before making to volume. The exact amount added is not so critical as the fact that *exactly the same amount* must be added to both standard and sample. With a concentrated lithium solution, use a microburette for volumes less than

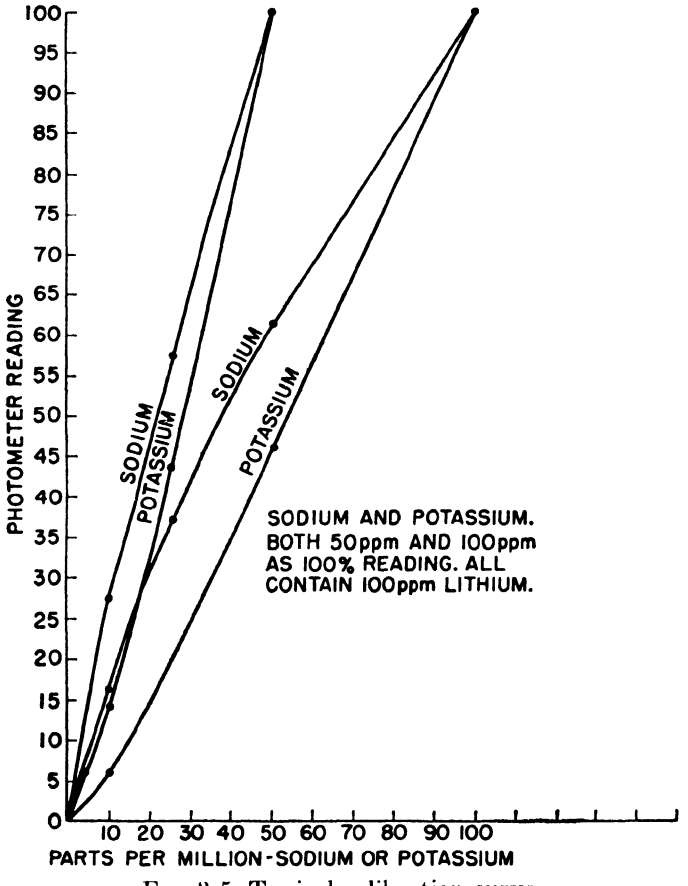


FIG. 3-5. Typical calibration curve.

5 ml. A 1,000-ppm concentrated lithium solution is obtained by dissolving 9.935 grams of cp anhydrous lithium nitrate, dried at 105°C, in a final volume of 1,000 ml. Store in a No-Solvit or polyethylene bottle.

When calcium standards are required, dissolve 24.962 grams of cp low-alkali calcium carbonate in just sufficient hydrochloric acid, just bring to a boil, cool, and make up to 1,000 ml to give 10,000 ppm calcium as metal. In general, use stable, nonhygroscopic, unhydrated salts of the elements required. Chlorides and nitrates give least effect due to the anion. It may even be necessary to remove sodium and potassium from calcium

carbonate by repeated leachings or by dissolving in acid, reprecipitating with ammonium carbonate, and thoroughly washing.

Elements and Other Salts. When it is not possible to obtain the sample solution free of salts, other than those of the element to be determined, these salts or acids must be added to the standard solutions if they are present in sufficient quantity to cause noticeable interference. Reference to literature cited above and experience will indicate when this is

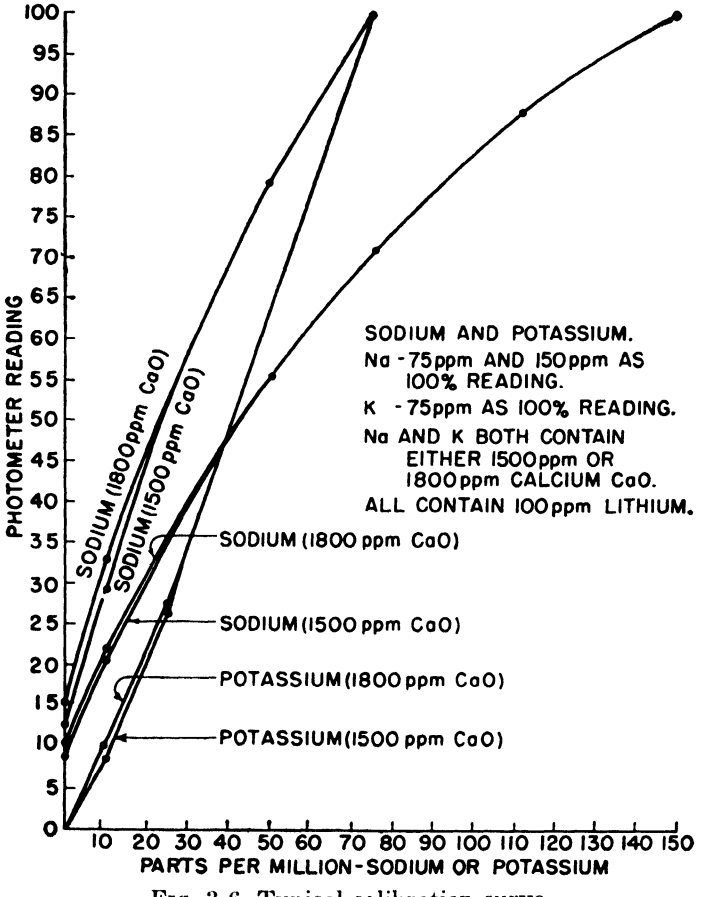


FIG. 3-6. Typical calibration curve.

necessary. In most cases, the amounts present should be known with a fair degree of accuracy and similar amounts, allowing for the final dilution, added to each standard solution. Proceed as indicated in the last section and add these salts or acids before making to final volume.

Standard Curves. After the various readings on the flame photometer with the standard solutions have been made exactly according to the instructions given in the manual for the instrument used, plot a calibration curve. Typical curves are given in Figs. 3-5 and 3-6. These show the effect of concentration and of the addition of a considerable amount

of calcium. The curves were used in the method for sodium and potassium in refractory materials given in ref. 3. These curves should be checked on one or two points, at least, each day the instrument is used for the specific element. Always check the 100 per cent point. The curves are used to convert the readings of the sample solutions to concentrations and save the trouble of continually making up fresh standard solutions.

AIR SUPPLY

The air supply should be passed through a dust filter, a liquid trap, and a pressure-regulating and -reducing device if compressed air is used. Approximately 2 cu ft of air per minute at pressures ranging from 8 to 15 psi should be available. A large tank between the supply and the valve helps to maintain even pressure. A manometer in the line between the valve and the instrument is useful in maintaining constant pressure. Small pressure variations may be important, especially if the burner is somewhat dirty. The latter, of course, should always be kept reasonably clean.

GAS SUPPLY

The compressed gas should be connected to the instrument through a pressure-regulating and -reducing valve capable of controlling gas pressure to the apparatus in the range of 2 to 10 psi. A manometer in the line is helpful in maintaining constant pressure. Some instruments advantageously use city gas at the usual pressure of supply.

TYPICAL DETERMINATIONS

Sodium and Potassium in Portland Cement. This method has been drawn up as a tentative method by the ASTM (C114-51T). Since lithium is sometimes present in small amounts in some cements, the direct-intensity method is used. When lithium is present in negligible amounts, the internal-standard method can well be employed.

Since portland cement normally contains approximately 63 per cent of calcium as oxide, it is necessary to add to the standards this amount of calcium. A difference of a few per cent of calcium from this average will not appreciably affect the accuracy of a determination when this amount is in the standard.

Calcium Chloride Stock Solution. Add 300 ml of water to 112.5 grams cp low-alkali calcium carbonate in a 1,500-ml beaker. Slowly add 500 ml concentrated hydrochloric acid. Cool to room temperature, transfer, filtering if necessary, into a 1,000-ml volumetric flask, dilute to volume, and mix well. This solution contains 63,000 ppm calcium as oxide.

Sodium–Potassium Chloride Stock Solution. Dissolve 1.8858 grams of cp sodium chloride and 1.5830 grams of cp potassium chloride, both completely dried at 105°C, in water, dilute to 1,000 ml in a volumetric flask, and mix well. This solution contains the equivalent of 1,000 ppm each of sodium as oxide (Na_2O) and potassium as oxide (K_2O).

STANDARD SOLUTIONS
(Prepare as follows)

No.	Designation of standard concentration of alkali as oxide, ppm	Content of standard		Final volume of solution, ml
		Calcium chloride stock solution, ml	NaCl-KCl stock solution, ml	
1	100	200	200	2,000
2	75	100	75	1,000
3	50	100	50	1,000
4	25	100	25	1,000
5	10	100	10	1,000
6	0	100	0	1,000
7	100	0	100	1,000

The calcium-free solution (No. 7) is for use only in determining the correct positions of the wavelength selector for maximum responses to sodium and potassium.

From these standards obtain readings exactly as prescribed in the manual accompanying the instruments and draw two curves, one for sodium containing calcium and the other for potassium containing calcium. These curves may be used for future work on portland cement. The standard solutions should be kept in appropriate bottles for occasional checking of the instrument and curves.

Preparation of Sample. Carefully disperse exactly 1 gram of the dried cement in a 250-ml beaker with about 20 ml of water. Add 5 ml of concentrated hydrochloric acid all at once and swirl the beaker. Immediately dilute to 50 ml and break up any small lumps of cement with a flat-ended Pyrex glass rod. Digest for 15 min and filter through a No. 40 Whatman filter paper into a calibrated 100-ml volumetric flask. Wash the beaker and the paper thoroughly with water, cool the flask and contents, make up to volume, and mix well.

Obtain readings on the flame photometer for both sodium and potassium at the same time that the standards are read. Using the curves obtained from the standard solutions, read off the amount of sodium and potassium in the cements.

Sodium and Potassium in Refractory Materials. The method[3] employed is essentially the initial steps in the classical J. Lawrence Smith gravimetric procedure, followed by photometric determination of these alkalies. The direct-reading method may be used or, if lithium is known to be negligible, the internal-standard method. As a matter of interest, lithium can be determined using potassium as internal standard. This can be allowed for and the internal-standard method used. It has been found that calcium is the only interfering element of any consequence present after preliminary treatment of the sample and that, in the normal procedure, and after making up to a volume of 250 ml, approximately 1,500 to 1,800 ppm as calcium oxide will be in solution. This amount will, of course, vary with other dilutions. It has also been shown that standard solutions of the alkalies containing either of these amounts of calcium will give correct results so long as the corresponding standard-solution curve is used.

Calcium Chloride Stock Solution. Add 300 ml of water to 17.857 grams of cp low-alkali calcium carbonate in a 1,500-ml beaker. Just dissolve by the careful addition of concentrated hydrochloric acid, drive off absorbed carbon dioxide by momentarily bringing to a boil, cool, and make up to 1,000 ml in a volumetric flask. This solution contains 1,000 ppm calcium as oxide.

Standards. Make these up as previously described (page 43) using concentrations compatible with the expected alkali contents. Before making to volume add the equivalent of calcium—under the conditions described this will be 1,700 ppm as oxide—expected in the sample solution. If necessary, add the equivalent of 100 ppm lithium and finally make to volume. Prepare curves in the usual manner.

Preparation of Sample. As in the usual J. Lawrence Smith method, intimately mix 0.5 gram of finely powdered sample with 4 grams of cp low-alkali calcium carbonate and 0.5 gram of cp ammonium chloride. Heat gently in a special long platinum or nickel crucible if available, or in a 30-ml platinum crucible with a well-fitting lid, inserted in an asbestos board, for about 15 min. At the end of this period no more ammonia is evolved. Raise the temperature until no more than three-fourths of the crucible is at a dull red heat. Maintain at this temperature for 1 hr. Allow to cool, remove the sintered mass, if possible, by gently tapping the inverted crucible. If this does not dislodge the mass, add water and carefully warm. Transfer to a platinum dish or a well-used Pyrex beaker, using a rubber policeman, if necessary, and heat with 50 to 75 ml of water for 30 min, disintegrating any lumps with a flat-ended Pyrex glass rod. Filter into a 250-ml volumetric flask and wash well with hot water, using as little as is necessary. Depending upon the expected alkali present, it may be advisable to use a 500- or a 1,000-ml volumetric flask. The cal-

cium is present, in the main, as chloride with some hydroxide. To prevent precipitation of the latter, neutralize with a few drops of hydrochloric acid.

To the sample solution add lithium if present in the standard solutions, and then make up to volume. Finally obtain flame-photometer readings and, using the appropriate curves, read off the amount of the alkalies in solution.

Calculation (assuming 250-ml volume):

$$\text{ppm alkali from curve} \times \frac{250}{10^6} \times \frac{100}{0.5} = \text{per cent alkali}$$

The possibility that elements other than the alkalies, calcium, and chloride might be present and so produce interference in the flame photometer should be considered. This possibility is rather remote since refractory materials do not normally contain materials other than the alkalies, calcium, and magnesium. The method of treatment, sintering with calcium carbonate and ammonium chloride, renders insoluble all metals other than the alkalies, calcium, and possibly minor amounts of magnesium, which would have a negligible effect on the photometer readings. Some sulfate as calcium sulfate might be present. However, sulfate is not usually present in refractory materials, and also the solubility of calcium sulfate is small. Experience has shown that 12 per cent boron as oxide (B_2O_3) in a borosilicate glass did not prevent accurate results from being obtained by this method.

SODIUM AND POTASSIUM IN BIOLOGICAL MATERIALS

The main difficulty with biological materials is to extract the alkalies into suitable solution. Each type of condition must be dealt with according to its merits.

A typical analysis of plasma shows, in milliequivalents per liter, sodium 140, potassium 5, calcium 5, magnesium 3, chloride 103, and bicarbonate 27. It can be seen from this that the relatively large amount of sodium can cause interference when the elements present in small amount are determined. Proteins and the viscosity of the material produce interference. Particles, clots, and sediments tend to clog orifices. Many of these interferences can be rendered very small by suitable dilution with water. Tissue can be broken down by simple treatment with dilute nitric acid at room temperature. Accuracy of results is essential because small differences are significant physiologically.

References 15 to 28 give some methods used in the biological field.

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CHAPTER FOUR

Visual and Ultraviolet Absorption Spectrophotometry

INTRODUCTION

Scope. Spectroscopy, a broad term for that division of science concerned with the study of spectra, has spectrophotometry as one branch. Spectrophotometry, in turn, may be considered as the study of the relative measurement of radiant energy as a function of wavelength. The term *relative* should be stressed since in spectrophotometry the radiant energy transmitted or reflected by a system is nearly always measured, not in terms of absolute units, but as related to some standard such as the solvent in which the substance being analyzed is dissolved. Spectrophotometry may be used to study fundamental properties of matter, such as molecular or atomic structures; it may be used to study and standardize color as such; and it may be used to identify substances, either in their pure state or in mixtures, and to determine their concentrations. It is only with spectrophotometry in the last aspect, as a technique of analytical chemistry, that this chapter is concerned. Furthermore, since the main analytical applications of spectrophotometry are concerned with the changes undergone by radiation during absorption, rather than during reflection, absorption spectrophotometry rather than reflection spectrophotometry will be stressed.

Solid, liquid, and gaseous samples are susceptible to analysis by absorption spectrophotometry, generally after being dissolved in an appropriate solvent. Gases may, however, be so analyzed without previous solution.

Chromophoric Grouping. Consideration of the kinds of compounds which may be studied qualitatively or quantitatively brings in the concept of the chromophoric grouping. Originally, as the name implies, this concept was applied to colored substances, particularly dyestuffs, for which it had been found that the presence of color was related to the presence in the molecule of certain atomic groupings which caused absorption bands in the visible spectrum. The same term has been retained for groupings which lead to the formation of absorption bands in the

ultraviolet region of the spectrum, even though, of course, these produce no visible effect. Table 4-1 lists a number of such chromophoric groups, those in the first column being more potent than those in the second column, since only one of the former will displace the absorption of the benzene ring sufficiently from the ultraviolet to the visible region to confer color, whereas more than one of the latter is necessary to do the same. The table also lists a number of auxochromic groups. These do not of

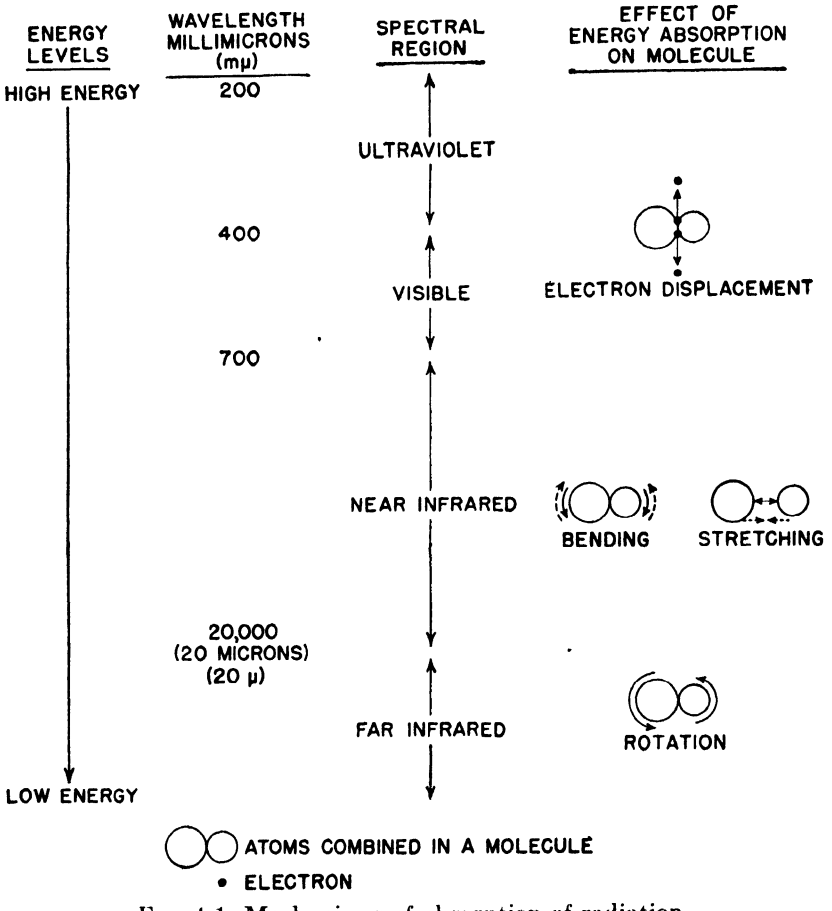


FIG. 4-1. Mechanisms of absorption of radiation.

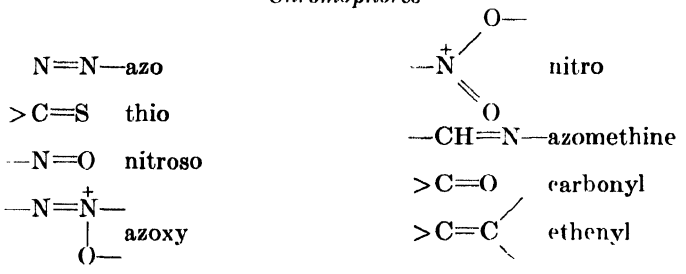
themselves displace the absorption of otherwise colorless molecules into the visible region and so do not produce color, but they augment such an influence of the chromophores. Their order of effectiveness decreases from the top to the bottom of each column.

It may thus be possible for an absorption to be strengthened, or for its maximum to be shifted, by the effect of changes in the molecule. Such a shift may even possibly be from a region outside of that susceptible to measurement by a particular technique or instrument to one thus susceptible. Figure 4-2 shows such an effect in the case of ethylbenzene and

styrene. The change from the structure $C_6H_5—CH=CH_2$ to $C_6H_5—CH_2—CH_3$ has resulted in a shift of the transmittancy minimum (or absorption maximum) both in wavelength and in intensity.

TABLE 4-1. CHROMOPHORES AND AUXOCHROMES

Chromophores



Auxochromes

—NR_2
—NHR
—NH_2
—OH
—OCH_3
—I
—Br
—Cl

Absorption Bands. In both the visible and ultraviolet regions of the spectrum, which extend for ordinary analytical purposes from a wavelength of about 200 mμ (millimicrons) to about 400 mμ for the ultraviolet region, and from about 400 to 700 mμ for the visible region, the underlying mechanism which accounts for the absorption bands is similar. In both regions the absorption of radiation is caused by the transfer of the energy of that radiation to electrons in the outer orbit of the molecule, which then suffer displacement. In the visible region the energy involved in this displacement is less than in the ultraviolet region, but qualitatively the displacements are of the same type. The absorption process is thus different from that which occurs in the infrared region, where the absorptions are governed by oscillations and displacements of atoms within the molecule (see Fig. 4-1). The differences thereby involved in the interpretation of the infrared spectra, as compared with the visible and ultraviolet, as well as differences in instrumental approach and in technique, make it desirable to treat infrared absorption separately from visible and ultraviolet absorption.

Colorimetry. Changes in absorption stemming from reactions which alter the molecular structure of substances are, of course, at the basis of that branch of absorptimetry (chemical analysis by means of measurement of optical absorption) which is oldest and most familiar to analytical chemists. It is what is commonly known as colorimetry. In colorimetric techniques reactions are carried out which usually convert colorless substances to colored, the color serving as a means of identification and its intensity as a quantitative measure of the amount of the substance under-

going reaction. A common example would be the identification of ferrous iron by the red color formed upon reaction with orthophenanthroline and the quantitative estimation of the ferrous iron thereby. For more of the many reactions which have been utilized for these purposes, the reader is referred to some of the many texts on colorimetry.

Allport,[1] Snell and Snell,[4] and Yoe[7] give comprehensive treatments of the subject of colorimetry, with considerable detailed information on procedures for the development of colors for colorimetric analysis. Chapter 1 of Mellon[2] has a systematic discussion of types of reactions

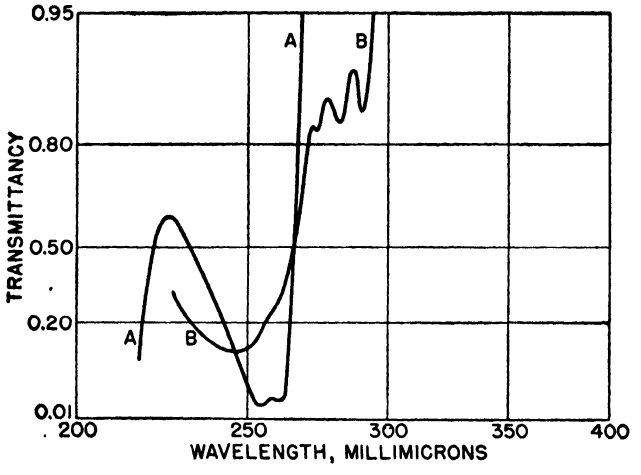


FIG. 4-2. Effect of structural changes on absorption. *A*. Ethylbenzene ($C_6H_5CH_2CH_3$). B. Styrene ($C_6H_5CH.CH_2$). Solvent, ethanol; molar concentration of $A = 0.01B$; $a_s = 144$ at 247 mμ for *B*. [*Adapted from R. N. Jones, Chem. Revs.*, **32**: *1* (*1943*), *Fig. 14.*]

which may be applied for color development. Sandell[3] is especially useful for applications to the colorimetric determinations of metals.

It should be noted in this connection that in general no distinction will be made between inorganic and organic compounds in either visual or ultraviolet absorptimetry. Substances of either type may be identified or determined when they yield absorption bands, or when they can be made to do so by reaction, regardless of whether the reaction is carried out by an organic or an inorganic reagent.

PRINCIPLES OF VISUAL AND ULTRAVIOLET ABSORPTION SPECTROPHOTOMETRY

Terminology. There is considerable confusion regarding spectrophotometric terminology. For the purposes of this chapter the system of terminology which seems to be gaining most widespread approval among analytical chemists in the United States will be used; namely, that in Mellon,[2] Chaps. 5 and 7.

The prevalent technique in analytical chemical absorption spectrophotometry involves passage of so-called monochromatic radiation (really radiation comprising a restricted range of wavelengths) through a liquid or gas confined between the windows of a cell. Designating as T_{soln} (transmittance of the solution) the ratio of the radiant energy leaving the cell containing the sample as a solute (or in gaseous admixture) to that entering the cell, and the corresponding ratio for the cell containing pure solvent or all the constituents of the solution minus the constituent being studied as T_{solv} (transmittance of the solvent), then $T_s = T_{soln}/T_{solv}$ = transmittancy of the sample ($100 \times T_s$ = percentage transmittancy) and $A_s = -\log_{10} T_s = \log_{10} 1/T_s$ = absorbancy of the sample.

Let b represent the length of the solution through which the radiation passes (or the cell thickness) and c the concentration of the solute or constituent being studied. Then $a_s = A_s/bc$ = absorbancy index of the substance.

The units in which b and c are expressed should always be specified, as should the temperature of the sample during measurement, when it is of importance. b is usually expressed in centimeters and c in grams per liter.

Another term $k_s = a_s c = \log_{10} (1/T_s)/b$, which is called the absorbancy coefficient, is also used. When b is expressed in centimeters and c in grams per liter (or approximately 1,000 cm^3), k_s is expressed in units of reciprocal centimeters.

a_x is the partial-absorbancy index of one constituent x of a multicomponent system.

a_M is the molar-absorbancy index, c being expressed in moles per liter and b in centimeters.

In the literature various alternative terms and symbols have been used in place of those given, which will be used in this chapter. Some of the more common follow: I for transmittancy in place of T_s, and similarly A and a in place of A_s and a_s; d, l, and x in place of b for cell thickness; the term optical density with symbol D, or extinction indicated by E, instead of absorbancy A_s; specific extinction or extinction coefficient k, and absorptivity, in place of absorbancy index a_s; and molecular-extinction coefficient K or ϵ for a_M, the molar-absorbancy index.

QUALITATIVE ANALYSIS

The use of spectrophotometric curves (see below under Plotting Data) as a means of determining the identity of an isolated single substance is essentially an empirical process, a comparison of the curve of the unknown with those of known substances. If sufficient similarity exists between the curve of a known substance and that of the sample in the position of an absorption maximum, or of several maxima, or in the relative intensity

of two or more maxima, one may draw conclusions concerning the identity of the unknown with the reference substance.

Types of Error. There are, however, two types of error which must be avoided: one, drawing a conclusion of identity on the basis of too few similarities; and the other, deciding on a lack of identity because of small differences brought about by the presence of a relatively low concentration of impurities or by differences in the conditions of measurement. The guiding principle which must be kept in mind is that identification is largely an application of probability. The more numerous the independent points of similarity between known and unknown, the greater the probability of identity. From this principle it follows that one should have for a good identification as complete a wavelength-absorbancy curve as possible, covering as much of the visible and ultraviolet regions (also, if possible, the infrared) as is feasible. In this way, the absorption effects of the various groupings and structures of the molecule are obtained, so that the conclusion that an identity exists because of identity between a chance group or two may be avoided. Yet, the fact must be borne in mind that, particularly in regions of high transmittancy, a relatively insignificant concentration of an impurity may cause a change in curve shape. This should, however, be ignored in order to avoid concluding that the unknown is a different substance from the reference material.

Changes in Conditions. Confirmation of an identification should be made by changing the conditions under which the curve is obtained. A change in the solvent, including a change in pH, may cause a change in the curve shape. The temperature of the measurement may cause an effect, particularly by changing the association or dissociation of the sample, by enhancing or diminishing a reaction of the solute with the solvent, or by altering the solubility of the substances being studied. In cases where it may be suspected that two compounds are different even though there is a similarity in curves, some of the solid known substance may be added to a saturated solution of the unknown and measurements made after suitable dilution of the filtered solutions. An increase in the absorption over that previously found at maximum solubility would indicate lack of identity. Of course, the fact that the addition of polymorphic forms which come to equilibrium slowly might increase absorption and yet not prove lack of chemical identity must be considered.

Chemical Reaction. Identification may be made, or confirmed, by subjecting the sample to chemical reaction and comparing the absorption of the products of reaction of the known and the unknown. This is, of course, the principle of colorimetric analysis and is not essentially different when the reaction produces a change in absorption in the ultraviolet region instead of in the visible region.

An example is given by the work of Williams and coworkers[6] on

vitamin B_1. A cleavage fragment of natural vitamin B_1 which exhibited an absorption maximum at 240 mμ was changed by hydrolysis to a substance with maxima at 229 and 275 mμ. This behavior was similar to that of a known dimethylaminopyrimidine, and led to the identification of the cleavage fragment as being such a derivative.

The identification of single substances in multicomponent systems may be made in a manner common to most chemical analyses by actually isolating single substances from the mixture or solution and identifying these in the usual manner. This may sometimes be done effectively without actual physical separation by effecting a chemical change so that the substance of interest continues to absorb in the spectral region under consideration, whereas the interfering substance does not. An example might be the identification of a red substance which is insensitive to changes of pH, in the presence of phenolphthalein, by adjusting the pH so that the latter becomes colorless.

Subtraction of Curves. An identification may sometimes be made without recourse to such devices. Since absorption at longer wavelengths is more apt to be specific for one component than that at shorter wavelengths, an identification of a constituent is made at a longer wavelength. Its known curve is then subtracted from the curve of the sample, leaving the resultant curve of the other constituents of the mixture. The same process is repeated with another suspected component absorbing at a longer wavelength and, if necessary, again and again, until a complete qualitative analysis is made. Finally, in order to make certain of the analysis, since sometimes the principle of additivity of absorption, on which this method is based, does not hold, a mixture of the suspected ingredients should be made and its curve compared with that of the original sample.

QUANTITATIVE ANALYSIS

The use of absorptimetric methods in the visible and ultraviolet regions for quantitative analyses constitutes one of the greatest single advances in analytical chemistry in recent years. As is true fairly generally for all chemical analyses, it is also true with this branch of analytical chemistry that a quantitative method is based on one of two suppositions. One must have either a knowledge of the identity and relevant properties of all the constituents present, or assurance that the sample being analyzed is substantially similar to the samples on which the method has been based, in respect to the nature and concentration ranges of the components other than those being determined.

Bouguer-Beer Laws. At the basis of all quantitative spectrophotometric absorptimetry are two laws: Bouguer's law relating absorptive capacity and thickness of the absorbing medium, and Beer's law (some-

times referred to as Lambert-Beer's law) relating absorptive capacity and concentration of a solute in a solution. The former states that each layer of equal thickness of a homogeneous absorbing medium absorbs an equal fraction of the radiant energy passing through it. In terms of transmitted energy, the intensity of the transmitted energy decreases exponentially as the thickness of the absorbing medium increases arithmetically. Beer's law states that the absorptive capacity of a solution is directly proportional to the concentration of the solute, or that the intensity of the transmitted energy is an exponential function of the concentration. The two laws may be combined in one equation to express the combined effects of changes in cell thickness and concentration:

$$T_s = 10^{-a_s bc} \tag{4-1}$$

or

$$a_s bc = -\log_{10} T_s = A_s \tag{4-2}$$

or

$$k_s = a_s c = \frac{-\log_{10} T_s}{b} \tag{4-3}$$

Since Bouguer's law is generally considered to be universally applicable, departures of actual systems from the combined laws, which are not of uncommon occurrence, are to be ascribed to the failure of Beer's law. This can be brought about by association, dissociation, solvation, or other changes in the nature of the solute with changes in concentration. It is therefore necessary to prove, rather than to assume, for any system under study, that Beer's law is applicable. Whenever it is applicable, concentrations of solute may then be calculated directly from the expression

$$c = \frac{A_s}{a_s b} \tag{4-4}$$

Plotting Data. A variety of systems is used for plotting spectrophotometric data. The abscissas may be expressed in terms of wavelength (in millimicrons, mμ, or angstrom units, A), frequency (in fresnels), wave number (in waves per centimeter), or logarithm of the wavelength. The ordinates may be expressed as per cent transmittancy, decimal fraction of transmittancy, absorbancy (formerly designated as optical density, or extinction), absorbancy index (formerly extinction coefficient), molar-absorbancy index (formerly molecular-extinction coefficient) or as the logarithm of any of these. Stress will be placed here upon a system which is useful for general analytical purposes, both qualitative and quantitative, as shown in Fig. 4-3. The ordinate is expressed in terms of transmittancy but has a logarithmic scale which is equivalent to log A_s or log log $1/T_s$. Plots made with this ordinate are valuable for qualitative identification since the curve shape will be independent of concentration and cell thickness and will depend solely upon log A_s, which is a function of wavelength.

If transparent plotting paper is used, the sheet containing the curve of an unknown may then be placed over that containing the curve of a known substance, so that the wavelength scales coincide, and the plot of lower transmittancy may be raised until coincidence of the two curves is obtained. Such coincidence is evidence (although not necessarily conclusive) of the identity of the two substances. The wavelength, expressed in millimicrons (mμ), is plotted on a scale based on the logarithm of the wavelength.

For quantitative analyses, this type of curve is most conveniently used with a transparent reference scale which is so drawn that each reading on the reference scale is equal to the $\log_{10}$ of the reciprocal of the corresponding reading on the above-mentioned transmittancy scale. By placing the

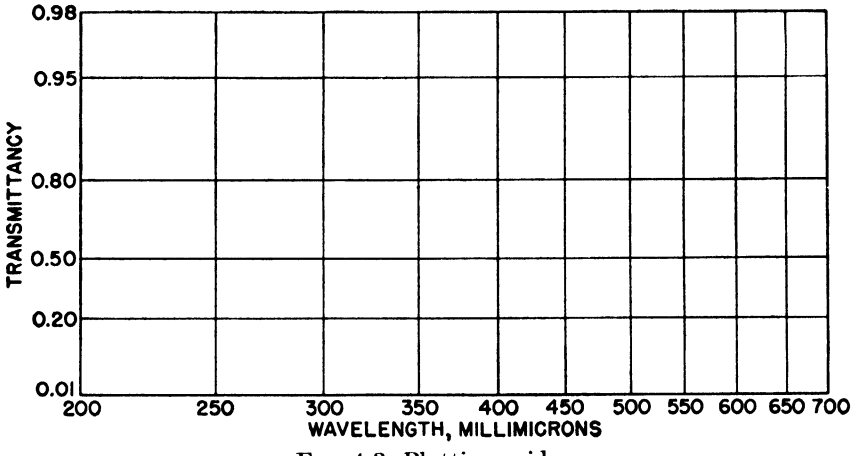


FIG. 4-3. Plotting grid.

reference scale on a curve which has been plotted on the transmittancy scale described so that the 1 mark of the reference scale falls at a point corresponding to 0.10 transmittancy, absorbancies may be read directly on this scale. If it is known that Beer's law is valid for the substance being studied, concentrations relative to that of a standard substance, the curve of which is also plotted on the log A_s scale, may be read directly from the reference scale by placing the 1 mark of the latter on the standard curve and reading the relative concentration from the intersection of the reference scale with the curve of the sample. Figure 4-4 gives an example of such a computation. The reference scale is shown placed at 480 mμ so as to cross two curves of a substance with an absorbancy maximum at that wavelength. A is the curve for a solution of twice the concentration indicated in A'. If the reference scale were placed with the 1 mark on A, the reading would be 0.5 on A' to indicate that the concentration of the solution A' is half that of A. By placing 1 to correspond to 0.10 on the

transmittancy scale, the respective readings on the reference scales have been made equal to the absorbancies.

The reference scale used in conjunction with the log A_s ordinate is convenient in qualitative analyses where two or more absorbing materials have additive absorbancies. If from the curve of a sample known to contain a substance, the curve of which is also known, the latter curve is subtracted, the curve of the remaining ingredient or ingredients may be constructed. By adding together two or more curves of separate ingredients, a curve for an admixture may be drawn.

Analytical Errors and Solution Effects. Most quantitative absorption analyses are carried out in solution. The nature of the solvent, as well as variations in a number of properties of the solution, or in the conditions to

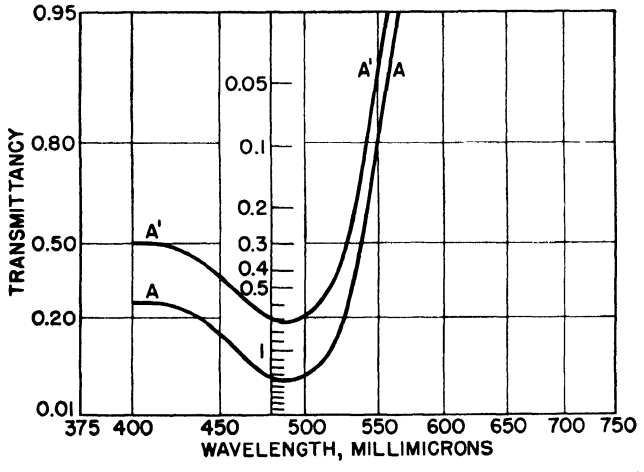


FIG. 4-4. Use of reference scale. *A*. Sample at concentration-1. *A'*. Sample at concentration-0.5. (*M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley & Sons, Inc., New York, 1950, Fig. 7-1. By permission of the publishers.*)

which a solution has been exposed, may exert a greater or lesser influence on the shape of the curves and on the positions and intensities of the absorption maxima. It is important to understand the kinds of change in the solution medium which may affect absorption curves, to consider these effects in setting up absorptimetric methods, and to adhere to the chosen conditions when making analyses.

To explain this point somewhat, as previously stated absorption of visible and ultraviolet radiation in solutions is dependent upon the arrangement and energy states of electrons in the outer shells of the atoms which are combined to make up the ultimate solute (and solvent) units. In considering a solution, it should not be assumed that any given substance, when put into solution in various solvents, will have the same ultimate absorbing units in all the solvents. The effect of the *solvent* may be such as to produce solvated molecules which may have different

absorptions from unsolvated molecules. A change from one solvent to another may thus result in a shift in the absorption maxima or in their intensities.

A change in *concentration* in the same solvent from a less dilute to a more dilute solution may cause a change in association or polymerization which will make Beer's law inapplicable in certain concentration ranges.

One effect which must be guarded against particularly is that caused by changes in pH. The most obvious illustration is that of ordinary acid-base indicators which evince changes in absorption of visible radiation with changes in pH. Not evident to the eye, but just as significant in ultraviolet absorptimetry, are the changes in absorption in the ultraviolet region, which may or may not be accompanied by changes in the visible

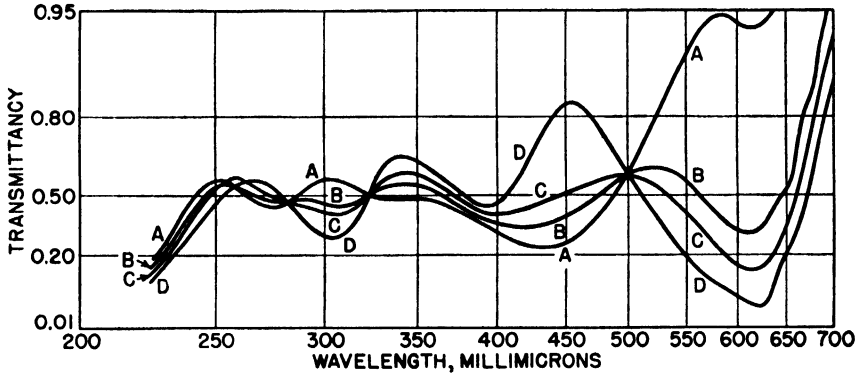


FIG. 4-5. Absorption changes due to pH changes. Absorption spectra of bromothymol blue at various hydrogen-ion activities. *A* = pH 5.45, *B* = pH 6.95, *C* = pH 7.50, *D* = pH 11.60. Solvent-water; a_s = 60.5 at 615 mμ for *D*. (*M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley & Sons, Inc., New York, 1950, Fig. 7-5. By permission of the publishers.*)

region. Figure 4-5 shows curves for the absorption of bromothymol blue at various pH values, which illustrate the changes in absorption in the ultraviolet which are coincident with those in the visible range. To avoid errors due to changes in pH, it is necessary, whenever a system sensitive to such changes is dealt with, to use an acid-base buffer in order to keep the pH within the required limits. Such a buffer must, of course, be chosen so that it will not itself contribute interfering absorptions.

Any influence which causes a *change in the chemical nature of the absorbing material* may cause changes in its absorption. In an aqueous medium hydrolysis may occur or one component of a solution may react with another. The substance may suffer decomposition during preparation of the sample solution because of sensitivity to light. In instruments where only a monochromatic beam is passed through the sample, the intensity is usually too low to cause much trouble from this source during the spectrophotometric examination but in instruments where the unmodified beam

from the source passes through the sample, the effect may be serious. Changes in the temperature at which a solution is measured may cause reversible changes in the absorption curves; or differences in the temperature at which dissolution is effected may cause irreversible changes. In brief, any change in conditions which may affect the nature of the solute chemically or in its state of *colloidal aggregation* or *polymeric condition* may affect the curve. Conditions known or suspected to cause such changes should always be fixed in order to avoid the introduction of variables in the analyses.

Other Sources of Errors. In addition to such variables which involve superficial or deep changes in the chemical nature of the solute, some other effects should be considered as possible sources of error. Absorptimetry as an analytical technique assumes that absorbed radiation is dissipated as heat. When, however, as with *fluorescent material*, the absorbed radiation is reemitted as energy of the same or longer wavelength, erroneous values may be found. Since the reemitted radiation is reemitted in all directions, its effect may be minimized by moving the photocell sufficiently far away, when the instrument permits, so that only a small fraction of the reemitted radiation falls upon it. *Turbidity* in the solution also introduces errors by scattering light. Another error may be brought about by *deposition of material* from solution on the adsorptive surface of the cell, which will later add to the absorption of a solution measured in that cell unless the cell has first been scrubbed with soap and water, rather than merely rinsed with solvent.

In view of these possibilities of error, the effect of small changes in any particular property found to be significant should always be considered in order to choose conditions for the analysis which will be least affected by small changes. In choosing these conditions, two points should always be tested. One is whether adequate reproducibility may be obtained on making up fresh solutions and carrying out repeated measurements, preferably not close together in time. Another is whether the solution exhibits good or bad aging properties; i.e., whether upon standing, the solution changes in transmittancy upon repeated measurements. Satisfactory behavior in these respects is essential for a good analytical method.

Optimum Transmittancy. Finally, reference must be made to the question of the optimum transmittancy at which to make measurements in order to determine concentration values with the greatest precision (the least random percentage error). Generally speaking, a low transmittancy increases the errors due to stray light in the instrument and to lack of adherence of the system to Beer's law; while a high transmittancy magnifies the effect of fingerprints or other dirt on the cells, turbidity of the solvent, and inaccuracy in the transmittance of the solvent-filled reference cell. A transmittancy in the range 10 to 50 per cent is usually satisfac-

tory. By varying both concentrations and cell lengths, it is almost always possible to set up a method for which the transmittancies will be within this range.

One-component Analysis. A common analytical problem is the determination of a single absorbing constituent in the absence of other constituents with interfering absorptions. Sometimes lack of interfering absorptions exists because of the nature of the sample; sometimes because the sample has been treated to develop absorption in only one of several constituents; and sometimes because an actual physical or chemical treatment has been made to remove interferences.

From the absorption curve of the substance being determined, the *best wavelength* at which to make the absorption measurement for the determination should be decided upon. Generally, this will correspond to the absorption maximum, since the curve flattens out there so that a small error in setting the wavelength scale of the spectrophotometer will not introduce a significant error in the transmittancy value. There may, however, be other considerations which will suggest making the determination at a wavelength other than that of the absorption maximum. The sensitivity of the photoreceptor may be sufficiently more favorable at a wavelength other than that of the absorption maximum to make its intensity more suitable for measurement. The resolution of the instrument may be better at some other wavelength so that a narrower slit width may be used, thus affording additivity of absorbancies which may not hold at the absorption maximum if it should be necessary to use a wider slit width there. Impurities absorbing at the wavelength under consideration must also be taken into account so that a region should be chosen where their effect may be absent or at a minimum. For example, in one method for potassium permanganate, it is recommended to work at a very steep portion of the absorption curve of that substance because of the presence of potassium dichromate, which absorbs strongly near the maximum of the permanganate curve.

When the most appropriate wavelength has been chosen at which to make the measurement, it is then necessary to test for *adherence to Beer's law* at that wavelength. This may be done by plotting absorbancy coefficients against concentrations and observing whether the plot so obtained is a straight line. If it is not, Beer's law does not hold over the concentration range plotted. (An alternative procedure is to observe whether a constant absorbancy index is obtained with changing concentration.) Even if a straight line is not obtained for the entire concentration range tested, it must be true for a limited range of concentrations that the curve is close enough to a straight line, which passes through the concentrations in question and also through the origin, so that the deviations from Beer's law over that concentration range may be

unimportant for the analysis in question. By plotting *logarithms* of absorbancy coefficients and of concentrations, a better estimate may sometimes be made of the relative (rather than absolute) deviations from Beer's law. If no concentration range can be found at which a satisfactory adherence to Beer's law is obtained, another more satisfactory wavelength may be available at which to make measurements. Other conditions may also be altered to bring about adherence to Beer's law.[5] The possibility that the failure of Beer's law may be due to a fault in the instrument leading to wide bands or stray light should be considered, particularly if similar errors recur for different analytical systems. In the discussion of methods of calculation which follows, it is assumed that Beer's law holds. Examples of failure of Beer's law should be relatively few if methods are set up with care.

Spectrophotometric analysis nearly always involves measurements against a *standard.* The standard should preferably be a pure sample of the absorbing substance which is taken as 100 per cent in strength. If no such pure material is available, the best available specimen of the substance is used as a 100 per cent standard. Care should be taken to avoid confusion if such a standard is used by reporting the values obtained as "percentage against standard," since it is possible to get values over 100 per cent, if the sample happens to be of a higher purity than the standard.

The absorption of a standard is measured under the exact conditions of the analysis to obtain $a_{s(st)}$, the absorbancy index of the standard. The sample is then measured to get $k_{s(x)}$, the absorbancy coefficient of the unknown. If Beer's law holds, then the concentration c of the constituent sought is obtained by the equation

$$c = \frac{k_{s(x)}}{a_{s(st)}} \tag{4-5}$$

If Beer's law does not hold and a measurement cannot be made at a concentration close to that at which the standard was measured, the linear equation (4-5) cannot be used. The concentration may then be determined graphically from the absorbancy coefficient by making use of the empirical curve relating absorbancy coefficient to concentration which was used to test for adherence to Beer's law.

Nomographic Method. Another method of making the calculation (the nomographic method) which is convenient involves the use of the transparent logarithmic reference scale with a standard curve plotted with log A_s ordinate. In Eq. (4-5) the reciprocal $1/a_{s(st)}$ is calculated and this value is placed on the reference scale (located vertically at the wavelength of standardization) to correspond to a transmittancy value on the ordi-

nate of 0.10. From the intersection of the curve with the reference scale, the concentration sought is read off the reference scale. If the length of the cell used for the measurement is not 1.000 cm, this operation will cause an error. The error, for cells differing in the third decimal place from 1.000 cm, is usually negligible, but it can if desired be taken into consideration. If the curve of a sample is plotted on transparent paper, it may then be placed to indicate the greater or lesser transmittancy which would have been obtained if the cell used had been 1.000 cm instead of a shorter or longer length. The reference scale is then placed over the curve as usual.

If it is desired to use the nomographic method when Beer's law does not hold, it is necessary to set up a nomograph with empirically determined values instead of the logarithmic scale. The curve of the sample is placed over this scale. The logarithmic reference scale is placed at the reference marks on both sides and the value corresponding to the point closer to the curve is taken.

Two-component Analysis. When two substances are present in a sample, each of which absorbs radiation, the usual procedure is to measure absorptions at two wavelengths in order to determine both substances. The curves of the individual pure substances must be known. Sometimes, as an alternative, two measurements may be made at the same wavelength before and after appropriate treatment of the sample, which affects the absorption of one substance at the wavelength in question differently from that of the other substance. Measurement at two wavelengths is the more common procedure.

Measurement at Two Wavelengths. Let c_a and c_b be the concentrations to be determined of the constituents a and b; $a_{s(a1)}$ and $a_{s(b1)}$ the absorbancy indexes of a and b at the first wavelength; $a_{s(a2)}$ and $a_{s(b2)}$ similar constants at the second wavelength; and $k_{(a+b)1}$ and $k_{(a+b)2}$ the absorbancy coefficients of the mixture of a and b at wavelengths 1 and 2. Then

$$c_a a_{s(a1)} + c_b a_{s(b1)} = k_{(a+b)1} \tag{4-6}$$

and

$$c_a a_{s(a2)} + c_b a_{s(b2)} = k_{(a+b)2} \tag{4-7}$$

Values for c_a and c_b are obtained by substitution in Eqs. (4-6) and (4-7) followed by an algebraic solution for c_a and c_b.

In order to choose the wavelengths at which to carry out the analysis with the best accuracy, the curves of the substances a and b are examined. From these curves the ratio a_{sa}/a_{sb} at a number of wavelengths is calculated and plots of that ratio as ordinate against wavelength as abscissa are made. The maximum and minimum points on the curve indicate the optimum wavelengths, but the choice should be modified by the considerations given above under the section on One-component Analysis A simpler method of choosing the two optimum wavelengths is

first to draw the transmittancy curves of each of the two pure substances, on the log A_s plot, on each of two transparent graph papers. The curve for substance a is placed above that for substance b and lowered until the former meets the latter. The point of meeting is chosen as one wavelength. The curve for substance a is then placed below that for substance b and raised until it meets that for substance b. The point of contact is taken as the second wavelength. These wavelengths correspond to those obtained from the a_{sa}/a_{sb} plot.

When two wavelengths have been chosen, tests should be made for *additive absorbancies* over the range of relative compositions and total concentrations to be met in the use of the method of analysis. A separate

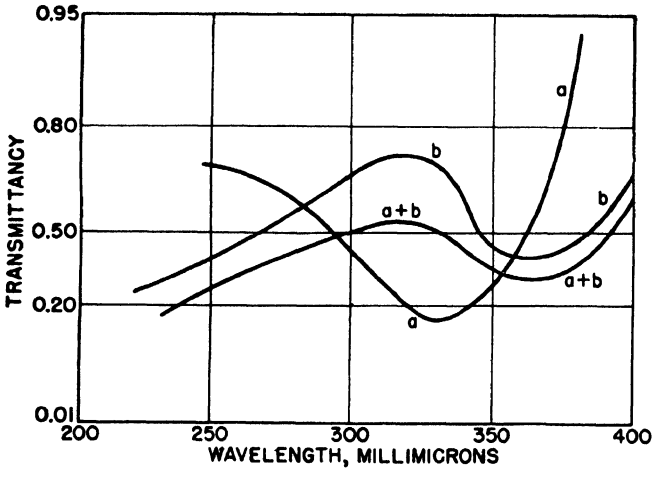


FIG. 4-6. Two-component analysis. *a*. Curve for one substance. *b*. Curve for second substance. $(a + b)$. Curve for mixture of a and b.

plot of the absorbancy coefficients of mixtures of various relative percentages of the two constituents for each of a selected range of total concentrations should form a straight line if Eqs. (4-6) and (4-7) are to be applicable. The test for additivity of absorbancies should be made even if it is known that each constituent alone follows Beer's law. This is to ensure the absence of interaction and solution effects of the two absorbing substances on each other.

If additivity of absorbancies does not exist, it is necessary to set up a *family of correction curves* over the range of total concentrations and relative concentrations of the two constituents with which the method is concerned.

Example of Calculation. For both cases, involving additivity or non-additivity, the concentrations may be calculated by using the log reference scale, or algebraically as in the following example.

Assume two substances a and b, the curves of which are represented in Fig. 4-6 and which are to be used as standard reference materials on

which to base a method of two-component analysis for mixtures of a and b. By one of the methods just given, the optimum wavelengths at which to carry out the analysis are chosen as 325 mμ (wavelength 1) and 375 mμ (wavelength 2). The transmittancy values for a and b have been determined at each wavelength in 0.975-cm cells, in a solution of each substance containing 0.040 gram per liter of that substance. From the T_s values the absorbancy indexes a_s are calculated [$a_s = -\log_{10} T_s/(0.975 \times 0.040)$]. Table 4-2 gives these values. Substituting these values in Eqs. (4-6) and

TABLE 4-2. TRANSMITTANCY AND ABSORBANCY INDEXES

Substance	T_{s1}	T_{s2}	a_{s1}	a_{s2}
a	0.190	0.755	18.494	3.130
b	0.725	0.437	3.581	9.219

(4-7), Eqs. (4-6′) and (4-7′) are obtained.

$$18.494\ c_a + 3.581\ c_b = k_{(a+b)1} \qquad (4\text{-}6')$$

$$3.130\ c_a + 9.219\ c_b = k_{(a+b)2} \qquad (4\text{-}7')$$

Equations (4-6′) and (4-7′) may now be used to calculate c_a and c_b for solutions of a and b of unknown concentrations of each. Suppose such a solution ($a + b$) is to be analyzed in a 1.010-cm cell. The transmittancy of this solution is found to be 0.504 at wavelength 325 mμ (T_{s1}) and 0.310 at 375 mμ (T_{s2}). Corresponding values of the absorbancy coefficients $k_{(a+b)1}$ and $k_{(a+b)2}$ are calculated ($k_s = -\log_{10} T_s/\text{cell length}$). These values are 0.295 and 0.504, respectively. These values are substituted in Eqs. (4-6′) and (4-7′), which are then solved for c_a and c_b in the usual manner.

$$c_a = 0.0057 \text{ gram/liter}$$

$$c_b = 0.0527 \text{ gram/liter}$$

Multi-component Analysis. Systems containing more than two components may be analyzed by an extension of the principles which were applied to two-component analyses. An absorbancy coefficient is needed for each component. These may be measured at different wavelengths, or under different conditions at the same wavelengths, or with a combination of both variations. If the absorbancies are additive, simultaneous equations may be set up equal in number to the number of components being determined. If the absorbancies are not additive, special methods are required.

Impurity Index. It happens frequently in industrial analysis that mixtures are encountered which contain, in addition to a known substance, one or more impurities whose identities are not known. If these

impurities exhibit absorption which is different from that of the known constituent, a value may be assigned to represent their combined concentration in a relative manner. Such a value is known as an impurity index (I.I.).

The chief use of the impurity index is as a numerical measure of the relative amounts of absorbing impurities in various batches of an industrial material. It can be obtained without an exact knowledge of the nature of those impurities, provided that they remain reasonably constant in a qualitative sense from batch to batch. Since the impurity index is additive, it may also be used to calculate the composition of a mixture of batches which have been blended. The index may also be used to correct

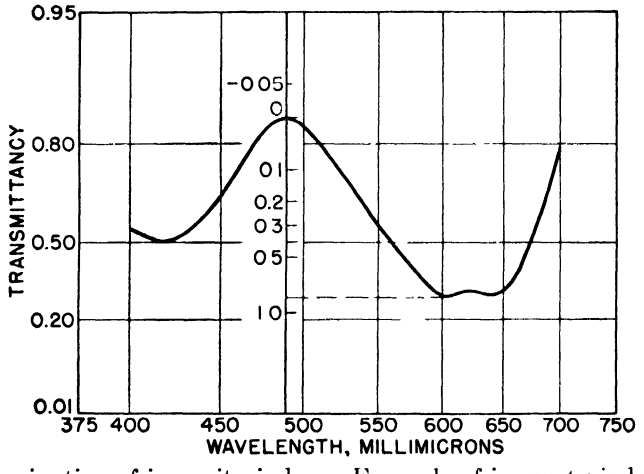


FIG. 4-7. Determination of impurity index. Example of impurity index. The numbers at 490 mμ are on the impurity index scale. (*M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley & Sons, Inc., New York, 1950, Fig. 7-49. By permission of the publishers.*)

the concentration computed for a compound if it is assumed that the impurity has a horizontal transmittancy curve with equal absorbancy indexes at wavelengths 1 and 2 which are also equal to the absorbancy index of the purified standard at wavelength 2. The concentration of a may then be calculated by multiplying the right-hand side of the equation for c_a by $(1 - p)$, where $c_a = k_{s(a_2)}/a_{s(\text{standard 2})}$; $k_{s(a_2)}$ is the absorbancy coefficient of a at wavelength 2 and $a_{s(\text{standard 2})}$ the absorbancy coefficient of the corresponding standard; and where

$$p = \frac{\text{I.I.}}{1 - a_{s(a_1)}/a_{s(a_2)}}$$

Since p varies directly with I.I., the term $(1 - p)$ becomes smaller as the impurity index increases, thus making the value of c_a lower, the greater the amount of impurity.

The impurity index may be calculated as in Eq. (4-8):

$$\text{I.I.} = \frac{k_{s(m_1)}}{k_{s(m_2)}} - \frac{a_{s(a_1)}}{a_{s(a_2)}} \tag{4-8}$$

$k_{s(m_1)}$ and $k_{s(m_2)}$ are the absorbancy coefficients of the sample at wavelengths 1 and 2, respectively, where 1 and 2 were chosen in the manner previously described. $a_{s(a_1)}$ and $a_{s(a_2)}$ are the absorbancy indexes of the purified standard at wavelengths 1 and 2, respectively, of the substance a which is being determined.

The impurity index may also be determined from the log A_s plot of the sample by means of a scale drawn as shown in Fig. 4-7 and constructed as follows: Place the reference logarithmic scale at the wavelength at which the impurity index is to be determined (usually corresponding to a transmittancy maximum) so that +1 is located at a transmittancy value equal to the value of the transmittancy minimum for the standard (e.g., 0.25). Make a mark on the scale to correspond to 1 plus this value (1.25). This mark becomes the value 1 on the impurity-index scale and the intersection of the scale with the curve becomes zero. Then mark off the scale into 10 or 100 parts using the reference logarithmic divisions for this purpose. [Each mark is the sum of $k_{s(a_1)}$ and I.I. $\times$ $k_{s(a_2)}$.] After such a scale has been set up for a given system, it may be used to determine the impurity index of a sample without the use of Eq. (4-8). The curve of the sample is superimposed on that of the standard curve at wavelength 2, and the impurity index is read at the intersection of the sample curve with the impurity-index scale.

INSTRUMENTS

In the discussion of absorption spectrophotometry thus far no consideration has been given to the instruments with which the type of information under discussion is to be obtained. In discussing instruments attention will be confined to types, and specific examples of those types, which are commercially available and which have given evidence of fairly widespread acceptance among chemists.

Instruments useful for optical absorptimetric methods of analysis may be classified into three types: (1) spectrophotometers, (2) filter photometers, and (3) comparators. Their versatility may be considered generally to decrease in the order given, along with a corresponding decrease in their complexity and cost.

Spectrophotometers. Spectrophotometers are instruments which measure transmittancies over an extended wavelength region of the spectrum at close wavelength intervals. Regardless of the type of spectrophotometer, they all have in common the following fundamental parts:

(1) a source of radiant energy; (2) a prism or a grating to produce dispersion of mixed radiation containing energy of various wavelengths so that so-called monochromatic regions, in reality narrow-wavelength regions, may be isolated before passage through a sample (or in some instruments after passage); (3) a device for holding the sample of which the absorbancy is to be measured, which makes possible the simultaneous or consecutive measurement of absorption in the sample and in the reference medium; and (4) a device for detecting and measuring radiant energy either visually or by means of electric currents produced by the effect of the energy upon appropriate barrier-layer or photoelectric cells. An extensive discussion of these components and the various ways in which they may be combined is beyond the scope of this chapter. Instead, mention will be made of spectrophotometers in common use and commercially available.

General Electric Recording Spectrophotometer. This instrument automatically records the per cent transmittancy (or reflectance) over the visible spectral range (400 to 700 mμ). Figure 4-8 gives a schematic representation. Radiant energy from a lamp source passes through a slit and is dispersed by a prism. A portion of the isolated band passes through a second slit, thus eliminating some stray energy. It is then dispersed again by a prism and more stray energy is removed by the interposition of a third slit. In this way, a band is obtained which has a minimum of stray energy and the width of which is determined by the width of the slits. As the spectrum is traversed, a system of cams changes the slit widths in order to allow a band to pass which is of constant width—generally 10 mμ.

The radiant energy from the third slit passes through an optical system so arranged that any lack of balance of the intensity of the light transmitted by (or reflected from) a sample, compared with the intensity of an unobstructed beam, acts in such a manner upon a phototube as to produce an alternating current. The latter drives a motor which turns in one direction or another, and to a greater or lesser extent, depending upon whether the energy transmitted (or reflected) by the sample is less or more than that from the unobstructed beam. A combination of optical, electrical, and mechanical parts translates these changes of intensity into movements of a recording pen upon the chart and also causes the second slit to move through the spectrum, thus causing the pen to move horizontally along the wavelength scale.

A typical set of transmittance curves is given in Fig. 4-9. Three calibration curves are shown: (1) the "zero curve" is run with the sample blocked off, (2) the "100 per cent curve" is run with no sample in either beam, and (3) the "didymium curve" is run with a calibrated didymium glass in the sample beam. This curve is used to correct the wavelength

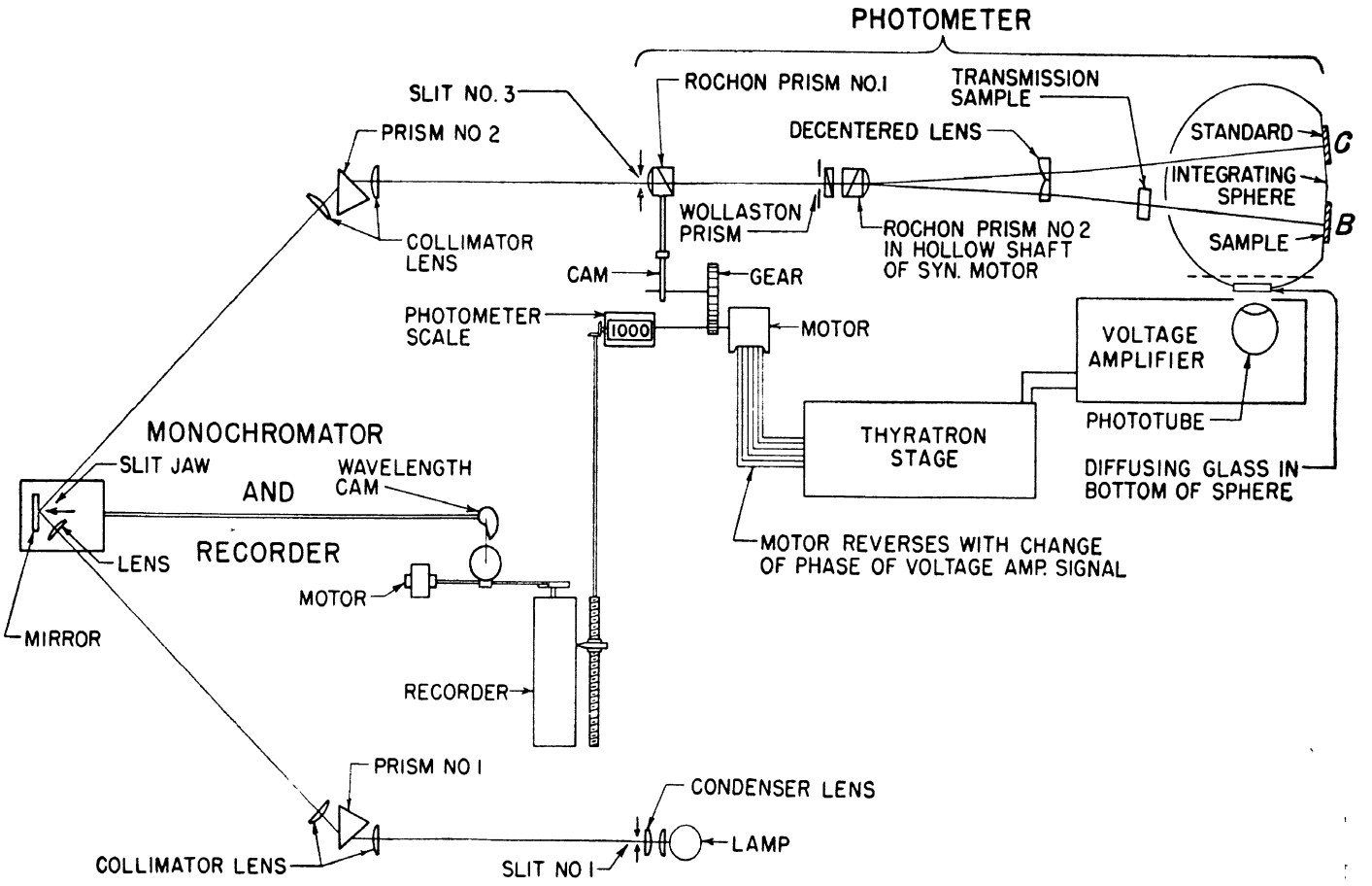


FIG. 4-8. Schematic diagram of General Electric photoelectric recording spectrophotometer. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 17.*]

scale. The sample curves were obtained with certain glasses. The "zero," "100-per cent," and "didymium" curves were repeated after the sample runs in order to detect erratic or gradual changes during the course of the run.

Beckman DU Quartz (Nonrecording) Spectrophotometer. The Beckman model DU spectrophotometer is a manually operated instrument which

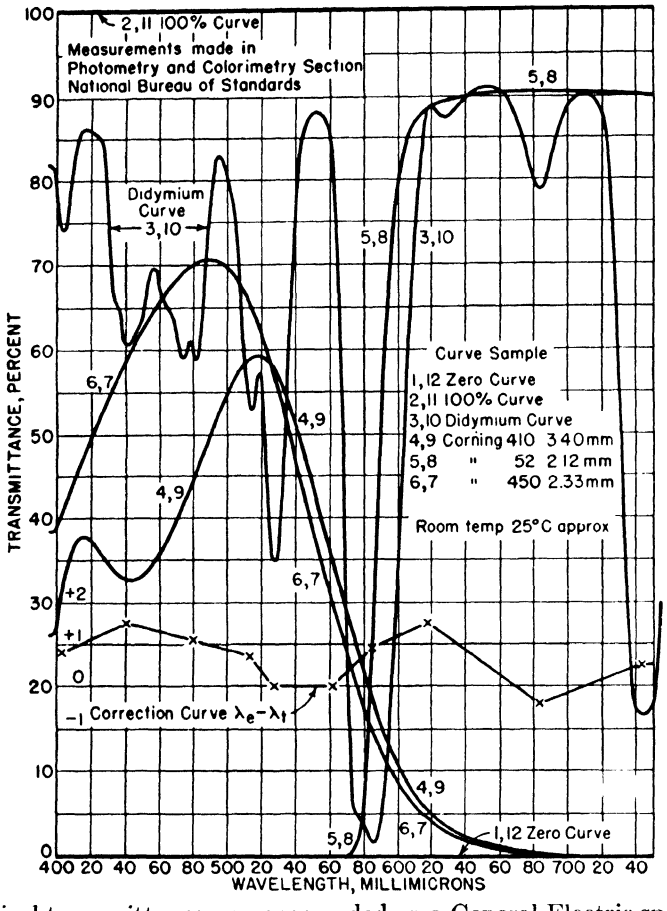


FIG. 4-9. Typical transmittance curves recorded on a General Electric spectrophotometer. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 18.*]

gives readings in terms of transmittancy T_s or absorbancy $-\log_{10} T_s$ relative to solvent in a 1-cm thickness, over the near ultraviolet and visible regions and beyond into the near infrared—or from about 200 to about 1,000 mμ. Figure 4-10 is a schematic diagram of the optics of the instrument. Radiant energy from the source is reflected into a prism, where it is dispersed, and an isolated band is reflected back through a slit into the sample, thence to impinge upon a phototube. The current produced is amplified and balanced by a potentiometer to give a reading on a scale in terms of transmittancy or absorbancy. Two sources are normally

used, an incandescent tungsten-filament lamp for the visible region and a hydrogen arc for the ultraviolet region. Two phototubes are supplied, either of which may be inserted as desired. One is a red-sensitive, cesium-oxide phototube which should be used for measurements above 620 mμ; the other a blue-sensitive, cesium-antimony phototube for use below 620 mμ. The lower limit of the range is about 320 mμ if the incandescent lamp and common glass phototube are used, but it is extended to about

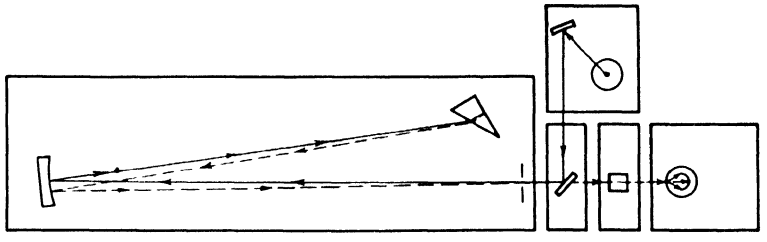


FIG. 4-10. Schematic diagram of optics of Beckman quartz nonrecording (DU) spectrophotometer. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 21.*]

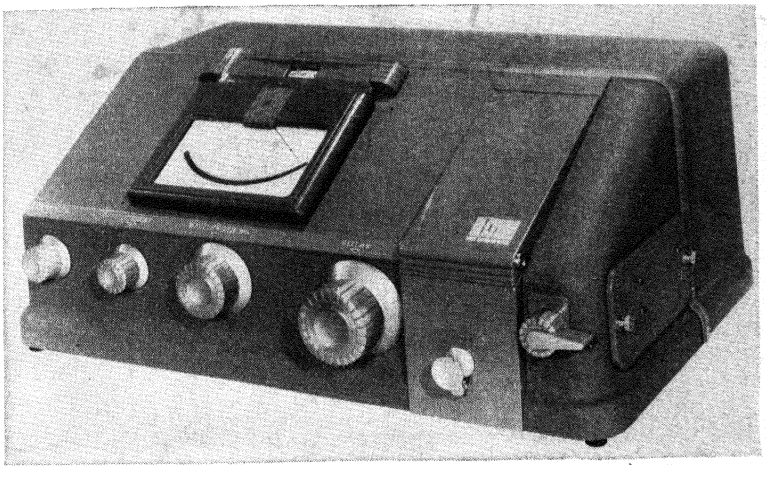


FIG. 4-11. Beckman model B spectrophotometer. (*Courtesy of Beckman Instruments, Inc.*)

200 mμ if the hydrogen-arc lamp is used with the phototube which has an envelope of Corning 9740 glass.

Matched cells are used. The cell containing the solvent is first inserted in order to fix the 100 per cent transmittance setting. The insertion of the sample in a similar cell makes possible direct transmittancy or absorbancy readings.

Beckman Model B Spectrophotometer. This instrument is less expensive than the model DU, having glass rather than quartz optics for use in the range 320 to 1,000 mμ. It is designed for rapid routine use in the more restricted range and does not give such high precision. Figure 4-11 is a photograph of the instrument.

Cary Recording Quartz Spectrophotometer. This instrument draws a curve automatically for the 200- to 700-mμ range. It is especially useful as a research instrument, having particularly good resolution.

Recording Attachments for Beckman DU. Both the Warren Spectracord (Fig. 4-12) and the Beckman model DR recording spectrophotometer are automatic recording attachments for the Beckman model DU spectrophotometer. They give chart recordings with good resolution in the ultraviolet and visible regions. The rapidity with which complete curves may be obtained together with the simplicity of use of these instruments make them highly desirable acquisitions to the analytical laboratory. The Beckman model DK (Fig. 4-13) in addition to covering the visible and ultraviolet regions also extends automatic recording into the near-infrared region.

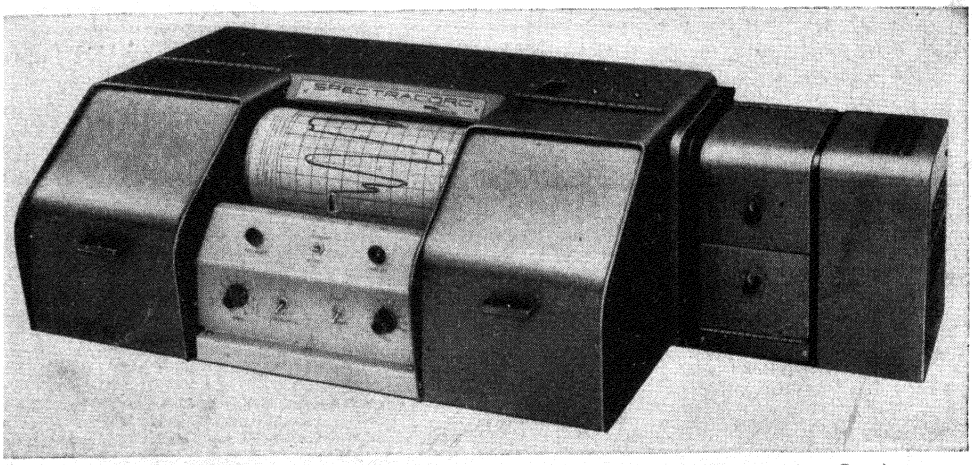


FIG. 4-12. Warren Spectracord. (*Courtesy of Warren Electronics, Inc.*)

Other Photoelectric Spectrophotometers. The following are among other photoelectric spectrophotometers commercially available: (1) the Cenco-Sheard spectrophotometer for the 325- to 750-mμ range which uses a concave reflection grating and a barrier-layer photocell; (2) the Coleman "double monochromator" spectrophotometer for the range 350 to 1,000 mμ, which uses a transmission grating; (3) the Coleman "universal" spectrophotometer for the 300- to 800-mμ range which uses a single grating with a barrier-layer cell; (4) the Coleman "junior clinical" spectrophotometer for the 400- to 700-mμ region, designed for clinical analysis but used also for other purposes; and (5) a Gaertner instrument using two spectrometers and a Martens photometer for the 450- to 820-mμ range.

For work requiring complete curves in the visible region, the General Electric recording spectrophotometer is convenient. The Cary, Warren, and Beckman DR instruments are convenient for the ultraviolet region as well. They are, however, considerably more expensive than the Beck-

man DU. The latter is a serviceable instrument of good precision and of sufficiently good resolution for most analytical purposes, serving for both the visible and ultraviolet regions. Complete curves may be plotted without too great an expenditure of time.

Filter Photometers. Filter photometers are essentially spectrophotometers in which spectral bands are produced by passing mixed light through a filter which transmits a restricted range of wavelengths, rather

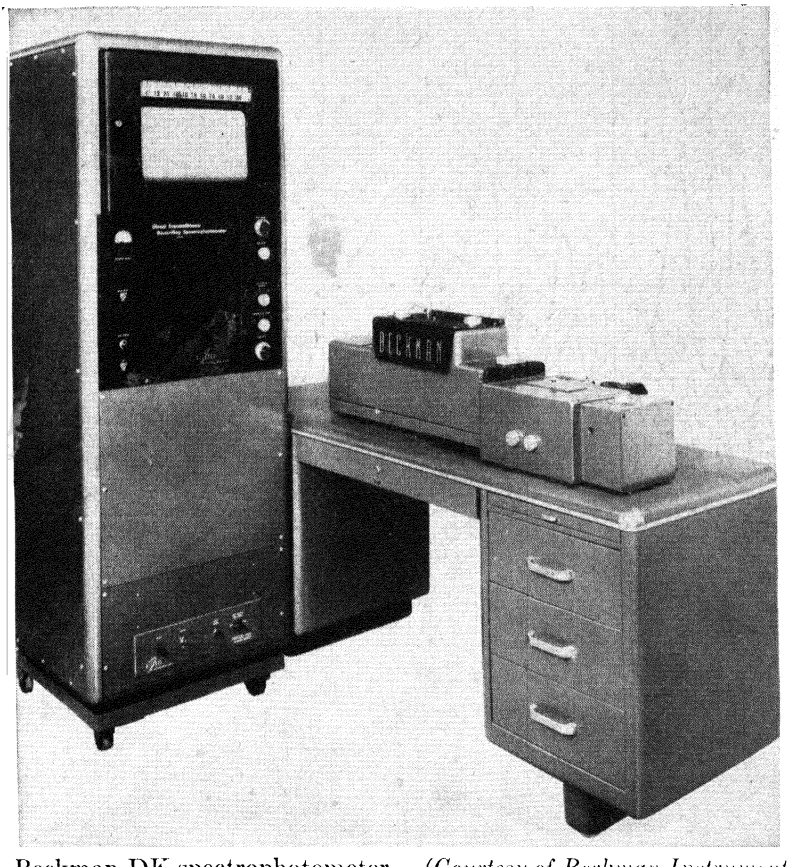


FIG. 4-13. Beckman DK spectrophotometer. (*Courtesy of Beckman Instruments, Inc.*)

than by dispersing it by means of prisms or gratings. In fact, filter photometers are sometimes referred to as abridged spectrophotometers.

Figures 4-14 to 4-17 give the spectral-transmittance curves of several types of filters. Information is usually available from the seller of a filter photometer concerning the characteristics of the filters supplied with, or recommended for, that photometer. It is generally desirable for a filter to transmit freely in a narrow region of wavelengths and not to transmit energy of other wavelengths which are present to any significant extent in the source, or to which the detector will be sensitive.

Several types of filters are available: (1) glasses, (2) a mixture of

dyes in solution or incorporated in gelatin, (3) interference filters, and (4) miscellaneous types.

Filter photometers have a field of usefulness intermediate between that of visual color comparators (see below) and that of spectrophotometers.

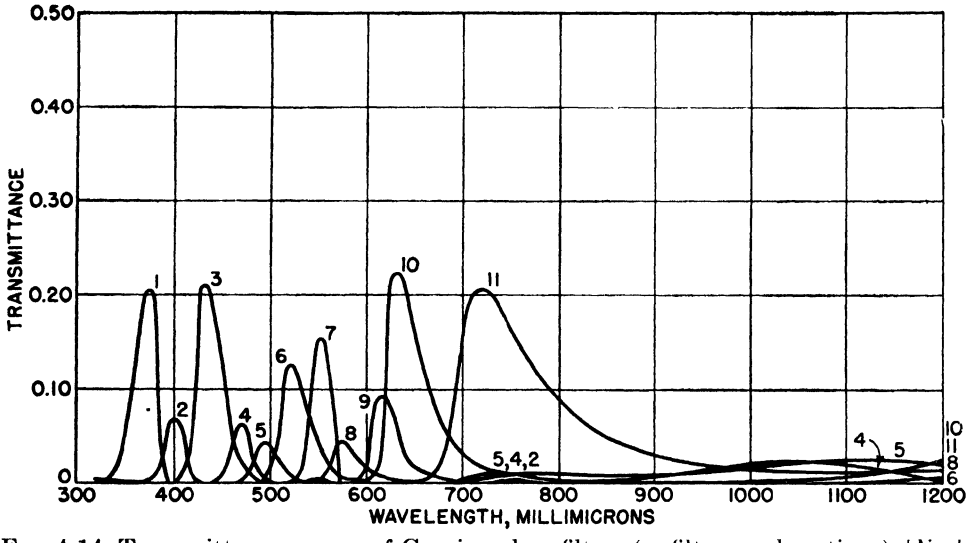


FIG. 4-14. Transmittance curves of Corning glass filters (or filter combinations). [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 23.*]

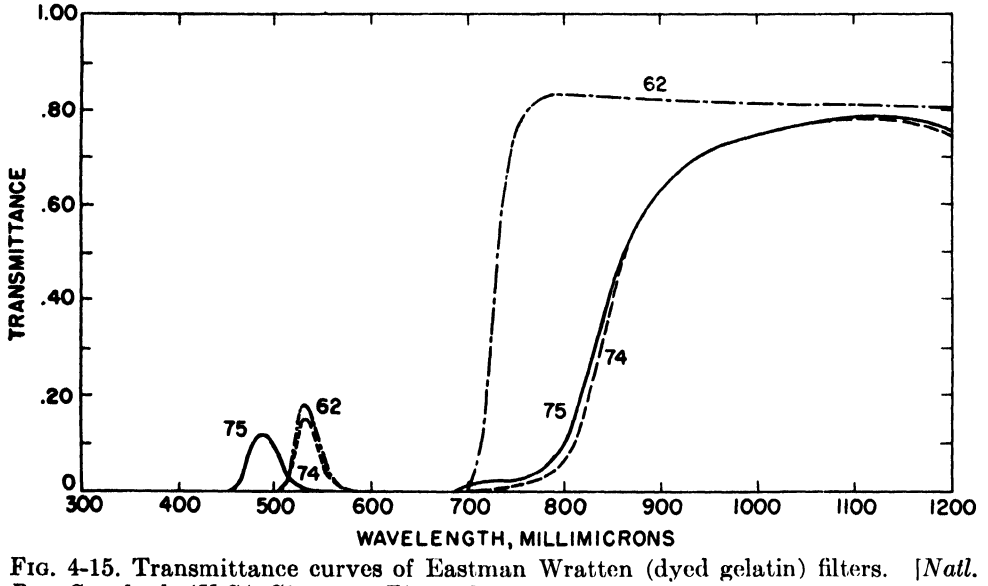


FIG. 4-15. Transmittance curves of Eastman Wratten (dyed gelatin) filters. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 24.*]

They do not suffer from the subjective errors associated with visual comparators, such as those brought about by shade differences between standard and sample, by errors caused by eye fatigue, and by personal differences of visual acuity, to say nothing of degrees of color blindness.

On the other hand, it is not possible in general to carry out with filter photometers two- or more-component analyses, which can be done by spectrophotometers. The reason for this is that it is not possible to iso-

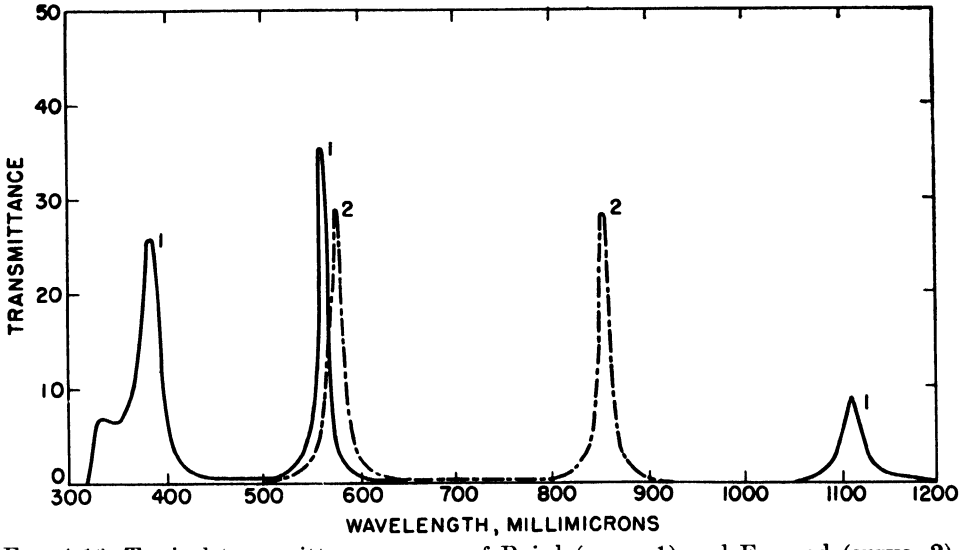


FIG. 4-16. Typical transmittance curves of Baird (curve 1) and Farrand (curve 2) interference filters. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 25.*]

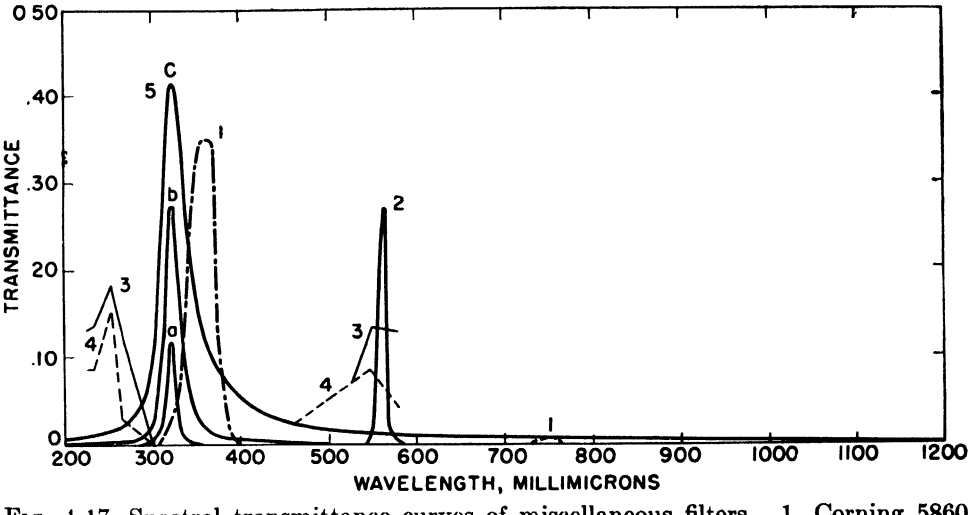


FIG. 4-17. Spectral transmittance curves of miscellaneous filters. 1. Corning 5860 glass. 2. Gibson four-component glass filter. 3. Quartz cell containing mixture of chlorine and bromine gas. 4. Quartz cell containing chlorine gas. 5. Fused quartz plates carrying silver films of the following thicknesses: (*a*) 0.0552 μ, (*b*) 0.0326 μ, (*c*) 0.0217 μ. [*Natl. Bur. Standards (U.S.) Circ. 484, Fig. 26.*]

late narrow enough spectral bands over a wide enough spectral range by combinations of filters. Nevertheless many filter photometers are used, particularly in routine industrial or clinical analysis. Where the types

of samples and the conditions of analysis are well standardized, these instruments may suffice in place of the more expensive spectrophotometer, but they are of only limited usefulness in analytical research.

A number of filter photometers are available commercially. Those requiring visual matching of two beams of light—only one passing through the sample—include the Pulfrich photometer, manufactured by Carl Zeiss, Inc.; the Leifo photometer manufactured by E. Leitz, Inc.; and the Aminco neutral-wedge photometer, manufactured by the American Instrument Company.

The photoelectric type of filter photometer is much more popular than the visual type. A number of manufacturers make such instruments, including the American Instrument Company, the Central Scientific Company, the Fisher Scientific Company, the Lumetron Corporation, and the Arthur H. Thomas Company (Klett-Summerson photoelectric colorimeter).

Visual Color Comparators. The simplest methods for colorimetric analysis call for the use of color comparators. There are a number of possible techniques, but they all ultimately involve matching the intensity of color of a solution containing the colored sample, or a colored reaction product derived from the sample, with a similarly colored standard solution (or a colored transparency such as a glass filter). These methods are simple, require inexpensive equipment, and may be run by technicians; but, on the other hand, they are of poorer precision than the photoelectric methods and may suffer in accuracy because of some of the subjective errors mentioned above.

A considerable variety of equipment is available commercially. It comprises such simple apparatus as test tubes, square bottles, and Nessler tubes, as well as many kinds of more intricate apparatus. Several types of methods may be distinguished. In the standard-series type, color standards of varying concentrations are used, against which the sample is matched.

The standards may be prepared as need arises or they may be permanent consisting of solutions, colored glasses, or similar transparencies. The apparatus varies in complexity from a block containing openings for viewing test tubes or bottles to elaborate roulette types (Fig. 4-18). In these, Nessler or other tubes with standard solutions may be rotated to bring one standard at a time in juxtaposition to the sample and in position to be viewed simultaneously by an optical arrangement. The Hellige comparator has colored glasses mounted in a circular disk against which the sample color is matched. A large variety of apparatus is available on the market.

In the duplication type, Nessler tubes are used and the color of the standard is brought up to that of the sample by adding measured amounts

of standard. In the dilution type the sample and standard are matched in Nessler tubes, or in an arrangement such as the Myers colorimeter, by diluting one or the other until they match when viewed through equally thick layers.

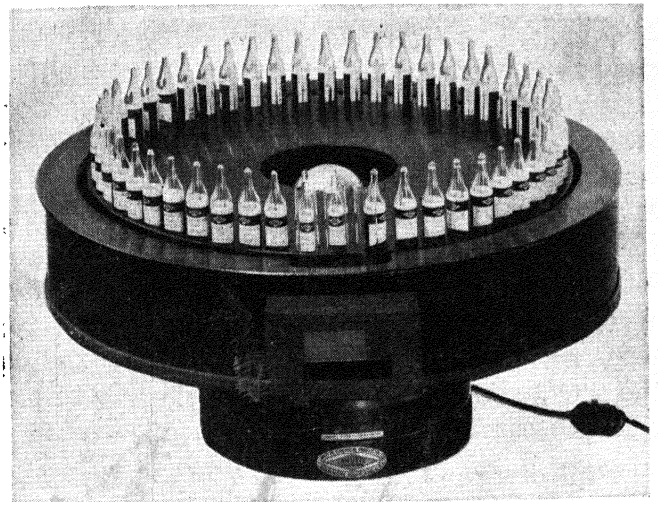


FIG. 4-18. Roulette comparator with permanent liquid standards. (*Courtesy of Arthur H. Thomas Co.*)

In the balancing type the sample and standard solutions are brought to a match by varying the depth of observation. A simple type consists of two graduated Nessler tubes or similar tubes containing, respectively, sample and standard. The former is added to a match and the depths are read. Various stages of elaboration exist, the most familiar being the Duboscq comparator (Fig. 4-19).

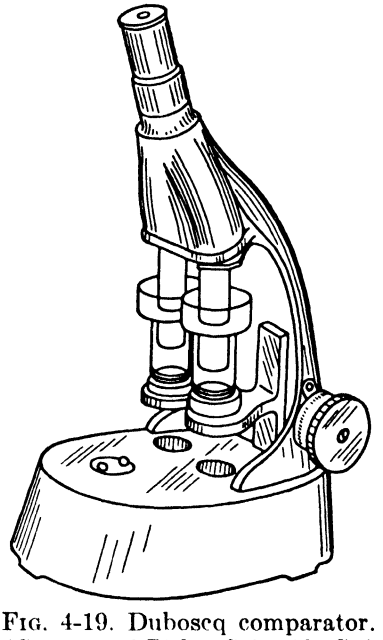


FIG. 4-19. Duboscq comparator. (*Courtesy of Fisher Scientific Co.*)

TYPICAL ANALYSIS

To give a detailed procedure for an absorptimetric analysis which would be generally applicable is impossible since too many variations are possible. The following procedure is for a hypothetical two-component analysis in the ultraviolet region. The directions would also be applicable for an analysis in the visual region with the additional possibility of the use of techniques of meas-

urement, such as filter photometry and direct visual matching, which are precluded in the ultraviolet region.

Given a sample of unknown composition, the problem is to identify the constituents of the sample and to set up an absorptimetric method for the constituents. If nothing at all is known about the possible constituents, it may be best to separate them by the usual chemical or physical methods and then to identify the separate constituents, perhaps by comparing their curve shapes with those of known substances. More often, however, something is known of the likely constituents of such a sample, so that it may be possible to identify the constituents spectrophotometrically without recourse to a separation. Assume that the sample is colorless. A solvent must be found which will completely dissolve sufficient of the sample to give a curve with a transmittancy which will lie in the region of about 10 to 50 per cent over the 220- to 400-mμ region. The solvent must transmit sufficiently well so as not to reduce very much the sensitivity of the instrument which is to be used. The following list comprises some of the more *commonly used solvents:*

Distilled water	Cyclohexane
Ethanol	Hexane
Methanol	Heptane
Concentrated sulfuric acid	Octane
0.1*N* hydrochloric acid	Isooctane
0.1*N* sodium hydroxide	

The solvents in the second column may have to be purified first by passage through a tube containing silica gel.

The following *solvents* are of *more limited application,* but are occasionally useful:

Pyridine	Orthodichlorobenzene
Toluene	Glacial acetic acid
Benzene	Cellosolve

The following *buffers* are satisfactory in the ultraviolet region:

pH	
3	Sodium dihydrogen phosphate and hydrochloric acid
5	Sodium acetate and hydrochloric acid
7	Potassium dihydrogen phosphate and sodium hydroxide
9–11	Boric acid, potassium chloride, and sodium hydroxide

Glassware should be cleaned scrupulously with warm soapy water, rinsed with distilled water, and allowed to drain. *Cells* should be similarly cleaned. The use of strong cleaning solutions is to be avoided since the last traces may be difficult to remove. Some detergents other than soap may also leave films which may introduce errors. If a solvent which

is not miscible with water is to be employed, the cell should be rinsed with the solvent before use.

With the usual 1-cm cell, a concentration of from 10 to 40 mg per liter, obtained by direct weighing of the sample, or by a second dilution of a more concentrated solution, will generally be suitable.

The details of manipulation of the instrument to be used will vary with the particular instrument and may be learned from the manufacturer's manual. It will generally involve first setting the 100 per cent reading with the cell filled with solvent, then taking readings with the cell filled with the solution.

The curve is plotted on the log A_s scale. It is then examined in a qualitative manner to try to identify its constituents. This is done by subtracting from the curve so obtained that of a suspected constituent also plotted on the log A_s scale. This is accomplished most easily with the log reference scale, as described previously. The curve remaining after the subtraction is then compared with known curves of substances suspected to be present, disregarding small deviations, particularly at regions of high transmittancy. When a tentative identification of the constituents has been made, its correctness should be confirmed as previously described in the section on qualitative analysis.

Having identified the constituents, either spectrophotometrically or otherwise, one may set up a quantitative spectrophotometric method of analysis. After a suitable solvent and an appropriate concentration range have been found, certain other possible effects must be investigated. The effect of *changes in pH* should be studied and a buffer chosen if necessary. If *heating* is necessary to effect solution, it must be ascertained whether such heating will cause alterations in the absorption curve and if, in spite of such alterations, it is still desired to use the particular solvent, whether those alterations will be reproducible. Other effects of heating involve change in solvent volume or change in the composition of a mixed solvent by volatilization. Another effect to look for is that of *irradiation* causing alterations in curve shape which may, or may not, be reversible on standing. Comparisons should be made of curves on a fresh solution, and on the same solution after irradiation and after storage in the dark, to allow for the possibility of reversibility. So-called *aging effects* must also be studied to see whether changes take place in the solution of the substance on standing and, if so, to fix conditions to eliminate or to standardize such effects. Adherence to *Beer's law* should be tested for by measurements of solutions with variations in concentrations within the range of interest. Finally, the effects of any ingredients should be determined which may not themselves absorb radiation but which may affect or alter the absorption characteristics of the constituents being determined.

After conditions for measurement which will ensure reproducible absorption curves under the conditions of the analysis have been decided upon, *wavelengths* appropriate for the measurements are chosen, as described previously, by examination of the curves of the purified constituents known to be present. Methods of calculation have already been discussed.

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CHAPTER FIVE

Infrared Spectrophotometry

Infrared absorption spectrophotometry might, from one point of view, have been logically included in the chapter on visible and ultraviolet absorption spectrophotometry. From that viewpoint it is merely an extension to radiation of longer wavelengths (lower frequencies) of the principles and techniques encountered in the visible and ultraviolet regions. Nevertheless, the points of similarity are outweighed sufficiently by the points of dissimilarity to make a separate treatment advisable. The peculiar characteristics of infrared spectrophotometry may be considered under two categories: first, the type of information obtained by absorption in the infrared region; and second, the kinds of apparatus and techniques used in that region.

ORIGIN OF INFRARED SPECTRA AND REGIONS

It has already been pointed out (Chap. 4) that, whereas absorption of visible and ultraviolet radiation depends upon the vibrations of electrons in a molecule, absorption of infrared radiation stems from the vibrations of the atoms in the molecule and from the rotation of the molecule itself. However, rotational effects (in the far infrared) are not brought out by the usual infrared instruments. A mechanical analogy[1] will illustrate the vibrational behavior of the molecule. Suppose that ball bearings, the weights of which are proportional to those of the atoms in a molecule, are connected by springs in positions analogous to those of the atoms in the molecule. Also assume that the tensions on the springs are proportional to the forces between the atoms. If such a model is set vibrating by a blow, the bearings execute complicated vibratory patterns. When such a vibrating model is illuminated with stroboscopic light definite frequencies are found for which the model seems to stand still. Each such model, representing a single molecule, will have a number of characteristic vibrations in which each ball bearing is moving in a definite path with the same frequency. If the model has N ball bearings, there will be $3N - 6$ characteristic modes of vibration.

By substituting atoms for ball bearings and chemical forces for springs and using the appropriate values for the masses and the forces, it is possible (for simple molecules) to calculate the frequencies of vibration characteristic of a given molecule. If radiation corresponding to a characteristic frequency of vibration of a molecule is caused to impinge upon that molecule, it is absorbed in quanta (thereby raising the energy level of the molecule) provided that the vibration at that particular frequency involves a change in the dipole moment of the molecule. (The dipole moment is dependent upon the location of the electrical center of the molecule.) Gases, in addition, often undergo a change in the rotational state of the molecule. Practically all organic compounds, and most inorganic compounds, have characteristic infrared absorptions; whereas only colored substances have characteristic visible absorptions and only certain classes of compounds, particularly aromatic compounds and compounds with conjugated unsaturation, have characteristic near-ultraviolet absorptions. These facts make infrared spectrophotometry of practically universal application. This is not to say, of course, that for one application or another, for one reason or another, ultraviolet or visible spectrophotometry may not be preferable. Some of the points to be considered in choosing one spectral range over another for a specific problem will appear during the discussion to follow.

Infrared Regions. The infrared spectrum may be considered as being divided into four regions: (1) the near-infrared or overtone region, comprising wavelengths from 0.75 to 2.5 μ (microns); (2) the infrared region, from 2.5 to 25 μ; (3) the far-infrared region, from 25 to about 350 or 400 μ; and (4) the microwave region, comprising an indefinite spread of wavelengths up to 10,000 μ (1 cm) or longer.

The *near-infrared* region comprises vibrations some of which may be considered extensions of the electronic vibrations characteristic of ultraviolet and visible radiation, and some of which may be considered as overtones and combinations of vibrations characteristic of the infrared region. Although this region possesses some interest, it has not been applied to any considerable extent to analytical chemistry. This is true in spite of the fact that there would be certain advantages to the analytical chemist in working in this region. One advantage is the fact that glass or quartz optics and windows may be used rather than the more expensive and inconvenient sodium chloride and similar optics and windows (see below) which must be used in the infrared region. Commercial instruments have recently appeared which make use of stable photoconductive and photovoltaic lead sulfide or thallous sulfide cells for the detection and measurement of near-infrared radiation, rather than of thermocouples and bolometers. These developments will permit the exploitation of that region of the spectrum for analysis.

The *far-infrared* region comprises pure rotation bands of light gases and certain frequencies of inorganic crystals and organic materials. This region too is of only slight interest for the analytical chemist, because of experimental difficulties in working there and because of the limited nature of the analytical information to be gained. The *microwave region* is one of overlaps between heat radiation and electrical radiation, including radiation characteristic of radar. It is mentioned merely for completeness; it is not yet of great analytical significance, although rising interest is being shown in its study.

The *infrared* region is the region of greatest analytical importance at present, and subsequent discussion will be confined to it. Such discussion will also be confined to what may be called empirical applications, as distinct from theoretical applications. The latter are derived from the fact that absorption of infrared radiation is related to fundamental energy, mass, and space relationships between the atoms of a molecule. There is therefore a considerable body of knowledge which is concerned with the study of infrared absorption as related to an elucidation of fundamental molecular forces. A knowledge of this branch of physical chemistry is not essential for the use of infrared as an empirical analytical tool.

QUALITATIVE AND STRUCTURAL ANALYSIS

The analytical chemist is interested in infrared absorption both for qualitative and for quantitative analysis. For qualitative analysis the most obvious application is that involving the use of absorption curves as "fingerprints." This application is similar to that in the visible and ultraviolet regions except that the "fingerprints" may be influenced by the presence of many more chance impurities because practically all compounds show infrared absorption. Water must be avoided because of its wide absorption. The background of carbon dioxide and moisture must be considered and is taken care of by some instruments. The ability to superimpose the curve of one substance upon that of another makes it practically certain that the two are identical. The infrared region leads to a greater certainty in this respect than the visible or ultraviolet since each molecular species usually has so many absorptions that the chance of superimposition without complete identity is negligible. To make best use of this means of identification a library of curves of known substances should be accessible. Such collections of curves have been published[2] and others appear occasionally in current literature. If these curves are properly codified and indexed for ready reference, they may make possible a ready identification. If the specific curve cannot be found, the chemist must make some guesses, based on other evidence as well as on structural evidence from the infrared curve itself (see discussion below). He may

then proceed to match the curve of the unknown with curves which he has prepared from compounds which he hopes may match that of his unknown material.

When the unknown sample is impure, it may be purified by the usual methods. The removal of impurities may be followed by noting the disappearance of certain bands from the infrared curve. This may, of

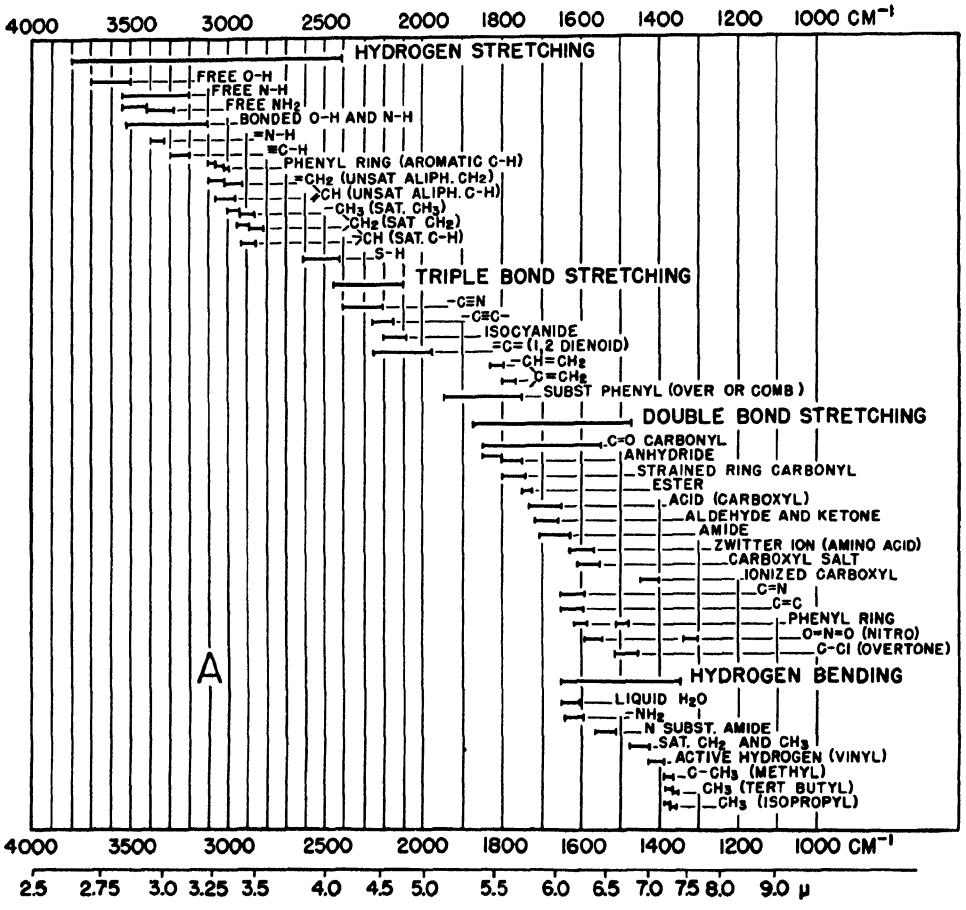
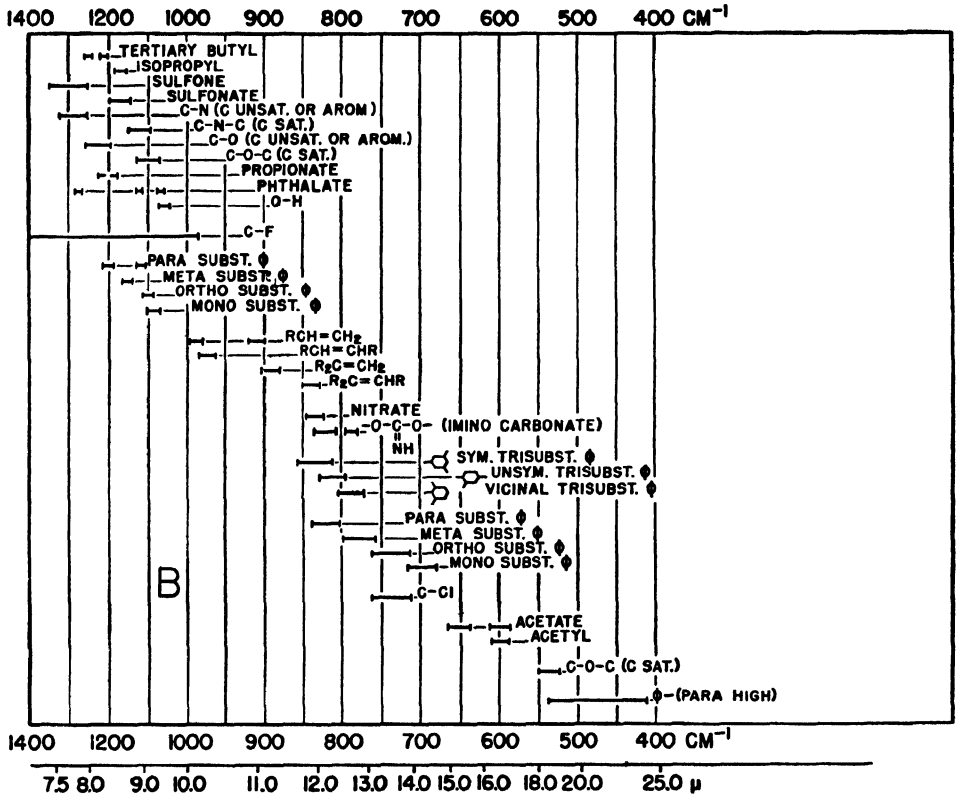


FIG. 5-1. Characteristic infrared absorptions of atomic groups.

course, be done without a knowledge of the identity of the impurities which are being removed.

Another application of infrared spectrometry to qualitative analysis is the obtaining of structural information. It has been found from a study of many compounds, and from calculations on simple molecules, that the presence of a given structural grouping in a compound will produce an absorption band in a definite wavelength region. Figures 5-1*A* and 5-1*B* indicate the wavelengths (and the corresponding wave numbers, cm^{-1}) at

which absorption bands may be found when the molecule contains certain groups and types of bond. The assignments in Fig. 5-1*A* (below 7.5 μ) are due mainly to absorption caused by vibrations of specific atomic groups and may be interpreted as being due to the structures indicated. The assignments in Fig. 5-1*B* (above 7.5 μ), on the other hand, are due mainly to absorption caused by the vibration of the molecule as a whole. The presence of a band at a particular wavelength region is presumptive, but not conclusive, evidence of the existence of the structure indicated in the chart since there is a possibility that the absorption may be due to



[*R. B. Barnes et al., Anal. Chem.*, **20**: *402 (1948), Fig. 3.*]

harmonics of other structures. The absence of such a band does indicate the absence of the structure. For example, the presence of a strong band near 13.0 μ does not conclusively prove the presence of a meta-substituted aromatic ring. If absorptions are present which indicate an aromatic ring (as at about 3.25, 6.3, and 6.7 μ) then the presence of the 13.0-μ band indicates the probability of a meta-substituted ring. Success in using this type of information requires considerable experience and judgment as well as the use of other chemical and physical information and of any

other correlative information on the material. This approach may, however, simplify exceedingly the oftentimes complex problem of chemical identification.

QUANTITATIVE ANALYSIS

In its general aspects quantitative analysis by absorption of infrared radiation is similar to quantitative analysis by absorption of visible and ultraviolet radiation. Measurement is made of absorptions at properly chosen wavelengths, and for two- or multicomponent systems, simultaneous equations are set up and solved for the concentration of individual components. There are differences which are caused in part by the peculiar characteristics of infrared absorption and in part by differences in spectrometers and cells.

Choice of Wavelength. As in the visible and ultraviolet regions, setting up a quantitative method of analysis usually starts with getting absorption curves for the individual components to be found in the expected samples. From these curves one wavelength is chosen at which a single component is the sole or major absorber. There are thus obtained as many wavelengths as there are components, each wavelength corresponding to a different component. (One wavelength fewer may be used, but this is not usually advisable.) Whenever possible, wavelengths corresponding to absorption peaks should be chosen. If this is not possible and a wavelength corresponding to the side of a band must be chosen, the accuracy attainable may be limited by the precision of the wavelength setting. It is good practice to choose wavelengths so that the absorbancies of the minor absorbers do not change by more than a factor of 2 over the wavelengths subtended by the slit widths being used.

Base-line Technique. Computations in the infrared region by the use of simultaneous equations are more complicated than in the visible or ultraviolet regions. One reason is that absorption coefficients are difficult to calculate because of the difficulty of accurate measurements of sample thickness and because of the variations in slit width and scattered light as the spectrum is scanned. Furthermore, Beer's law is not always followed exactly. For certain gases the absorption of infrared radiation is dependent not alone on the number of molecules of the gas in the path of the radiation but also on the pressure of the gas. The addition of gases which do not themselves absorb radiation in the region in question, e.g., air, hydrogen, or oxygen, will increase the absorption coefficient of the gas of interest. This is the so-called "pressure-broadening" effect. For liquids and solids Beer's law may not hold because of intermolecular effects such as, for example, that due to hydrogen bonding.

Because of such complications, a simplified method of calculating concentrations of single components in a multicomponent system, the base-

line technique has gained popularity. This method is one in which substances already present in the sample serve as standards in determining the substance of interest. Cell thickness and other instrumental conditions need not be reproduced and analytical accuracy is increased. The steps in the method are as follows: First determine the spectra for all the compounds to be determined in a mixture. Next, select appropriate absorption peaks, at each of which one compound is to be determined, in such a manner as to minimize interference by the peaks of other compounds. In Fig. 5-2, A illustrates such a chosen wavelength. Measure I, the distance from the recorded zero line to the selected absorption peak. Draw a straight line, the base line, between two points M and N taken at wavelengths on either side of the absorption peak, but on the same absorption band. M and N are chosen, if possible, where there is little absorption. Measure the distance I_B from the zero line to the base line at the same wavelength A at which I was measured. Calculate $(A_s)_B = \log_{10}(I_B/I)$ where $(A_s)_B$ is the base-line absorbancy. Set up a series of simultaneous equations using values of $(A_s)_B$ for each component instead of $-\log T_s$ (absorbancy), such as were described for visible and ultraviolet absorption calculations (page 66). When it is desired to determine only one constituent in a mixture in which other constituents do not absorb in the region where that constituent absorbs, the latter constituent may be determined by setting up a graph of $(A_s)_B$ vs. percentage of the constituent. If Beer's law is obeyed, such a graph will be a straight line.

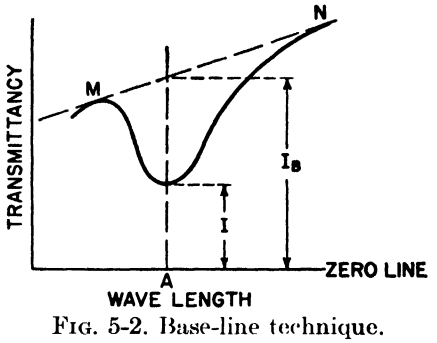


FIG. 5-2. Base-line technique.

Slit Width. The slit width to be used in an analysis at a given wavelength should be chosen judiciously and must, of course, be used subsequently in measurements at that particular wavelength. A slit width as narrow as possible should be chosen, particularly when the measurement is to be made on the side of an absorption band or at the peak of narrow bands. With wide bands wider slit widths are permissible. Narrow slits also tend to reduce the extent of deviations from the Bouguer-Beer law. It is sometimes necessary, however, to sacrifice some of these advantages by using a wider slit, in order to get sufficient energy to be able to measure transmittancies with sufficient precision.

Cell Length. As in the visible and ultraviolet regions, the cell length should be properly chosen so as to give absorbancies between 0.2 and 0.8 in order to attain good accuracy in the absorption measurement. The optimum value for the absorbancy is 0.4343, which corresponds to a

transmittancy of 37 per cent. With gases, optimum transmittancy may be attained by using a cell of fixed length and altering the gas pressure until a suitable transmittancy is reached. With liquids a variable length cell must be used or a fixed-length cell within the desired range.

False Energy. One source of error which must be considered is that of false energy. This is energy of wavelengths other than that which it is desired to transmit, and which reaches the thermocouple or bolometer by scattering from the walls or by gas in the system and for other reasons.

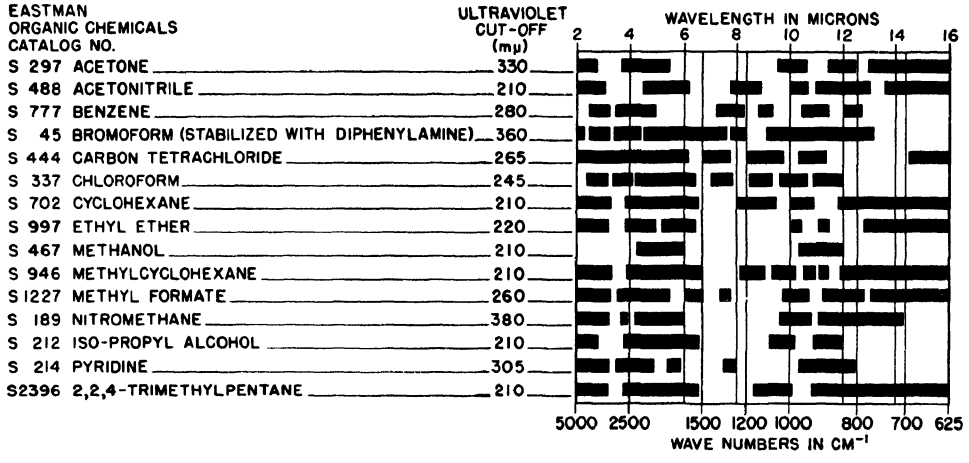


FIG. 5-3. Solvents for spectrophotometric use. (*By permission of Eastman Kodak Co.*) The ultraviolet cutoff given is the wavelength at which the absorbance (optical density) of a 1-cm layer is about 1. Below 200 mμ, cutoff values should be determined in the user's own equipment because of instrumental variations in wavelength calibration, stray light, and effective slit width.

The white "windows" in the chart show the infrared regions for which these liquids have been found useful in the cell thicknesses commonly employed.

For wavelengths below 11 μ this may be satisfactorily eliminated from spectrometers by the use of shutters which pass only a restricted spectral range. For higher wavelengths transmittancies should be corrected for this false energy. In more recent types of infrared spectrophotometers a device is used to convert the desired energy to alternating current, whereas the stray energy is not so converted. Since only the alternating current is measured, the effect of false energy is eliminated.

Preparation of Samples for Measurement. *Gaseous samples* offer no great difficulties in their preparation for measurement. Fairly long cells may be used to make possible the detection or the determination of low concentrations of a constituent of a gaseous mixture. With a fixed-length cell the pressure of the gaseous sample may be varied to achieve a suitable absorbancy in the wavelength regions of interest.

Liquids may be examined unchanged for qualitative analysis by using cells which vary in thickness from about 0.01 mm to several millimeters,

or the liquid may be squeezed between flat salt plates. Where even such an extremely thin film of liquid sample is too thick to permit proper resolution of absorption bands or when a quantitative analysis is desired, a solvent may be used.

Several methods of mounting *solid samples* are in use.[3] Solids with low melting points may be melted on silver chloride or mica plates. For higher-melting solids a heated cell has been described.[4] Plastic solids may be examined as a film. A very common technique is to mull the sample in a medium such as mineral oil (Nujol) or, for wavelength regions where mineral oil is opaque, in perfluorokerosene. Still another technique is to mix the pulverized sample with polyethylene and press the mixture into a film. A recent technique involves pressing the sample into a plate with potassium bromide.[6,7]

Finally, solid or liquid samples may be examined in *solution*. For exact quantitative analysis the use of solutions is practically imperative. Yet the fact that no molecules are completely transparent to infrared radiation makes the choice of a solvent difficult. Water may not be used because of its high absorbance. Two solvents, carbon tetrachloride and carbon bisulfide, are useful because of the wide range of frequencies for which they show low absorbance. But they are not good solvents for many substances. Other compounds such as acetone and pyridine, which are good solvents, have fewer regions of usefulness. The chart (Fig. 5-3) indicates regions of usefulness for a number of solvents. Absorption curves for many solvents are given by Torkington and Thompson[5] and by Pristera.[3]

INSTRUMENTS

Several types of infrared spectrometers may be purchased. They all have in common the following components: (1) a source of continuous infrared radiation; (2) a means for dispersing this radiation into a spectrum; (3) an optical system and a system of slits for collimating and selecting narrow-wavelength portions of the spectrum; (4) a system of detecting, amplifying, and recording the intensities of radiation which has passed through the sample; and (5) absorption cells and accessory equipment for samples.

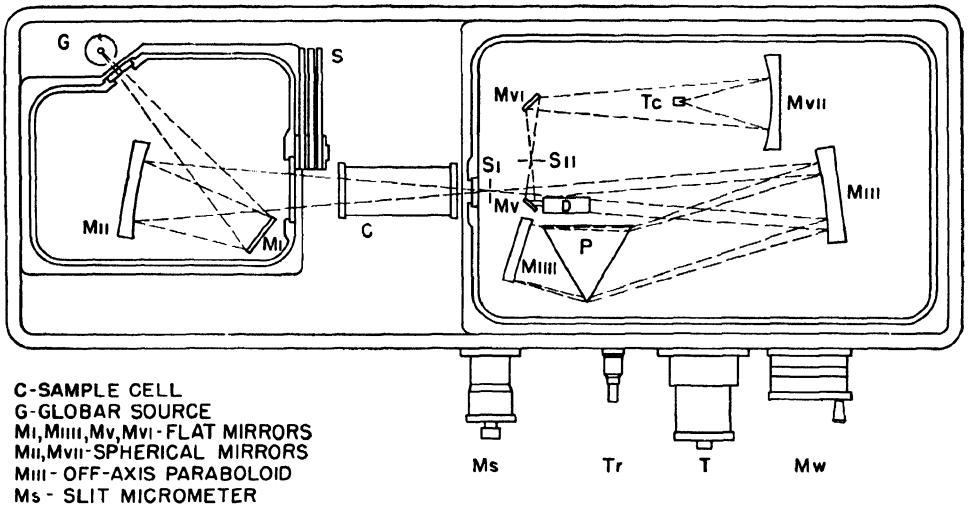
Sources. Various kinds of heated filaments have been used to provide continuous infrared radiation. The two most common are the Globar and the Insulcon or Nernst glower. The former is a bonded silicon carbide rod and the latter a rod made up of a mixture of rare earth oxides. Each type has some advantages and disadvantages relative to the other, but practically, the buyer of an instrument must use the type which comes with that instrument. (For the near-infrared region a tungsten lamp may be used.)

Dispersive Media. Dispersion of the continuous infrared radiation from the source may be accomplished, as in visual or ultraviolet spectrometry, by a grating or a prism. The prism type is used on commercially available instruments intended mainly for chemical analysis. Gratings offer higher dispersion and so better resolution than prisms and are used on some special research instruments. The grating reflects radiation with frequencies which are multiples of those desired. It must therefore be used either with appropriate filters or in series with a (low-dispersion) prism to remove unwanted radiation. The latter combination is used since suitable filters are not yet available, although they are being studied. For molecular structural studies of some complexity, and for some analytical problems, a grating instrument is desirable, but for most analytical purposes the lesser dispersion of the more generally available prism instrument is sufficient.

As is true with solvents for infrared use, so it is also true with prisms that the great tendency for substances to absorb infrared radiation complicates the selection of prism materials. No one substance transmits radiation throughout the entire infrared region. It is accordingly necessary for best results to choose prism materials according to the spectral region of interest. The following are common prism materials, together with the highest wavelength at which they are useful: quartz 3.0 μ, lithium fluoride 6 μ, calcium fluoride 9 μ, sodium chloride 15 μ, potassium chloride 20 μ, potassium bromide 25 μ, and potassium iodide 30 μ. Sodium chloride is used most commonly since it covers most of the spectral range of interest in analysis, but advantages in dispersion and resolution may be obtained by using calcium fluoride or lithium fluoride for the low-wavelength region and potassium bromide for the high-wavelength region. A disadvantage of both sodium chloride and potassium bromide, not shared by lithium fluoride or calcium fluoride, is their hygroscopicity. This makes it necessary to protect the prisms and cells from atmospheric humidity by the use of drying agents, and by other means, and, of course, from excessive moisture in samples.

Optical Systems. The optics of infrared spectrometers are essentially the same as for the visible and ultraviolet regions, but with modifications required by the peculiar characteristics of the infrared radiation. Large apertures are needed to get sufficient energy, and mirrors are used since lenses which are sufficiently achromatic over the desired wavelength region are not available. Figure 5-4 gives a schematic diagram of the optical system of an infrared spectrometer. Such a simple spectrometer leads to the need for laborious and time-consuming computations in converting thermocouple readings obtained with a sample to transmittancy or absorbancy values, calculated against solvent or reference blanks. To eliminate the need for such computations, two types of instruments are available which make this comparison automatically.

One type, exemplified by the Beckman IR-3, uses a *single beam* and the so-called memory-standardization system. In this system a reference spectrum is first obtained with the same cell and solvent as will be used for the sample, but without the sample. The slit widths are varied during the course of the run by means of a servomechanism in order to provide a constant energy output. The schedule of slit widths is recorded on a magnetic tape and the recording is fed back to the system when the sample is run in order to reproduce the same sequence of slit-width



C-SAMPLE CELL
G-GLOBAR SOURCE
MI,MIIII,MV,MVI-FLAT MIRRORS
MII,MVII-SPHERICAL MIRRORS
MIII-OFF-AXIS PARABOLOID
MS-SLIT MICROMETER
MW-WAVELENGTH MICROMETER
P-PRISM
S-SHUTTERS
SI-ENTRANCE SLIT
SII-EXIT SLIT
T-TURRET DRUM
TR-TURRET RELEASE
TC-THERMOCOUPLE
D-TEMPERATURE COMPENSATOR

FIG. 5-4. Optical path of small prism infrared spectrometer. [*R. B. Barnes et al., J. Appl. Phys.*, **16**: 77 (*1945*), *Fig. 3.*]

changes. In that way true percentage transmittancy or absorbancy readings are automatically obtained and plotted.

Another type of automatically recording percentage-transmittancy spectrometer is based on the use of a *double beam* and the optical-null method. This instrument (Fig. 5-5) utilizes two radiation beams taken from a single source. One beam goes through the sample cell and the other through a reference cell. By means of a suitable mechanical and optical arrangement each of these beams is made to strike the detector alternately. If their radiation intensities are different, an alternating current is produced which operates a servomechanism which, in turn, actuates an optical wedge in the reference beam. This maintains a balance of radiation intensity from the sample and reference beams. The

position of the wedge is recorded as transmittancy, thus producing an automatic percentage-transmittancy vs. wavelength curve. (The double-beam principle has also been embodied in the Beckman DK and the Warren Spectracord instruments, which extend the range of the Beckman DU to the near infrared, with automatic recording.)

Double-beam instruments have an advantage over the single-beam type in the infrared region. Absorption due to moisture and carbon

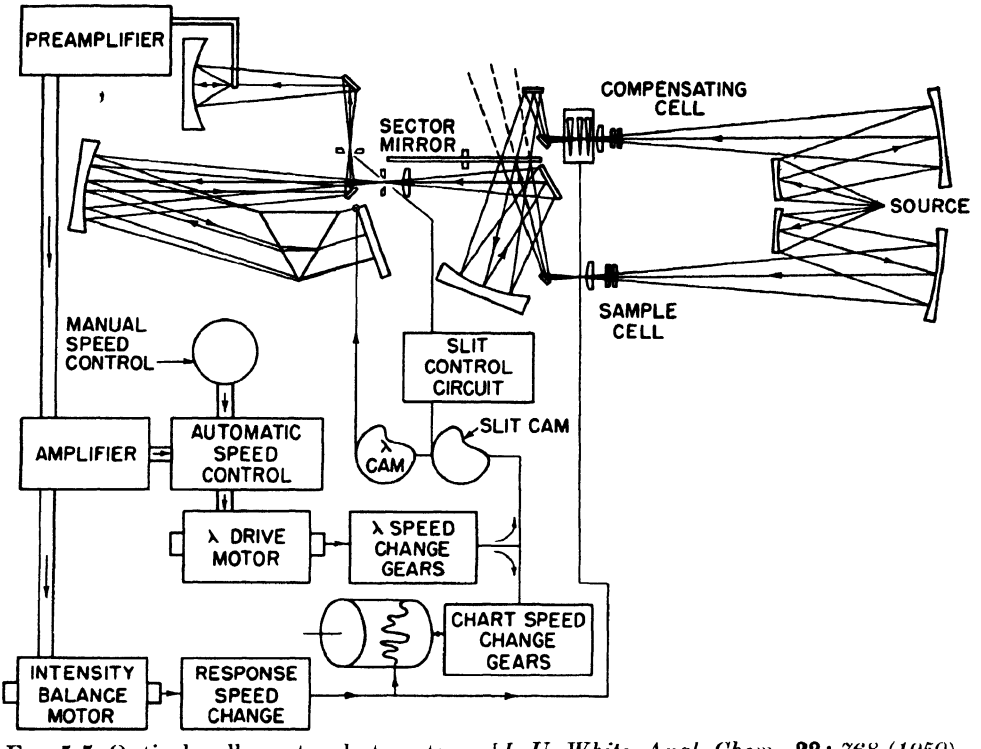


FIG. 5-5. Optical-null spectrophotometer. [*J. U. White, Anal. Chem.*, **22**: 768 (1950), *Fig. 1.*]

dioxide (as well as adventitious impurities in the air in the optical path) is automatically compensated and does not affect the absorption curve.

Detectors, Amplifiers, and Recorders. Two types of detectors are employed, each of which depends upon the heating properties of infrared rays. One type is the *thermocouple*, enclosed in an evacuated tube, which develops a current by virtue of temperature changes produced by the incident radiation. The other type is the *bolometer*, consisting essentially of a strip of metal in a suitable electrical circuit. The heating effect of the infrared rays changes the conductivity of the strip. By means of the conductivity the intensity of the radiation may be measured. (The Beckman DK and the Warren Spectracord utilize *lead sulfide detectors* for the near-infrared region.) In the manually operated instruments the

signal produced by the radiation actuates a galvanometer which is read at each wavelength setting, and the reading is plotted manually. In the automatically recording instruments, the signal is amplified electronically and fed into a commercial recorder to furnish an automatic plot.

Absorption Cells. The absorption cell is placed in the undispersed beam between the source of radiation and the entrance slit. This is preferable to placing it in the monochromatic beam after dispersion, because in the latter position slight variations in the temperature of the cell affect the detector. The former arrangement also simplifies some optical requirements of the prism.

The sample cell is the weakest link in modern infrared spectrometry. Except for gaseous samples, such a thickness of sample is generally used

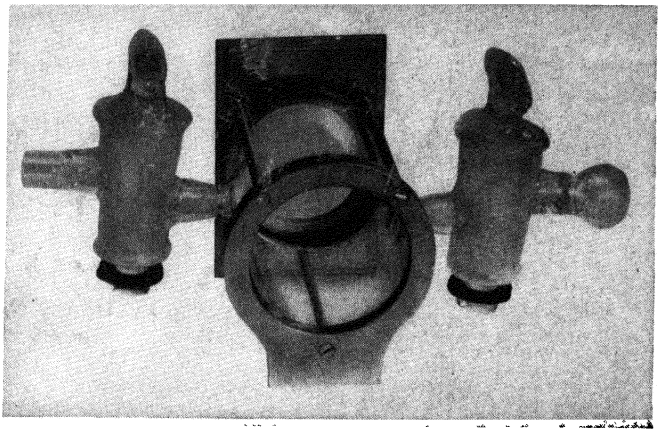


FIG. 5-6. Gas absorption cell. (*Courtesy of The Perkin-Elmer Corporation.*)

which will cause about 80 to 95 per cent absorption of the radiation at the wavelengths of the strongest bands. With the uncertainties of thickness and of the transmittance of the cells used, infrared-absorption data cannot be given in terms of specific extinction coefficients. They are presented rather as percentage transmittancy, together with the best estimate of sample thickness.

Gas-absorption cells (Fig. 5-6) vary in length from 1 to 20 cm and have provisions for utilizing pressures of from a few millimeters of mercury for strong bands to atmospheric pressure for weak bands. *Nonvolatile liquid* samples being studied for qualitative information may be spread on a rock-salt or other suitable plate, covered with a cover plate, and inserted in a cell holder (Fig. 5-7). Metal foil spacers may be inserted to give a rough thickness variation of from, perhaps, 0.01 to 0.5 mm. For *volatile liquids*, or for reproducible thickness, a series of cells with graded spacers is used. The cells may be filled and emptied by means of cutoff hypodermic needles. *Solids* may be studied, as mentioned previously, in the

molten condition, as deposits left after evaporating a solution, as Nujol mulls, or in solution. Window materials have been discussed previously.

A technique for working with solid samples[6,7] has been published which would seem to be better than the usual procedure of grinding with mineral oil on a rock-salt plate. By this technique the sample is ground with solid potassium bromide and the mixture is pressed under high pressure into a thin plate. This is then used instead of the usual cell containing the sample. Several advantages are claimed for this technique: (1) There are no scattering losses, especially in the short-wavelength region. (2) There is no obscuring of any spectral region because potassium bromide transmits out to 25 μ. (3) Better-separated and sharper bands are obtained because of the practically molecular dispersion of the sample. (4) There are no background effects or bands; therefore, quantitative

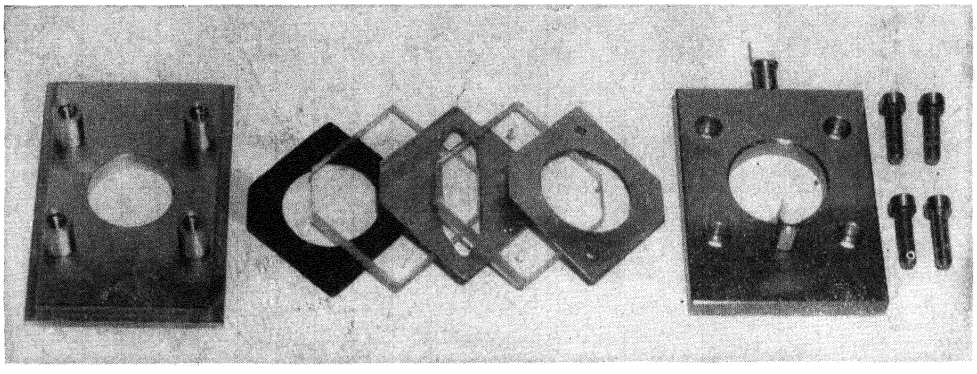


FIG. 5-7. Cell holder and cell for rock-salt plate. (*Courtesy of The Perkin-Elmer Corporation.*)

work is simpler and more accurate. Only the proportion of potassium bromide to sample must be known. (5) Samples may be stored without danger of evaporation of solvent or changes in composition. (6) The expense for cells is reduced.

Gas Analyzers. Mention should also be made of the nondispersive type of infrared gas analyzer, which is of value for the determination of a single component in a gas stream. It may be used for the continuous monitoring of industrial or laboratory processes. These instruments use no prisms or other means of dispersing the beam from the infrared source. They are of two types: the positive- and the negative-filter types, as shown in diagrammatic sketches in Fig. 5-8.

In the positive type (Fig. 5-8*A*) infrared radiation from the source *So* is collimated by the mirrors M and M' through the sample cells S and S', a filter cell F, and two detector cells D and D'. The cells D and D' constitute two bulbs of a gas thermometer and are joined by a thin metal diaphragm which is incorporated as a plate of a variable condenser. If

it is desired, for example, to determine carbon dioxide, both D and D' are filled to the same pressure with carbon dioxide. The gas in which carbon dioxide is to be determined passes through cell S (S' is a dummy cell). Radiation of wavelengths at which carbon dioxide is absorbed is removed by the sample to a degree dependent upon the concentration of carbon dioxide, but the same radiation is not removed in S'. (If the sample gas contains other constituents which have absorptions that overlap those of carbon dioxide, such interfering constituents are placed in F, thus making both D and D' insensitive to these interferences.) To the extent to which frequencies which could be absorbed by the carbon dioxide have been removed from D, but not from D', D is cooled in relation to D' and the diaphragm registers the difference in pressure that is thus produced.

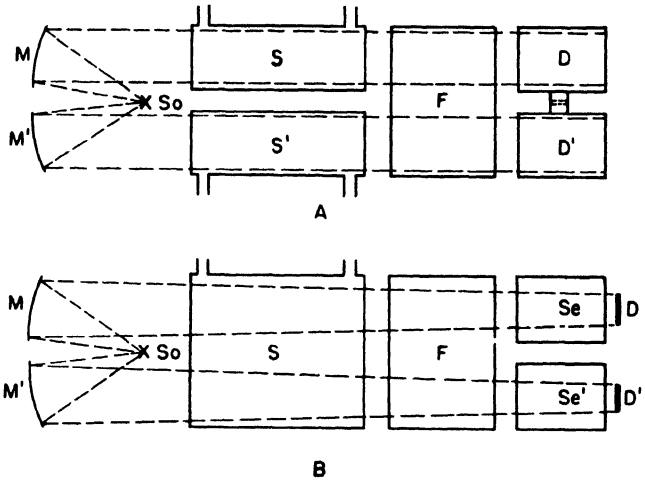


FIG. 5-8. Nondispersive infrared gas analyzers. [*V. Z. Williams, Rev. Sci. Inst.*, **19**: *135* (*1948*), *Fig. 19.*]

In the *negative-filter* type (Fig. 5-8*B*) all the radiation passes through the sample cell S and the filter cell F. The latter serves the same function as in the positive type. The radiation is then split to pass into the sensitizer or selector cells Se and Se' and thence to the thermopile or bolometer detectors D and D'. Se contains the gas which is to be detected, e.g., carbon dioxide, and Se' a gas which does not absorb infrared radiation, such as nitrogen or air freed from carbon dioxide. If the sample in S contains carbon dioxide, the detector D will be unaffected since, even without the sample, Se has already caused absorption due to carbon dioxide. The detector D' will be cooled further by the extent of the absorption caused by the carbon dioxide in the sample. The difference in temperature between D and D' measures the concentration of carbon dioxide.

EXAMPLES OF QUANTITATIVE ANALYSES

As an example of a simple determination, in which the base-line technique is used, there may be cited the determination of methylene chloride in chloroform.[8] A series of known mixtures of methylene chloride in

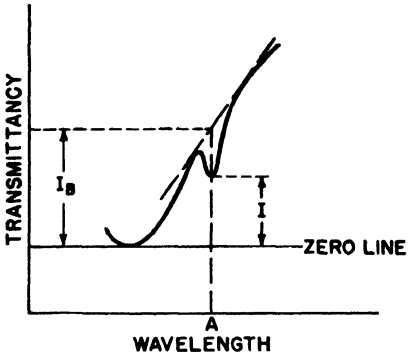


FIG. 5-9. Curve of methylene chloride–chloroform mixture. [*N. Wright, Ind. Eng. Chem., Anal. Ed.*, **13**: *1 (1941), Fig. 8.*]

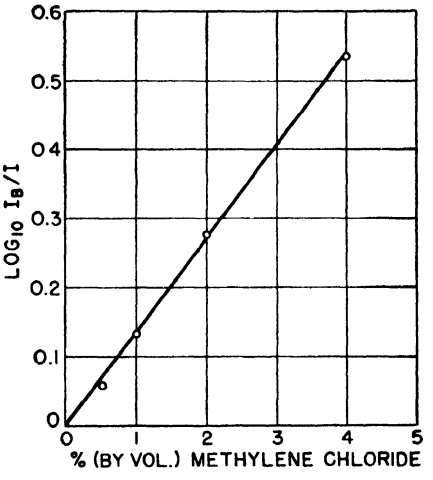


FIG. 5-10. Working curve for methylene chloride–chloroform mixtures. [*N. Wright, Ind. Eng. Chem., Anal. Ed.*, **13**: *1 (1941), Fig. 8.*]

chloroform is made up ranging from 0.0 to 4.0 per cent. The curves of the mixtures are measured in the same cell (0.1 mm thick) over the spectral interval from 7.50 to 8.35 μ, which includes the methylene chloride band at 7.93 μ. Figure 5-9 illustrates one such curve. $\log_{10} I_B/I$ is calculated for each concentration of methylene chloride and the graph (Fig. 5-10) is set up. By making similar measurements with samples, the percentage of methylene chloride may be read from the graph with an error of about ± 0.05 per cent of the total sample and with a sensitivity as low as 0.05 per cent of methylene chloride.

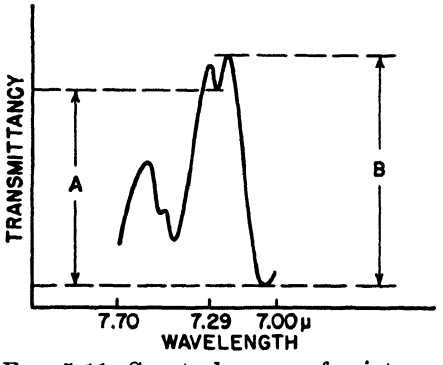


FIG. 5-11. Spectral curve of mixture of 1,2- and 1,3-dibromopropane. [*N. Wright, Ind. Eng. Chem., Anal. Ed.*, **13**: *1 (1941), Fig. 9.*]

As an example of a determination which is not so simple as the foregoing, in that a band for the constituent to be determined must be chosen which is close to that of a band of another constituent, the determination of 1,2-dibromopropane in 1,3-dibromopropane may be cited. Figure 5-11

shows a portion of the curve of the mixture of 1,2-dibromopropane with 1,3-dibromopropane. The former has an absorption band at 7.29 μ and the latter has one in close proximity. The analysis for such a mixture is set up by plotting per cent 1,2-dibromopropane as abscissa against the ratio $(B - A)/B$ as ordinate, without involving a base-line measurement. Furthermore, it is unnecessary to get a curve for each analysis; instead galvanometer deflections at the two wavelengths may be read.

Analyses by means of the base-line technique have been extended to more and more complicated systems, involving in one reported example[9] the determination of seven hydrocarbons in the presence of one another in petroleum-distillation cuts. Because of overlapping in absorption bands such a system must be handled by solving a number of equations and by applying a series of corrections. The original reference should be consulted for details.

One advantage of the base-line method is that it can be extended to the analysis of difficultly soluble solids, as well as of solutions, by working with a Nujol mull.

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CHAPTER SIX

Raman Spectroscopy

Raman spectroscopy is based on a phenomenon discovered by C. V. Raman, an Indian physicist, in 1928. It has not yet attained the practical importance to the analytical chemist which has been reached by visible, ultraviolet, and infrared absorption spectroscopy. Since its use is on the rise, however, it should be discussed briefly.

Principles. Raman spectroscopy utilizes the fact that if a substance is irradiated with monochromatic radiation (commonly the 4,358 A blue line of the mercury-arc spectrum) a line spectrum is emitted. The extent of the shift in position of the lines from that of the exciting source depends upon the molecular structure of the sample. The intensities of the lines depend upon the concentration of the molecular groups or linkages from which they have arisen. Both infrared and Raman spectra, therefore, respond to similar molecular vibrations and rotations. However, infrared spectroscopy utilizes the absorption of radiation by the molecule, whereas Raman spectroscopy utilizes the scattered radiation which is emitted. [Frequently, the Raman shift expressed in wave numbers (cm^{-1}) is the same as the infrared absorption expressed in the same frequency units.]

Hence for *qualitative analysis* both systems of spectroscopy utilize the same physical-chemical principles. For *quantitative analysis* the use of Raman spectra is intrinsically simpler. It is based upon the simple fact that the intensity of the lines scattered into a Raman spectrum by a single component in a fixed volume is a simple linear function of the number of molecules of that component which are present. Quantitative infrared analysis, in contrast, is generally based upon the validity of Beer's law (which is logarithmic rather than linear) under the special conditions of the analysis. When molecular interactions occur in Raman spectroscopy (as in infrared spectroscopy) simple working curves may be prepared.

Raman Spectra and Frequency Shifts. Figure 6-1 gives examples of the Raman spectra of cyclohexane and of carbon tetrachloride. Such spectra would be obtained upon photographing the light emitted from those substances as a result of their having been irradiated with the

4,358 A blue line of the mercury arc. Table 6-1 lists a few of the Raman frequency shifts which are characteristic of various structures and linkages.

Raman spectroscopy may be applied to gases and solids, as well as to liquids, by properly chosen techniques and equipment. Relatively simple inorganic compounds, such as mercuric bromide, lead tetrachloride, and carbon bisulfide, commonly have Raman spectra consisting of one or two

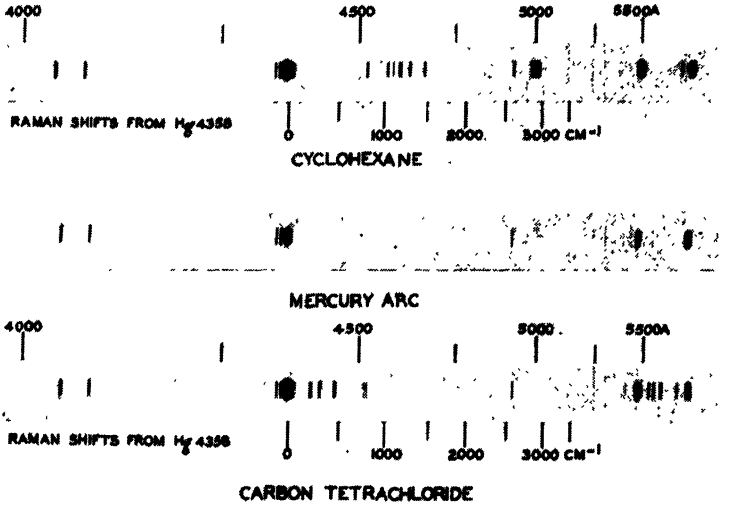


FIG. 6-1. Raman spectra of cyclohexane and carbon tetrachloride. (*Courtesy of Applied Research Laboratories.*)

prominent bands (which appear as lines under the conditions of resolution which ordinarily prevail). In this respect, the Raman spectrum is simpler than the usual arc- or spark-emission spectrum. It is also simpler than the infrared-absorption spectrum. The latter consists of

TABLE 6-1

Structure	*Frequency Shifts, cm⁻¹*
C—H benzene	3,045–3,070
C—H aliphatic, saturated	2,850–3,300
C=C aliphatic	1,600–1,680
C=O acids, unsubstituted, aliphatic	1,645–1,666
C=O aldehydes, aliphatic	1,720 (avg)
C=O ketones, aliphatic	1,710 (avg)
C=O anhydrides	1,745–1,754, 1,804 (avg)
S—H aliphatic	2,568–2,572
O—H alcohol, aliphatic	3,325–3,450
C≡C aliphatic	1,960–2,320
C—X halogen, aliphatic	500–725
C≡N nitrile, isonitrile	Near 1,100; 2,150

bands rather than lines and it generally has many more bands than the Raman spectrum has lines.

Advantages and Disadvantages. Raman spectroscopy has a number of advantages over infrared spectroscopy. The Raman spectrum is usually simpler than the infrared and is therefore easier to apply to quantitative analysis. The equipment involves glass optics rather than the several types of salt optics and sample cells necessary for infrared, with the attendant dangers from humidity. Furthermore, because of the glass optics, an entire Raman spectrum may be recorded in a single run. With infrared at least two separate runs must be made with different prisms to cover even the range between 2.5 and 25 μ, and even that range does not exhaust the useful spectral regions. Finally, because water is not a strong emitter, as it is a strong absorber in infrared spectroscopy, Raman analyses may be carried out on aqueous solutions.

One disadvantage of Raman spectroscopy is that there has not yet been sufficient development of instruments and techniques, and reported analytical data, to take the method quite out of the field of research and to make it a rugged tool for applied analysis. In particular, difficulties caused by the interference of colored substances and fluorescent materials await for their elimination the development of a choice of suitable light sources.

Instrumentation. Most reported work has been done with specially constructed instruments. Commercial production is, however, under way. The Applied Research Laboratories manufactures Raman equipment which may be used for either photographic or photoelectric recording (Fig. 6-2). Hilger and the Applied Physics Corporation (Cary) also manufacture Raman spectrographs. Undoubtedly there will be an accelerated development of commercial instruments in the near future.

Since the field of Raman instrumentation is in a state of flux, no attempt will be made to discuss it in any detail. Figure 6-3 is a schematic drawing of one arrangement for a Raman spectrograph which illustrates the general principles of the instrumentation needed. The light source must be monochromatic in order to avoid overlapping spectra since a complete series of Raman lines is formed for each exciting frequency. The 4,358 A mercury line is most commonly used. In order to eliminate the 4,047 A mercury line, filter solutions or filter glasses must be used. Sodium nitrite[1] and praseodymium ammonium nitrate[2] as well as other materials have been suggested. Since an intense source is needed to provide a sufficiently energetic signal, the filter must not cause too great a loss of intensity. The light source consists of two or more mercury-arc lamps or, more recently, a helical mercury-vapor lamp. This surrounds the sample tube, which is irradiated from the sides. A typical arrangement of mercury arcs, filters, and receiving cells is shown in Fig. 6-4. The

Raman radiation is emitted at right angles to the direction of the incident light and is sent through a spectrographic slit. The spectrograph must have high speed, good resolution, and reasonable dispersion.

The dispersed spectral lines may be recorded on a photographic plate as in the usual emission spectrograph. With such a system, their densities would be evaluated for quantitative measurements. In the apparatus illustrated in Fig. 6-3 the radiation emitted from the sample is

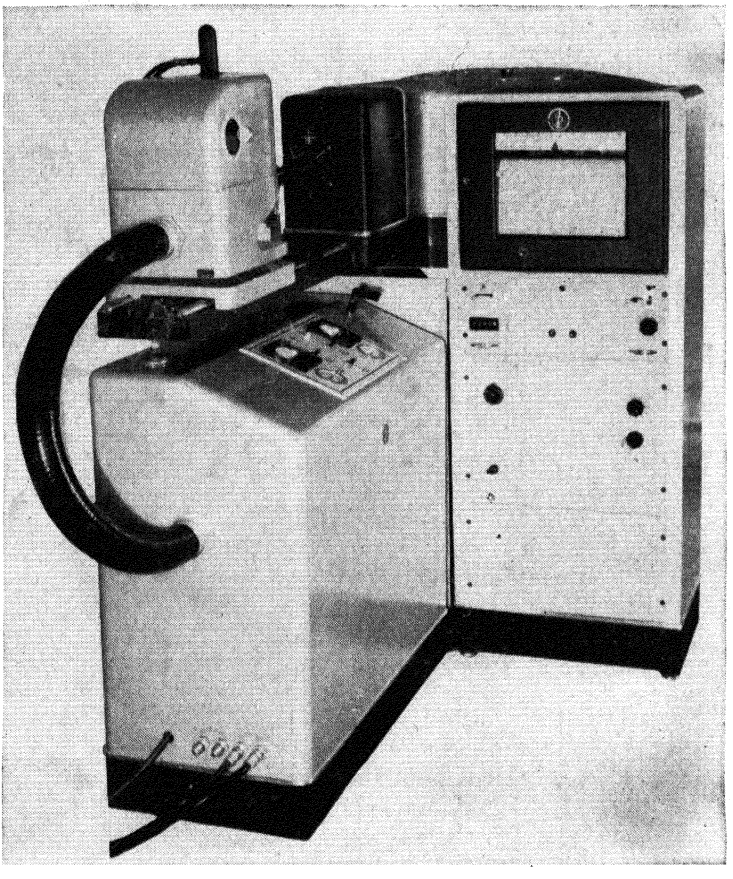
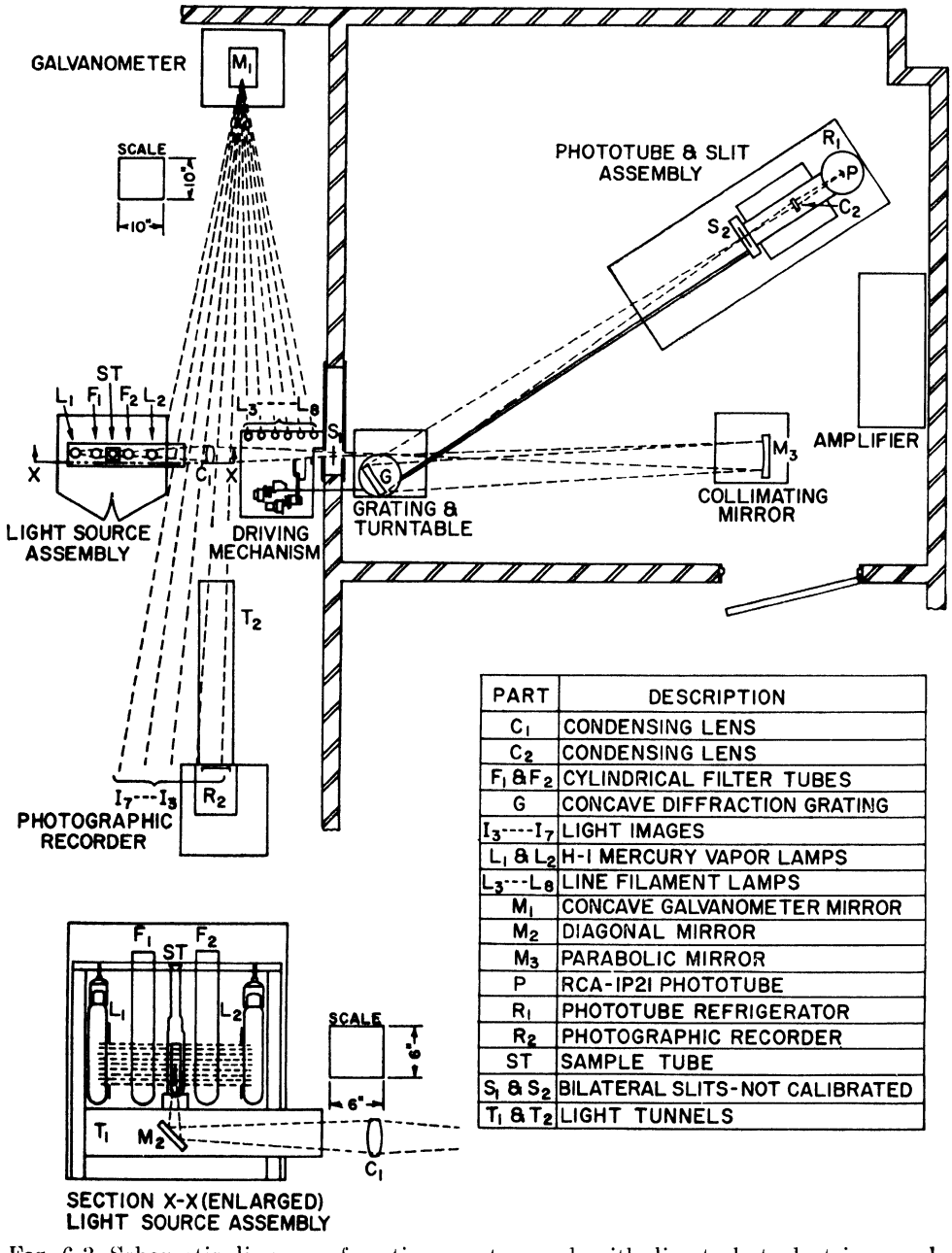


FIG. 6-2. Raman spectrophotometer. (*Courtesy of Applied Research Laboratories.*)

dispersed by a grating. The grating revolves on a turntable so that the energy at successive wavelengths is caused to impinge upon the photomultiplier tube. The signal from the tube is amplified to actuate a galvanometer which throws a light beam upon a photographic plate to trace a curve in which the ordinate represents intensity of radiation (distance through which the galvanometer needle is deflected) and the abscissa wavelength. The line-filament lamps L_3 to L_8 are arranged so that the driving mechanism (which also operates the grating turntable) causes the lamps to light in such a sequence as to indicate wavelength settings on



PART	DESCRIPTION
C_1	CONDENSING LENS
C_2	CONDENSING LENS
F_1 & F_2	CYLINDRICAL FILTER TUBES
G	CONCAVE DIFFRACTION GRATING
I_3----I_7	LIGHT IMAGES
L_1 & L_2	H-I MERCURY VAPOR LAMPS
L_3---L_8	LINE FILAMENT LAMPS
M_1	CONCAVE GALVANOMETER MIRROR
M_2	DIAGONAL MIRROR
M_3	PARABOLIC MIRROR
P	RCA-IP21 PHOTOTUBE
R_1	PHOTOTUBE REFRIGERATOR
R_2	PHOTOGRAPHIC RECORDER
ST	SAMPLE TUBE
S_1 & S_2	BILATERAL SLITS-NOT CALIBRATED
T_1 & T_2	LIGHT TUNNELS

FIG. 6-3. Schematic diagram of grating spectrograph with direct photoelectric recording. [*D. H. Rank and R. V. Wiegand, J. Opt. Soc. Amer.*, **36**: *325 (1946), Fig. 1.*]

the photographic curve. In more recent instruments (see Fig. 6-2) the phototube is arranged to actuate a pen-and-ink recorder rather than to make a photographic curve.

Sample Preparation. The fact that the Raman spectrum is emitted at right angles to the path of the exciting radiation makes it necessary

to eliminate all extraneous scattered radiation. Even small amounts of *dust* in suspension will scatter the exciting radiation. This will cause fogging of the background. To avoid this effect, filtration of the sample through activated silica gel and sintered glass may be necessary, with perhaps a distillation also. Care must be taken that the activated-gel treatment does not cause a change in composition.

Fluorescent materials must be absent, such as high-molecular-weight hydrocarbons or decomposition products produced photochemically by the exciting radiation. Treatment such as that indicated for removing dust may be needed. Sometimes quenching agents may be used to remove the fluorescence.

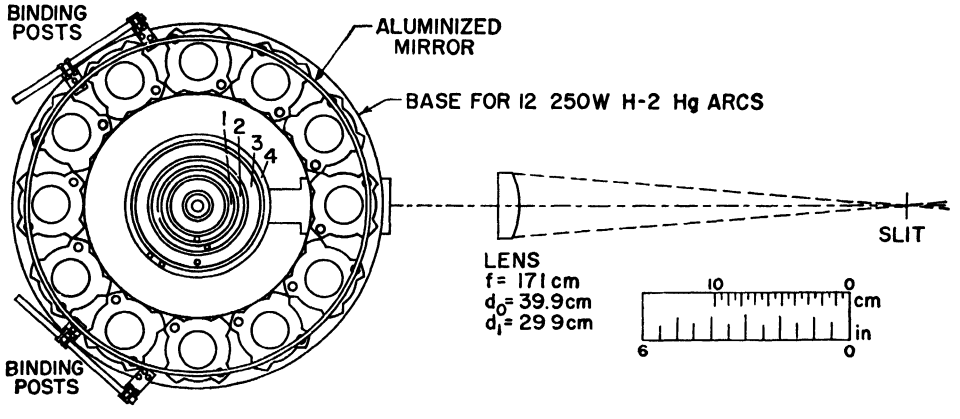


FIG. 6-4. Typical arrangement of mercury arcs, filters, and receiving cells. 1. $PrCl_3$, 5 mm, saturated solution. 2. Rhodamine SGDN extra, 5 mm, 0.0750 gram per liter aqueous solution. 3. $NaNO_2$, 1 cm, 600 gram per liter aqueous solution. 4. H_2O-cooled base plate. [*R. F. Stamm, Ind. Eng. Chem., Anal. Ed.*, **17**: *318 (1945), Fig. 1.*]

Colored substances may cause trouble by absorbing the exciting or emitted radiations. If the color is intrinsic to the sample, and thus incapable of removal without altering the sample, the only recourse is to use an exciting radiation of a wavelength which is not absorbed and from which the emitted Raman frequencies are not absorbed.

Impurities in concentrations below the sensitive level (about 1 per cent) need not be removed since they do not cause any serious error. The reason for this is that the intensity of Raman spectra is proportional to the concentration of the individual components when there is no intermolecular interaction.

Qualitative Analysis. As indicated in Table 6-1, there are characteristic Raman shifts for various atomic groupings. The presence of characteristic lines in any of these particular regions can be used as an indication of the presence of the groups characterized by the particular shift. However, the exact location of the Raman lines for a definite group is

influenced by the nature of the rest of the molecule. This brings about the possibility of identifying compounds rather than merely groupings. In other words Raman spectra may be used as "fingerprints" as are spectra in other regions of radiation. Figure 6-5 illustrates this point. Raman lines are given for ethyl chloride, propyl chloride, and butyl chloride. The vertical height of a line is an indication of the relative intensity of the line. It may be seen that, for this homologous series, the lines are similar because of the similarity of the compounds but with differences due to their dissimilarities.

It may be noted that compounds which contain *covalent chemical bonds*, in which electrons are shared between the nuclei of the atoms of the molecule, exhibit Raman lines. Most organic compounds are of this type and, as indicated, exhibit Raman spectra. Compounds containing *electrovalent bonds*, in other words saltlike compounds, possess no Raman spectra. The ionic inorganic compounds, such as sodium chloride, would come into this classification. Inorganic compounds which possess covalent linkages

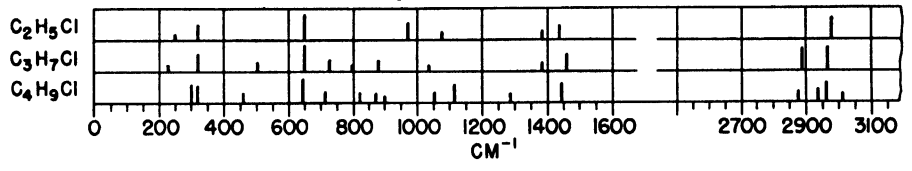


FIG. 6-5. Raman spectral lines for ethyl, propyl, and butyl chlorides. (*W. G. Berl, "Physical Methods in Chemical Analysis," vol. 1, p. 413, Fig. 4, Academic Press, Inc. New York, 1950. By permission of the publisher.*)

exhibit Raman spectra. Examples would include sulfur monochloride, mercuric bromide, water, titanium tetrachloride, boric oxide, carbon bisulfide, and lead tetrachloride and gases such as nitrogen, hydrogen, sulfur dioxide, ammonia, and nitrous oxide. Compounds which contain both electrovalent and covalent bonds exhibit Raman spectra which are characteristic only of the latter. For example, sulfate, nitrate, perchlorate, phosphate, and ammonium ions produce Raman spectra which are not influenced by the other ion which is present. An interesting example is hydrogen chloride which exhibits a Raman spectrum as the un-ionized gas but not as ionized aqueous hydrochloric acid.

Quantitative Analysis. Quantitative Raman spectroscopic analysis is most useful for solutions of relatively high concentration. (In this respect it supplements absorption spectroscopic methods which are most useful for regions of relatively low concentrations.) For substances which scatter light strongly a lower useful limit may be set at around 5 per cent and for substances which scatter light poorly, at around 10 per cent. A relative precision of from 1 to 5 per cent of the concentration of single ingredients in a mixture may be expected by a measurement of the

intensities of the spectral lines, if specific lines can be ascribed to single substances.

As has been pointed out in the discussion of instrumentation, Raman spectra may be recorded *photographically*, as with the usual emission spectrograms, or *photoelectrically*. Photographic recording has all the disadvantages for quantitative analysis which prevail with emission spectrography. The quantitative evaluation of a substance is made from the optical density or opaqueness of a Raman line of the substance. Yet it is well known that the density of a photographic line does not depend only upon the intensity of the radiation which produces the line. It is also affected by the time of exposure, the frequency of the radiation, the type and age of the plate, the conditions of development of the plate, the presence of fluorescence, and the background caused by scattering of the spectrum of the arc. It is thus necessary to control these variables rigidly in order to achieve quantitative results. A more satisfactory method is to measure the intensity of Raman lines directly by photoelectric means rather than indirectly through the interposition of the properties of a photographic plate. If the photoelectric system is arranged to actuate a pen-and-ink recorder, rather than to trace a curve on a photographic plate (which latter is illustrated in Fig. 6-3), an even more convenient system is achieved.

There are several general methods of quantitative Raman analysis. One method involves the use of *internal reference* standards. These standards consist of such substances as carbon tetrachloride or carbon bisulfide[3,4] which have a few strong Raman lines far removed from those of the sample being analyzed. A definite concentration of the standard is added to solutions of known concentrations of the substances A and B which are to be determined. A line characteristic of A and one characteristic of B are chosen and the ratios of the intensities of these lines to that of a line of the reference standard are calculated (the scattering coefficients). A calibration curve is then drawn for each of the substances A and B relating the scattering coefficients of each substance to the ratios of the concentrations of the substances to those of the standards. A concentration of standard similar to that used in preparing the calibration curves is added to the solution of the unknown. The scattering coefficients for the lines for A and B are calculated and used to read the concentrations of A and B in the unknown from the calibration curves.

A variation of this method uses similar reference materials such as carbon bisulfide or carbon tetrachloride but avoids contaminating the sample with the reference material. The *external reference standard* is introduced into a tube which is of identical shape and scattering potential as that for the sample, and which is placed in the same location. With photoelectric recording, intensities of the Raman lines may be measured

directly from the heights of the recordings, since the relationship is linear. A ratio of peak height of sample line to peak height of reference line is obtained (the scattering coefficient). It is also obtained for the pure materials. The percentage of a given substance in a sample is then calculated as 100 × (scattering coefficient of sample ÷ scattering coefficient

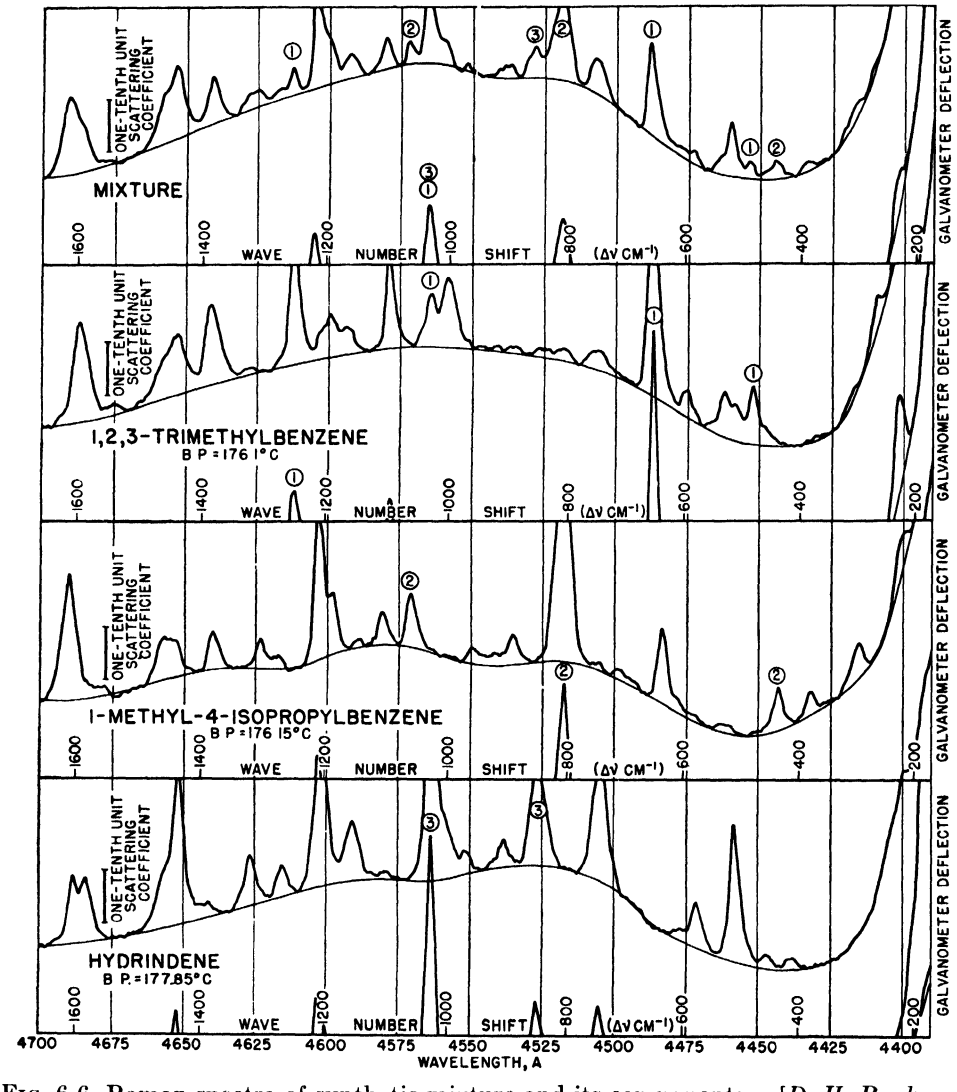


FIG. 6-6. Raman spectra of synthetic mixture and its components. [*D. H. Rank and R. V. Wiegand, J. Opt. Soc. Amer.*, **36**: *325 (1946), Fig. 3.*]

of the pure material). Figure 6-6 contains photoelectric recordings of three individual substances and of a mixture of the three. Table 6-2 contains the analytical values obtained from these curves.[5] Table 6-3 gives the analysis by this method of a sample of an aromatic concentrate from a special gasoline.[5]

The use of reference standards is convenient. It eliminates the effects of variations, chiefly that of the intensity of the light source. However, the intensity of Raman lines, as has been noted previously, bears a linear relationship to the number of exciting molecules. If then there is no molecular interaction between the compounds in a solution, their concentrations may be calculated directly from the intensities of their Raman lines. For practical analysis the use of reference standards is to be preferred.

Stamm[4] has presented a detailed discussion of several other approaches to methods of quantitative analysis other than those requiring the use of reference standards.

TABLE 6-2. ANALYTICAL VALUES FOR FIG. 6-6*

Synthetic sample	Volume per cent known	Volume per cent determined
1,2,3-Trimethylbenzene	28.2	28 7
1-Methyl-4-isopropylbenzene	43.8	43.5
Hydrindene	28 0	28 3
Total	100 0	100 5

* D H. Rank and R. V. Wiegand, *J. Opt. Soc. Amer.*, **36**: 325 (1946).

TABLE 6-3. ANALYSIS OF A SAMPLE OF AN AROMATIC CONCENTRATE FROM A SPECIAL GASOLINE*

Component	Per cent of volume from analysis of	
	Fractions	Original sample
o-Xylene	2 5	1.4
Isopropylbenzene	0 7	2 5
n-Propylbenzene	2 6	
m-Ethyltoluene	18 5	21 7
p-Ethyltoluene	8.7	10 5
1,3,5-Trimethylbenzene	13 2	14 2
o-Ethyltoluene	4 5	7 2
1,2,4-Trimethylbenzene	41 5	40 5
1,2,3-Trimethylbenzene		3 0
Not analyzed†	7 7	
Total	99 9	101 0

* D. H. Rank and R. V. Wiegand, *J. Opt. Soc. Amer.*, **36**: 325 (1946).

† The last fractions of the fractionation and the residue and holdup were not submitted for Raman analysis. Distillation data showed these to be essentially 1,2,3-trimethylbenzene.

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CHAPTER SEVEN

Mass Spectrometry

As is so often the case with modern analytical instruments, the principle behind mass spectrometry was discovered long before instruments became available. About fifty years ago, Sir J. J. Thomson devised what may be termed the first mass spectrometer. His colleague, F. W. Aston, began a systematic study of isotopes in the entire atomic table using this method. At the same time, A. Dempster in this country built a mass spectrometer for a similar purpose.

Since then, but virtually since 1940, the mass spectrometer has become a most useful tool for analytical purposes and for research in such diverse fields as chemistry, geology, biology, and medicine. It is still quite expensive and the number of instruments in use is comparatively small. The basic principle involved is simple and the scope is great. Its unique property is that it is sensitive to the mass of an element or compound introduced in attenuated gaseous form in its ion chamber. Discovery of new isotopes and the correct isotope ratios can be attributed to this method.

Basically the mass spectrometer is an equipment for sorting and identifying atoms or molecules. The particles are given an electric charge (ionized) by impact with a stream of electrons and then passed across a magnetic field by which they are separated into individual beams, each containing ions of only one specific mass. The lighter ion streams are bent more than the heavier ones. The amount of deviation from the original path and the intensity of each beam can be accurately measured. From these data, together with the known speed of the particles, the relative masses of the various ions can be precisely calculated.

Should the stream of ions be caught on a photographic plate, the instrument is called a mass spectrograph. When it is detected and recorded by electrical means, the apparatus is called a mass spectrometer.

In Fig. 7-1 will be seen a diagrammatic representation of an analytical mass spectrometer. In practice the gas is introduced into the ion chamber through a molecular leak after successive expansions. These neutral molecules are bombarded by a magnetically collimated stream of elec-

trons, the energy of which is sufficient to ensure the formation of positive ions of all species of molecules contained in the sample. In effect, these positive ions have essentially zero energy. After acceleration through 2,000 volts they are reduced to a fine stream by means of successive slits and plates. The resultant beam is a heterogeneous mixture of all the constituents of the original gas. This beam enters a d-c magnetic

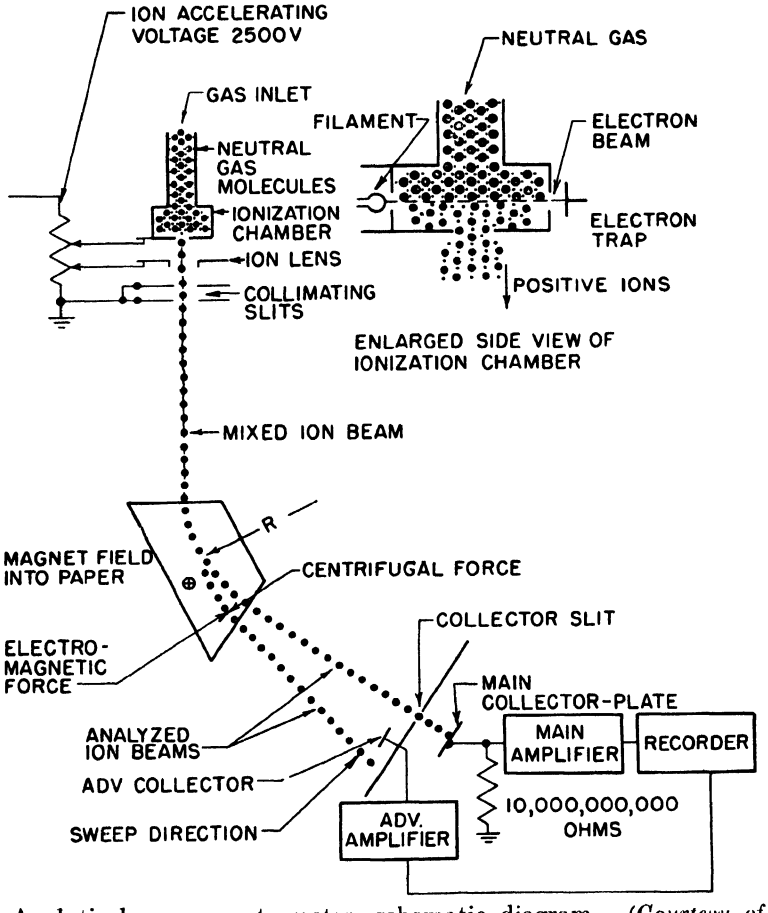


FIG. 7-1. Analytical mass spectrometer, schematic diagram. (*Courtesy of General Electric Co.*)

field which separates it into individual beams. This is governed by the fundamental equation expressing the relation between the mass-to-charge ratio, the radius of curvature of the tube R, and the magnetic and electric fields H and V, as follows:

$$\frac{m}{e} = K\frac{H^2R^2}{V}$$

In a given tube R is fixed. Hence, by varying H or V the separated beams of ions can be swept as in a cathode-ray oscilloscope. A properly

designed and positioned slit will successively select masses m as the values of the field successively satisfy this equation. The beams impinge on a plate coupled to a d-c amplifier. Low currents are thus measured and recorded. The plot of these ion currents vs. field strength is called a mass spectrum. The former is a measure of the quantity of each gas component, the latter a measure of their respective masses.

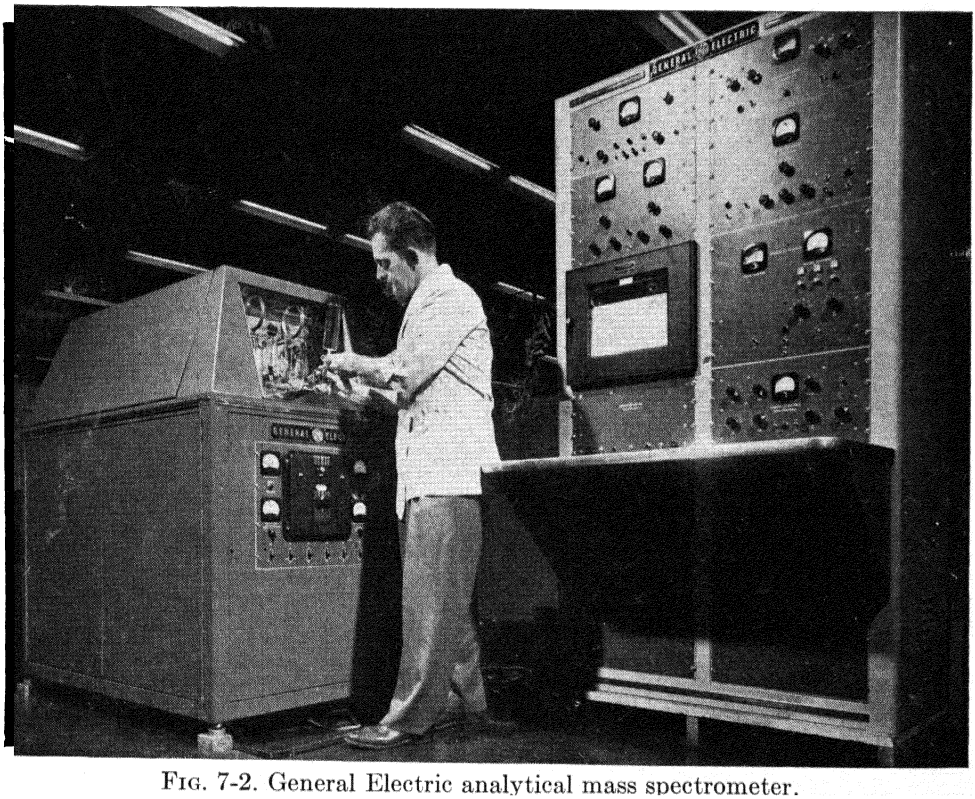


FIG. 7-2. General Electric analytical mass spectrometer.

There are three main types of mass spectrometers: the analytical mass spectrometer, the isotope-ratio mass spectrometer, and the leak-detector mass spectrometer.

THE ANALYTICAL MASS SPECTROMETER

This may be regarded as the basic and probably the most useful type of instrument. Some models employ a galvanometer to record the spectra and can be used to pass a beam of light across photographic paper. In other instruments the spectra are recorded by a pen-and-ink recorder. The magnetic field may be changed by various means depending upon the scope of the instrument. All perform the functions outlined previously. A commercial analytical mass spectrometer is shown in Fig. 7-2.

A mass spectrometer is purchased with a general idea of the class of

materials it will be used to analyze. Some large instruments have wide mass ranges from about 2 to 150. These are used for a wide range of work, usually research. Others operate from mass 2 to 100. Instruments made for specific purposes may range between any two selected mass numbers.

This type of mass spectrometer is largely used in the petroleum field. It can be used to record automatically all the known components in a gas mixture, e.g., H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_6, etc., or just one of these.

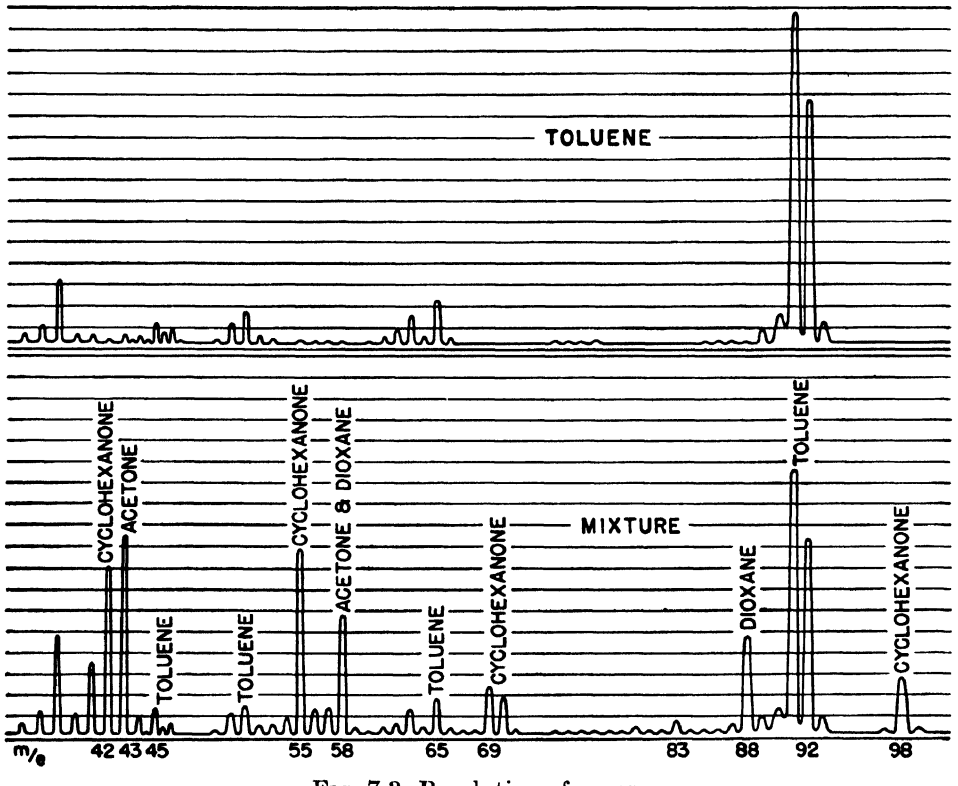


FIG. 7-3. Resolution of gases.

Complex mixtures of less simple gases can be resolved (Fig. 7-3). Wherever gas analysis is required, one of the quickest and most accurate methods of analysis is to use the analytical mass spectrometer. Inorganic materials can also be analyzed. They will be touched upon later.

THE ISOTOPE-RATIO MASS SPECTROMETER

Radioisotope-tracer techniques (Chap. 14) are widely used. To supplement these, stable-isotope tracers are not uncommonly employed in geological analysis, metabolism study, and work on catalytic action. These are used when the desired radioisotopes are not available or are

inconvenient or dangerous. They might also be used in preference to radioisotopes if a mass spectrometer is available. The isotope-ratio mass spectrometer is used to trace the course of reactions with molecules tagged with heavy isotopes of the commoner elements. A commercial isotope-ratio mass spectrometer is shown in Fig. 7-4.

The *isotope-dilution* method is employed in elemental analysis and for the determination of individual compounds in mixtures. In either case



FIG. 7-4. Consolidated Engineering isotope-ratio mass spectrometer.

it involves the addition of measured amounts of isotope to mixtures being analyzed and the subsequent determination of the extent of dilution of this isotope in the mixture, or, with compounds, the extent of dilution of the enriched compound. With this method the quantitative separation of the material being determined is not necessary. Amounts of the order of parts per billion have been determined by this method.

The instrument used in this method differs from the analytical spectrometer only in the fact that there are two ion collectors instead of one. Through proper control of the magnetic field and the accelerating voltage, ions of a specific mass are made to strike one collector. Ions of lighter and adjacent mass fall upon the other collector. The intensities of the

two beams are balanced by proper attenuation and the ratio of the beams obtained from the relative amplification.

A lengthier explanation of the isotope-dilution method, which is the same in principle as the method used for stable isotopes, is given in the chapter on Radioactivity (Chap. 14).

THE LEAK-DETECTOR MASS SPECTROMETER

This use of the mass spectrometer is not quantitative in character but is of considerable commercial importance. The leak detector is, in essence, a small portable instrument sensitive only to the mass of the inert gas helium, which is used as a probe gas. Leaks as low as 10^{-9} ml per sec are detectable and the exact location of the leak is readily found. The detector is connected directly to the vacuum system and a fine stream of helium gas is sprayed upon the outer surface. The instrument is so adjusted that only helium gas will give a response.

ANALYSIS OF GASEOUS MIXTURES

Natural and other gases, through the C_4 hydrocarbons, can be completely analyzed and information obtained concerning heavier hydrocarbons if present. The following constituents may be determined in such mixtures: methane, ethane, ethene, propane, propene, isobutane, butane, butenes, pentanes, pentenes, hexane, carbon dioxide, hydrogen sulfide, sulfur dioxide (the two latter will react if originally coexistent), argon, helium, neon, nitrogen, and oxygen. Hydrogen can be determined if present in amounts of 0.1 per cent or greater. Hydrocarbons heavier than C_6 may be indicated on the spectrogram but their determination must be made separately on a concentrate.

The spectrogram of the mixture is solved against the mass spectra of each of the pure molecular species constituting the mixture.

Reference Standards. The gases used to calibrate the spectrometer must be approximately pure. Any impurities must be such that they can in turn be "calibrated out" of the mass spectra. As a rule the spectrometer is able to detect impurities and their contributions to the spectrum can be removed. The necessary gases may be purchased or prepared in the laboratory. The Phillips Petroleum Company, Bartlesville, Okla., has available an extensive list of research-grade hydrocarbons. Many pure hydrocarbons prepared by the American Petroleum Institute Research Projects are listed by the National Bureau of Standards. Purified helium is obtainable from the U.S. Bureau of Mines, Amarillo, Tex. The "prepurified" grade of nitrogen should be used. The remaining gases should be the best available.

Operation of the Mass Spectrometer. Procedures for standardizing the apparatus and for introducing the gas sample should be those given by the manufacturers, or the American Society for Testing Materials Method D1137-53 should be followed. Should the approximate composition of the mixture not be known, a preliminary run over the complete operating mass range is made. When the composition is known, the calibrating gases are run just before the mixture and in an order depending upon the composition of the mixture. The methane calibration is run last, immediately before the mixture if natural gas, which is principally methane, is being analyzed. This will condition the inlet lines, ionization chamber, etc. The minor component calibrating gases up to C_4's should be run in the order of increasing mass. Isomers, if present, should be run in succession if they are to be separated in the analysis. If required, the C_4's and heavier compounds are run after the mixture. Introduce the calibrating gases and the mixture through the inlet system at approximately the same pressure. The mass spectra of all the gases must start at the same ion-accelerating voltage (for the same magnetic field).

When the peak heights of the spectrograms of the calibrating gases have all been measured and corrected for any background, the most abundant ion of the molecule is normally given the value of 1.000. The abundancies of the other peaks are calculated in proportion to this ion. The method of computing the analysis from the mixture spectrogram and the calibrating patterns is illustrated in ASTM D1137-53. The method requires a mechanical calculator, but an electronic computer especially designed for solving simultaneous equations may be employed.

Precision and Accuracy. Table 7-1, based on considerable cooperative work on a standard gas mixture, gives the probable precision and accuracy of this mass-spectrometric method (from ASTM D1137-53).

TABLE 7-1

Gas	Probable accuracy, per cent	Reproducibility	
		Different laboratories and apparatus, per cent	One laboratory and apparatus, per cent
Methane (>70 per cent)	1 0–0.5	0.5	0.2
Ethane	0.5	0.3	0.1
Propane	0.1	0.06	0.02
Propene	0.05–0.02	0 04	0.02
Carbon dioxide	0.1	0.03	0.02
Nitrogen	1.0	0.3	0.2
Calculated heating value	1.0	0.5	0.2
Specific gravity	0.6	0 6	0.2

ANALYSIS OF ORGANIC COMPOUNDS

Although gases are more readily adaptable to analysis by mass spectrometer, it is also possible to use this method for the identification of more complex organic materials.

One method[1] is to use correlations that relate mass spectra with molecular structure. Basically, this method consists of the use of mass spectral correlations to identify structural groups in unknown compounds. Supplemental chemical and physical data are employed to complete the identifications. By this means thiophene and benzene homologues have been identified.

Certain types of nonvolatile materials may be pyrolyzed to give characteristic volatile decomposition products which can be analyzed in a mass spectrometer.[2] A few tenths of a milligram of sample are coated on, or placed inside the coils of, standard receiving-tube filaments and heated in a vacuum. Rapid heating at temperatures above 800°C will often give monomers when linear homopolymers are present. Slow low-temperature heating is not advisable as a complicated mixture may result. By standardizing the conditions of pyrolysis, characteristic mixtures may be obtained which are compared with known materials for characterization.

ANALYSIS OF INORGANIC MATERIALS

The analysis of not readily vaporizable inorganic materials is not at present so firmly established as is the analysis of organic materials, which can be more readily vaporized. It is the difficulty in vaporizing inorganic materials that makes them less amenable to this type of analysis. Considerable progress has been made, although instruments for this specific purpose are not yet commercially available.

There are three basic methods of solid inorganic analysis: (1) the Dempster vacuum-spark method, (2) the ion-bombardment method, and (3) the isotopic-dilution method. This last method normally analyzes for only one element at a time. It is very sensitive, more so than methods 1 and 2. These are analogous to emission-spectrographic methods in that all elements present are determined in one tracing of the spectrum. These three methods are fundamentally different only in the method of producing the ion source. The type of mass-sensitive analyzer to be used in conjunction with the source is dictated by the characteristics of the source used.

The Dempster Vacuum-spark Method. Figure 7-5 shows mass spectra of the light-element impurities in a sample of uranium metal. To obtain this spectrum, the vacuum-spark discharge was maintained between

two electrodes of the uranium metal. When nonconducting solids are analyzed, the sample is packed in a 0.004-in.-diameter nickel tube and the discharge maintained between that tube and a second pure tantalum or nickel electrode. Consequently, the lines due to nickel and tantalum are not characteristic of the sample. The spectrum is of a sample of known chemical composition. The exposure was for 3 min, about 10 mg of the metal being evaporated. There are almost no restrictions as to the physical form of the solid sample.

The sensitivity of this spark method can be determined by a comparison of Fig. 7-5 with Table 7-2, which lists the composition of the

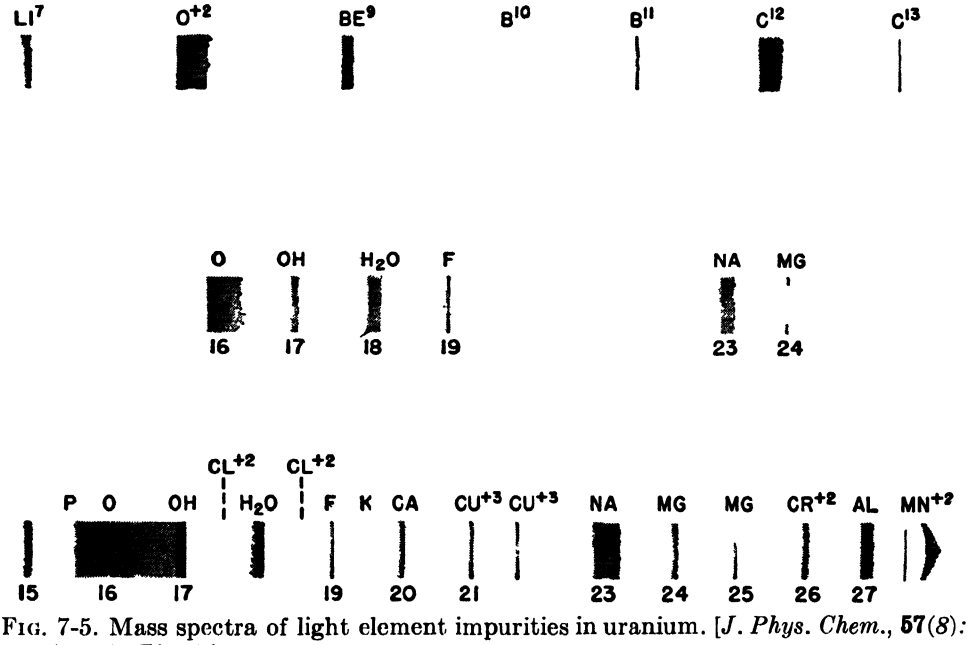


FIG. 7-5. Mass spectra of light element impurities in uranium. [*J. Phys. Chem.*, **57**(*8*): *810* (*1953*), *Fig. 1.*]

calibration sample used. The strong line at mass 9 marked Be is complicated by triply charged ions of aluminum. It is seen from this figure that light elements of the order of 1 ppm are detectable with relatively short exposures.

Difficulties encountered in quantitative measurements parallel those met with in optical spectroscopy. It is seen from Table 7-2 that the sensitivities vary from element to element because of their different ionization efficiencies. Hence, as with optical spectroscopy, calibration with standards is necessary. On the other hand, there are no blind spots as in optical spectroscopy. Elements difficult to determine by optical methods such as nitrogen, carbon, phosphorus, oxygen, and sulfur appear in mass spectra with sensitivities comparable with other elements. There is no evidence that any impurity evaporates preferentially with time.

Background is a limiting factor. Lines appear which are due to residual gas pressure in the instrument. Obviously excellent vacuum conditions are essential. Scattering of the intense ion beams forms a continuous background, particularly when peaks are close together, i.e., at the higher masses. Again, good vacuum conditions minimize this difficulty. The Dempster method suffers from the following problems: (1) handling the large amounts of r-f power necessary to run the source in proximity to sensitive electrometers, (2) the inherent instability of a spark, (3) the high rate of consumption of sample due to spattering of large pieces of the electrodes, and (4) space-charge defocusing due to the pulsed nature of beam. These limitations are largely removed by using an ion-bombardment type of source.

TABLE 7-2*

Impurity	Known chemical composition, ppm	Electrode consumption, mg, to give detectable line	Weight of trace element just detectable, grams
Li^7	5		
Be^9	0.02	2.0	0.4×10^{-10}
B^{10}	0.3	0.4	1.2×10^{-10}
C^{13}	4	0.2	8×10^{-10}
N^{14}	24	0.01	2.4×10^{-10}
O^{16}	40	0.002	0.8×10^{-10}
F^{19}	1.1	0.08	$0\ 9 \times 10^{-10}$
Na^{23}	10	0.005	$0\ 5 \times 10^{-10}$
Mg^{24}	14	0 025	$3\ 5 \times 10^{-10}$

* *J. Phys. Chem.*, **57**(8): 809 (1953).

The Ion-bombardment Method. In this method, high-energy ions are directed against the surface to be analyzed. Ions characteristic of the surface are produced and are accelerated and analyzed with a mass spectrometer. It is unfortunate that the ion beam produced by the bombardment has a large energy spread. For high sensitivities a double-focusing spectrometer is necessary.

Positive or negative ions can be used to bombard the material to be examined. The resultant positive or negative ions may be accelerated and analyzed. Since negative-ion production is very selective it should be used only for special problems. The more usual arrangement is to use positive ions for bombardment. A high-intensity source of this type has been described.[3]

This method has not been extensively applied to analytical problems. Dempster[4] first used secondary rays. More recent work[5] has been done on the bombardment of surfaces.

The chief disadvantages of this method are that it requires a special double-focusing mass spectrometer and that the best sensitivity obtainable is about 1 ppm. The advantages are that, as it is a d-c source, r-f and pulsed beams are not a problem; as with the spark source, all elements present are ionized; and sample consumption is very small.

The Isotope-dilution Method. This is referred to on page 115. For many purposes sensitivities of better than 1 ppm are desirable. This method, essentially an internal-standard method, has been used by biologists for a number of years[6] to determine the elements and compounds of hydrogen, carbon, and nitrogen. More recently the Atomic Energy Commission has made available separated isotopes of many elements. In a number of cases the sensitivity has far surpassed any other known analytical method. For example, the uranium content of a sample of ammonium nitrate has been determined as 0.075 part per billion with an error of 0.004 part per billion.

In brief, the procedure is to dissolve a weighed sample in an appropriate solvent and to this add an aliquot of a stock solution of a separated tracer isotope of the impurity under examination. The "impurity" element together with its diluent is extracted chemically. This last step may or may not be necessary but depends upon the element and the required sensitivity. The change in isotopic composition of the impurity element due to dilution with the tracer is determined by the isotope-ratio mass spectrometer. Since in usual cases normal and tracer materials consist of mixtures of isotopes, it is necessary to set up and solve two simple simultaneous equations.

The advantages of this method are several. It is not necessary to separate the constituents. If, during processing, part of one isotope is lost, at the same time an equal proportion of the other isotope would be lost, as they cannot be chemically separated. No corrections are needed to obtain the final result—the method is absolute. Many elements can be detected when only 10^{-12} gram of material is present. Sodium, potassium, rubidium, and cesium can be easily detected in the 10^{-14} gram range. Simple mass spectrometers can be used as the method does not depend upon a particular source. The method is extremely sensitive. Trace amounts of gases in solids have been measured with gas contents of less than 1 part per trillion.[7] At the same time the range of concentration detectable is wide. Accuracy is of the order of 1 per cent or higher.

On the other hand, normally only one element at a time can be determined. The method has been used for the rare earths and also for the alkalies to determine up to four elements at a time. This is unusual and is due to the fact that the chemistry of the elements in each of these sets is similar.

In order to use the method, samples of the desired element having

isotopic compositions considerably different from normal are necessary. Some elements just do not have a second isotope which can be used as a diluent. Up to now the following elements cannot be determined by this method: fluorine, aluminum, phosphorus, scandium, manganese, cobalt, arsenic, yttrium, columbium, rhenium, praseodymium, terbium, holmium, thulium, tantalum, and gold.

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CHAPTER EIGHT

X-ray Diffraction

Within forty years since it was first used by von Laue, X-ray diffraction has grown to a science of very considerable importance. Crystallography, formerly largely dependent upon microscopic and angle measurements, has now become a powerful and versatile tool. Whereas only the outer macroscopic form of crystals was formerly measured, it is now possible to examine accurately the basic forms of such crystals and to determine exactly interatomic spacings. In most cases, previous work has been verified and in much shorter working time.

It is only within the past fifteen years that X-ray diffraction has been generally recognized in industry as a useful analytical tool. Commercial equipment has been made available during this time and is being continually refined. The reason for the usefulness of this means of identification lies in the significant fact that the wavelengths of X rays are of the same order as the distances between atoms. The latter are built up in the form of regular lattices with the constituent atoms arranged, in crystalline material, in regular patterns determined by (1) the kind and number of atoms present, (2) the atomic radii of these atoms, and (3) their valence and their coordination numbers.

Complete structural determination can be made of crystals of sufficient size so that they can be geometrically oriented with respect to the direction of the X-ray source. In many cases, because of the complexity of the molecule this is a time-consuming and difficult piece of work, as, for example, when the constitution of penicillin was worked out. In a large number of cases, however, molecules are comparatively simple and it is possible to identify the substance completely. Specific substances give specific patterns. Like thumbprints, no two patterns are completely identical, although occasionally they may be very similar. As a result single-crystal diffraction analysis is a unique method of chemical identification, giving not just the amounts of each element present as in normal chemical analysis, but identifying the compound as such. When more than one compound is present, the patterns are additive and can often

be resolved. Of course, the more components present, the more difficult is the interpretation.

Other useful determinations may also be made using X-ray diffraction means. Crystallite-size determination is frequently made from X-ray line broadening and from low-angle-scattering data particle size may be measured. In metallurgy much can be learned in respect to the composition and the solid and physical state of alloys. The thickness of thin coatings has been measured. Molecular weights can be determined.

These methods are useful in constructing phase diagrams and in the study of fibers giving information relative to orientation and consequent strength and also as to crystallinity.

As a means of identifying crystals, X-ray diffraction is of paramount importance. As a supplementary tool together with other analytical procedures, X-ray diffraction is a most useful mode of analysis. In many cases it is the only method that will give the desired result. The amount of sample may be very small (e.g., about 0.01 mg). The sample is not destroyed.

Even in cases where materials are amorphous or semiamorphous, X-ray diffraction can be of considerable use. The clarity, or otherwise, of patterns produced indicates the state of crystallinity or of aggregation of the material. Substances in which the atoms are randomly oriented or in which the crystal pattern is distorted give useful information by this means. Indeed, the question as to when a material is amorphous or is crystalline becomes almost academic. There is no sharp line of distinction between the two phases. Sharp X-ray diffraction patterns are obtained when the material consists of crystallites of 500 A or more in diameter. Below 500 A the pattern becomes increasingly broadened and below 75 A the pattern is usually not recognizable.

PRINCIPLE OF ANALYSIS

When monochromatic X rays are scattered by a periodic array of atoms in space such as exists in a crystal, interference phenomena occur and under certain circumstances reinforced X-ray beams are observed in certain specific directions (Fig. 8-1). Consider two X-ray beams X and X' diffracted from atomic layers a distance d apart. It will be seen from Fig. 8-1 that, when the difference in length of these beams ABC equals some multiple n of the wavelength λ, constructive interference occurs and reinforcement will result. By simple theory,

$$n\lambda = ABC = 2AB$$

but $AB = d \sin \theta$, where θ is the incident angle of the beam. Hence

$$n\lambda = 2d \sin \theta$$

This equation, known as the Bragg equation, is the simple basis for the calculation of atomic distances. For a given wavelength every value of d will produce a reinforcement at a certain angle θ. The letter n stands for the order of the reflected X-ray beam in the same manner as it does in formulas explaining the operation of the grating spectrograph. In most calculations n is made equal to 1.

It will also be seen from Fig. 8-1 that the angle of scattering, i.e., the angle between the original beam direction and that of the scattered beam, is equal to 2θ, where θ is the angle of incidence of the original beam.

When the Bragg equation is satisfied, reinforcement of the diffracted beam occurs. For a single crystal this scattering will consist of a few specific beams; for a powder of randomly oriented crystals, it will be localized in the surfaces of right-circular cones.

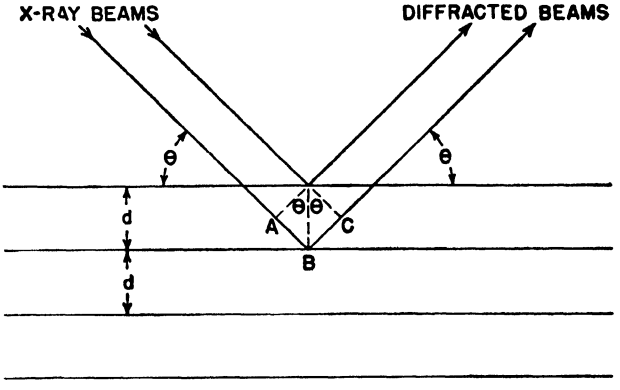


FIG. 8-1. X-ray diffraction from lattice.

In practice, scattered radiation is recorded on a photographic film. The specific beams from single crystals appear as more or less intense dots. With randomly oriented powders, they appear as arcs when cylindrical-section cameras are used, or as circles on flat cassette cameras. Instead of the photographic method, an X-ray-sensitive Geiger counter spectrometer may be used, employing direct counting or using an automatic recording device.

Since the diffraction effects are a function of the interplanar distances, and since atomic configurations are different, the recorded pattern must be characteristic of the material tested. For this same reason the intensities of the diffracted beams vary. The intensities can be measured and are generally given as a fraction of the intensity of the heaviest line or point.

PROPERTIES OF X RAYS

X rays are electromagnetic waves of short wavelength, covering approximately the region from 0.06 to 1000 A and overlapping soft gamma

rays on the shorter side and the extreme ultraviolet on the longer side. For diffraction work, wavelengths between 0.7 and 2 A are generally used.

The spectral distribution emitted from targets consists of a continuous (white) radiation upon which are superimposed characteristic line spectra. These depend upon the target metal and upon the peak voltage applied to the tube. The following formula shows the relation between the minimum wavelength cutting off the white radiation and the voltage applied.

$$\lambda_{min} = \frac{12{,}350}{V}$$

where λ_{min} is in angstrom units and V is the peak potential in volts.

The wavelengths of the characteristic lines are independent of the voltages used and depend upon the target material. These lines originate in electron jumps to electron shells within the atoms of the target. The various sets of lines (K, L, M, etc., in order of decreasing energy or increasing wavelength) are produced only when sufficient energy is present to ionize the respective shells.

It is usual in X-ray diffraction work to use the characteristic K lines and particularly the K_α doublet. The nearby K_β line is removed by using a filter. The peak potential applied should be from 3.5 to 4 times the excitation potential of the K shell for minimum background interference. This potential can be obtained by substituting the wavelength of the K absorption edge given in Table 8-1, in the above equation.

TABLE 8-1. WAVELENGTHS AND ABSORPTION EDGES OF K LINES OF TARGET AND FILTER MATERIALS*

Target metal	Atomic No.	Wavelength, A			
		$K_{\alpha 2}$	$K_{\alpha 1}$	$K_{\beta 1}$	K absorption edge
Titanium	22	2.75236	2.74871	2.51407	2.4962
Vanadium	23	2.50718	2.50340	2.28430	2.2676
Chromium	24	2.29352	2.28962	2.08479	2.0701
Manganese	25	2.10570	2.10174	1.91016	1.8954
Iron	26	1.93991	1.93597	1.75654	1.7429
Cobalt	27	1.79279	1 78890	1.62073	1.6072
Nickel	28	1.66168	1.65783	1.50008	1.4869
Copper	29	1.54434	1.54050	1.39217	1.3802
Zinc	30	1.43894	1.43510	1.29520	1.2831
Zirconium	40	0.79010	0.78588	0.70169	0.6888
Molybdenum	42	0.71354	0.70926	0.63225	0.6197

* W. L. Bragg, *J. Sci. Instr.*, **24**: 27 (1947).

Absorption edges are wavelengths at which a sharp step in the absorption of X rays by an element takes place.

According to Moseley's law, for corresponding lines of the spectrum, the higher the atomic number of the emitting atom, the shorter the wavelength (or the higher the frequency). Quantitatively, the square root of the frequency of corresponding lines from different elements increases linearly with the atomic number Z, $\sqrt{\nu} = K(Z - \sigma)$ where K is a constant for corresponding lines from all elements and σ is another constant.

As with other electromagnetic radiations, the X rays are absorbed according to the equation

$$I = I_0 e^{-\mu t}$$

I_0 is the incident beam intensity, I the intensity after traversing a thickness t, and μ the linear absorption coefficient. The mass absorption coefficient $\mu_m (= \mu/\rho$ where ρ is the density of the specimen) is often used. It is independent of the chemical and physical state of the absorber. For a given element, it is a function of the wavelength of the radiation absorbed. The linear absorption coefficient is helpful in determining the best specimen size. When a cylindrical specimen is used with a beam of diameter greater than the cross section of the specimen, the optimum specimen diameter is $2/\mu$ cm.[1]

A filter material is chosen, the K edge of which lies between the wavelengths of the K_α and K_β lines, so that the latter are highly absorbed and the former little absorbed. For the most frequently used copper targets, nickel filters are employed. With nickel foil of 0.021-mm thickness, the CuK_β line will be reduced to one six-hundredth of that of the CuK_α line. The latter will also be cut to 40 per cent of its original intensity. Sometimes the absorption edges will dictate the choice of radiation. For example, as the K_α line of copper will excite the K level of iron to produce a heavy background of fluorescent radiation, diffraction patterns of materials containing much iron should not be obtained with copper target tubes. A list of suitable filters is given in ref. 2.

CRYSTAL STRUCTURE

A crystal is a regular three-dimensional enlargement of a fundamental atomic or molecular arrangement. The size and shape of this basic cell and the distribution of the atoms and molecules can be determined by X-ray diffraction measurements. The external form of a crystal is by no means always the same as that of its basic molecular shape. This is due to irregularities of growth. It is important to note that, whatever the actual shape of the crystal and whatever the relative sizes of the faces, the angles between the faces are always the same as those in the basic molecule. Consequently it is the directions of the faces and not the

shape of the crystal that is essential. If from any single point within a crystal, perpendiculars, supposed produced if necessary, are drawn to the faces and beyond if necessary, the radiating bundle of normals so obtained depends only upon the directions and not upon the sizes and shapes of the faces. Imagine a sphere described about the single point which is the origin of the normals as a center. This sphere will intersect the normals in a set of points. The arrangement in space of these points will be dependent only on the directions of the faces. According to the usage of crystallographers, this radiating set of normals, or the corresponding array of points on the sphere, describes the geometrical form of a crystal.

Crystal Form. As indicated before, the form of the basic molecule depends to a large extent upon the size of the component atoms. As an example, silicon atoms are much smaller than oxygen atoms. The silicon radius is 0.39 A and the oxygen radius 1.32 A. In all known silicates the silicon atoms always lie at the center of nearly regular tetrahedra composed of four oxygen atoms. In orthosilicates these tetrahedra form independent SiO_4 groups which act as anions. Closed groups in which two tetrahedra are linked by one common oxygen atom give the Si_2O_7 group. When three tetrahedra form a ring in which two common oxygens are shared the Si_3O_9 group is obtained. The group Si_6O_{18} forms a ring of six tetrahedra. Each ring has the composition $(SiO_3)_n$. Sometimes endless chains of tetrahedra form, each adjacent pair having a common oxygen atom. Yet again, two adjacent chains may lie side by side and be joined by cross linkages to form bands of hexagonal rings each sharing an edge with those on either side. Fibrous minerals such as asbestos contain such rings and chains.

The tetrahedra may also be joined, and always through oxygen atoms, to form sheets of hexagonal rings extending indefinitely in two directions to give layerlike minerals such as talc and mica. Finally, cagelike structures in three dimensions may be formed, giving minerals like the zeolites and feldspars.

It is of real interest to see that an actual molecular entity does not always exist with the silicates. Even with such a simple compound as sodium chloride (NaCl) each Na atom stands in the same relationship to six Cl atoms and similarly each Cl atom to six Na atoms and no simple NaCl molecule exists. In such cases it is convenient to speak of a *unit cell* which is regularly repeated in the crystal. However, there is a well-defined molecule in many, particularly organic, crystals. The atoms in these molecules are linked by a covalent bond and not by ionic or electrostatic forces. The crystal is built up of such molecules held together by residual forces of attraction. These crystals are usually much softer and with lower melting points than the ionic-type crystals.

Crystal Symmetry. The symmetry of a crystal is due to the regular arrangement of its atoms in a space pattern. The crystal is built up of units of this pattern. Thus, if a point, say the center of an atom, is taken in each of these units, a series of points in space is obtained each of which is situated similarly to all other such points. When such a space is divided into parallelepipeds by three sets of parallel planes, the spacing of each set being constant but not necessarily the same for all sets, the sets making any angle with one another, then the points of intersection of these planes give a system of regularly situated points which is called the *space lattice* of a crystal.

It might be thought that the number of possible lattices would be infinite. Measurements of all known crystals by the goniometer show that this number is strictly limited. X-ray measurements confirm this.

The directions parallel to the three edges of a simple parallelepiped are called the *axes* of the crystal. In a crystal belonging to the cubic system these axes are equal and at right angles relative to each other. Suppose the lengths of the three sides of such a parallelepiped are a, b, and c and that a crystal plane intercepts these axes at A, B, and C, respectively, then $a/OA : b/OB : c/OC = h : k : l$, where hkl are the so-called *Miller indices* of this crystal plane. Taking the case of a plane making intercepts 2, 3, 6, than $h = a/2$, $k = b/3$, $l = c/6$. In a cubic system, $a = b = c = 1$; so $h = \frac{1}{2}$, $k = \frac{1}{3}$, $l = \frac{1}{6}$. Converting these to whole numbers, $h = 3$, $k = 2$, $l = 1$, and this plane is called the 3,2,1 plane. Should the intercepts be made on the negative side of the three axes, the plane notation would be $\bar{3}, \bar{2}, \bar{1}$. The faces of a crystal of salt are (1,0,0), (0,1,0), (0,0,1), etc., according as they are parallel to the plane containing the b and c axes, the a and c axes, and the a and b axes, respectively.

Crystals differ in regard to the relative lengths and angles of intersection of the axes, or in other words, in their *symmetry* and their interfacial angles. Three kinds of symmetry exist: (1) axes of symmetry, (2) planes of symmetry, and (3) centers of symmetry. *Axes of symmetry* are divided as follows: (1) Digonal, round which, if a crystal is rotated through 180°, the position is the same as at the start except that a different face replaces the original one. Six such axes occur in a cube—three diagonals joining opposite corners and three lines through the middle of opposite sides. (2) Tetragonal, such that a rotation of 90° brings the crystal to a position exactly similar to the original. A cube has three such axes. (3) Trigonal, such that a rotation of 120° gives the original position. (4) Hexagonal, in which a rotation of 60° gives the original position.

A plane of symmetry is such that the structures on each side have the same relation as object and mirror image.

A center of symmetry is a point in a crystal such that any line drawn through it to the surface of the crystal is bisected at that point.

It has been shown that there are 32 possible *classes of crystals*. These classes are divided into 7 systems. For more detailed information such books as Bunn's "Chemical Crystallography" and Evans's "Crystal Chemistry" should be consulted.

METHODS OF DETERMINING X-RAY DIFFRACTION SPECTRA

The Laue Method. From the Bragg law it follows that, if a given wavelength is passed in a given direction through a stationary crystal, diffraction is, in general, not likely to occur. This is so because only at one specific angle will the formula be satisfied and reinforcement of diffracted rays take place. However, if instead of a single wavelength, the continuous (white) unfiltered radiation from an X-ray tube is used, a considerable number of conditions occur under which reinforcement will take place, since the wavelength varies continuously. As a result, a series of regularly placed spots will be observed on the photographic plate. These spots lie on a series of ellipses which pass through the central spot. This is what Friedrich and Knipping did under the direction of von Laue in the classical experiment that first showed the diffraction of X rays by atomic structures. This is the Laue method. In practice, a narrow beam of white X radiation, limited by suitable lead slits, is passed through a thin slice of a crystal and then allowed to fall normally on a photographic plate wrapped in black paper. It can be shown that the spots formed occur at the positions to be expected from the Bragg law. The method is useful, but the fact that the spectra are formed by many different wavelengths makes them difficult to interpret.

The X-ray Spectrometer. Other methods simplify interpretation of results by using X rays of a single (monochromatic) wavelength, and by varying the angle of incidence in one way or another. In 1913, Sir William H. Bragg devised an X-ray spectrometer in which the crystal, mounted on a goniometer, was allowed to rotate about the axis of the instrument. The face of the crystal from which the desired reflections were to be obtained was mounted so as to contain this axis. The X rays were collimated by passing through a series of slits which absorb stray diffracted rays. This stray radiation comes from the edges of previous slits and to a large extent from the air. A narrow beam of X rays was allowed to fall upon the crystal face. The usual telescope of the spectrometer was replaced by an ionization chamber—nowadays a Geiger counter is often used—which could rotate about the axis of the instrument. The chamber was provided with an aluminum-foil window and limiting slits. In the original equipment the diffracted X rays entered the chamber and set up an ionization current in the gas of the chamber. This current was detected by an electroscope. Electronic counters or recorder charts are used in present instruments.

In operation, the crystal was slowly rotated. The chamber was simultaneously rotated at twice the rate of the crystal since, as seen before, the angle of reflection is twice that of incidence. Signals were obtained when the equation $n\lambda = 2d \sin \theta$ was satisfied. As θ and d (the distance between atomic planes) were continuously changing, the number of integrated reflections was far greater than when the crystal was stationary. The angle θ was readily measured to within a few minutes of arc. Consequently, the d spacings could be easily calculated for the different angles of incidence. The relative intensities of such reflections were measured by the electroscope.

The spectra can be denoted as the product of the Miller indices of the planes at which they are reflected, with their order. The first order from a (111) face would be called 111, the second order 222, and so on.

Conversely, using a crystal of known d spacings it is possible to determine the wavelength of unknown monochromatic X radiation.

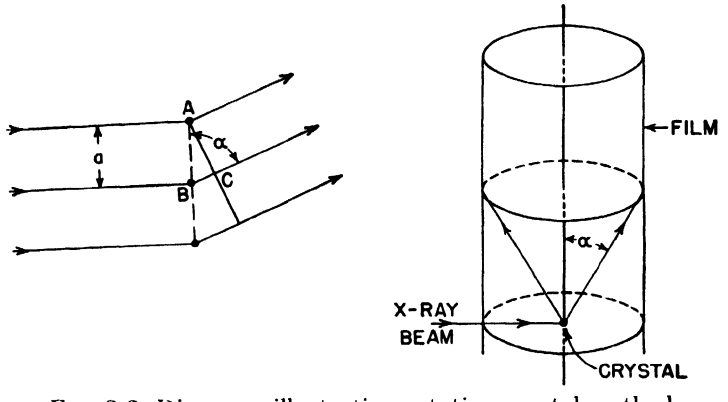


FIG. 8-2. Diagrams illustrating rotating-crystal method.

The Rotating-crystal Method. In this method the crystal is slowly rotated, the X-ray beam is monochromatic and constant in direction, and the reflections are caught on a cylindrical photographic film, the axis of which is also the axis of rotation of the crystal. Under these conditions the sets of planes move successively into their reflecting positions and a beam is emitted. The beam produces upon the photographic film a pattern of spots known as a rotation photograph. A very large number of rotations is necessary to produce appreciable photographic intensity.

Consider the crystal so mounted that the a axis (Fig. 8-2) is parallel to the axis of rotation to which the X-ray beam is perpendicular. Consider a spectrum formed in a direction making an angle α with the axis. It is clear that a spectrum cannot be formed unless $a \cos \alpha = n\lambda$, where a is the lattice translation parallel to the a axis, and n is a whole number. Such diffracted beams as do occur must be on the surface of cones, the vertices of which are at the crystal and the semivertical angles α of which

are obtained by replacing $n = 0, 1, 2, \ldots, -1, -2 \ldots$ in the above formula. This set of cones will intersect the cylindrical film in a series of circles which lie in planes perpendicular to the axis of rotation. These show as a series of spots in parallel straight lines called *layer lines*, on the film. Each layer line is denoted by its corresponding n value.

The cone for $n = 0$ is a plane perpendicular to the axis and contains the direction of incidence of the X-ray beam. The intersection of this with the film is called the zero layer line, or the equatorial. Should the rotation occur about the a axis, and the index of the spectrum be called hkl, all spots on the zero line would have $h = 0$; those on the first layer lines above and below the zero layer line $h = 1$ or -1, respectively, and so on. Spots with the same values of h and k, but varying values of l, all lie on one of a series of curves called *row lines*, which are transverse to the layer lines.

From the spacing of the layer lines, the lattice translation can be determined. This is the distance in which the pattern repeats itself in a direction parallel to the axis of rotation. With a known distance of the film from the crystal, the distances of the layer lines from the zero layer line give the values of the angle α and consequently, since λ is known, the value of a. When rotating photographs are taken separately about all three axes, the translations a,b,c, and therefore the dimensions of the unit cell of the crystal, are determined. It is thus evident that three rotation photographs give very considerable information. Complete rotation would give so many spots that confusion would result. In practice the crystal is usually rotated backward and forward through about 15°.

A special application of this method is due to Weissenberg. The crystal is continuously rotated back and forth through 180°. The cylindrical camera moves at a constant speed backward and forward, parallel to the axis of rotation. The relative movements of the camera and the crystal are such that a given position of the former corresponds accurately to a definite angular position of the latter. As a result, the coordinates of a spot on the film give both the reflection angle and the position of the reflecting plane. A metal cylinder with an equatorial slit a few millimeters in width is placed between the crystal and the film so that the spots of only one layer line can pass through it. The Weissenberg photograph thus records all spots belonging to that layer line, spread out on a single film. These can be readily identified. The exposure time is much longer than with an ordinary oscillation photograph. However, the information afforded would at times require many more of the ordinary photographs.

The Powder-crystal Method. Very many naturally occurring crystals are too small to be examined by the spectrometric or rotating-crystal method. It is not possible to align such crystals accurately along their

different crystal axes. A method devised by Debye and Scherrer and by Hull is used with considerable success for such materials. It is so convenient that a large amount of commercial work in X rays is done by this method even on materials that occur in large crystals. The method is simple and fast and usually gives sufficient information to identify the material. It is a powerful method for determining simple crystal parameters under certain circumstances. Cubic, tetragonal, and hexagonal crystals as, for example, most metals and alloys and a number of simple binary compounds which do not give large crystals, have had their structures determined by this means. When the crystal axes are not at right angles, the number of lines is so great that it is not feasible to attempt to identify them.

A monochromatic X-ray beam is allowed to fall on a small specimen of the crystal ground to a fine powder. The orientation of the small crystal fragments is completely random. As a result some of them will lie with any given set of lattice planes and thus make exactly the proper angle with the X-ray beam for reflection to take place. The reflections occur as cones, the axes of which are in the direction of the incident beam. There is a cone for each set of planes and for each order of spectrum. These cones intersect the photographic film set normal to the incident beam and so form a series of concentric halos. The rays are refracted at an angle of 2θ from the incident beam where θ is the angle of incidence. The d spacings of the crystal lattices can be calculated from the Bragg equation once θ is determined, as shown later (pages 141–143).

The powder pattern of a substance is characteristic of it whether it is simple or complex and can be used to identify it definitely, as will be seen later.

Analysis of Crystal Structure. In general it may be stated that the complete determination of a crystal structure is quite a complex operation involving many calculations. It is not possible to enter into the complete method in this chapter. The methods depend upon the angle of incidence of the X-ray beam, the distribution of electrons in the individual atoms, and the parameters or arrangements of the atoms themselves. It may even be necessary to measure a thousand or more X-ray spectra. At least several hundred are usually required. Certain considerations may considerably lighten the labor involved. Methods of trial and error are employed until one atomic arrangement is found that satisfactorily agrees with the experimentally obtained parameters. The size of the constituent atoms is of great importance. From symmetry considerations a certain structure may appear feasible, but if the atoms present cannot be fitted into it because of their size, that structure must be discarded. Proper balance of the constituent positive and negative ions must be looked into as also the question of proper coordination forces. The prin-

cipal refractive indices of the crystal will give important information as to the possible structure. Other physical properties can be used to limit structural possibilities.

W. L. Bragg has shown that the mathematical Fourier coefficients of a crystal can greatly aid in solving the structure. An infinitely extended crystal structure, with lattice translations a,b,c, is periodic in three dimensions. With these periods and the density of the scattering matter in it, thought of as continuously distributed, and as having maxima at the positions of the atoms, the structure can be expressed as a triple Fourier series. The coefficients of this series are simply related to the amplitudes of the spectra of the crystal, and there is one term in the series for each spectrum. If these Fourier coefficients can be determined, the density of scattering matter at any point and therefore the structure can be determined by summing the series. This is a useful method of solving crystal structure. It involves considerable calculation. Much less work is necessary if the projection of the scattering matter on one or more of its faces is determined. This projection is periodic in only two dimensions; so the number of terms involved is usually less than two hundred. Calculating machines which are necessary with the three-dimension series are thus not necessarily required.

COMMERCIAL X-RAY DIFFRACTION EQUIPMENT

X-ray Units. A number of firms manufacture either complete units or accessories for diffraction apparatus. Figures 8-3 and 8-4 show the most recent equipment manufactured in this country by the North American Philips Company and the General Electric X-Ray Corporation, respectively. A smaller unit made by North American Philips is shown in Fig. 8-5.

All units are high-quality precision instruments and are arranged so that several cameras can be used at one time for photographic work. Spectrometers are attached and means provided for counting the diffracted pulses and for the use of chart recorders. Attachments for fluorescent spectrometry are also available.

The British-made Hilger & Watts unit (Fig. 8-6) differs from the American units in that the X-ray tube is on a continuous pump system and not permanently sealed. This has the disadvantage of continuous pumping but it does enable target elements to be readily changed. In the American units a separate tube is necessary for each element used as target.

The most commonly used target is copper. Tungsten (wolfram), molybdenum, cobalt, iron, and chromium targets are also available. Filters are provided with the tubes.

Cameras. Figure 8-7 shows typical cylindrical *X-ray diffraction powder cameras.* The sample is placed in the center of the camera and provision is made to revolve it slowly and completely. Two collimating tubes reach on either side nearly to the sample in the center and minimize scattering of the beam by air. A fluorescent screen, covered by protective lead glass, is mounted at the outer end of the exit collimating tube. This facilitates camera alignment and allows observation of the specimen shadow during exposure. Cameras of various diameters are available.

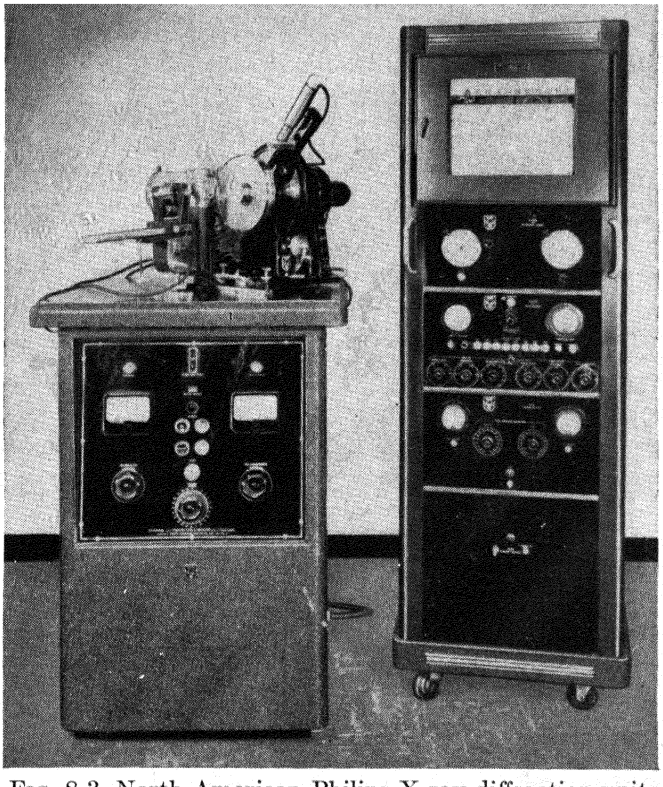


FIG. 8-3. North American Philips X-ray diffraction unit.

A *back-reflection* camera (Fig. 8-8) takes advantage of the fact that, with large angles of scattering, the dispersion is proportionately much greater than with small angles. This follows from the values of sin θ in the Bragg equation.

For use with microscopic sections of substances, fibers, and microtomed sections, a *microcamera* (Fig. 8-9) is available.

When rapid general surveys of the atomic arrangements of a material are desired, a *flat-plate camera* (Fig. 8-10) is used. This is also useful for work with single crystals in obtaining Laue diagrams. For measurements of very small values of θ a flat camera is used with a long (15 to 50 cm) specimen-to-film distance.

Special cameras are also available such as the Weissenberg goniometer



FIG. 8-4. General Electric X-ray diffraction unit.

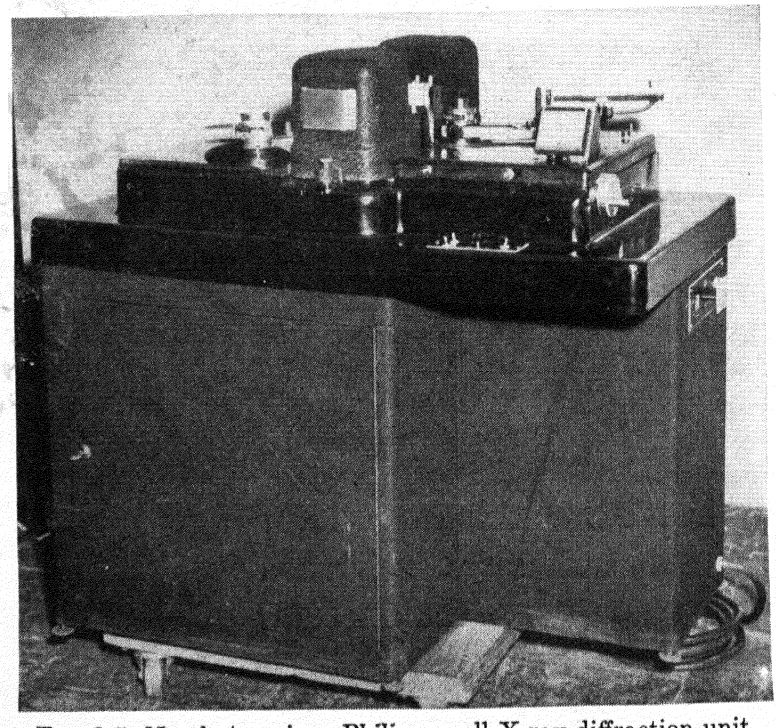


FIG. 8-5. North American Philips small X-ray diffraction unit.

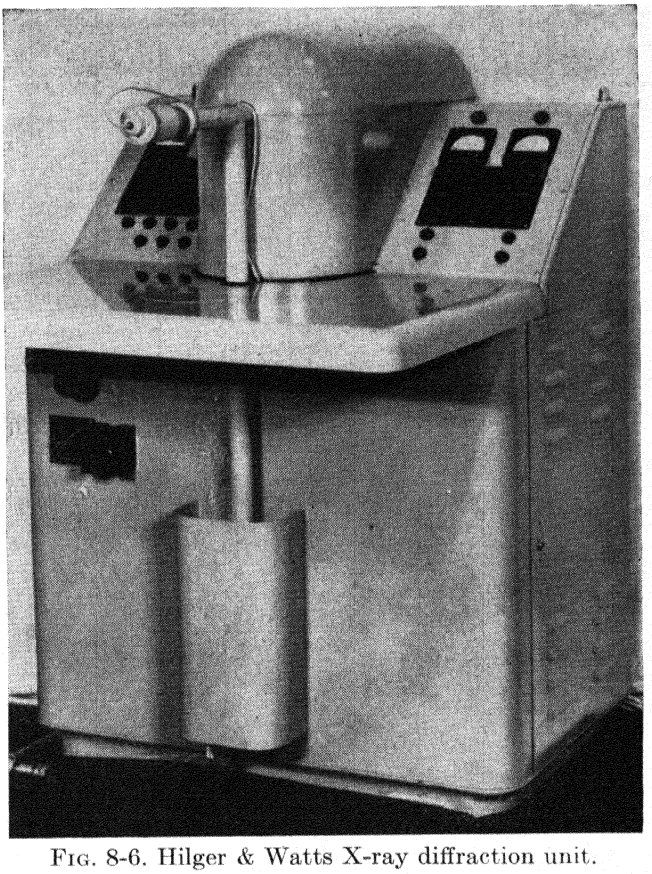


FIG. 8-6. Hilger & Watts X-ray diffraction unit.

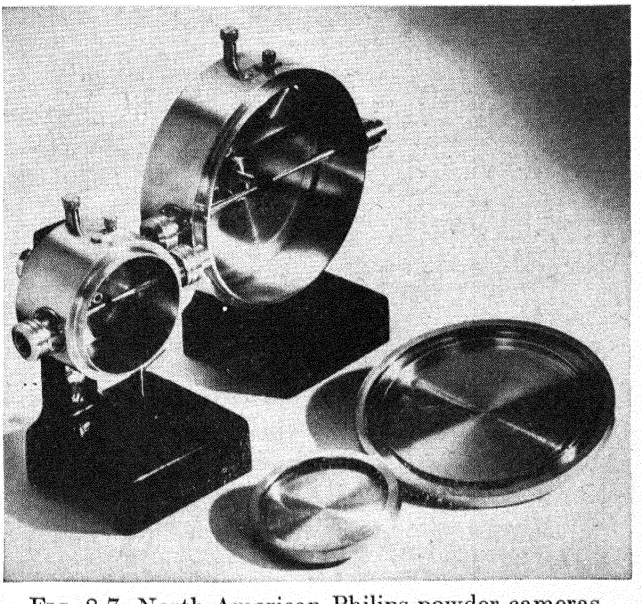


FIG. 8-7. North American Philips powder cameras.

(page 132), the precession camera, the Universal Unicam, and the low-angle scatter camera.

Focusing cameras are sometimes used. These are cylindrical but differ from the usual powder cameras in that the defining slits, specimen, and

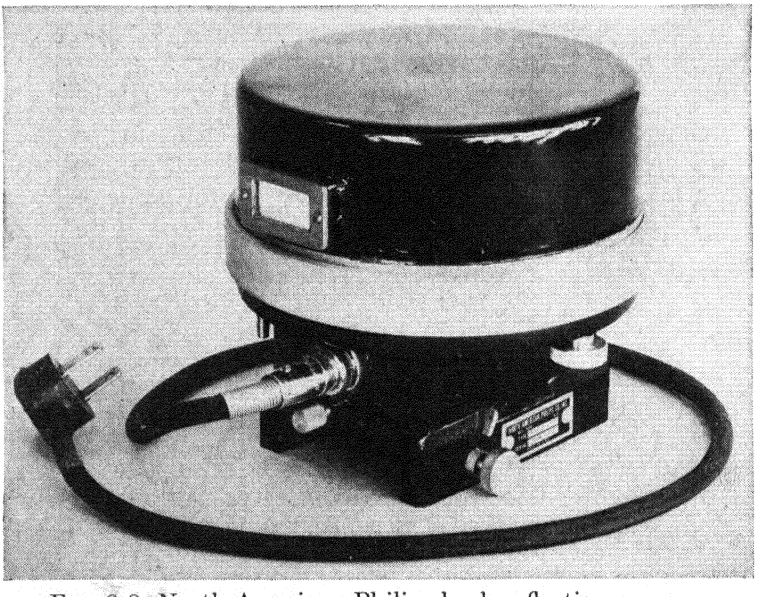


FIG. 8-8. North American Philips back-reflection camera.

film lie on a circle, the circumference of the cylinder. The specimen has a large surface and the geometry of the camera is such that the incident beam diverges somewhat. A large area of the specimen thus receives the X rays. The diffracted rays reconverge and focus on the circle so that a sharp line is formed on the film. These cameras give rapid exposures and have twice the dispersion of the usual cameras of similar radius. For this reason they are used in the study of complex materials where the number of lines is great.

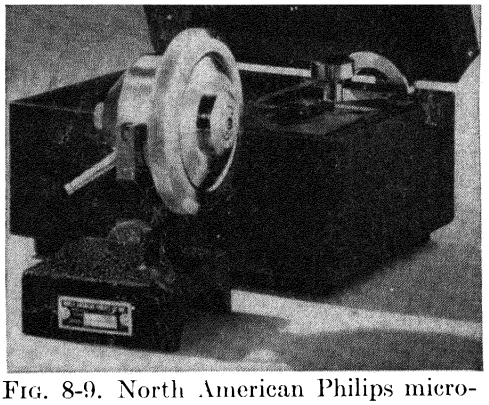


FIG. 8-9. North American Philips micro-diffraction camera.

Special cameras for high temperatures and others for low temperatures are used. At present these cameras are not generally available commercially but are built to individual specifications.

Various Equipment. A typical unit utilizing fluorescent light and mainly used to illuminate and measure 35-mm films is shown in Fig. 8-11.

A *film punch and cutter* (Fig. 8-12) serves the important dual purpose

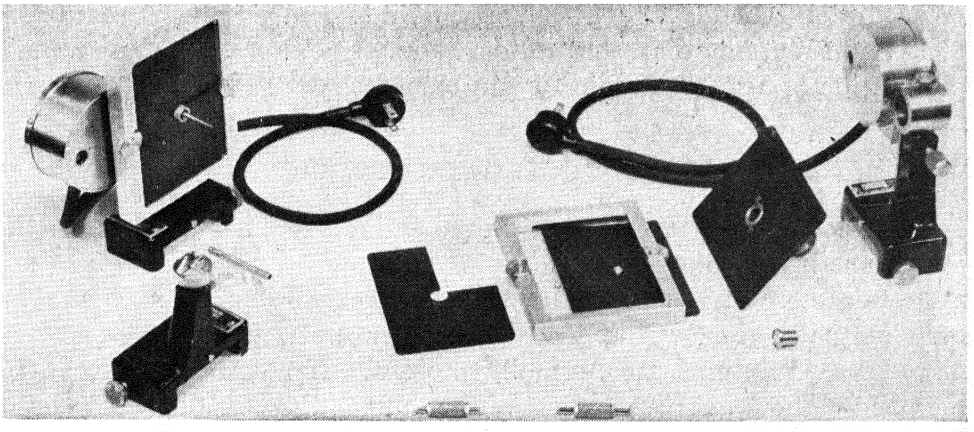


FIG. 8-10. North American Philips flat-plate camera.

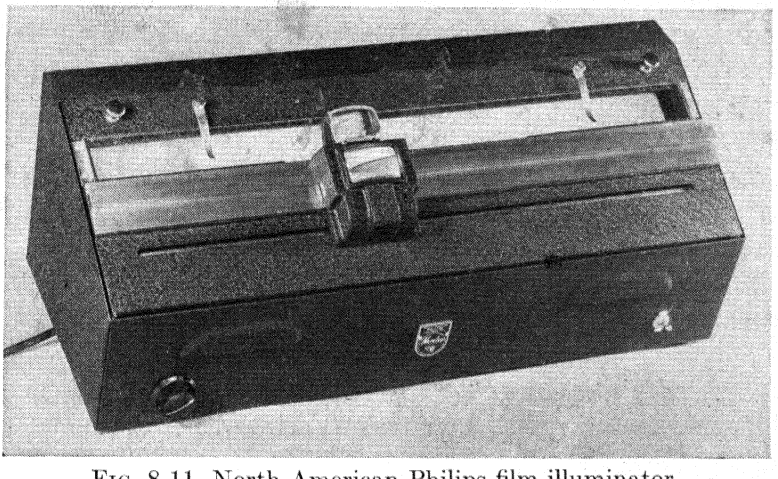


FIG. 8-11. North American Philips film illuminator.

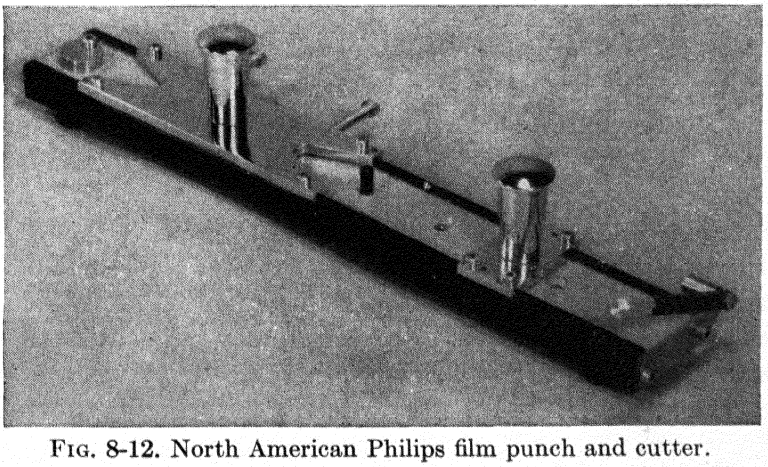


FIG. 8-12. North American Philips film punch and cutter.

of accurately cutting and perforating 35-mm film at proper points for 57.3- and 114.6-mm-diameter powder cameras, and of permitting central perforation of 5- by 7-in. film for flat cameras.

POWDER-DIFFRACTION TECHNIQUES

As these methods are so largely used in industry, some details of the operations involved are given.

Pretreatment of Powder-diffraction Samples. Identification of materials is usually greatly simplified when other substances are absent. In many cases mixtures are normally present. If any materials can be removed without altering the rest of the sample, the possibility of definite identification is greatly enhanced. One or more of the following simple procedures may be followed: (1) dissolve out materials with water or organic solvent; (2) treat for about 30 min with 1:6 hydrochloric acid, wash and dry; (3) treat for about 30 min with 1:14 nitric acid, wash and dry; (4) treat similarly, using 1:3 acetic acid; (5) shake continuously or intermittently with 5 per cent ammonium chloride solution, wash and dry.

Treatment (1) separates soluble from insoluble materials. Each fraction can be separately examined by the powder method. The hydrochloric acid treatment will remove carbonates, hydroxides, and some phosphates. However, partially soluble materials may be attacked. This applies to the nitric acid treatment which may also dissolve many metallic materials. For such cases the acetic acid treatment may be less drastic. Ammonium chloride will dissolve calcium and magnesium hydroxides and sometimes carbonates. Variations of these methods may be usefully employed.

Air-dry the residues from these treatments or wash with alcohol and ether. The use of a centrifuge is helpful for very small samples. Gravity separation can be helpful at times.

Powder-camera Method. Samples are usually prepared in the form of a cylinder, either sealed in thin-walled glass capillaries, adhering to a thin glass fiber using an adhesive such as shellac which has a low X-ray absorbance, or in extruded form. These are, in most cameras, embedded in plasticine on the camera mount so that they can be centered properly.

Lindemann glass (high in lithium) is often used as well as Pyrex glass. The latter has four times the X-ray absorbance of the former. For normal purposes a capillary with internal diameter 0.012 to 0.02 in. and walls 0.003 in. thick may be used. Grind the sample to at least 200 mesh. Seal one end of the capillary using a microburner. Push the open end into the ground sample, and hold vertically. By tapping fingers on the

bench or by stroking the capillary gently with a fine file, cause the powder to fall to the closed end. Repeat until approximately ⅛ to ¼ in. depth is obtained. Compact by using a fine glass hair as a ramrod.

It has been suggested that, for samples with a high coefficient of absorbance μ, a glass fiber 0.003 in. in diameter be used and that the sample be diluted with an inert nonabsorbant material such as nitrocellulose cement or shellac. Quartz and clay, which have a moderate μ value, can be used undiluted and placed on a fiber 0.005 to 0.008 in. in diameter. For materials such as organic preparations possessing a low μ value, use a capillary as above. This is for general identification work. For high-precision work use a diluted sample on a fiber 0.003 in. in diameter. For general work, however, the capillary-tube method is frequently employed. It may save time to examine the sample first under a reflecting polarized-light petrographic microscope in order to detect and possibly to separate different crystals.

For forward reflection, the intensity of diffraction lines is a maximum for a certain thickness of sample which can be calculated from the mass absorption coefficient μ_m. The intensity decreases as the sample becomes thinner since fewer crystals are present, and also decreases as the sample thickness increases over the optimum since the diffracted rays are then absorbed by the specimen. For flat specimens, the optimum thickness is $1/\mu_m$ and for circular specimens it is $2/\mu_m$. A variation of 50 per cent from this value is not serious. Samples that have a high absorbance, like heavy-metal powders, can be diluted with low-absorbing nonrefracting material such as starch or powdered gum tragacanth.

When the optimum specimen thickness cannot be determined, a wedge-shaped specimen can be used with a low-absorbing nonrefracting binder such as shellac. If the X-ray beam is directed to the tip of the wedge, in all likelihood some portion of the tapered tip will have the optimum thickness.

The glancing-angle technique can be used if the specimen cannot be ground or broken. The X-ray beam strikes the specimen at a small angle. The diffracted beams are thus recorded on only one side of the film and the specimen absorbs the diffracted rays from the other side. In such a case it will be necessary to add a substance with known spacings since only one side of the film has markings.

Measurement of Spacings and Intensities. The Straumanis film technique which follows is most frequently used for obtaining diffraction-pattern measurements.

Many cylindrical cameras have a diameter of 114.59 mm. With this camera 1 mm on the circumference is equivalent to 1°. The distance S between the centers of the two holes on the film (Figs. 8-13 and 8-14) in

such a camera is equal to half the camera circumference, i.e., $\pi r = 180$ mm. The angle of the diffracted ray can be calculated as follows:

$$S = \frac{2\pi r}{2} = \pi r$$

s is subtended at the reflection angle 2θ.

$$\theta \text{ in radians} = \frac{s}{2r}$$

$$\theta \text{ in degrees} = \frac{s}{2r} \times \frac{180}{\pi} = \frac{90s}{\pi r} = \frac{90s}{S}$$

When, as with above camera, $S = 180$, θ in degrees $= 90s/180 = s/2$ mm, where s measured in millimeters is the radius of the right circular cone of

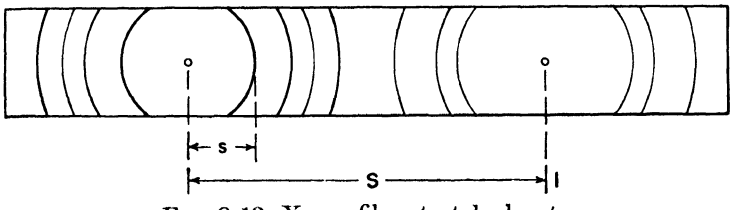


FIG. 8-13. X-ray film stretched out.

the diffracted ray as it cuts the film (half the distance between corresponding concave and convex lines on the film).

This method allows for correction due to film shrinkage when both s and S are measured. In the majority of cases, except for very refined work, S is considered constant when modern X-ray films and proper development procedures are employed. Another method is to use an internal standard giving spacings with all known measurements.

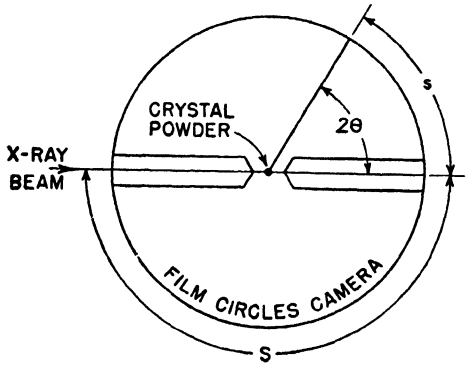


FIG. 8-14. X-ray film camera diagram.

When a camera is first used, it is well to calibrate it by making a pattern of a standard substance such as rock salt or quartz and to use the known spacings to obtain the radius.

For flat cassette cameras, $2\theta = \tan^{-1} s/2r$ where r is the specimen-to-film distance.

To measure the s distances, a vernier-equipped scale and viewer such as depicted in Fig. 8-11 is employed. After the angle θ has been found

and knowing the wavelength λ of the incident X rays, it is a simple matter to calculate the d spacings from the Bragg equation. Convenient tables are made up for known values of λ so that d may be directly read from the value of s.

Scales calibrated in 2 sin θ values have been proposed by Fankuchen.[3] These are independent of wavelengths but a separate scale is required for each camera radius. Scales may be calibrated to read d/n directly, but a different scale must be used for each different wavelength and for each different camera size. The scales are inverse with units which vary greatly over their length and are thus difficult to read accurately. Scales of either of these types do not give very great precision but may be accurate to within a percentage satisfactory for many compound identification problems.

The *line intensities*, which depend upon the atomic distribution within the unit cell and also to some extent upon the condition of the sample, must now be read. In the majority of cases, relative intensities are sufficient. Most available data are given in terms of I/I_0 where I is the intensity of the desired line relative to I_0, that of the strongest line taken as unity. Visual examination with the naked eye is normally sufficiently sensitive to quite small changes in intensity and is usually employed. Such listings as *h* (heavy), *m* (medium), *l* (light), *vl* (very light) and *vvl* (very, very light) are often used. Photometric devices may be used where extreme accuracy is desired. The multiple-film technique also gives accurate results. In this method the known absorption of a sheet of film is used to calculate the relative intensities of lines recorded simultaneously on superimposed films. It has been found that Kodak "no-screen" double-coated film absorbs 75 per cent of Cu K_α radiation.

These methods of intensity measurement can give results within ± 10 per cent of the actual amount present. In some cases a $\pm$ 5 per cent accuracy may be obtained. More precise measurements can be made with Geiger-counter spectrometers.

Geiger-counter Spectrometer Method. The introduction of the Geiger-counter X-ray spectrometer in 1945 gave greater possibilities for accurate quantitative analysis. This spectrometer provided excellent resolution and made possible intensity measurements of high accuracy without the difficulties resulting from film graininess, intensity-blackening relationships for X-ray film, and the microphotometer technique.

A single diffracted d line may be all that it is necessary to measure. Under exactly similar conditions of sensitivity and amplitude, the amount of a substance present is, with certain reservations, directly proportional to the line height on the chart. Alternatively, the actual number of rays emitted can be counted with the scaler and counter. By increasing the amplitude and possibly the sensitivity, spacings which give only weak

lines on a film can be made to give quite measurable chart lines. Quartz in silicate materials may be estimated when present to the extent of only 0.5 to 1 per cent by these methods. Furthermore, if the normally most favorable line of the material to be determined is common to that of another substance present, or is close to it, a weaker line may be used and amplified. Quick analyses may be made by these means since it is not necessary or desirable to record the whole X-ray spectrum.

The reproducibility and precision obtainable depend upon: (1) instrument stability and reproducibility, (2) mounting of the specimen, (3) crystallite size of the sample, (4) proper mixing of any internal standard with the sample, (5) the type of counting technique used, and (6) correction for counter dead-time losses. In modern instruments the mechanical details have been brought to a high degree of dependability and accuracy.

The sample for use in this method must be uniformly mixed, the particle size very small, and the sample thickness sufficient to give maximum diffracted intensities. The specimen must be ground so that the maximum crystallite size does not exceed a value that limits the random orientation of the powder components. For quartz this is about 5 μ.[4] Mixing may be performed in a ball mill or by mechanically shaking in a flask, with an inert liquid in either case. Rapid filtration is desirable to prevent segregation. The sample is then dried.

A useful *sample holder* is a square aluminum plate $\frac{1}{8}$ in. thick, surface ground to a tolerance of 0.002 in., with a rectangular hole 2 by 1 cm. Place the holder on a clean glass slide, fill the cavity with the specimen, press lightly, and make sure that no air pockets are present. Place a second glass slide on top and invert the whole assembly. Remove the first glass slide and expose this side to the X-ray radiation. By this means the surface is not touched and any tendency toward preferred orientation of the components of the specimen through mechanical action is minimized. The specimen-holder mount is geared to the Geiger-counter traversing mechanism in such a way that the angle between the face of the specimen and the incident X-ray beam is in correct relationship to the Geiger-counter receiving slit. This angle must be one-half the angle between the incident beam and the direction of the Geiger-counter slit in order to satisfy the Bragg-law relationship.

Provision is made to drive the goniometer arm and crystal at various multiple speeds and also to measure the actual 2θ angle. Slits are variable in width at the emergence of the X rays and also at the receiving end of the Geiger counter where the diffracted rays enter.

Response is measured by a scaled counter or may be recorded on a strip-chart recorder. Sensitivity and amplitude controls are present. A typical chart recording is shown in Fig. 8-15. The peaks of diffraction lines can usually be located on spectrometer charts with an error no

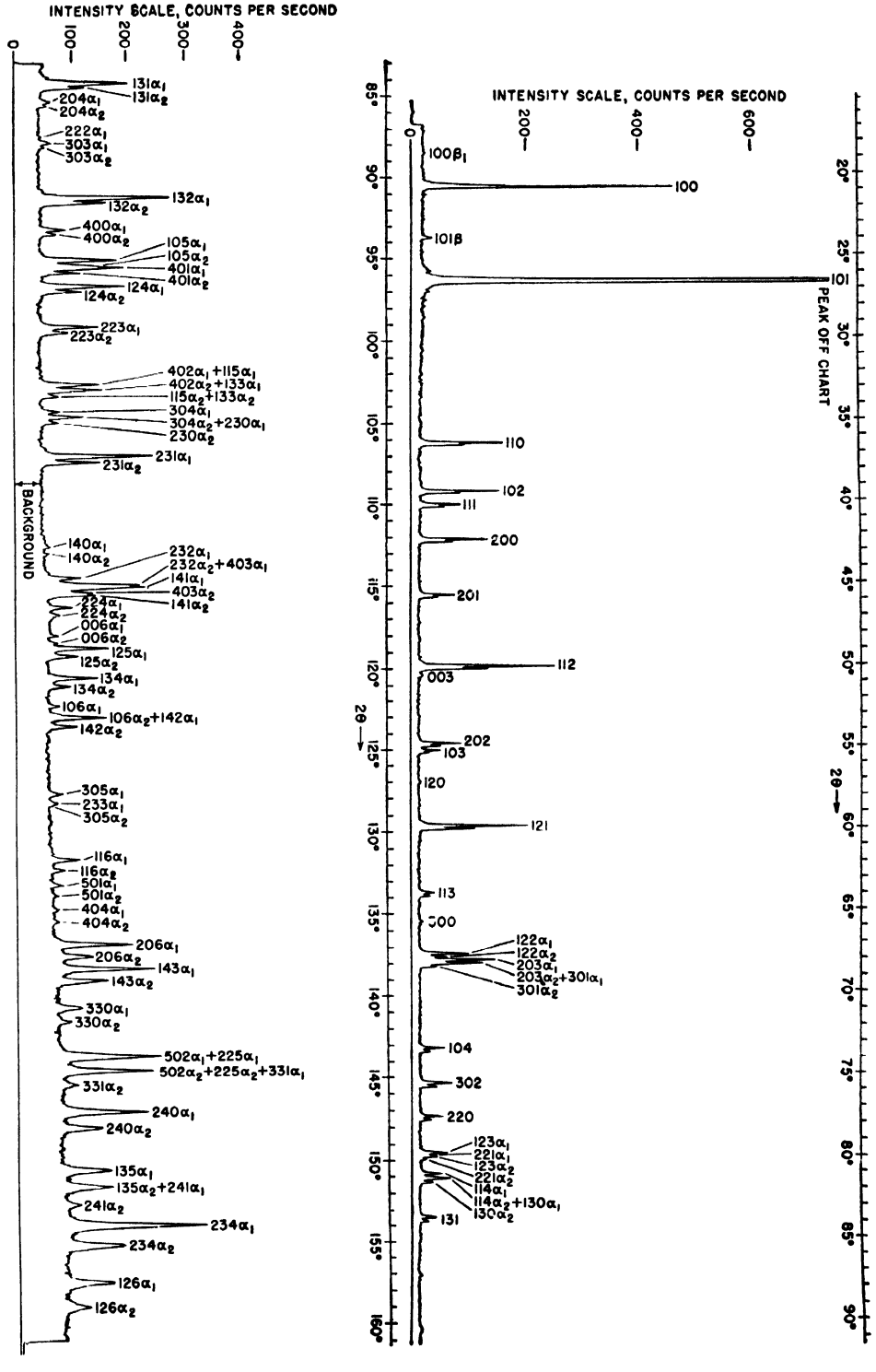


FIG. 8-15. Spectrometer charts for silica. (*North American Philips.*)

greater than $\pm 0.02°$, compared with $\pm 0.1°$ generally inherent in photographic diffraction measurements.

The resolving power is frequently beyond that obtainable by photographic means. The resolution of two diffraction lines obtained from one lattice plane (a spacing of d) with two slightly different wavelengths, as Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ (1.54050 and 1.54434 A), is used as a criterion. It is seen from the Bragg equation that the angle difference for two such lines increases with angle θ (or diminishing d). With the spectrometer, Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ are readily distinguishable even at $\theta = 30°$ and are fully resolved at $\theta = 40°$. With a film taken with a conventional 114-mm-diameter powder camera, resolution of these lines starts only at $\theta =$ about $50°$ and complete resolution is not obtained before $\theta =$ about $60°$.

Quantitative measurements are obtained by measuring the relative heights of the peaks, or the relative areas under the curves, a great advantage over the photographic method. With special techniques it is possible to measure lines at very low Bragg angles (spacing values up to 150 A).

It is of great importance to remember that charts obtained with the spectrometer give no indication as to whether or not the intensity along the diffraction line is uniform. Hence special precautions are necessary in the preparation of flat specimens so as to avoid preferred orientation of the crystallites (or texture formation). This would give rise to a variable intensity distribution and so introduce errors into the intensity measurements.

Absorption Effects. These are of considerable importance, particularly when mixtures are being investigated. When both weak and strong X-ray absorbing materials are together special precautions must be observed. A mathematical relationship between pattern intensity and the absorptive properties of the sample has been worked out and takes the following form:

$$I_1 = \frac{KX_1}{\rho_1[X_1(\mu_1 - \mu_m) + \mu_m]}$$

where I_1 = intensity of a selected line of the unknown component, X_1 its concentration, ρ_1 its density, and μ_1 its mass absorption coefficient. Referring to the rest of the mixture as the matrix, μ_m is its mass absorption coefficient, and K is a constant. When this relationship is applied to actual analytical conditions, three important cases arise, depending upon the number of components and the equality or nonequality of μ_1 and μ_m.

Mixtures of n Components, μ_1 Equals μ_m. This is a rather unusual case. The above equation reduces to $I = KX$, i.e., the intensity is directly proportional to the concentration. Direct linear analysis is possible.

Mixtures of Two Components, μ_1 Is Not Equal to μ_2. The components

are known. A direct analysis is possible by reference to a calibration curve prepared from synthetic mixtures of the two components.

Mixtures of n Components ($n > 2$), *and* μ_1 *Is Not Equal to* μ_m. This is the general case. The absorption coefficients are unknown. Indirect analysis by means of an internal standard is necessary. It has been shown[5] that, when the internal standard is added in a constant proportion, the concentration of the unknown component is proportional to the intensity ratio I_1/I_s.

The Geiger-counter spectrometer has been used in the routine analysis of industrial materials. Besides giving more information on the mineral composition than would be obtained by chemical analysis its use results in a considerable reduction in labor relative to chemical methods. For example, in the analysis of run-of-the-mine bauxite samples[6] the principal peaks for kaolinite, boehmite, gibbsite, goethite, quartz, and hematite were discernible. The relative heights of the peaks and of the general background level are related to the proportions of the various minerals present. It is not necessary to record the entire pattern in routine quantitative analysis. The intensities at the six diffraction angles of the principal peaks and one background intensity are all that is required. The exact angular settings are determined in advance.

Interpretation of *d* Spacings. By whatever method the *d* spacings have been obtained—by the powder camera or spectrometer methods—it is necessary to find out what they signify. For single substances this is quite simple if a record of the *d* spacings of the same material is at hand. Mere comparison will show correspondence. When mixtures of crystals are present, the interpretation becomes progressively more difficult the greater the number of components. The relative quantities of the latter may be different and must be considered. It is usual first of all to investigate the line of highest intensity and, when compounds have been found with this line as the heaviest, to observe further if the next dense line of the sample and of the material suspected are the same both in spacing and in relative intensity.

The American Society for Testing Materials has issued *X-ray diffraction-data cards.* These consist of five sections and can be purchased either on plain (3 by 5 in.) or Keysort (4 by 6 in.) cards. On each card are given the d/n values with their relative intensities, crystallographic information, optical data, and additional information such as source of mineral, method of preparation, and heat-treatment. For regular workers in this field these cards are essential.

The published data are under constant revision by a Joint Committee Fellowship at the National Bureau of Standards. Crystallographic information may be obtained from the "Strukturbericht," vols. I to VII, "Structure Reports," vols. 8 to 13; and from Wyckoff's "Crystal Struc-

tures," vols. I, II, III, and "Structure of Crystals," 2d ed., 1931, with supplement for 1930–1934. Starting with *Analytical Chemistry*, **20**: 274 (1948), a monthly series of new crystallographic data of organic compounds is being published.

Continued use may familiarize a worker with a small number of patterns but it is not possible to remember data of the many thousands of common materials met with in an industrial laboratory. Lists of compounds with their diffraction data are often compiled from day-to-day work in a busy laboratory. These are of particular use in the special field of investigation.

There are, of course, limitations to the use of X-ray diffraction as a method of analysis. This has been pointed out in regard to complex mixtures. In organic chemistry difficulty is encountered when, for example, homologous series of compounds are being examined. Such patterns look very much alike, and the long spacings must be used to differentiate as far as possible. It is often not possible to determine the identity of the compounds with certainty without knowing something of their chemistry. Longer wavelengths obtained from cobalt and chromium targets are being used to elucidate large organic molecules.

Low-angle X-ray Scattering. Low-angle scattering is used for the measurement of the sizes of particles or pores smaller than 0.25 μ, which is the limit of application of the light microscope. The analytical development of the method has been worked out by Guinier.[7] In the simplest method of measurements the filtered X-ray beam passes through two collimating apertures and then through the sample. A beam stop is provided for the primary rays. The scattered rays are measured by a Geiger counter. In more precise methods a reflecting crystal eliminates the first aperture by allowing only parallel rays to pass the second aperture. A curved crystal will effectively narrow the beam and achieve both monochromatization and focusing at once. A double-crystal spectrometer is also sometimes used.

The analytical expression deduced by Guinier for the approximate curve is

$$I = \exp(-K^2\bar{R}^2/3)$$

where I = scattered intensity, $K = 2\pi\epsilon/\lambda$, ϵ = scattering angle, λ = X-ray wavelength, and $\bar{R}$ = particle gyration radius. The gyration radius $\bar{R}$ may be computed from the slope of the curve of log I vs. K^2 or ϵ^2. For a known or assumed particle shape $\bar{R}$ is at once related to the actual particle dimensions. When samples are not uniform in size, the nonlinear curves obtained may be interpreted only very approximately.

This method has been used on many materials[8] such as inorganic solids, organic particles, oil-water emulsions, gases near their critical points,

bacteria, sols, and viruses. It supplements methods such as light scattering, ultramicroscopy and electron microscopy, surface adsorption, and sedimentation.

LOW-TEMPERATURE X-RAY CRYSTALLOGRAPHY

Many substances which are liquids or gases at room temperatures form crystal structures at low temperatures and can be examined by means of X-ray diffraction. This technique not only serves for identification purposes but makes it possible to follow phase transformations in the compounds under study.

The procedure involves cooling the sample, previously sealed into a thin-walled glass capillary tube, with a stream of cold dry gas. The progress of single-crystal growth and orientation is observed and controlled with the aid of a polarizing microscope mounted on the X-ray camera. The light source is placed behind the X-ray collimator slit. The light source is removed when crystals of appropriate size are grown and properly oriented. The camera and cooling stream are then moved along the track to the X-ray source. From this point the examination proceeds as with solids at room temperature.

It has been pointed out[9] that collecting X-ray data at low temperatures offers one of the simplest means of improving precision of determination of bond lengths and bond angles, particularly in relatively low melting crystals. The amplitude of thermal vibration at room temperature, in substances like these, is so great that to locate the true centers of the broadened atomic peaks is often difficult. In electron density projections, serious overlapping of adjacent atomic peaks is often encountered. These peaks, at low temperatures, are effectively sharpened.

FLUORESCENT X-RAY SPECTROSCOPY

Because of the small number of lines in a characteristic X-ray spectrum and because of the direct relation of the relative intensity to the amount of element present in the examined material, the X-ray region offers considerable advantages in some respects over the visible and ultraviolet region for spectrochemical analysis. Until quite recently this possibility could not be used because of inadequate means of measuring the relatively feeble fluorescent rays. The development of high-intensity sealed-off X-ray tubes and efficient Geiger-counter spectrometers and scintillation detectors has enabled this method to become of considerable use. Largely because of the absorption of fluorescent rays and their diffraction by air, up to very recently only elements with higher atomic number than titanium could be detected and determined. The use of helium and also

of vacuum, in place of air as path for the rays, and of very-high-intensity X-ray tubes, makes it possible to determine elements of even lower atomic number.

The basic problems encountered are resolution and intensity. The resolution is effected by the analyzing crystal and by the proper arrangement and alignment of collimator slits used for the X-ray beam.

The four methods that have been used are briefly outlined in Fig. 8-16. They differ mainly in their geometry, as in each case a sealed-off X-ray

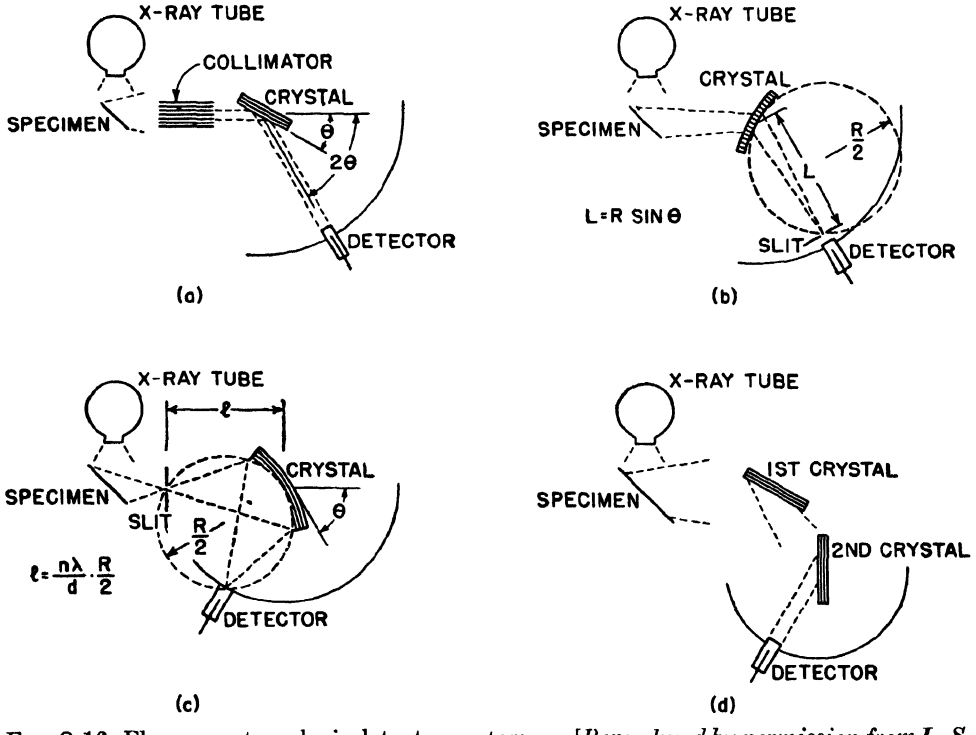


FIG. 8-16. Fluorescent analysis detector systems. [*Reproduced by permission from L. S. Birks, E. J. Brooks, and H. Friedman, Anal. Chem.*, **25**: *693, 694 (1953)*.]

tube is used to excite the spectrum and a Geiger-counter spectrometer with analyzing crystal is used to detect the fluorescent rays.

The simplest of these methods as shown in Fig. 8-16*a* is self-explanatory. The sample emits the characteristic X-ray spectra of all the elements present. This fluorescent radiation is collimated by a system of nickel tubes (Soller slits) so that only a parallel beam of the polychromatic radiation strikes the analyzing crystal. The single-crystal Geiger-counter spectrometer analyzes this beam in the usual manner. The positions of the various components of the beam and their intensities are measured. These are specific for the various elements. The more perfect the analyzing crystal, the better the resolution.

The second method (Fig. 8-16*b*) employs a curved focusing crystal as analyzer. The crystal is bent to a radius equal to the diameter of the focusing circle. The detector slit is placed at the proper point on the periphery of this circle. In order to keep the distance L from crystal to detector slit constant, the bending radius R of the crystal must be automatically changed with angle θ so as to satisfy the equation $L = R \sin \theta$, where θ is determined for a particular λ by the Bragg equation. In this method, resolution depends on the perfection of the crystal and the slit size in front of the detector. The intensity depends on the perfection

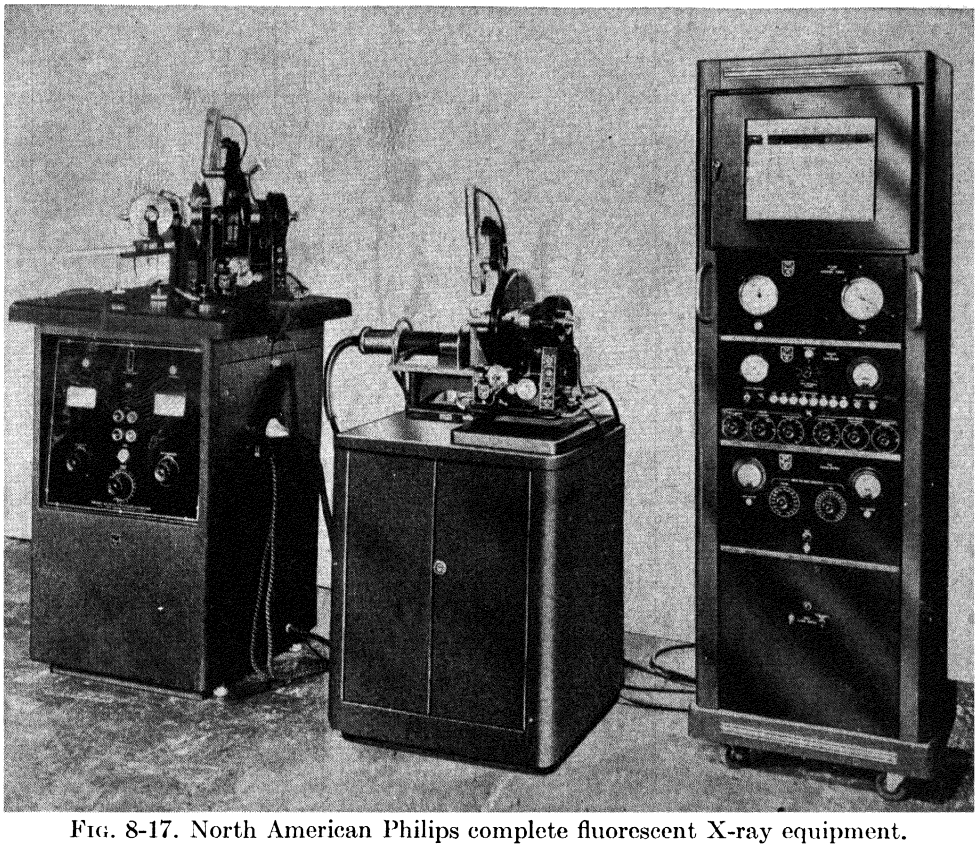


FIG. 8-17. North American Philips complete fluorescent X-ray equipment.

of the crystal and its thickness. Radiation from heavy elements will too easily pass through thin crystals without being diffracted, while radiation from light elements will be absorbed by a thick crystal.

The third method (Fig. 8-16*c*) is similar to the second method except that the crystal is of fixed curvature R and is used in the reflection rather than in the transmission condition. A fourth method (Fig. 8-16*d*) uses a double-crystal spectrometer.

Analyzing Crystals. For the flat-crystal method (Fig. 8-16*a*), a sodium chloride crystal has been most generally used because of its availability

and good working properties. Lithium fluoride crystals give about 1.5 times the intensity of that obtained with sodium chloride. Crystals of potassium chloride, potassium iodide, potassium bromide, quartz, aluminum, calcium fluoride, gypsum, and topaz have also been used.

Applications. Elements can be determined in both minor and major amounts. Measurements of plating thickness can also be effected by this means. It is usual to set up calibration curves for intensity vs. amount of element present. These are made with known standards, which need not be very close to the unknown in composition and often need not contain all the same elements. If the components of a mixture have very different absorption coefficients or excitation energies, the corresponding standards must be more carefully chosen. The intensity varies almost linearly with the amount present and to a much less extent with the composition of the matrix.

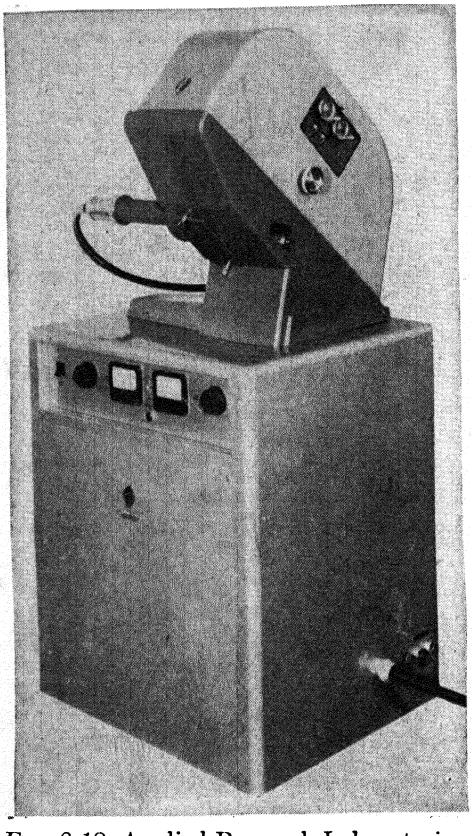


FIG. 8-18. Applied Research Laboratories X-ray scanning spectrometer and power supply.

Analysis of metal alloys is most usefully effected. For elements present from a few to 100 per cent, values correct to a fraction of a per cent for counting times of less than 1 min are obtainable. Elements present in parts per million are not readily determined. However, when parts per 10,000 are present, excellent results are obtained with longer counting times (5 to 10 min). Sulfur in oil,[10] lead and bromine[11] in gasoline, iron in blood, and uranium[12] in solution can be quantitatively determined. For plating thickness[13] calibration curves are readily set up. An example is the determination of the thickness of silver on silver-plated copper. This is found by measuring the reduction in intensity of the fluorescent copper spectrum which is partially absorbed by the silver. As an alternative the intensity of the silver K_α radiation can be measured and used.

Apparatus. Figure 8-17 shows the fluorescent X-ray spectroscopy equipment produced by North American Philips. The goniometer of the regular diffraction apparatus is employed.

For rapid routine measurements the Applied Research Laboratories manufacture an X-ray scanning spectrometer (Fig. 8-18).

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CHAPTER NINE

Survey of Electroanalysis

Electrical phenomena lie at the root of chemical reactions. It is therefore not surprising that they should be made use of in analysis. It follows also from the many ways in which they are exhibited that there should be many types of analytical methods based on them. In fact the variety of electroanalytical methods may give a disjointed appearance to their study. An attempt will therefore be made in this chapter to weave together some of the separate strands into a coherent pattern in order to impart some semblance of unity to this body of methods. Some of the individual methods which appear to be of lesser current importance analytically will be referred to only briefly, whereas a few of the more important methods will be discussed at greater length in subsequent chapters. Table 9-1 will serve as the basis of a discussion of electroanalysis.[1]

Most electroanalytical methods make use in some way of the chemical or physical effects associated with the flow in solution of (negative) electrons toward the positive electrode (the anode) and away from the negative electrode (the cathode). Such methods are listed in Table 9-1 under *A*, Electrolysis; *B*, Electrotitrations; and *C*, Analysis by measurement of electrical properties. Under *D*, Miscellaneous electrical methods, are listed some of the types of methods which are based not so much upon the phenomena occurring at electrodes but rather upon effects associated in various ways with stresses set up in a system by the existence of electrical forces.

In most electroanalytical methods two electrodes are immersed in a solution containing the substance to be analyzed, sometimes among other solutes. For some methods an electrical current generated externally to the solution is passed through the solution and the analysis is carried out by virtue of the effects produced in the solution by this current. (More rarely, as in electrographic analysis, no external source of current is used.)

Electrolysis is essentially a process of *reciprocal oxidation* (donation of electrons by a solute to the anode) *and reduction* (acceptance of electrons by a solute from the cathode). In the case of ionizable substances,

inorganic or organic, the anion and the cation are each driven, under the impulse of the applied current, to the anode and cathode, respectively. There oxidation and reduction of the respective ions (or of other more reactive substances in place of them) occur because of the gain or loss of electrons. Nonionizable substances, mainly organic molecules, on the other hand, cannot, of course, be driven to an electrode by virtue of the electrical charges involved in the ionization process. In order to bring such substances up to an electrode for oxidation or reduction, recourse must be had to diffusion forces, sometimes aided by mechanical stirring. Under such circumstances the current is carried by electrolytes added to the solution.

TABLE 9-1. ELECTROANALYTICAL METHODS

A. Electrolysis
- I. In preparation for nonelectrical measurements
  - *a.* Oxidations or reductions prior to titrations
  - *b.* Reduction and collection at cathode of groups of metals
  - *c.* Internal electrolysis
  - *d.* Electrographic analysis
  - *e.* Electrophoresis or cataphoresis
- II. For analysis directly by electrical measurements
  - *a.* Polarography
  - *b.* Determination by measuring current at controlled potentials
  - *c.* Coulometric analysis
    1. By measuring current used in carrying electrolysis of sample to completion
    2. By titrating sample with a measured quantity of electrolytically generated reagent to potentiometric or other end point

B. Electrotitrations
- I. Potentiometric
- II. Conductometric including high-frequency oscillometry
- III. Coulometric (also under Electrolysis)
- IV. Amperometric titrations

C. Analysis by measurement of electrical properties
- I. Polarography (also under Electrolysis)
- II. EMF measurement
- III. Conductance (resistance) measurement

D. Miscellaneous electrical methods
- I. Dielectric-constant measurements
- II. Magnetic effects
- III. Magnetic-electrostatic effects
- IV. Thermoelectric effects
- V. Photoelectric effect
- VI. Ionizing radiations
- VII. Piezoelectric effect

Electrolytic Methods. The process of electrolysis is used in analytical chemistry for two broadly different purposes. One is to effect separations of substances in order to aid subsequent analysis by methods which

do not involve electrical measurements (*AI*). The other purpose is to carry out electrolytic reactions so that substances may be identified or determined by measurement of electrical effects which are connected with such electrolyses (*AII*).

Under *AI* the process of electrolysis is an adjunct to the main method of analysis. It serves the same purpose as might be served by techniques such as distillation, crystallization, precipitation, and other methods of separation and purification, or by the application of chemical reagents prior to further analysis. Electrolytic techniques of this type may be applied prior to any method of determination, electrical or otherwise.

One category into which such techniques may be grouped consists of *oxidations* or *reductions* aimed at changing substances to a state suitable for titration. Elements such as titanium, vanadium, and uranium have been reduced by electrolysis with a mercury cathode and the reduced forms of the elements then titrated. (During such reductions elements like iron, chromium, copper, nickel, and others may at the same time be removed.[2]) Oxidations prior to titration have not been used so extensively but published reports indicate the possibility of oxidizing cerous ion for such a purpose.[3] Such preparation for titration can be clean-cut, efficient, and sparing of an analyst's time, which might otherwise have to be spent in carrying out extensive manipulations and chemical separations.

A related group of procedures involves *cathodic reduction* not merely for subsequent titration (although this too may be done) but primarily as a means of separating and collecting one metal (or group of metals) in the presence of others by changes in potential, by complexing agents, or by other devices. Subsequent determination is often gravimetric, as in the classical procedures for plating out metals at a platinum cathode. These techniques have also been used for reducing metals at a mercury cathode, collecting them in the mercury, and subsequently isolating them by removing the mercury by distillation. The metals are then dissolved and determined polarographically or spectrophotometrically.[7] The development of potentiostats, instruments for automatically maintaining the potential of an electrode at a desired voltage, has made it possible to separate many metals in solution from each other by plating them out in succession at their own deposition potentials.[13,14,15]

In *internal electrolysis*,[8] so called because no external source of current is employed, a soluble anode of zinc or some other suitable metal is used to displace the desired metal or metals from solution. They are deposited upon a platinum cathode which is connected to the anode metal.[8,9]

In *electrographic analysis*, minute amounts of substances may be detected in the surface of a metallic sample. A test paper which is impregnated with reagents suitable for detecting or determining the

desired constituent is applied to the metal surface. The sample is made to serve as one electrode. A second electrode is applied to the test paper. Trace constituents may thus be electrolyzed and caused to travel through the test paper. Here they react with the test reagent to produce a coloration or other visible evidence of their presence.[10,11,12] Commercial apparatus is available.

Finally, in this group of methods there should be mentioned *electrophoresis* or *cataphoresis*. These techniques have been especially important in the solution of biochemical problems where extremely complex mixtures are often encountered. Substances which are ionic in nature will wander at different rates toward the anode or cathode and may thus be separated.[4,5,6] These techniques are particularly useful when the migration is made to take place in paper impregnated with an electrolyte. When electrolysis is stopped, the various constituents may be located on the paper by application of suitable reagents.

Under *A II* are methods utilizing electrolysis not as a means of preparing a sample for detection or analysis by some other method, but in order to obtain analytical information from *some property of the electrical system* itself. In *polarography* electrolytic reductions or oxidations are carried out at a cathode or anode usually consisting of falling droplets of mercury. The method furnishes qualitative or quantitative analytical data from the magnitude of the current at known voltages and from changes in the current.

Somewhat akin to the information obtained polarographically is that which may be obtained by measuring current at controlled potentials. The previously mentioned potentiostats are used. Hickling[16] used a potentiostat to obtain current-voltage curves from which it was possible to make determinations of substances reduced at the cathode or oxidized at the anode. Figure 9-1 shows a curve of some of Hickling's data relating current and potential for the reduction of several metals. From the current value it is possible to estimate the quantity of the constituent in question. Generally, however, this sort of information may be obtained more conveniently polarographically.

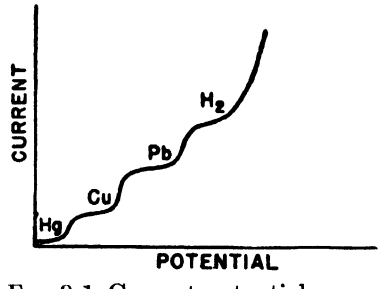


FIG. 9-1. Current-potential curves for several metals. [*A. Hickling, Trans. Faraday Soc.*, **38**: *27* (*1942*), *Fig. 4.*]

Finally in the category of analysis by electrical measurements is *coulometric analysis*, which is growing in importance. Coulometric analysis involves carrying out an electrolytic reaction with 100 per cent current efficiency and determining the reacting substance from the amount of current used. In the case of coulometric titrations this is done by titrating with electrolytically generated reagent to any acceptable end

point and determining the number of equivalents of titrant from the amount of current used in generating it.

Electrotitrations. Under *B*, Electrotitrations, are included several methods in which an electrical effect is used not to carry out a reaction, as under *A*, Electrolysis, but as a method of determining when a reaction has been carried to completion. *Potentiometric titrations* are carried out by measuring the potential developed at zero current during the addition of titrant. From the curve for change of potential with volume of added titrant the end point of the titration may be determined.

In *conductometric titrations* the end point is determined from a break in the titrant volume–conductivity curve. A more recent technique, titrations using *high-frequency oscillometry*, is somewhat similar in principle to conductometric titrations, except that it is unnecessary to use internal electrodes. This condition may be of advantage in some circumstances. There are also some other differences from conductometry.

Amperometric titrations involve the determination of the end point of a titration by a break in a titrant volume–current curve. They are based on polarographic principles.

Analysis by Measurement of Electrical Properties. Under *C* are included methods which utilize the measurement of the magnitude of electrical potential, conductance, or current as a measure of a substance being determined. These methods differ from electrotitrations in that the measured electrical property gives a direct estimate of the substance being determined and not merely an indication of an end point in a titration. *Polarography* also involves electrolysis and has already been mentioned. The use of *electromotive force* (*emf*) *measurements* for such a purpose is exemplified mainly by the widespread practice of determining pH by means of the glass electrode and the pH meter, which determines emf and translates it into pH units. Otherwise, there have been reported only a few isolated methods in which a concentration cell is set up containing a known solution in one cell and the unknown in another cell. The emf developed is measured. In this way the purity of redistilled mercury and other substances has been measured,[17,18] chloride[19] and fluoride[20] have been determined, and the kinetics of hydrolysis or of oxidations with ceric sulfate have been studied.[21]

Conductance (or resistance) measurement is used considerably in industry to test for the presence of dissolved electrolytes in water, effluents, and process liquors and to determine moisture in wood, paper pulp, and other solids. A method has been reported for determining water in acetone-insoluble liquids or solids by measuring the conductance of a 10 per cent solution of oxalic acid in anhydrous acetone after mixing it with the sample.[22,23] A method for analyzing binary mixtures of fatty acids by conductance has been reported.[24] Methods of gas analysis are

widely used which depend upon changes in the conductance of a heated wire caused by variations in composition of the gas surrounding it.[26,28] Gaseous mixtures are also analyzed for reactive components by mixing with conducting liquids and measuring the change in conductance of the liquids.[1]

Miscellaneous Electrical Methods. Under *D* are listed a number of miscellaneous electrical methods: *Dielectric-constant* measurements have been used for determining moisture[29] and isomers in certain mixtures such as the chlorobenzenes. *Magnetic effects* are utilized for determining oxygen in gaseous mixtures[27] in studies on rare earths and in tests for free radicals. *Magnetic-electrostatic effects* are essential in the mass spectrograph. *Thermoelectric effects* are utilized for temperature compensators

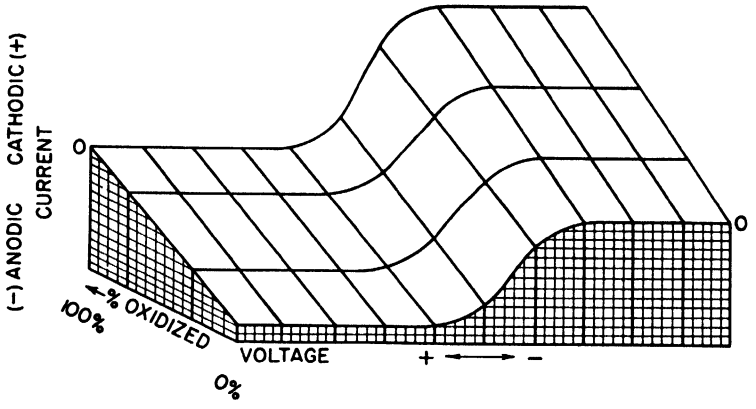


FIG. 9-2. Three-dimensional model for interpreting electrometric processes. [*C. N. Reilley et al., Anal. Chem.*, **23**: *1226 (1951), Fig. 1.*]

in pH meters, in conductance instruments, and elsewhere. *The photoelectric effect* makes possible certain photometric instruments. *Ionizing radiations* are of importance in radiochemical methods of analysis. The *piezoelectric effect* (electrical changes produced by strains in crystals) serves in controlled-frequency devices and in interferometers used for the analysis of gases and liquids.

Spatial Representation. Perhaps the best way to bring some of the electroanalytical methods into a common framework is to use the device of a three-dimensional model reported by Reilley, Cooke, and Furman.[25] Consider an electrode such as a platinum wire or falling mercury droplets in a solution containing a reversible oxidation-reduction system as, for example, ferrous and ferric ions or quinone and hydroquinone. The relationship between the percentage of oxidized form, the current, and the voltage, when the electrode and solution are made part of an electrical circuit, may be expressed by a three-dimensional surface (Fig. 9-2). This is based upon an equation set up in terms of the usual physico-

chemical properties. (The original paper may be referred to for the equation and a detailed discussion.) If planes drawn in various ways in the solid figure are examined, the theoretical basis of several electroanalytical techniques may be visualized.

If sections are cut parallel to the voltage-current surface at any value of "per cent oxidized," a polarographic curve will be obtained. Figure 9-3*a* shows such a plane for per cent oxidized equal to about 50 per cent,

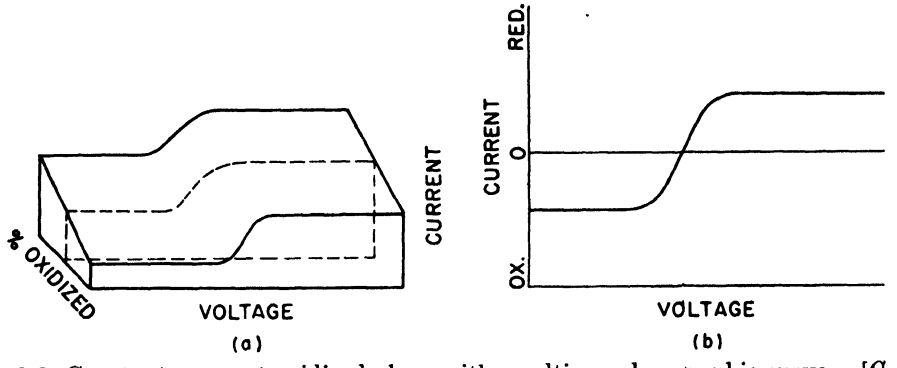


FIG. 9-3. Constant-per cent oxidized plane with resulting polarographic curve. [*C. N. Reilley et al., Anal. Chem.*, **23**: *1226 (1951), Fig. 2.*]

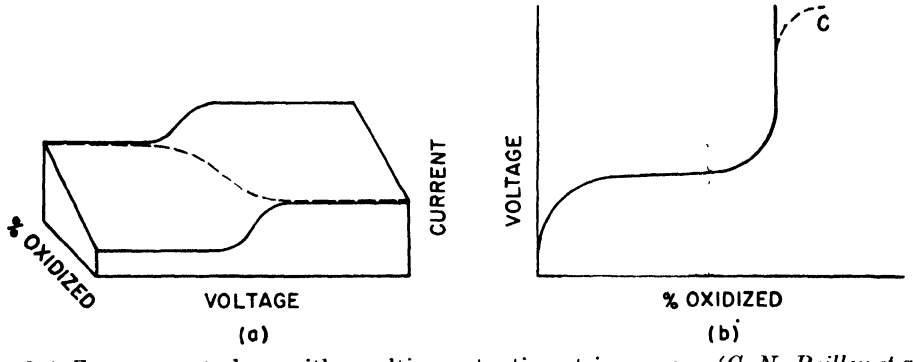


FIG. 9-4. Zero-current plane with resulting potentiometric curve. (*C. N. Reilley et al., Anal. Chem.*, **23**: *1226 (1951), Fig. 3.*]

and Fig. 9-3*b* shows the resulting two-dimensional, typical polarographic curve.

Figure 9-4*a* shows a plane at zero current cut parallel to the voltage–per cent oxidized plane. This gives Fig. 9-4*b*, which is a typical curve for a potentiometric titration. The dotted line *C* is the beginning of the curve obtained upon adding another oxidation-reduction system after the end point. For example, if the first part of the curve is that of the ferrous-ferric couple obtained by titrating ferrous ion with ceric ion to form ferric ion and cerous ion, the second curve would be that of the ceric-cerous couple after all the ferrous ion had been converted to ferric.

Figure 9-5*a* shows a plane at constant voltage cut parallel to the per cent oxidized–current plane. Figure 9-5*b* gives the resulting straight-line relationship which is obtained in amperometric titrations and in polarographic determinations. The dotted line gives the course of the curve upon the addition of another couple after the end point, such as ceric-cerous after the ferric-ferrous couple.

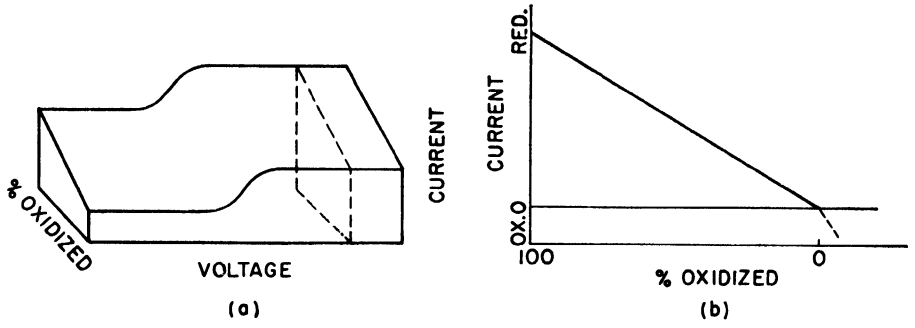


FIG. 9-5. Constant-voltage plane with resulting linear relationship. Basis for quantitative polarography and amperometric titrations. [*C. N. Reilley et al., Anal. Chem.*, **23**: *1226 (1951), Fig. 4.*]

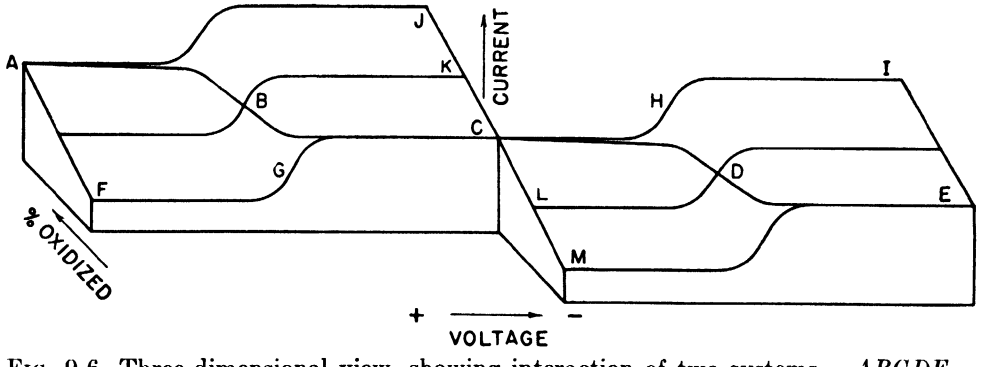


FIG. 9-6. Three-dimensional view, showing interaction of two systems. *ABCDE*—potentiometric curve. *JKC-CLM*—amperometric-titration curve. *FGCHI*—polarogram of solution at end point. [*C. N. Reilley et al., Anal. Chem.*, **23**: *1226 (1951), Fig. 5.*]

In Figure 9-6 are shown the relationships which exist when two reversible systems, such as ceric-cerous and ferric-ferrous, are properly aligned along their respective voltages axes. *ABCDE* represents the course of a titration of ceric ion with ferrous ion. *B* and *D*, respectively, represent the points where each system is 50 per cent oxidized, and *C* is the end point. A polarogram made on the solution at the end point would give a curve such as *FGCHI*, where *FG* represents the wave for the oxidation current of the higher-voltage couple (ceric-cerous) and *HI* the wave for the reduction current of the lower-voltage couple (ferric-ferrous). An amperometric titration would be shown by the two lines *JKC* and *CLM* with their intersection at *C* representing the end point of the ampero-

metric titration, as well as that of the potentiometric-titration curve *ABCDE*.

As has been indicated, later chapters will elaborate on some of the methods brought together in this chapter for a bird's-eye view of electroanalysis.

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CHAPTER TEN

Polarography

Polarography, as a method of analysis, is that branch of analytical chemistry which is concerned with identifying substances by means of the electrical potentials at which they are electrolytically reduced or oxidized and with estimating their concentrations by the magnitude of the electrolytic current involved. In an electrolytic cell oxidation occurs at the anode and an electrically equivalent reduction at the cathode. In polarography one electrode usually consists of a steady succession of mercury droplets falling into a solution of the substance being studied. The falling mercury droplets generally serve as the cathode. The anode is a quiet pool of mercury or a half-cell, such as a calomel half-cell. Sometimes the falling mercury droplets serve as the anode and the quiet pool of mercury or the calomel half-cell as the cathode. For purposes to be discussed later, the falling mercury droplets may be replaced by a platinum electrode.

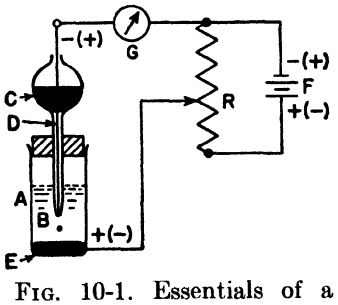


FIG. 10-1. Essentials of a polarograph. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. I-4. By permission of the publishers.*)

Essentials of a Polarograph. Figure 10-1 gives the essential parts of a polarograph. *A* is the electrolysis vessel containing solution *B* in which there is dissolved an electroreducible (or electro-oxidizable) substance. *C* is a mercury reservoir from which small mercury droplets fall at the rate of about one drop every 2 to 4 sec from the tip of the capillary *D*. The internal diameter of the capillary at the tip is about 0.03 mm and the mercury droplets have a maximum diameter of about 0.5 mm. *E* is a pool of mercury which serves as the anode when the dropping mercury serves as the cathode, and vice versa. (The pool of mercury is often replaced as the electrode by a calomel half-cell.) The potential across the cell may be varied by means of the variable resistance *R*, which is shunted across the battery *F*. A galvanometer *G* measures the current flowing through the system.

Actual polarographic instruments embody one or more elaborations upon the bare essentials given in Fig. 10-1. Some instruments require setting the desired potentials by hand at each voltage at which a current reading is wanted. Others have a device which varies the potential automatically at a uniform rate. Of the latter, some make a photographic recording of the potential-current curve and others produce a curve drawn by pen and ink.

Ideal Polarographic Curve. Figure 10-2 represents an ideal curve which might be obtained upon reducing a substance electrolytically at the dropping-mercury cathode. The first part of the curve indicates a constant, or only slowly rising, current, which is known as the "residual current." This is not dependent upon the nature or concentration of the reducible substance but, in the absence of reducible impurities, is equal

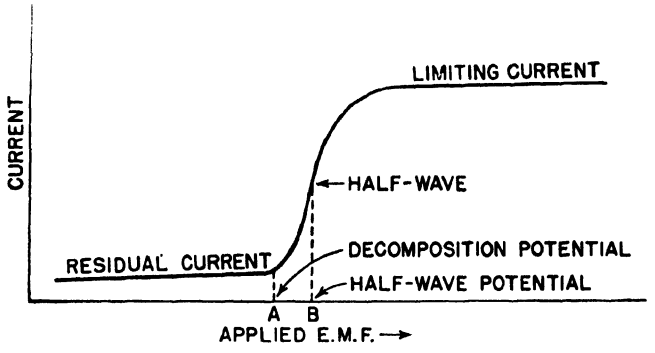


FIG. 10-2. Idealized polarographic curve. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. I-5. By permission of the publishers.*)

to the so-called "condenser or charging current" which is an electrical effect depending upon both the mercury electrode and the solution. In practice the residual current is usually somewhat greater than the charging current because of the presence of traces of reducing impurities. It also increases with increasing negative potential, and in accurate work a "background" correction should be applied for it. When the "decomposition potential" *A* is reached, reduction starts and the current rises abruptly to form a "polarographic wave." Finally, with continually increasing voltage the curve levels off to give again a constant, or slowly rising, current-voltage curve at a current value known as the "limiting current." The difference in magnitude between the residual current and the limiting current serves as a quantitative measure of the concentration of the reducible substance. The point on the wave halfway between the residual current and the limiting current is known as the "half-wave" and the corresponding potential as the "half-wave potential." The half-wave potential is characteristic of a given substance, under given conditions, and barring interferences, may be used to identify the substance.

Scope and Precision. Generally speaking, and within limitations and restrictions which will be discussed later, the polarographic method may be considered to be applicable to any substance which can be reduced or oxidized electrolytically. It has been used in the analysis of alloys and other materials for the determination of cations such as those of lead, zinc, cadmium, copper, iron, chromium, and other metals. Methods have been reported for the determination of anions such as chloride, bromide, bromate, and cyanide. Oxygen has been determined in gases and in industrial effluents. An ever-increasing number of organic substances is being analyzed polarographically. Among these are nitro compounds, carbonyl compounds, sulfur compounds, peroxides, azo compounds, and many others.

The usual precision of polarographic methods, with adequate control of temperature and other conditions, is about ± 2 per cent in the concentration range from about 10^{-4} to 10^{-2} molar, and about ± 5 per cent in the concentration range from about 10^{-5} to 10^{-4} molar. Thus the precision, which is not so good as for the most refined chemical methods, makes polarography of most interest for the determination of low concentrations, where relative errors of ± 2 to ± 5 per cent may not be important. But in view of the relative simplicity of the methods and their rapidity, they may often be preferred to more precise but often much more complicated and time-consuming methods.

GENERAL BACKGROUND

Considerable work has been done and many publications have appeared in an attempt to explain the underlying mechanisms on which polarography is based. Only enough of the theoretical background will be discussed here to make it possible for the analytical chemist to understand the use of polarography as an empirical tool.

Diffusion Current. Assume that zinc ion is being reduced at the dropping-mercury cathode. If the zinc salt furnishing zinc ions (Zn^{++}) is merely dissolved in water and an electrical potential is applied between the anode and the cathode, the magnitude of the current passing between the electrodes is dependent upon two forces: (1) the diffusion of zinc ions to the surface of the mercury droplets at which they are reduced to metallic zinc, which thereupon forms an amalgam with the mercury; and (2) the electrical migration of the current with the zinc ions. The current due to diffusion is proportional to the concentration gradient of zinc ions at the surface of the cathode; the current due to electrical migration is proportional to the electrical potential gradient at the cathode. If then the sole electrolyte is a zinc salt, the rate of discharge of zinc ions at the cathode will vary not only with the concentration of zinc ions, but

also with changes in the emf. If a small amount of an electrolyte which contains a cation reducible at a considerably higher potential than zinc ion, e.g., potassium chloride, is now added, some of the current formerly carried entirely by zinc ions is now carried by potassium ions (K^+). As the concentration of potassium chloride is increased, the potassium ion carries an increasing proportion of the current until finally when the ratio of potassium chloride to zinc salt is about 25:1 or 50:1, practically none of the zinc ions is carried to the cathode by electrical migration. (A ratio of 100:1 is used in practice.) Under such conditions, the magnitude of the reduction current depends entirely upon the rate of diffusion of zinc ion to the mercury droplets. This rate, in turn, is governed by the gradient between the concentration of zinc ion at the surface of the droplet and that in the bulk of the solution.

With this description of the underlying mechanism of the diffusion current in mind, the course of a current-voltage curve for a solution of a zinc salt in the presence of an indifferent electrolyte such as potassium chloride will be followed. (Reducible oxygen has been removed by blowing nitrogen through the solution.)

Residual Current. As the potential is slowly increased, before the decomposition potential of zinc ions is reached, a small residual current is produced. This is caused in part by the reduction of traces of impurities (including traces of oxygen) and in part by the discharge of a current due to the potential impressed upon the mercury by the mercury anode or the calomel half-cell.

Decomposition Potential. The residual current either remains constant or rises slowly, until the decomposition potential is reached. Zinc ions then start being reduced at the surface of the mercury droplets with an accompanying sudden increase in current. A slight increase in potential then causes a great increase in the number of zinc ions reduced during the time interval during which the mercury droplet is attaining its maximum size before falling. A condition of so-called complete *concentration polarization* is soon reached. This means that the average concentration of reducible zinc ions at the surface of the mercury droplets soon becomes so low that the concentration gradient, which governs the diffusion of zinc ions to the surface, is practically equal to the concentration of zinc ions in solution. A constant reduction current is accordingly attained equal to the limiting current. The magnitude of the latter is then proportional to the concentration of zinc ions in solution and may be used as the basis of a quantitative method of determining zinc.

What has been said about the diffusion and migration currents of reducible ions, such as zinc ions, applies also to oxidizable ions, e.g., halide ions. Uncharged reducible and oxidizable molecules, such as many organic compounds, do not, of course, ionize and so do not carry a current.

Even in the absence of a high concentration of electrolyte the reduction current due to such molecules is mainly a diffusion current. Dipolar uncharged molecules, however, will undergo orientation and acquire motion toward the electrode, producing in effect a migration current. But here too the presence of electrolyte will correct this condition.

The Polarogram. Figure 10-2 shows the polarogram as a smooth line. Actually what may be obtained in practice is a saw-toothed line such as is indicated in Fig. 10-3. The oscillations in the polarogram have two causes: The first is the periodic growth of the mercury droplets followed by their fall, with the consequent rise and fall of the electrolytic current. The usual galvanometer in a polarograph does not give a response which is rapid enough to record the true current values corresponding to the growth cycle of the mercury droplet. It is therefore not accurate to measure either the top or the bottom of the oscillations. The average of these oscillations should be measured as the best indication of the true average current value. The second cause applies to some automatic recording instruments in which unfiltered alternating current gets through to the recording. This fault is less pronounced in some makes than in others.

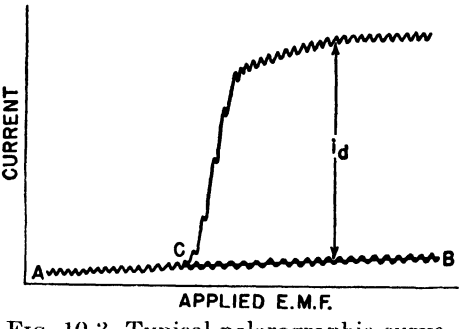


FIG. 10-3. Typical polarographic curve.

To get an accurate measurement of the diffusion current, it is important to correct properly for the residual current. This may be done by actually running a "blank" polarogram on the medium in which the reducible substance is to be run. In Fig. 10-3 this would be represented by the line ACB. The diffusion current i_d is then measured, as indicated, between the curve of the limiting current for the reducible substance and the curve of the residual current. Usually, however, it is not necessary to make a separate determination of the residual current. The latter generally rises linearly and uniformly so that the curve of the reducible substance may be extended by extrapolating AC as a straight line toward B. The diffusion current is then measured to the straight line CB instead of to the corresponding measured residual-current wavy line CB.

This device is particularly useful when a polarogram comprises several waves due to the presence of several reducible substances, such as are shown in Fig. 10-4. With such a mixture, where the waves of the consecutive constituents are separated sufficiently, e.g., with a mixture of cobalt and manganese, it is possible merely to extrapolate the curve of the limiting current of one substance, cobalt ion (Co^{++}), and to use the resulting line to measure the diffusion current of the next reducible sub-

stance, manganese ion (Mn^{++}), as indicated. Where the waves are not well separated, as with zinc ion and cobalt ion, no device can give an accurate measurement of the diffusion current, although approximations of limited accuracy may be obtained.

Ilkovic Equation. The diffusion current may, with some limitations, be calculated theoretically by means of the Ilkovic equation:

$$i_d = 605\ nD^{1/2}Cm^{2/3}t^{1/6} \tag{10-1}$$

In this equation, i_d is the average current in microamperes during the growth cycle of a single droplet of mercury; n is the quantity of electricity in faradays required for the electrolysis of 1 mole of the substance undergoing the electrode reaction; D is the diffusion coefficient of that

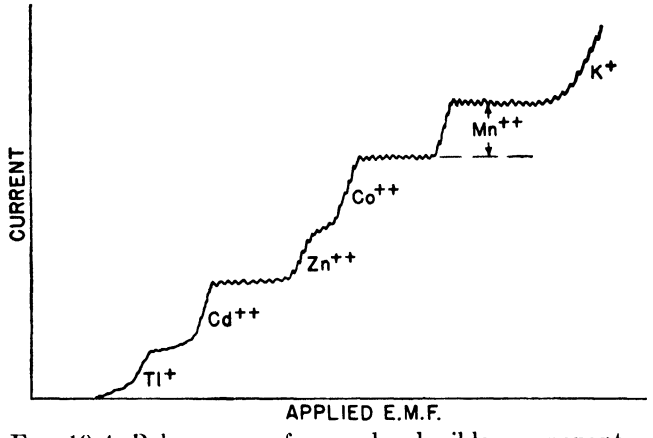


FIG. 10-4. Polarogram of several reducible components.

substance expressed in the units $cm^2\ sec^{-1}$; C is its concentration in millimoles per liter; m is the weight of mercury flowing from the capillary per unit time, and is expressed as mg sec^{-1}; and t is the drop time, or the time in seconds between successive droplets of mercury. Corrections of the Ilkovic equation have been worked out and published in attempts to bring it into closer adherence to the facts.[1,2] Nevertheless, it would appear that adherence of a system to the equation, at least to an approximate degree, may be used as a criterion of whether the current is controlled by diffusion alone or not.

It should be apparent from the Ilkovic equation that it could be used for the purpose of analysis. If the characteristics of the capillary have been established so as to fix the value of the term $m^{2/3}t^{1/6}$, and a given substance is undergoing a definite electrode reaction so that n and $D^{1/2}$ are also fixed, then for that particular system under those exact conditions,

$$C = ki_d \tag{10-2}$$

In other words, the concentration of the substance in question may be

calculated from the measured diffusion current. It might accordingly be inferred that, after the diffusion coefficient D has been established for any particular analytical application, it would be a simple matter thereafter to determine that substance without having to use an empirical calibration against a standard. Actually, the diffusion coefficient for a given substance varies with the concentration of the substance and with the ionic strength of the solution, so that for practical analysis it would have to be redetermined for the various conditions of concentrations of electrolytes and impurities which might be encountered. The equation is therefore not used very much for analysis. It is, however, important for theoretical uses, particularly for calculating n, the number of electrons involved in the electrode reaction, and for an understanding of the effects of some variables in polarographic analysis.

Polarographic Maxima. One variable, not predicted by the Ilkovic equation, which must be controlled is the polarographic maximum. It is found very often that, instead of waves which round off nicely as the limiting current is approached, waves with maxima are obtained. These may have sharp peaks or they may be well rounded. Figure 10-5 shows some of the types of maxima which may be obtained. Maxima are reproducible in a given solution and may be retraced in the direction either of increasing or of decreasing potentials. The maximum current, like the diffusion current, remains constant regardless of the length of time of electrolysis at a given potential. Unfortunately, the height of the maximum bears no simple relationship to the concentration of the electroreducible or electro-oxidizable substance involved. In addition, it is affected by the presence or absence of chance impurities, and by changes in their concentration. In general, maxima decrease in size with increasing drop time and increase with an increase in electroactive material. Practically, the analytical chemist must use "maximum suppressors" so as to do away with maxima.

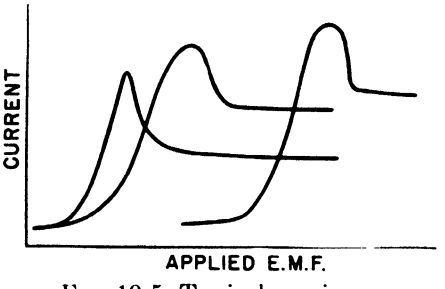


FIG. 10-5. Typical maxima.

The reasons for the formation of maxima are complicated and not yet completely understood. Nevertheless, a few brief remarks should be made about the theoretical background to serve as an introduction to a consideration of maximum suppressors.

If the drop time, or the surface tension at the interface between the mercury droplets and the solution, is plotted against the applied potential, the so-called "electrocapillary curve" (Fig. 10-6) is obtained. This indicates that the surface tension goes through a maximum (the electro-

capillary zero) at about −0.5 volt vs. the saturated calomel electrode. The surface tension is roughly proportional to the drop time t and, according to the Ilkovic equation [Eq. (10-1)], the diffusion current is proportional to the one-sixth power of t. Therefore, the diffusion current for a given electrode reaction will depend upon the relationship of the half-wave potential to the potential of the electrocapillary zero, in addition to other factors.

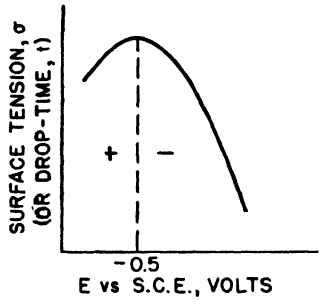


FIG. 10-6. Electrocapillary curve. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. VIII-2. By permission of the publishers.*)

If now polarographic maxima are again considered, it is seen that they may be classified, by reference to the electrocapillary curve, as positive maxima or negative maxima, depending upon whether they come at a more positive or more negative potential than that of the electrocapillary zero. Polarographic maxima are caused by mechanisms which undoubtedly involve both surface activity and electrokinetic phenomena. Positive maxima occur under conditions where the mercury droplets have a positive charge, and negative maxima where they have a negative charge.

Maximum Suppressors. Although some surface-inactive ions have some suppressive effect on maxima, the greatest effect is produced by surface-active ions or surface-active nonelectrolytes. Surface-active cations, which, of course, have a positive charge, are usually most effective in suppressing negative maxima, and surface-active anions in suppressing positive maxima. Thus traces of acid dyes, such as the sodium salt of methyl red indicator, a surface-active anion (in less than 0.001 per cent concentration), suppresses the positive lead maximum; but the lead maximum is not suppressed by methyl red in an acid medium, where the dye acts as a cationic surface-active compound. The positive thallium maximum is suppressed by acid fuchsin (an anionic surface-active substance). The negative nickel maximum is not suppressed by acid fuchsin, but it is by (cationic) basic fuchsin. However, there are exceptions to this regularity of behavior. For example, some positive dyes are as effective as negative dyes in suppressing the positive oxygen maximum.

Surface-active nonelectrolytes are very often effective suppressors. Gelatin in low concentrations is particularly good. A concentration of 0.02 per cent completely suppresses the lead maximum. When gelatin is present in a concentration greater than 0.01 per cent, its effect in decreasing the diffusion current must be taken into account. Sulfur-containing organic substances, alpha naphthol, and naphthalene, serve as suppressors. Oxygen suppresses the maxima of various metal ions, even

though in its own reduction pronounced maxima are found. In fact, so many substances serve as maximum suppressors that often unpurified or crude samples may contain impurities which act as suppressors. But unless it is certain that such impurities will always be present in suitable concentrations, it may be better to add a suppressor. To minimize possible side effects, which may sometimes occur, such as a shift in the half-wave potential or the magnitude of the current, the suppressor should always be used in as low a concentration as is effective.

Temperature. Another variable which must be controlled is temperature. In the Ilkovic equation [Eq. (10-1)], every term except n is a function of temperature to a lesser or greater extent. Even the constant 605 holds only for 25°C and increases with the decrease in the density of mercury as the temperature rises—but only by 0.012 per cent per degree. The temperature coefficient of D, however, is about +2 per cent per degree for most ions, since it is determined by, and is practically equal to, the temperature coefficient of the equivalent conductance of the ions. For uncharged substances, the temperature coefficient of D is probably of a similar magnitude. The temperature coefficient of the concentration C equals that of the density of the solution and is usually small (about −0.025 per cent per degree) for aqueous solutions; for solutions containing organic solvents it may be greater. The temperature coefficient of m depends upon that of the density and viscosity of mercury and is in the vicinity of +0.3 per cent per degree. The temperature coefficient of the drop time t depends upon that of the interfacial tension at the mercury-solution interface and is small enough to be neglected. The resultant of these temperature effects is such that the diffusion current will increase by from 1.3 to 2.3 per cent with each degree increase in temperature. Furthermore, the half-wave potential also changes appreciably with temperature. For practical analytical purposes, the temperature should be controlled to within ±0.5°C in order to keep variations due to temperature changes within ±1 per cent. It is recommended to work at 25°C. Although thermostatic temperature control is convenient, it is not essential. A large vessel of water to which hot or cold water is added as needed is satisfactory for most purposes.

Catalytic Waves. Another phenomenon of which the polarographer must be aware is that of the catalytic wave. This may, if recognized, be useful as a quantitative tool but, if unrecognized, may lead to confusion. The catalytic wave is caused by current which arises not by diffusion but, as the name implies, by the effect of a substance in catalyzing the reduction of a second substance. The catalytic wave which is most often encountered is the hydrogen wave. Hydrogen ion is not generally reduced, to be then discharged as free hydrogen, at the equilibrium potential for the hydrogen–hydrogen ion system. The reduction usually

occurs at a more negative potential, the difference being known as the "hydrogen overvoltage." The exact value of the hydrogen overvoltage depends upon the nature of the electrodes and the composition of the medium. If there are introduced into a solution exhibiting a characteristic hydrogen overvoltage small amounts of certain substances, the reduction of hydrogen is catalyzed so that the overvoltage is decreased and a hydrogen wave is obtained at a less negative potential than would be characteristic of the system in the absence of the catalyst. The catalytic hydrogen current will increase with the concentration of the catalyst, although usually not in a linear manner. The hydrogen current can therefore be used for the quantitative determination of the catalytic substance by setting up an empirical calibration curve.

As examples of catalytic waves, the following may be noted: Platinum reduces the hydrogen overvoltage and produces a "catalytic" wave, the height of which is some twenty times greater than that caused by the simple reduction of platinum. This effect has been used to determine platinum in the presence of palladium, which does not produce a catalytic wave.[3] Perrhenate produces a catalytic wave which has been used to determine traces of rhenium in manganese salts.[4] Quinine, quinidine, cinchonine, cinchonidine, codeine, morphine, narcotine, hydrastin,[5] and strychnine[6] yield catalytic waves. Probably the most important catalytic waves, which are of great significance in biological studies, are those obtained with traces of cysteine and with proteins containing a sulfhydryl group, in the presence of cobalt (ref. 7, p. 850).

Influence of Polarographic Medium. Oxidations and reductions of most organic substances and of some inorganic substances involve hydrogen ions. The half-wave potential for those systems will accordingly be influenced by the pH of the medium. It is therefore necessary to use buffers to maintain constant pH during the course of most polarographic analyses. If a sufficient concentration of buffer is used, it may furnish enough electrolyte to eliminate the migration current without the necessity of adding additional electrolyte. A solution containing the necessary buffer, electrolytes, and maximum suppressor is termed a "supporting electrolyte." It has been shown, however, that for some systems it is necessary to specify the nature of the supporting electrolyte even more rigorously to avoid changes in the half-wave potential.[8] The latter may change with a change in the chemical composition of the buffer and with a change in the total concentration of ionic material. For a given electroactive material, and with a given type of buffer, it may be possible to find a pH at which the half-wave potential is fairly independent of the ionic strength of the medium within wide limits. Such a pH would be particularly favorable for analysis, unless it should be necessary to work at a different pH in order to be able to take advantage of a separation in

half-wave potentials of two or more constituents which could be achieved by working at some other pH. The contribution of the sample itself to the ionic strength of the electrolysis solution may also have to be considered where a large sample must be taken for the analysis of a minor constituent.

Interference of Oxygen. Oxygen is reduced at the dropping-mercury cathode to give two waves, the first representing reduction to hydrogen peroxide and the second reduction of hydrogen peroxide to water or hydroxyl ion. The first wave has a half-wave potential vs. the saturated calomel electrode of about −0.1 volt. The $E\ ½$ of the second wave is at −0.9 volt, but the wave is drawn out over a range of from −0.5 to −1.3 volts. These waves interfere with many polarographic determinations so that oxygen in the solution must be removed before proceeding with the analysis. This is done usually by bubbling nitrogen through the solution in the electrolysis cell by means of the lower arm of the cell. After about 10 min bubbling of nitrogen, the nitrogen line is removed from the bottom tube and attached to the upper tube so as to maintain an atmosphere of nitrogen and prevent reabsorption of oxygen. Agitation of the solution by bubbling during the analysis must be avoided. Ordinarily, commercial nitrogen may be used without purification since its oxygen content is too low to do any harm. For special purposes it may be necessary to pass the gas over heated copper. To avoid volatilizing the solvent in the cell, the gas should be bubbled through water, for an aqueous solvent, or through whatever solvent is being used.

In neutral or alkaline solutions, where sulfite is not reduced polarographically, the addition of about 0.1 gram of anhydrous sodium sulfite per 100 ml will remove oxygen, in about 10 min, more completely than sweeping with nitrogen. This technique is a practical one where sulfite is known to cause no interference. In some analyses oxygen does not interfere and its removal may be avoided.

APPARATUS

Instruments. Two general types of instruments are used in polarography, the *manual* type and the *automatic* type. With the former, a potential setting is made by hand and a current reading is observed. This process is repeated at as many individual potential settings as are required. With the automatic type of instrument, the potential settings are varied continuously and mechanically over a chosen range and the corresponding current readings are plotted automatically against the potential values. An automatic apparatus is convenient and saves time but is naturally more expensive than manual instruments. The latter are just as accurate as the former, so that one should not be deterred from

the use of polarographic methods by the misapprehension that expensive equipment is needed.

The essential requirements for a polarographic circuit, as indicated in Fig. 10-1, are a means of applying a known voltage to the cell and a means of measuring the corresponding current, which is usually smaller than 50 microamperes (μa). Such circuits have been described by a number of authors and may be easily constructed of commonly available and

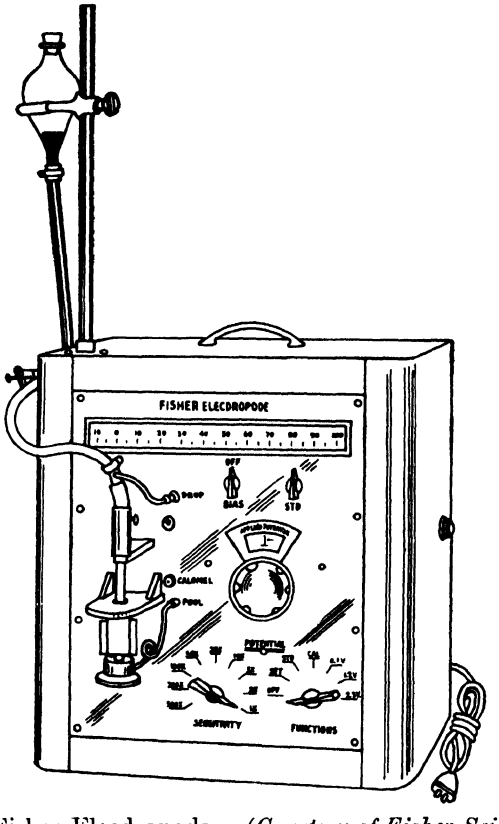


FIG. 10-7. Fisher Elecdropode. (*Courtesy of Fisher Scientific Co.*)

inexpensive parts. Kolthoff and Lingane,[7] Lingane,[9] Rulfs,[10] and Müller[11] have described the construction of such instruments.

Manual Instruments. Several commercial manual instruments are available which are compact and convenient. The Fisher Elecdropode (Fig. 10-7) is a serviceable instrument, but if used in a laboratory which is subjected to vibration, it should be mounted on a base designed to reduce vibration such as alternate layers, starting from the bottom, of felt, sheet lead, sponge rubber, and again sheet lead. The electrolytic cell provided with the instrument should also be replaced by one which can be placed in a bath for temperature control. The Aminco polarometric analyzer is a portable manual instrument. The Sargent manual

indicating polarograph model III (Fig. 10-8) is a practical rugged instrument which is not very sensitive to laboratory vibrations. The Cambridge Voltamoscope is a manual instrument made by the Cambridge Instrument Company, New York, N.Y.

Automatically Recording Instruments. The original automatically recording polarograph was that invented by Heyrovský, the originator of polarography. In the present instrument, a polarographic curve is traced on photographic paper, provision being made for recording several curves on the same sheet of paper. The need for developing the photographic recordings and the impossibility of observing the curve as it is



FIG. 10-8. Sargent manual polarograph, model III. (*Courtesy of E. H. Sargent and Co.*)

being traced make this instrument less convenient than the more recently developed pen-recording instruments. It is, however, less expensive.

The Sargent model XXI polarograph (Fig. 10-9) and the Leeds and Northrup Electro-chemograph, type E (Fig. 10-10) are pen-recording types which are of the utmost utility where a sufficient volume of polarographic work is contemplated to justify their cost. Papers by James J. Lingane[12,13] and manufacturers' literature discuss their respective merits. The Leeds and Northrup instrument would seem to have some advantages over the Sargent polarograph. The Voltamograph, an apparatus made by the Cambridge Instrument Company, is a pen-recording instrument also (ref. 13, p. 91).

The automatically recording instruments are particularly useful in studying new or unknown systems. Curves may be obtained rapidly under varied conditions for the purpose of obtaining qualitative information or for the purpose of studying suitable conditions for quantitative

analysis. After these conditions have been fixed for a given system, it may then be possible for routine purposes to set up the analysis on a manual instrument, with as few as two single readings of current at predetermined voltages serving for the analysis, without the necessity of obtaining a complete curve.

Oscillographic Polarographs. In oscillographic or cathode-ray polarographs the whole range of potentials of interest is rapidly scanned, the



FIG. 10-9. Sargent polarograph, model XXI. (*Courtesy of E. H. Sargent and Co.*)

complete polarogram being traced on a cathode-ray screen.[14] Such instruments have a potential usefulness in following rapidly changing chemical systems.

Derivative Polarographs and Vibrating Electrodes. Some other developments, which are at present still in a highly experimental stage, include derivative polarographs,[15,16,17] which are designed to plot the first derivative of the current against voltage, thus giving peaks at the half-wave potentials; and the vibrating electrode,[18] which is a device whereby the mercury droplets are knocked off the capillary before reaching full growth, thus eliminating some of the oscillations in the polarograms caused by the growth of the droplets.

Dropping Electrode, Cells, and Assembly. *Cells.* The original type of cell devised by Heyrovský consisted merely of a small Erlenmeyer flask, with side tubes for introducing an inert gas and for electrical contact with a pool of mercury which served as the anode. In the presence of chloride ion, sufficient mercurous chloride is formed for the pool of mercury to serve as a calomel electrode. But this reference electrode does not give a constant enough reference potential for all work, so that

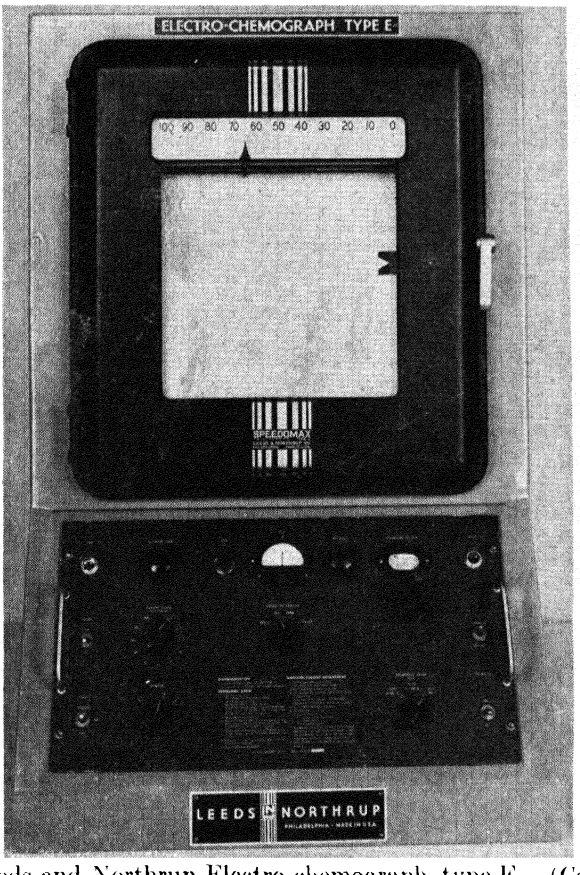


FIG. 10-10. Leeds and Northrup Electro-chemograph, type E. (*Courtesy of Leeds and Northrup Company.*)

it is more common to use a cell with which a saturated calomel electrode may be connected as the reference electrode. Figure 10-11*a* is a sketch of a type described by Lingane and Laitinen[19] which is generally useful.

Instead of including the saturated potassium chloride solution, mercury, and calomel in the side of the cell, as indicated in Fig. 10-11*a*, a more convenient arrangement is to have a separate calomel electrode as illustrated in Fig. 10-11*b*. The bottom of the indented tube is prepared by covering the lower end with a sheet of rubber or plastic and filling the tube with hot agar-agar solution containing potassium chloride, prepared

as described below, and allowing it to cool. The rubber is removed and the well at the upper end of the tube is charged with a mixture of calomel, mercury thoroughly mixed with calomel, and saturated potassium chloride solution also saturated with calomel. This mixture must cover the top of the agar plug. The calomel half-cell may be set into the right side of the electrolysis cell as shown in Fig. 10-12. Other types of cells have been described,[20] including some for use with small volumes of solution for micropolarography.[20,21]

The sintered-glass disk must be fused in the cell properly and of such porosity that, on the one hand, no leakage occurs and, on the other hand,

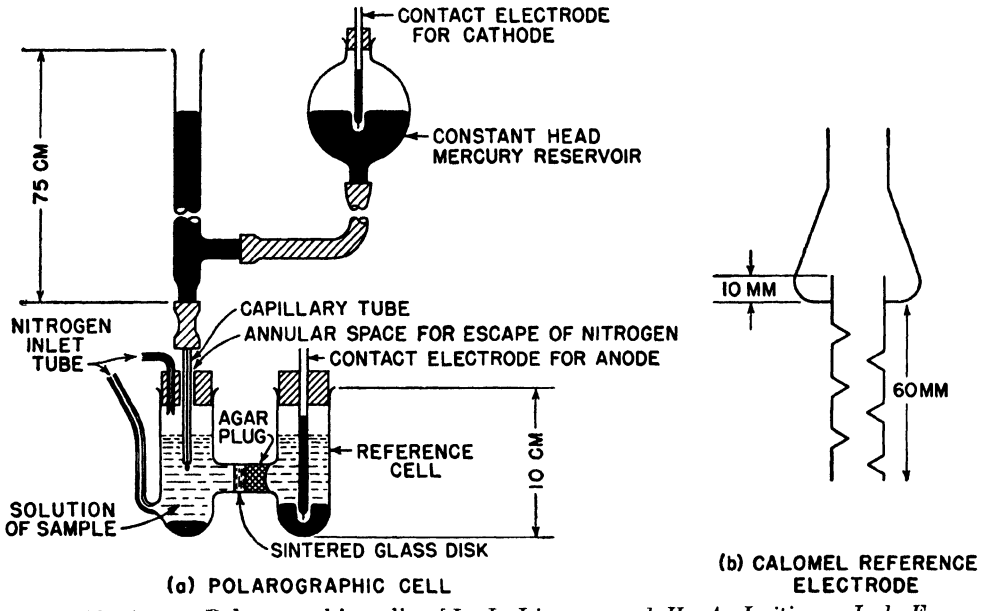


FIG. 10-11. *a.* Polarographic cell. [*J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem., Anal. Ed.*, **11**: *504 (1939)*.] *b.* Calomel reference electrode.

too great a resistance is not introduced. A disk approximately 20 mm in diameter should pass about 20 to 50 ml of water per min, under a pressure of from about 5 to 15 mm of mercury, produced with a vacuum pump or an aspirator. The agar plug may be made by heating 3 grams of powdered agar-agar in a solution of 75 ml of saturated potassium chloride solution and 30 ml of distilled water, pouring the hot solution onto the disk, and allowing it to cool. Kolthoff and Lingane (ref. 7, p. 362) describe a convenient device for making the agar plugs. If the cell is used daily, it should be cleaned at 2- to 4-week intervals in order to prevent too great an increase in resistance. This is done by removing the agar, washing the cell successively with hot water and chromic–sulfuric acid cleaning solution by the aid of slight vacuum, and rinsing thoroughly.

Capillaries. Capillaries should be about 7 to 8 cm long, with a uniform internal diameter of about 0.05 mm. "Marine barometer tubing" (made by the Corning Glass Works, Corning, N.Y.) is quite satisfactory. The tip of the capillary should be quite horizontal because otherwise the mercury droplets push against the glass before they attain full size. Absence of vibration is necessary to prevent the drops from falling before reaching full size. Connections are best made with Tygon tubing which may be

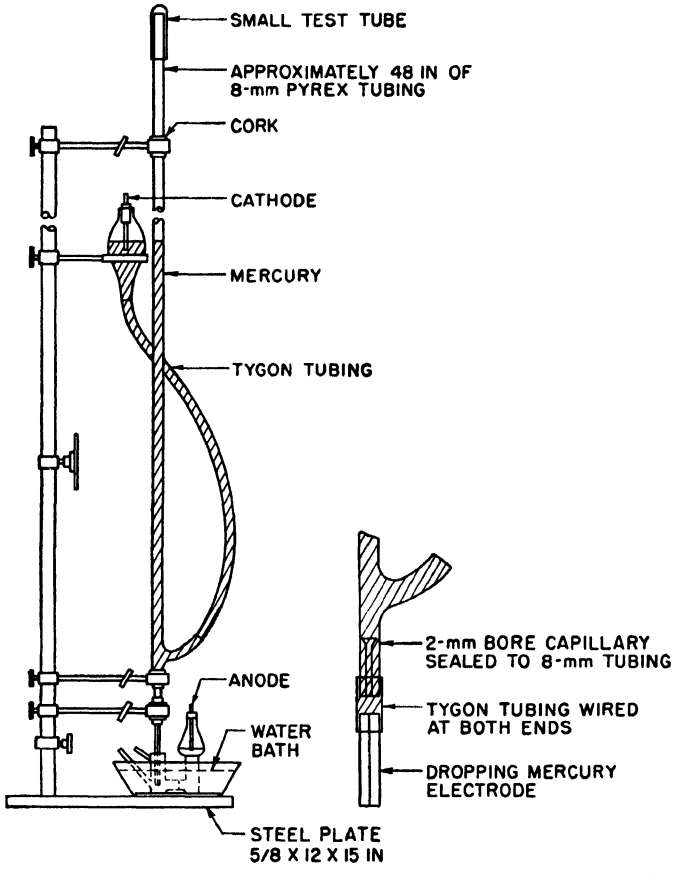


FIG. 10-12. Dropping-mercury electrode assembly. [*W. Seaman and W. Allen, Sewage and Ind. Wastes*, **22**: *912 (1950), Fig. 1.*]

used without any more elaborate cleaning procedure than just rinsing with water. If rubber tubing, or preferably neoprene, is used, surface impurities should be removed by soaking for several hours in hot concentrated sodium hydroxide solution, rinsing with water, and drying. Tygon is advantageous also because of its transparency, which makes possible the detection of undesirable air bubbles, and because of its tight adhesion to glass.

Mercury Pressure. A system for keeping the mercury pressure constant is important because the diffusion current depends upon the square

root of the pressure. Elaborate all-glass equipment has been proposed for this purpose, but the simple arrangement indicated by Lingane and Laitinen (Fig. 10-11)[19] is quite satisfactory.

Care of Capillary. After use, the capillary should be removed from the cell and washed with distilled water while the mercury is still flowing.

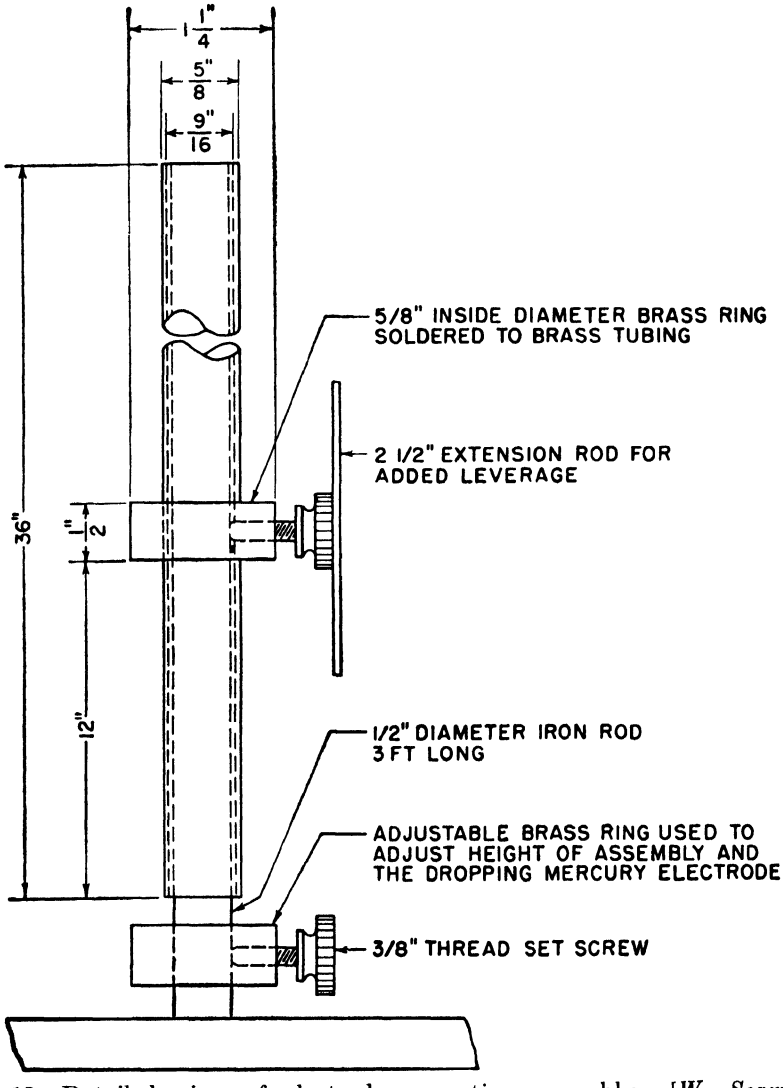


FIG. 10-13. Detailed view of electrode-supporting assembly. [*W. Seaman and W. Allen, Sewage and Ind. Wastes*, **22**: *912 (1950), Fig. 2.*]

The mercury pressure should then be decreased, while the capillary is secured by a clamp, until the flow stops. The capillary should not be placed in the cell or in water while mercury is not flowing because the entrance of water or solution into the tip may dirty it and lead to erratic behavior. If the tip becomes dirty, it may usually be cleaned by immers-

ing it in concentrated nitric acid while the mercury is flowing and then rinsing it thoroughly with distilled water. Capillaries properly used seldom require replacement.

Cell and Capillary Assembly. Figures 10-12 and 10-13 show a detailed arrangement which has proved convenient in practice for adjusting the height of the mercury reservoir and for inserting and removing the cell from under the capillary.[22] The stand consists of a ½-in. metal rod, approximately 3 ft long, and threaded at one end, and a heavy metal plate, approximately ⅝ by 12 by 15 in., drilled and threaded to take the ½-in. rod. A brass tube of slightly larger inside diameter than the outside diameter of the iron rod is fitted with a clamp so that it may be set at any desired position on the rod. The capillary is attached to an 8-mm Pyrex glass tube, about 4 ft in length, by means of a short length of Tygon tubing. A glass *T* is sealed to the glass tubing 2 in. above the top of the capillary, and a 3-ft length of ¼-in. Tygon tubing is connected between a glass leveling bulb and the capillary. The entire assembly is mounted by means of clamps to the brass tube.

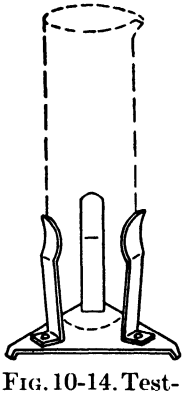


FIG. 10-14. Test-tube support for polarographic cell. (*Courtesy of Arthur H. Thomas Company.*)

Calibration of the instrument and subsequent analysis of samples are carried out at a fixed dropping rate of mercury. The dropping rate is measured at the start of a series of determinations, and as it is unnecessary to change the height of the mercury column when placing the capillary in the cell, the manipulation of the electrode is more convenient than by the usual method. The cell, in a test-tube support (Arthur H. Thomas, Philadelphia; see Fig. 10-14), is placed in a porcelain pan, which is filled to a depth of about 2 in. with water. The anode (Fig. 10-12) is placed in the calomel reference electrode (described in Fig. 10-11*b*). This assembly is convenient to insert and remove from the electrolysis cell. Electrical contact is made through a platinum wire sealed in the anode tube which contains mercury. The calomel half-cell needs to be renewed only infrequently.

Quality and Care of Mercury. Only highly purified and redistilled mercury should be used for the dropping-mercury electrode. Atmospheric dust should be kept out of the system by the use of a cotton plug. The mercury in the reservoir should not be permitted to reach a low level to prevent small fibers or particles of dust or oxide that may be floating on the surface from reaching the capillary. If foreign matter is noticed on the surface, it is advisable to pour off the mercury and replace it with clean mercury.

A simple test for detecting impurities in mercury[23] is to filter the mer-

cury through a chamois or a pinhole in a paper cone and to observe the filtered mercury. Impure mercury will form a film or deposit on the glass almost immediately after filtration. Even the purest mercury may show such a film after long standing. Another test[24] is to shake the mercury in a thoroughly clean flask with distilled water containing no organic matter. Pure mercury forms a fairly stable foam which disappears gradually in from 5 to 15 sec. Very dirty mercury does not foam at all. Mercury containing mere traces of impurities produces a foam which is stable for only 1 or 2 sec and then collapses suddenly.

According to O. H. Müller (see Bibliography, "Polarography," p. 1863), mercury which has been used should be purified by shaking it with water in a heavy separatory funnel and then drawing air through it by applying suction at the top and properly regulating the stopcock. After the impurities have been floated off into the water layer as a thick scum, the lower layer is allowed to drop through the ungreased stopcock in a fine stream of small drops into a solution of nitric acid and mercurous nitrate in a heavy-walled separatory funnel. After having been shaken for several minutes with the acid, the mercury is transferred in a similar manner to distilled water and washed, a second time if necessary, to remove acid. If a stable foam is not obtained, a second washing with acid is needed. Mercury so purified should leave no deposit on glass after filtration (as above) and is suitable for a "pool" mercury anode. For a dropping electrode it should be vacuum-distilled. Those desiring to avoid purifying mercury may purchase satisfactory "triple-distilled" mercury.

APPLICATIONS

Generally speaking, the dropping-mercury electrode may be used either as a cathode (for reductions) or as an anode (for oxidations). Practically, however, the latter application is limited by the fact that the oxidation of mercury to mercurous ion starts at zero potential and becomes very large at about +0.45 volt vs. the saturated calomel electrode. The application of most anodic reactions must therefore be carried out at metal electrodes. A platinized platinum electrode has been recommended for this purpose.[25] The use of the dropping-mercury electrode as a cathode is limited by reduction of ions, such as Na^+, K^+, or those of other alkali metals, in the supporting electrolyte. Since these reductions take place at fairly high negative potentials (around −2 volts) they usually offer no difficulty. Where the alkali metals do interfere, or where they themselves are to be determined, a supporting electrolyte consisting of tetraalkylammonium salts or hydroxide may be used.

Inorganic Analysis. Inorganic polarographic analysis is usually concerned with the reduction or oxidation of simple metallic or other ions

from one oxidation stage to another; e.g., $Fe^{III} \rightarrow Fe^{II}$, $Cr^{VI} \rightarrow Cr^{III}$; or with the reduction of simple metallic ions to the free metal; e.g., $Cu^{II} \rightarrow Cu$ or $Cu^{I} \rightarrow Cu$. The metal may either dissolve in the mercury as an amalgam or it may precipitate. There may also be two or more consecutive steps, involving first a change in the state of oxidation of an ion, followed by a reduction to the metal, in which case the polarogram may consist of two or more waves; e.g., $Cr^{III} \rightarrow Cr^{II}$ followed by $Cr^{II} \rightarrow Cr$. The types of wave obtained will depend upon whether the systems are reversible or not, as illustrated in Fig. 10-15. Lack of reversibility due to a slow electrode reaction gives a curve such as curve 4, because more or less overvoltage is required to initiate and maintain the reaction.

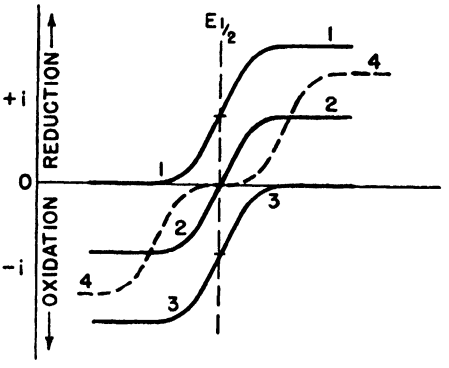


FIG. 10-15. Polarographic waves of oxidized and reduced forms of metals and other substances. (1) Cathodic wave of oxidized form. (2) Composite cathodic-anodic wave of mixture of the oxidized and reduced forms. (3) Anodic wave of the reduced form. (4) Composite cathodic-anodic wave for irreversible electrode reaction. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. XI-4. By permission of the publishers.*)

Complexing Agents. An important phase of inorganic polarography is the use of complexing agents. The half-wave potentials of simple metal ions are shifted, and usually to a more negative value, by complex formation. By the choice of suitable complexing reagents it is thus possible to broaden the scope of inorganic polarography, making it possible sometimes to enhance differences in half-wave potentials of different ions and otherwise to prevent interferences. Some examples of such complexes are oxalate complexes of ferric or ferrous ions, ammonia complexes of copper ion, tartrate complexes of various ions, and others.

The reduction of inorganic substances may also occur with un-ionized molecules. Thus nitric oxide may be reduced to ammonium ion; cyanogen to cyanide ion; oxygen to hydrogen peroxide; and hydrogen peroxide to water.

Organic Analysis. It has been suggested[26] on the basis of data available on the reduction of organic compounds that in general those compounds are reducible at the dropping-mercury electrode which are reducible by chemicals (including dissolving metals) as contrasted with catalytic reduction. Since reductions of most organic compounds are irreversible, or contain irreversible steps, less is known of the interpretation of their waves than is known for most inorganic substances. Furthermore, many of the older recorded reductions are not reported in terms of the half-wave

potential. Rather so-called "reduction potentials" are given. In some, the emf at the point of contact with the curve of a 45° tangent to the wave was taken as the reduction potential; in others the emf at the point of maximum curvature was taken; and in still others that emf was taken at which an increase of 10 mv caused an increase in current of 0.019 μa. Such potentials are not constant for a given system, as is generally true for half-wave potentials, but change with the concentration of the reducible substance, with the sensitivity of the galvanometer, and with the drop time and the rate of flow of the mercury.

Standardization of Conditions. Each system to be used analytically should be standardized with respect to a number of conditions, as follows: Acid-base buffers should be used because hydrogen ions usually enter into organic reductions. The composition of the solvent should be fixed, particularly since mixtures of water with solvents such as alcohols, acetic acid, and others may be used, as well as nonaqueous media, and these may affect not only the half-wave potential but also the pH of the buffer being used. The half-wave potential of irreversible reactions is also sometimes affected by changes in the concentration and kind of electrolytes present. The nature of metal ions reduced previous to that of the organic material may influence the course of the reduction of the latter since the reduction may then be taking place at a dropping-mercury amalgam rather than at pure mercury.

Classes of Reducible Organic Compounds. Polarographic reductions have been carried out on the following classes of organic compounds, to mention only a few as illustrations of the scope of organic polarography: aliphatic carbonyl compounds, including aldehydes, ketones, hydroxy carbonyl compounds, sugars (ketoses), and dicarbonyl compounds; aromatic carbonyl compounds, including aldehydes, ketones and phenylalkyl ketones, halogen-substituted aldehydes, dicarbonyl compounds, α-β-unsaturated ketones; sex hormones; unsaturated carboxylic acids, such as fumaric and maleic acids; nitrogen compounds including quaternary salts of amines, amino acids (by effect upon the cobalt-catalyzed hydrogen wave), heterocyclic compounds, nitro compounds, and azo compounds. Organically bound halogen is generally reducible. Considerable application has been made of polarography to the study of biological systems. The reader is referred to the current literature, the Bibliography at the end of the chapter, and to the following bibliographies:

"L & N Bibliography of Polarographic Literature—Bibliography E-90 (1)," Leeds and Northrup Company, Philadelphia, Pa., 1950—from 1903 to mid-1949, arranged chronologically and indexed by authors and subjects.

"Bibliography of Polarographic Literature, 1922–1945," E. H. Sargent and Company, Chicago, Illinois—arranged chronologically and indexed by authors and subjects.

Stanley Wawzonek, Organic Polarography, *Anal. Chem.*, **21**: 61 (1949); **22**: 30 (1950); **24**: 32 (1952)—literature references and discussion by individual members and classes of organic compounds.

G. Semerano, Bibliografia Polarografica, *Ricerca sci.*, suppl. A, vol. 19 (1949)—comprehensive bibliography up to 1949.

J. Heyrovský, *Collections Czechoslov. Chem. Communs.*, **10**: 153 (1938); **11**: 98, 667 (1939); **12**: 156 (1947); **13**: 481 (1948); **14**: 569 (1949)—periodic bibliographical series.

Practical Application. The details of manipulation of any given polarograph will vary from one make of instrument to another. Since such directions are provided by the manufacturer, no attempt will be made to describe them here except in a general manner, but an attempt will be made to describe the approach to the two problems of devising a method of analysis for a system of materials not previously studied polarographically and for setting up a routine method of analysis.

If the sample of interest is a single substance or a mixture of known materials, curves should be obtained for each of the known materials (in a reasonable state of purity) alone and in admixture in proportions such as may be encountered in practice. If the material to be analyzed contains unknown impurities, a qualitative analysis may be conducted in any appropriate manner and then an examination may be made of synthetic mixtures of known ingredients. Sometimes with complex industrial samples this may be rather involved, if at all possible. It may, however, suffice to gain information concerning the presence of definite substances by making additions of those substances to the original sample and noting whether any given wave increases in height; furthermore, after noting the increment for a definite added amount of the known material, calculations may be made for the amount of that substance in the original sample. With both these approaches, data will be obtained relating the diffusion current to concentration at each voltage reading of interest for a particular substance. A linear relationship will usually be obtained so that concentrations may be calculated directly from wave heights. Sometimes, as when utilizing the catalytic hydrogen wave for analysis, the relationship may not be linear and must be plotted for use.

Pilot-ion Technique. Sometimes, in order to avoid the careful standardization of conditions, including temperature control, which these methods require, the so-called "pilot-ion" technique may be used. In this method, a known amount of foreign reducible material, known to be absent in the sample under consideration, is added to the solution being analyzed. The known added ion must have a characteristic half-wave potential sufficiently different from that of the unknown being investigated so that two clear-cut reduction waves will result. In order to minimize the effect of changing drop rate, the half-wave potential of the added standard should be as close as feasible to that of the unknown

being measured. Usually a difference of 0.2 to 0.6 volt between the half-wave potential of the unknown and the internal standard will suffice.

A series of solutions is prepared containing known variable quantities of the substance the concentration of which is to be measured and a fixed quantity of the internal standard. Polarograms are then obtained for these solutions and a plot is made of the concentration of desired constituent against the ratio of diffusion current of desired constituent divided by the diffusion current of the internal standard. This plot should result in a straight-line relationship.

In determining the concentration of an unknown solution, the concentration of internal standard previously chosen is added and the diffusion-current ratios are measured with the dropping-mercury electrode. From the previously made calibration chart the concentration of desired constituent in the unknown solution may be directly determined.

The use of the internal-standard method has the following advantages: only one calibration curve is needed and it may be used irrespective of changing dropping rates or capillaries. Temperature fluctuations over a limited range have no effect upon the calibration. It is thus only necessary to be able to prepare duplicate samples of the internal-standard solution from time to time in order to be able to use a fixed technique for routine determinations. In using this technique it must be remembered that the relative diffusion-current constants of a series of different substances vary somewhat with the temperature and with the kind of supporting electrolyte. A separate set of calibration curves is therefore necessary for each particular set of conditions. Where polarograms are to be run frequently, it is usually simpler to have proper temperature control and to standardize conditions rather than to use the "pilot-ion" technique.

Solution Make-up. In making up solutions for polarographic measurement, the principles discussed earlier should be kept in mind. Wherever possible, aqueous solvents are used, but water dilutions of organic solvents and even nonaqueous solvents may be used. There must be added a sufficient concentration of indifferent electrolytes; a maximum suppressor, in a fixed concentration at the lowest level found to be effective; and, unless the analysis is known not to be affected by changing pH, an acid-base buffer.

Supporting Electrolytes. Substances which are used as supporting electrolytes are diverse and great in number. There would seem to be no restriction on the kinds of electrolytes which may be used (assuming, of course, lack of electroactivity of the substance in the region under consideration), except that differences in electrolytes may produce differences in the half-wave potential and the diffusion current for a given electroactive material. Where buffers are needed, they may themselves

serve as the supporting electrolyte or they may be mixed in with the supporting electrolyte in a common stock solution. The maximum suppressor may also be added to the stock solution, except for gelatin, which is unstable and should be prepared fresh each day.

Maximum Suppressors. Two of the most useful maximum suppressors are methyl red and gelatin. Since methyl red is in itself an electroreducible material, care must be used in adjusting its concentration. In concentrations greater than 0.001 per cent the current due to the reduction of the methyl red itself must be deducted from the normally measured diffusion current. For this reason the concentration normally employed for methyl red is less than 0.001 per cent. Gelatin has a general suppressing effect upon diffusion currents in solution. Therefore, the concentration normally employed is no greater than 0.01 per cent. If higher concentrations are used, corrections must be made for the effect on the diffusion currents. Acid fuchsin, basic fuchsin, alpha naphthol, naphthalene, starch, methyl cellulose, organic soaps, alkaloids, fatty acids, and other substances have been used as maximum suppressors.

Buffers. Most common buffers, such as the phosphate buffers and the acetate buffers, are usually suitable. The carbonate buffer may not be suitable,[27] evidently because it cannot furnish or remove hydrogen ions from the surface of the mercury droplet as rapidly as the other electrode reactions occur. In general, a concentration of buffer one hundred times that of the reacting material is sufficient to assure adequate buffering.[28] For best control of the hydrogen-ion concentration at the interface of the mercury droplet and of the solution, a buffer with equal concentrations of acid and salt is desirable.

Solvent Media and Removal of Air. Curves should be run with a sufficient number of solutions, with variations in the media used, in order to establish the best medium for the analysis in question. In making these runs, air should be removed by adding sodium sulfite (about 0.1 gram anhydrous Na_2SO_3 per 100 ml of solution) where it does not interfere, or by bubbling in nitrogen, followed by the maintenance of a nitrogen atmosphere above the surface of the solution. When volatile solvents are used, the nitrogen should first be passed through some of the solvent used for making up the solutions, previous to entering the polarographic cell, in order to avoid evaporation of the contents of the cell with changes in concentration of the solutes. Sometimes this procedure is not advisable. Thus with acetone the solubility of air increases with an increase in the acetone concentration in aqueous solutions. Furthermore a rapid stream of nitrogen would cause a drop in temperature because of evaporation so that it is better merely to seal off the system.

Making Polarographic Determinations. Having found a suitable medium, polarograms may be run with known concentrations of purified

standard material under standard conditions of dropping rate and temperature. (This should be repeated in the event that the capillary is changed.) The tip of the capillary is immersed in the solution in the cell, which is thermostated, conveniently at 25°C (+0.25°C), and the height of the mercury column is adjusted until a proper drop rate is obtained (about 3 to 5 sec per drop). The height of the mercury in the column is marked and this height is maintained by periodic addition of triple-distilled mercury. The sensitivity is then adjusted by setting the instrument so that the galvanometer reading, with the sample in solution, will be about midway on the scale at a voltage just a few tenths of a volt less negative than that at which hydrogen discharge starts, or at which the supporting electrolyte is reduced, whichever comes sooner. If in doubt as to this voltage, the voltage at which the sensitivity is being tested is changed to a value a little more positive and then a little more negative to make sure that there is no great change in current. The sensitivity should also be such as to ensure the absence of too high a residual current. With conditions fixed, waves may be obtained for a sufficient number of concentrations of the substance being analyzed to establish linearity of the current vs. voltage curve for the range of interest, or to set up a curve if linearity does not hold.

Checking Constancy of Calibration. The constancy of calibration should be checked daily against a standard in order to avoid errors which may arise from changes in mercury pressure, in the characteristics of the capillary, or in the measuring instrument. Since, particularly with some organic substances, a pure standard may be difficult to preserve, a stable secondary standard may be used. A solution which is 0.005*N* in potassium dichromate and 0.1*N* in sodium hydroxide is a good secondary standard. Constant conditions of measurement can be assured by setting the instrument to give a definite reading with that solution.[29]

Simplified Routine Methods. After a system has been studied by means of complete polarograms, it is usually possible to set up a simplified system for routine analysis. From the complete polarograms, voltages are chosen at usually two points for each constituent, one before and one after the steep section of the wave, where small changes in emf will not produce large changes in current. Then in routine analyses it is necessary merely to get the difference between two current readings in order to be able to calculate the concentration of reducible material. The relatively less expensive manually operated instruments are suitable for this purpose. Current readings do not, of course, have to be expressed in electrical units but may be expressed in galvanometer scale readings or distances read off on a chart.

Polarography with Platinum Electrodes. The dropping-mercury electrode, as noted previously, suffers from the disadvantage that it is itself

oxidized at positive potentials close to zero, so that it cannot be used for many anodic reactions. Furthermore, many organic reactions are catalyzed by various electrode materials. Platinum electrodes have therefore been used to obtain current-voltage curves. The use of *stationary platinum electrodes* requires that the cell have good protection from thermal and mechanical disturbances. In addition, it is necessary to wait 2 min or longer between readings in order to get steady readings. Furthermore, with the stationary platinum electrode, the diffusion current has a high temperature coefficient. A platinized electrode[25] has been recommended which is claimed to furnish larger anodic currents which are reproducible to 2 per cent.

To overcome the disadvantages of the platinum electrode the *rotated platinum electrode* was introduced. This consists of a small wire suitably mounted on a stirrer which is rotated at a constant speed by means of a synchronous motor. This type of electrode has a limited applicability in some specific determinations, such as that of dissolved oxygen, bromine, iodine, chlorine, and silver of which (ref. 7, p. 411) even traces may be determined. Generally speaking, the electrode reactions are accompanied by polarization effects which complicate the polarograms as contrasted with those obtained with the dropping-mercury electrode. The rotated platinum electrode is of greatest utility in amperometric titrations, which will be discussed next.

AMPEROMETRIC TITRATIONS

"Amperometric titrations" is the designation of a system of titrations whereby the end point of the titration of a substance or substances with a standard reagent is measured by means of changes in current (amperage) at a fixed emf which are brought about by changes in concentration of the electroactive participants concerned. Amperometric titrations are thus different from potentiometric titrations, where changes in potential are measured, and from conductometric titrations, where changes in conductivity are measured.

General Types of Titration. There are several general types of amperometric titration depending upon whether the reaction involves oxidative-reductive systems or precipitations; and for the latter, upon whether the substance being titrated or the standard reagent or both are electroactive. The several types may be illustrated most easily by some concrete examples.

Consider first the titration of sulfate with lead. If to the solution containing sulfate in a polarographic cell an emf is applied which is sufficiently negative to give a diffusion current with lead ion, and the solution is titrated with a standard lead nitrate solution, no reduction current will

be obtained as long as the added lead is precipitated as lead sulfate. With each addition of lead in excess, an increasing diffusion current is obtained. A curve such as that shown in Fig. 10-16*A* is obtained. The intersection of the dotted extensions of the two lines indicates the end point. Such a curve is typical of those titrations in which an inactive substance (sulfate) is precipitated with an electroactive reagent (lead).

A second type is that of the reverse titration—lead nitrate with sodium sulfate. This is illustrated by Fig. 10-16*B*. This type of curve is char-

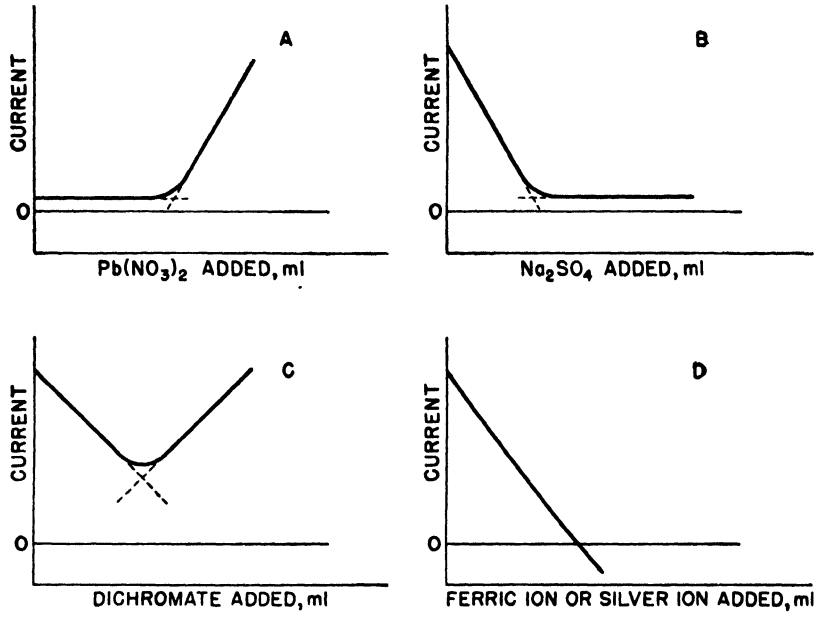


FIG. 10-16. Types of amperometric-titration curves. (*Otto H. Müller, "The Polarographic Method of Analysis," 2d ed., Chemical Education Publishing Company, Easton, Pa., 1951, Fig. 31. By permission of the publishers.*)

acteristic of precipitations of an electroactive substance with an inactive reagent.

If both the substance being titrated and the reagent are reducible at the emf chosen, as in the precipitation of lead with dichromate ion, the curve is typified by Fig. 10-16*C*. As the titration progresses, the concentration of lead is continuously lowered by precipitation with dichromate with a resulting continuously decreasing diffusion current. After the end point has been reached, the diffusion current starts to rise again because of the reduction of excess dichromate. Again the intersection of the extended lines indicates the end point.

A fourth case, shown in Fig. 10-16*D*, is that of an oxidative-reductive titration; e.g., titanous ion titrated with ferric ion, or of a precipitation of an anodically oxidizable anion with a cathodically reducible cation; e.g., chloride titrated with silver ion. The potential must be set at such

a voltage that either the negative diffusion current of the oxidizable ion or the positive current of the reducible ion may be obtained, depending upon which one is present during the titration. The negative current, indicative of the presence of oxidizable ion, decreases as the latter is oxidized or precipitated by the cathodically active substance. The current becomes zero when the oxidizable substance has reacted completely and none of the reducible titrant is present in excess, and then becomes increasingly positive as the cathodically active reagent increases in concentration. The slopes of the two lines need not necessarily be equal.

Choice of Electromotive Force. The choice of a suitable emf for the titration presupposes a knowledge of the polarographic curves of the substances contained in the sample. For example, consider Fig. 10-17, which gives a schematic curve of the waves due to two mutually precipitable substances A and B, one of which, A, has a wave with a limiting current that starts at the potential A, and the other of which, B, has a decomposition potential starting at B volts. If a titration is carried out at a voltage anywhere between A and B, A (and all other substances which are reduced before A) will give a diffusion current the magnitude of which will be proportional to the concentration of A (plus such other previously reducible substances) whereas B (and substances reduced beyond B) will not give any current. Thus, if B is used to titrate A, a curve such as Fig. 10-16B will be obtained. If A is used to titrate B, a curve such as Fig. 10-16A will be obtained. If a voltage C is chosen, a curve such as Fig. 10-16C will be obtained regardless of whether A is used to titrate B or vice versa.

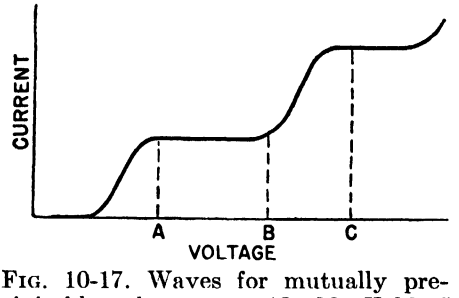


FIG. 10-17. Waves for mutually precipitable substances. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. XLVII-1. By permission of the publishers.*)

For oxidative-reductive titrations consider Fig. 10-18, a schematic diagram of the cathodic and anodic waves of the Ti^{IV}-Ti^{III} system in an acidified tartrate solution (curve 1) and the cathodic wave of the reduction of Fe^{III} to Fe^{II} in the same medium (curve 2). At voltages more negative than C (to the right of C) Ti^{IV} is reduced to Ti^{III}, and at voltages more positive than C (to the left of C) Ti^{III} is oxidized to Ti^{IV}. At B the full diffusion current of the oxidation of Ti^{III} is obtained. At voltages more negative than A (to the right of A) the full diffusion current due to the reduction of Fe^{III} is obtained. If then Ti^{III} is titrated with Fe^{III} according to the reaction

$$Ti^{III} + Fe^{III} \rightarrow Ti^{IV} + Fe^{II}$$

at a potential between A and B, a curve such as Fig. 10-16D will be obtained. A similar situation will exist when anions such as halides, sulfite, thiosulfate, thiocyanate, and sulfide, which yield anodic waves, are precipitated by cations which yield cathodic waves. An example would be the titration of iodide with mercuric ion.

General Procedure. Amperometric titrations may be carried out either with the dropping-mercury electrode or with the rotated platinum

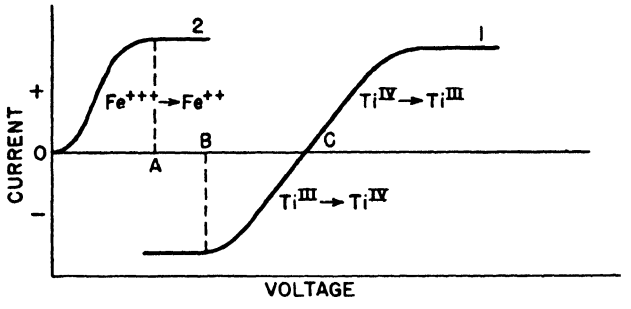


FIG. 10-18. Schematic curves for titanium and iron in a tartrate medium. (*I. M. Kolthoff and J. J. Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York, 1952, Fig. XLVII-6. By permission of the publishers.*)

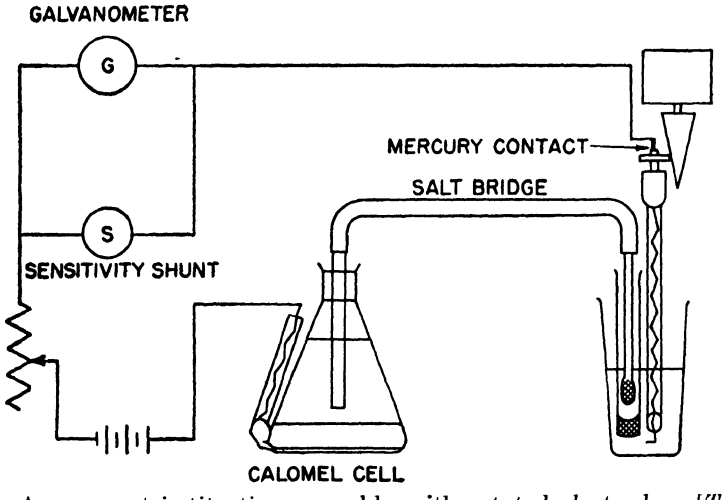


FIG. 10-19. Amperometric-titration assembly with rotated electrode. [*T. D. Parks and L. Lykken, Anal. Chem.*, **22**: *1444 (1950), Fig. 3.*]

electrode (ref. 7, p. 887, ref. 30). For the former, the conventional polarographic equipment is used with cells suitably modified to allow of the addition of the titrating reagent (ref. 7, p. 903). For the rotated platinum electrode a simpler arrangement may be used.[31] Figure 10-19 is a schematic diagram of such an arrangement. The rotated platinum electrode is more generally applicable since it may be used at positive potentials where the mercury anode may not be used. With both types it is necessary to remove oxygen if the electrolysis is conducted at an emf

at which oxygen would have a diffusion current. It is also generally necessary to add a supporting electrolyte containing, if needed, a maximum suppressor.

Advantages of Amperometric Titrations. Amperometric titrations have a number of advantages over polarographic measurements or potentiometric or conductometric titrations, which account for their increasing popularity. Highly dilute solutions may be titrated with generally better precision than is possible with polarographic determinations. Precipitation reactions involving relatively soluble reaction products may be utilized for titrations because the points near the end point, where the solubility would be greatest on account of the absence of excess common ions, are disregarded, and only points considerably removed from the end point are used. Here the common ion effect reduces the solubility. Rapid titrations are possible because only a few points are needed to plot the lines necessary to determine the end point. However, the necessity of plotting curves is sometimes disadvantageous. For routine work, a simple apparatus may be used; the essential instrument is a sensitive galvanometer with variable sensitivity. It is also not necessary to work at a definite temperature, provided that the temperature does not change during the titration, and wide variations in the supporting electrolyte and other conditions, such as the capillary characteristics, are not important so long as these conditions are constant during a titration.

Although the presence of foreign electrolytes is not harmful, the presence of electroactive impurities may be undesirable. If such impurities cause a high diffusion current, they may reduce the relative magnitude of the changes in diffusion current due to the reaction of interest and thus reduce the precision of the titration. To meet such a situation, chemical separations may be necessary or suitable conditions must be found to eliminate the diffusion current of the interfering substance.

Examples. Following are a few examples of the numerous amperometric titrations which have been reported: chloride, iodide, and bromide with silver nitrate, separately[32] and in mixtures;[33] phosphate with uranyl acetate;[34] lead with dichromate;[35] sulfate with lead nitrate;[36] molybdate with lead nitrate or perchlorate;[37] nickel with dimethylglyoxime;[38] cobalt, copper, and palladium with α-nitroso-β-naphthol;[39] copper with salicylaldoxime;[40] fluoride with thorium or lanthanum (ref. 41, ref. 7, p. 935); ferrocyanide with zinc;[42] titanous chloride with iron, dichromate, chlorate, bromate, and ferricyanide;[42,43] chloride with mercurous nitrate (ref. 7, p. 937); iodide with mercuric nitrate (ref. 7, p. 937); α-tocopherol with auric chloride;[44] 8-quinolinol (oxine) and phenol with potassium bromate;[45] *p*-aminosalicylic acid with bromate;[46] pyrazolone or naphthol coupling compounds with diazotized aromatic amines;[47,48] sulfhydryl groups with silver;[49] sulfhydryl groups in amino acids and proteins with

silver;[50] primary and tertiary mercaptans with silver and iodine.[51] Bibliographies are given in ref. 30.

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CHAPTER ELEVEN

Potentiometric Analysis

It is convenient to treat in one chapter potentiometric titrations and analysis by electromotive force (emf) measurement (measurements of potentials). This follows from the fact that a potentiometric titration usually consists of a number of measurements of potentials made for the purpose of determining when an increase occurs in the rate of change of potential with added titrant, as evidence of the end point in a titration. But individual emf measurements are also of great importance, particularly in pH determinations.

Potentiometric methods are based on the properties of galvanic cells. Galvanic cells are systems which are arranged to permit the energy of chemical reactions to be converted to electrical energy. The potential drop, or emf, of a galvanic system is dependent upon a number of factors, such as the nature of the electrodes, the temperature, and the concentration of the substances participating in the reactions at the electrodes. Analytical applications depend upon the relationship of concentration to emf when either the other factors are kept constant or corrections are applied for variations in those factors.

Galvanic cells always consist of two half-cells. At the electrode of one half-cell an oxidation reaction occurs, or in other words, a substance loses electrons which the electrode (the anode) takes up. At the electrode of the other half-cell, a reduction of a substance occurs, or in other words, the substance takes up electrons which it receives from the electrode (the cathode). If both electrodes are joined in a circuit the electrons given up to the electrode in one half-cell are transferred to the electrode in the other half-cell to effect the reduction there. This transfer of electrons constitutes the electric current which the galvanic cell produces. The emf of this current is dependent upon the concentrations (or more strictly activities) of the substances involved.

POTENTIALS OF GALVANIC CELLS

The potential of a galvanic cell is the resultant of the potentials of the half-cells involved and that of the liquid junction formed by the solutions concerned.

Consider the half-cell reaction

$$mA \rightarrow pB + ne$$

according to which a substance A is oxidized at one electrode to form the substance B with the release of n electrons. According to the Nernst equation, the potential of such a half-cell is represented by

$$E' = \frac{RT}{nF} \ln \frac{[B]^p}{[A]^m}$$

At the other electrode a reduction takes place with the absorption of n' electrons:

$$qC + n'e \rightarrow rD$$

the potential of which is

$$E'' = \frac{RT}{n'F} \ln \frac{[D]^r}{[C]^q}$$

R is the gas constant, T the absolute temperature, F the faraday, and the bracketed letters are concentrations (or activities) of the substances mentioned.

Since it is necessary to join the two cells by two different electrolytes at the same concentration, or by two different concentrations of the same electrolyte, or by two solutions of different concentrations of different electrolytes, a potential Ej, the liquid-junction potential, is also set up. The potential of the galvanic cell E is

$$E = E' + E'' + Ej$$

It is usually impossible to determine liquid-junction potentials accurately. Galvanic cells are therefore ordinarily arranged to minimize the liquid-junction potential (by using a salt bridge) and the latter is then disregarded. A *salt bridge* consists simply of a tube containing an electrolyte in high concentration which connects the two cells. It is arranged in some manner, sometimes by the use of an agar plug, so as to avoid diffusion of the contents of the bridge.

The potential of a galvanic cell can be measured accurately, but not that of the half-cells involved, because an isolated half-cell produces no flow of current until it is placed in a circuit with another half-cell. However, the relative magnitudes and signs (positive or negative) of half-cells to one another are of the utmost importance in electrochemistry. The

convention has therefore arisen of referring all half-cell potentials to that of the half-cell reaction

$$H_2 = 2H^+ + 2e \qquad (11\text{-}1)$$

The standard potential E^0 produced by this reaction, which is the potential when H_2 is at a pressure of one atmosphere and the activity of H^+ is unity, is taken to be zero at all temperatures.

This leads to a consideration of the hydrogen electrode which is fundamental to the measurement of pH and to potentiometric acid-base titrations.

POTENTIOMETRIC pH MEASUREMENT

Perhaps the most common potentiometric measurement is that of pH. pH was defined originally as $-\log C_{H^+}$ or $\log 1/C_{H^+}$, where C_{H^+} is the concentration of hydrogen ion. Today instead of C_{H^+} one would write A_{H^+}, the activity of hydrogen ion. For weak acids it is possible to get an approximate value for the activity from the degree of dissociation calculated from the equivalent conductances of the acid at a given concentration and at infinite dilution. For strong acids the activity cannot be obtained. The experimental determination of pH potentiometrically leads to a value which is neither strictly concentration nor activity of hydrogen ion but something in between.

Hydrogen Electrode. When hydrogen gas is dissolved in a solution containing hydrogen ions, an equilibrium occurs of the constituents of both sides of Eq. (11-1). In this system the activity of the hydrogen gas will depend upon its solubility or partial pressure. The emf E of such a system is calculated from the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{A_{H^+}}{A_{\frac{1}{2}H_2}}$$

where E^0 is the emf of the normal hydrogen electrode with

$$A_{H^+} = A_{\frac{1}{2}H_2} = 1$$

E^0 is defined as equal to zero, so that the emf of a hydrogen electrode becomes $E = RT/nF \ln(A_{H^+}/A_{\frac{1}{2}H_2})$ when measured against a normal hydrogen reference electrode. By converting $\ln A_{H^+}$ to $-\log_{10} A_{H^+}$ (= pH), transposing, collecting terms, and introducing corrections for temperature effects and the actual partial pressure of hydrogen, pH can be calculated. At 25°C the pH may be expressed by the equation

$$\text{pH} = \frac{E}{0.05915} \qquad (11\text{-}2)$$

where E is equal to the observed potential minus the potential of the reference electrode.

Hydrogen gas, not being metallic, cannot conduct electrons and thus cannot serve as an electrode for a half-cell. The hydrogen electrode is prepared by immersing a platinum wire, which has had its surface area increased by electrolytically depositing platinum black upon it, in a solution containing hydrogen ion and bubbling hydrogen gas over it.

Although fundamental as a reference electrode, the hydrogen electrode is not a convenient one for general use for the determination of pH. Oxygen interferes. Many substances such as traces of arsenious oxide, arsine, or hydrogen sulfide poison the electrode. Organic substances which may be hydrogenated and oxidizing and reducing substances cause errors. Volatile acids and bases, such as carbon dioxide and ammonia, are removed by the stream of hydrogen.

Standard Calomel Cell. The most convenient reference electrode is usually the calomel (mercurous chloride) electrode which consists of a potassium chloride solution over solid mercurous chloride and metallic mercury. The potential of this cell is governed by the half-cell reaction

$$2Hg \rightarrow Hg_2^{++} + 2e$$

The activity of the mercurous ion is determined by the solubility of mercurous chloride in the chloride solution. The concentration of potassium chloride must therefore be well controlled. This is sometimes done by using standardized $0.1M$ or $1M$ potassium chloride solutions, which must be protected from evaporation to prevent concentration changes. Much more commonly and conveniently, however, saturated potassium chloride (containing solid potassium chloride) is used. Since both excess solid mercurous chloride and potassium chloride are present, passage of current results in solution of either mercury or chlorine, in accordance with the requirements of the solubility product of mercurous chloride. The composition of the solution is thus maintained constant (at constant temperature) and the potential therefore remains constant. The temperature coefficient of this electrode is greater than that of the $0.1M$ or $1M$ KCl cells, but for most titration purposes the cell may be used at room temperature with no other control

Many varieties of calomel reference cells have been described and are available commercially. The essentials are as indicated in the reference electrode in Fig. 11-1. This consists of a tube containing a layer of metallic mercury, to which electrical contact is made with a platinum wire, a layer of solid mercurous chloride and potassium chloride, and a saturated solution of potassium chloride saturated also with mercurous chloride. The cell is connected with the solution being tested by means of the long arm shown, or by other means which make possible electrical contact with a minimum of diffusion. Commercially available calomel reference cells substitute for the salt bridge devices which permit the

reference cell to be immersed directly into the test solution. One such device is an asbestos thread contained in a capillary in the bottom of the cell. Since this is kept moistened by the solution in the cell, contact is thereby established with the test solution. Another device is a ground-glass cap on the bottom of the cell. The thin layer of solution between the cap and the cell is sufficient to establish contact with the test solution. With these devices electrical contact with the mercury is established otherwise than as shown in Fig. 11-1.

A number of pH electrodes have been proposed but of these only two have been widely used—the quinhydrone electrode and the glass electrode. The latter is by far predominant.

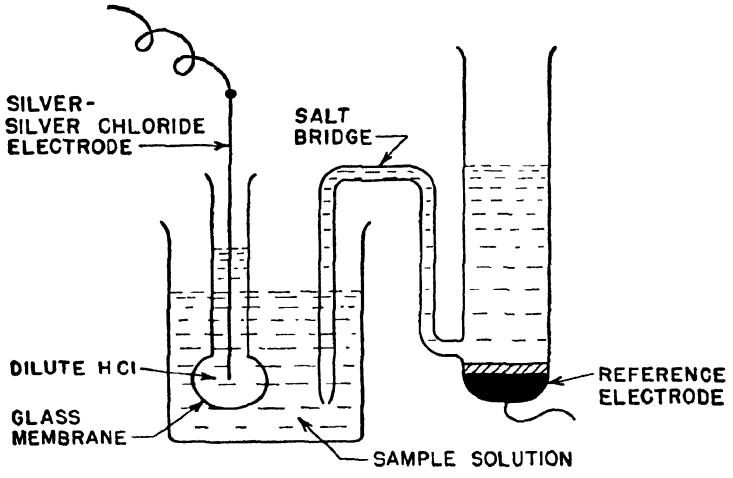


FIG. 11-1. Schematic diagram of glass electrode.

Quinhydrone Electrode. The quinhydrone electrode consists of a bright platinum or gold wire immersed in a solution saturated with quinhydrone. Quinhydrone is a slightly soluble molecular complex consisting of 1 mole of benzoquinone and 1 mole of benzohydroquinone. This compound dissociates as follows:

$$2QH(s) = Q + H_2Q$$

where $QH(s)$ is quinhydrone in the solid state, Q is benzoquinone, and H_2Q is benzohydroquinone. The half-cell reaction is

$$H_2Q = Q + 2H^+ + 2e$$

If the cell is made up as indicated by dissolving quinhydrone in the solution, then $[H_2Q] = [Q]$ and pH is expressed by Eq. (11-2).

Like the hydrogen electrode, the quinhydrone electrode is affected by oxidizing or reducing substances which would react with quinone or hydroquinone. Since hydroquinone is a weak acid, the quinhydrone

electrode cannot be used in alkaline solutions (above pH 8.5). In addition, it is oxidized by air in a strongly alkaline medium. The electrode is useful mainly for locating end points in acid-base titrations where indication of a rapid change in pH is more important than exact determinations of pH.

Glass Electrode. The most useful pH electrode is the glass electrode. Figure 11-1 is a schematic diagram of a glass electrode. The galvanic cell may be represented as follows:

Ag|AgCl(*s*), HCl|glass|sample solution|salt bridge|reference electrode

Each vertical line represents a phase boundary in the cell. It has been found experimentally that the value of the pH of the sample solution at 25°C may be represented by the relationship

$$\text{pH} = \frac{E}{0.05195} \tag{11-3}$$

over a pH range of from about 0 to 10 where E is the observed potential minus the potential of the reference electrode.

The mechanism for the behavior of the glass electrode in measuring pH is not thoroughly understood. It seems to act as a semipermeable membrane which transmits hydrogen ion. The amount of current involved in the transfer of hydrogen ion has been found to approximate what would be expected from Faraday's law. The presence of water is essential and the functioning of the electrode as an accurate indicator of pH is impaired by allowing it to dry out or by immersing it in a dehydrating liquid such as absolute ethanol or concentrated sulfuric acid. Soaking in water restores its usefulness. However, the electrode can be used to determine end points in nonaqueous solvents where pH values are in themselves of no significance.

The behavior of the glass electrode depends to a considerable degree on the composition of the glass. Hard glasses like Pyrex are not useful. Most commonly used is a soda-lime glass, Corning 015. In strongly alkaline solution Eq. (11-3) does not hold. There is an "alkaline error" which depends upon the type of glass, the pH, and the concentrations and kinds of salts in the solution. Up to about a pH of 9, with Corning 015 glass, the alkaline error is negligible. Above pH 9 the pH values are too low. Types of glass electrodes are, however, commercially available which are made of glasses of special composition to minimize the alkaline error. One such electrode, made of lithium glass,[1] shows a negative error of only 0.12 pH unit in the presence of 2M sodium ion at a pH of 12.8. The Corning 015 glass electrode exhibits a corresponding error of 1.5 units.

The glass electrode does not suffer from the disadvantages of the

hydrogen electrode and the quinhydrone electrode. Strong oxidants or reductants do not interfere; the physical condition of the sample is unimportant so that even viscous or semisolid samples may be tested; and adsorption of high-molecular-weight substances, such as proteins, causes no difficulty. Very rugged electrodes are available, and electrodes of many sizes and shapes, so that pH values may be determined on small biological samples or in process lines and tubs. The glass electrode is quite adaptable to automatic recording and automatic control.

POTENTIOMETRIC ACID-BASE TITRATIONS

Potentiometric titrations of acids and bases consist of a number of pH determinations which are made after the addition of measured increments of standard acid or base. If pH values (or less preferably emf values) are plotted on the ordinate against volume of titrant on the abscissa, curves such as those indicated in Fig. 11-2 are obtained. The end point of the titration is indicated by the inflection point. The abruptness of the inflection depends in part on the degree of dissociation of the acids and bases concerned and in part on their initial concentrations. A sharp inflection, such as in curve *A*, would be characteristic of strong acids and bases and a gradual inflection, such as in curve *B*, would be characteristic of weak acids and bases.

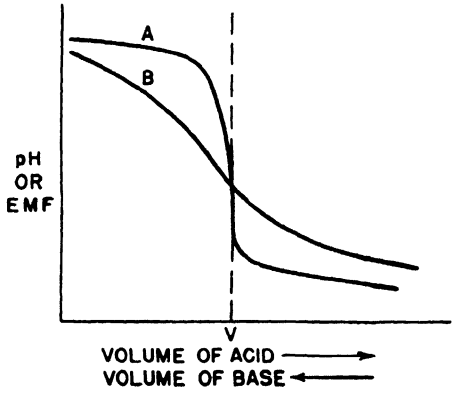


FIG. 11-2. Acid-base titration curves.

In actual titrations with a glass electrode or a quinhydrone electrode, the sample may be contained in a small beaker in which are placed the indicator electrode, one end of a salt bridge (usually an inverted U tube containing an agar gel saturated with potassium chloride), and a mechanical stirrer. The salt bridge is connected to a reference electrode, usually a calomel electrode. If a base is being titrated it is desirable to exclude carbon dioxide by titrating in a flask through which carbon dioxide–free air may be bubbled. Large increments (several milliliters) may be added at the start of the titration, but as the equivalence point is approached, small equal increments (0.1 to 0.2 ml) should be added. Equilibrium is attained rapidly in acid-base titrations, but sufficient time should always be allowed between increments so that the potential becomes constant. This may be considered attained when a drift of no more than 1 or 2 mv per min (about 0.02 to 0.04 pH unit) occurs. Normally, there is no need to measure the potential any closer than to about 1 mv.

Graphical Determination of End Point. For titrations with sharp inflection points, such as in curve *A*, Fig. 11-2, it is easy to determine the inflection point (indicated by intersection with the dotted line) by inspection of the curve. With curves such as *B*, this is sometimes difficult. By plotting values for the slope of the titration curve ($\Delta E/\Delta V$) against volume of titrant (Fig. 11-3) (the first-derivative curve) it is easier to locate the end point. The stoichiometric end point corresponds to the maximum of this curve when the curve is symmetrical. The curve will be symmetrical if the half-cell reaction is reversible, if the number of molecules or ions reacting is equal to the number of molecules or ions of the product, and if the indicating electrode acts in a reversible manner. (The latter would not be true, for example, with the quinhydrone electrode above pH 8.5.) For most titrations of practical interest the error caused by failure of these conditions is negligible.

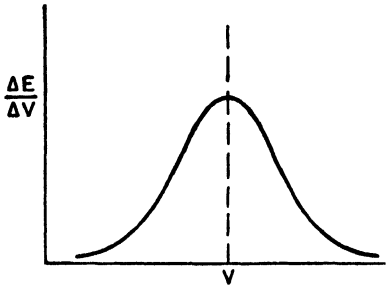


FIG. 11-3. First-derivative titration curve.

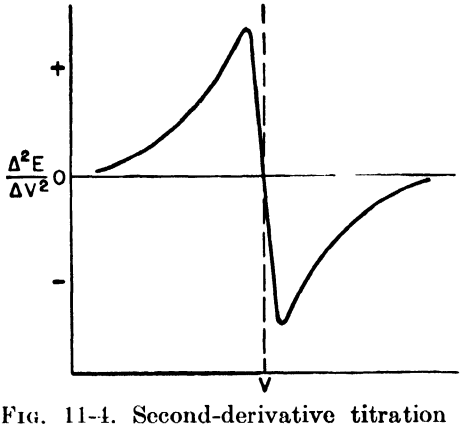


FIG. 11-4. Second-derivative titration curve.

Determination of End Point by Second Derivative. It is frequently more convenient to determine the inflection point of a potentiometric titration by means of the second-derivative curve (Fig. 11-4). In such a curve the second derivative passes through zero at the inflection point. However, this determination is best done not graphically but by computation.[2] To do this, titrate with small equal increments of titrant and calculate from the data the volume at which the second derivative becomes zero. The hypothetical example shown at the top of p. 204 will illustrate the process.

Simplified Methods of End-point Determination. A number of methods of titration have been devised with the purpose of simplifying potentiometric titrations. The greatest simplification, of course, is the automatic carrying out of the titration to an end point or the automatic recording of a curve from which the end point may be taken. These approaches will be discussed below. Three other approaches will now be mentioned briefly.

If the potential of the indicator electrode (the electrode which is respon-

V, ml	emf, mv	$\Delta E/\Delta V$, mv/0.1 ml	$\Delta^2 E/\Delta V^2$
20.10	312		
		7	
20 20	319		+2
		9	
20 30	328		+19
		28	
20 40	356		+60
		88	
20 50	448		−21
		67	
20 60	515		−4
		63	
20 70	578		

$$V \text{ inflection} = 20.40 + 0.1\left(\frac{60}{60 + 21}\right) = 20.474 \text{ ml.}$$

sive, directly or indirectly, to changes in concentration of the constituent being determined) is known from previous information about the potentiometric titration, then the equivalence point may be determined merely by titrating to that potential without bothering to record any data.[3] The potentiometer, or pH meter, is set to the desired value, standard solution is added, dropwise near the end point, and the addition is stopped when no deflection of the galvanometer needle, or a reversal of direction of the deflection, occurs upon momentarily closing the tapping key. The accuracy attainable with this procedure depends upon the reproducibility of the equivalence potential from one titration to another and upon the magnitude of $\Delta E/\Delta V$ at the equivalence point.

The Pinkhof-Treadwell method[4,5] accomplishes the same objective without requiring a knowledge of the equivalence potential. An indicator electrode is immersed in the sample solution. An identical electrode is immersed in a reference solution which has the same composition which the sample solution will have when it has been titrated to the end point. The electrodes are connected to a galvanometer, a resistance, and a tapping key. At the end point the current will be zero.

The reference solution need not necessarily be a replica of the sample solution at the end point. The essential point is that its potential be correct. For example, if an acid is being titrated with a base to pH 7 the reference solution might be a pH 7 buffer solution. It is not even necessary for the indicator electrodes to be identical, provided that the proper potential is indicated.

Finally, mention should be made of the differential-titration method,[6] which furnishes a direct measurement of $\Delta E/\Delta V$ vs. V without requiring a reference electrode. The method is, however, no more accurate or

precise than other techniques and is slower and more cumbersome than titrating to a known equivalence potential. In one variation of this method[7,8,9,10] an apparatus is used such as that shown in Fig. 11-5. A portion of the solution, which is kept in the medicine dropper, is forced into the main body of the sample after each increment of standard solution has been added. In this way the potential difference between the identical indicator electrodes corresponds directly to $\Delta E/\Delta V$. By keeping the volume of solution surrounding the "retarded electrode" small compared with the main volume the error caused thereby may be made negligible.

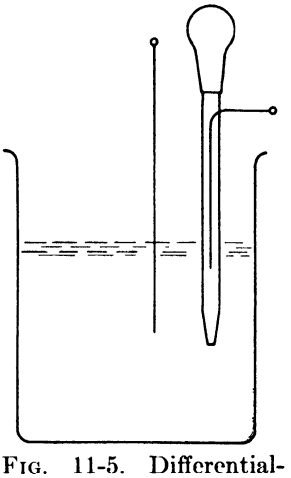


FIG. 11-5. Differential-titration apparatus. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. V-2. By permission of the publishers.*)

Types of Acid-Base Titration Curves. *Strong Acids, Strong Bases.* The titration of strong acids with strong bases, or the reverse, involves merely the reaction

$$H^+ + OH^- = H_2O \qquad \text{with} \qquad K = \frac{1}{Kw} = 10^{14}$$

where Kw is the ionization constant of water. At the end point, at 25°C,

$$[H^+] = [OH^-] = 10^{-7}$$

and the pH = 7. The equivalence point is pH 7.00 (at 25°C) regardless of the initial concentration of the strong acid or base being titrated. However, the rate of change of pH at the end point decreases with decreasing initial concentration of acid or base.

Weak Acids, Strong Bases. Titration of a weak monoprotic acid (an acid which is capable of liberating, per mole, a maximum of 1 gram equivalent of hydrogen ions) with a strong base involves two reactions:

$$HA = H^+ + A^- \qquad Ka = \frac{[H^+][A^-]}{[HA]}$$

and

$$H^+ + OH^- = H_2O$$

The net reaction is therefore

$$HA + OH^- = A^- + H_2O \tag{11-4}$$

and

$$K = \frac{[A^-]}{[HA][OH^-]} = \frac{Ka}{Kw}$$

since $[H_2O]$ is constant.

Reaction (11-4) represents an equilibrium which does not proceed completely to the right. There are, therefore, always some hydroxyl ion

and some undissociated weak acid left at the end point (when 1 equivalent of strong base has been added to 1 mole of weak acid). The pH at the end point of a weak acid–strong base titration is therefore always in the alkaline region—above 7. The weaker the acid (the smaller Ka is) the smaller is the ratio Ka/Kw and the higher is the concentration of hydroxyl ion at the end point for a given initial acid concentration. For extremely weak acids, reaction (11-4) becomes so incomplete that the change of pH with added base becomes too small to be precisely measurable. In other words, curve B (Fig. 11-2) becomes flatter and flatter. Finally, it becomes so flat that it is impossible to determine the end point, and the titration cannot be carried out.

Strong Acids, Weak Bases. The situation in titrating a weak base with a strong acid is exactly the reverse of that just described. The pH at the end point is always less than 7.

Other Acid-Base Combinations. The feasibility of titrating a polyprotic acid (one which is capable of liberating, per mole, a maximum of more than 1 gram equivalent of hydrogen ion) such as carbonic, phosphoric, or oxalic with a strong base, or a mixture of weak acids or weak bases with a strong base or acid, depends upon the absolute magnitude of the ionization constants of the constituent acids or bases and upon their ratios. In general the greater the ratio the more pronounced will be the separation between the titration curves of the several constituents. It has been calculated[11] that a ratio of K_1/K_2 greater than 16 is necessary to get two inflection points in the titration of a diprotic acid (one which is capable of liberating, per mole, a maximum of 2 gram equivalents of hydrogen ion) but for good accuracy a much greater ratio is needed.[12]

A salt containing the anion of a weak acid, e.g., sodium carbonate, sodium cyanide, etc., may be titrated with a strong acid. Likewise, salts containing the cation of a weak base, e.g., ammonium chloride, anilinium sulfate, etc., may be titrated with a strong base. The pH at the end point will be that of the solution of the weak acid or weak base. The titration curve is identical with that obtained by titrating the weak acid with a strong base or the weak base with a strong acid. The precision with which the titration may be performed, which depends upon the steepness of the slope at the end point, will be better the weaker the acid or the base. Thus sodium cyanide ($K_{HCN} = 7.2 \times 10^{-10}$) may be titrated more precisely than sodium acetate ($K_{HAC} = 1.75 \times 10^{-5}$) and similarly for salts of weak bases.

Acid-Base Titrations in Nonaqueous Solvents.[13,14,15] There are many organic acids, bases, and salts which cannot be titrated accurately in aqueous solution because of limited solubility in water. Very many also cannot be titrated because they are too weakly acidic or basic in aqueous solution. An increasingly great number of such titrations are being

carried out in nonaqueous solvents. Aside from the matter of enhanced solubility, the success of this approach stems from the fact that a weak acid becomes a stronger acid in a basic solvent and a weak base becomes a stronger base in an acidic solvent. This explanation may be put in a more concrete form by reference to Brönsted's concepts of acidity and basicity. On the older ionization theory of acids and bases, acidity was considered merely in terms of dissociation into, or hydrolysis leading to the formation of, hydrogen ions, and basicity in similar terms with respect to hydroxyl ions. The solvent was considered merely as a medium in which this process could occur. According to the newer concepts, the solvent plays a more essential role. Thus when an acid dissociates, HA forms H^+ and A^-, but H^+ is merely a proton and does not act as an acid until it enters into combination with a solvent (is solvated). The tendency of the proton to be solvated is thus an essential factor in determining the strength of an acid. It follows then that a given acid may be very weak in one solvent and much stronger in another. An acidic solvent like glacial acetic acid has less tendency to solvate a proton to form $CH_3COOH_2^+$ than water (which forms H_3O^+) and which in turn has less tendency to solvate the proton than a base like liquid ammonia (which forms NH_4^+). Standard bases which are used to titrate acids in nonaqueous solvents are mainly metallic alcoholates such as sodium methoxide, potassium methoxide, and lithium methoxide dissolved in benzene-alcohol; sodium aminoethoxide (prepared from ethanolamine) in ethylenediamine as solvent[16] and sodium triphenylmethane in benzene-ether. They are best standardized against National Bureau of Standards benzoic acid either potentiometrically or with suitable indicators.[13,14] The titration of bases in nonaqueous solvents (as well as in water) depends upon the proton-accepting role of the base. In the familiar example of the basicity of ammonia in water, the following reactions occur:

$$\begin{aligned} H_2O &= H^+ + OH^- \\ NH_3 + H^+ &= NH_4^+ \\ \hline NH_3 + H_2O &= NH_4^+ + OH^- \end{aligned}$$

The hydroxyl ion formed is the base which is titrated by the standard strong acid used. With very weak bases, e.g., urea, the proton-accepting property is too slight in water to liberate enough OH^- to make a titration possible. However, in a more acidic solvent such as glacial acetic acid, the following reactions occur readily:

$$\begin{aligned} CH_3COOH &= H^+ + CH_3COO^- \\ RNH_2 + H^+ &= RNH_3^+ \\ \hline RNH_2 + CH_3COOH &= RNH_3^+ + CH_3COO^- \end{aligned}$$

CH_3COO^- is a strong base in glacial acetic acid, just as OH^- is in water,

and can be titrated with a strong acid in a nonaqueous solvent. Perchloric acid in glacial acetic acid is generally used and may be standardized potentiometrically or by means of a visual indicator (crystal violet) against National Bureau of Standards potassium acid phthalate.[17,18,19,20]

POTENTIOMETRIC PRECIPITATION AND COMPLEX-FORMATION TITRATIONS

An ion may be removed from solution either by precipitation or by formation of a soluble complex. A titration involving such ions may be followed potentiometrically in several ways. The changing concentration of the ion may alter the potential of an indicator electrode consisting of the metal corresponding to the ion. For example, in precipitating silver with chloride, or chloride with silver, a silver electrode may be used.

The indicator electrode may also be one responsive to an anion. For example, an inert electrode (platinum) in a solution containing iodide ion and free iodine will respond to changes in the concentration of iodide ion since such changes alter the ratio $[I_2]/[I^-]$ upon which the potential of the cell depends. Such electrodes, which are directly responsive to changes in concentration of an ion, are known as electrodes of the first order. Electrodes of the second or third order have also been described. With such electrodes the response is to a change in concentration of an ion which is not involved in the titration itself but which is controlled at second or third hand by a change in the concentration of an ion which is involved in the titration. Such a titration has been described[21] for calcium ion with oxalate ion in which a silver-silver oxalate electrode is used. The potential of the latter depends upon the concentration of silver ion. This in turn depends upon the solubility product of silver oxalate so that, as the oxalate-ion concentration increases, the silver-ion concentration decreases, and vice versa. In its turn the oxalate-ion concentration changes with the concentration of calcium ion, so that indirectly the silver-silver oxalate electrode indicates changes in calcium ion.

Instead of titrating an ion with another by forming an insoluble precipitate with it, the same effect may be achieved by titrating with an ion which forms a complex ion with the first. The effect upon the potential due to a change in the concentration of the first ion is similar to that obtained by precipitating it. For example, the soluble complex $Ag(CN)_2^-$ has been utilized in determining cyanide with silver potentiometrically.[22]

POTENTIOMETRIC OXIDATION-REDUCTION TITRATIONS

Oxidation-reduction reactions are of great importance in analytical chemistry, and the potentiometric determination of the end point in such

reactions is frequently the best available method. Titrations may be followed potentiometrically either with oxidants such as permanganate, cerate, dichromate, iodine, iodate, bromate, hypochlorite, and ferricyanide or with reductants such as ferrous ion, arsenite, chromite, titanous ion, or thiosulfate (only for the titration of iodine). The general techniques and methods for locating end points are similar to those described for other types of potentiometric titrations.

Need for Inert Indicating Electrodes. As in all electroanalytical methods, it is necessary to have a reaction which will produce a flow of electrons, but potentiometric oxidation-reduction titrations differ from acid-base, precipitation, and complex-formation titrations in an important feature. This is the fact that the indicating electrode used for oxidation-reduction titrations must be inert; i.e., it must not itself participate in the reaction. (The reference electrode is usually a calomel-mercury electrode.) The indicating electrode serves merely to transfer to the reductant through the external circuit the electrons which are given up to it from the solution by the oxidant. The noble metals platinum and gold are frequently used and under some conditions mercury or silver. The conditions necessary for the use of any metal as an inert electrode are that the solution should not contain ions of the metal and that the oxidation potential of the solution should be lower than that necessary to oxidize the electrode.

Platinum and Mercury Electrodes. Platinum with its high oxidation potential is usually satisfactory. However, in the presence of a high concentration of chloride ions the oxidation of platinum to $PtCl_4^=$ occurs at a lower oxidation potential. Accordingly, in the presence of chloride ions strong oxidants such as permanganate or cerate may react with a platinum electrode, even though perhaps slowly, to give erroneous potential readings. However, even though the actual potential readings may not be reliable under those conditions, the inflection point may still be useful as an end-point indication.

Platinum may also give erroneous potential readings when it is used with reducing agents, such as acidic chromous solutions, which are more strongly reducing than hydrogen on platinum. Under these conditions, to use chromium as an illustration, Cr^{++} reacts with H^+ to yield Cr^{3+} and H_2. This reaction is catalyzed by finely divided metals and by the surface of a platinum electrode. Accordingly, at the surface of the electrode the ratio Cr^{3+}/Cr^{++} is increased over that in the body of the solution being titrated and false potential readings are obtained. To remedy this difficulty, a mercury electrode may be used. Mercury has a higher hydrogen overvoltage than platinum, or to put it otherwise, it does not catalyze the reduction of H^+ to H_2. At the same time its oxidation potential is sufficiently high so that it will not be oxidized by many strong

oxidants. It has, accordingly, been recommended for the titration of Ti^{4+} with acidic chromous solutions[23] since it indicates true potentials for the Cr^{3+}-Cr^{++} couple.[24] However, one difficulty with the use of a mercury electrode is that it is oxidized at fairly low potentials when used in solutions containing anions, such as chloride, which form complex ions with mercuric or mercurous ions.

Bimetallic Electrodes. Bimetallic electrodes of various kinds are sometimes used instead of a metallic indicating electrode and a reference electrode. These may comprise a platinum and palladium couple,[2] a platinum and tungsten couple, or other combinations.[25,26,27,28,29,30,31,32,33,34] They are effective by virtue of the fact that one of the metals (palladium for the first example, tungsten for the second) is much more sluggish in reaching equilibrium than the other, so that a difference of potential is established which is most pronounced at the end point. Such combinations do not give true potential readings and are most useful for the determination of end points when the titration is run rapidly. It is questionable whether bimetallic electrodes offer sufficient advantages over the conventional systems to offset their lack of theoretical predictability.

Special Characteristics. Oxidation-reduction reactions have several special characteristics which should be considered when carrying out potentiometric titrations. They are generally less rapid than acid-base or precipitation reactions because of the more complex mechanisms involved, particularly for oxygen-containing oxidants such as dichromate or permanganate. It is therefore necessary sometimes to run the titration at an elevated temperature or to add a catalyst, as is done when iodide ion is added to catalyze the oxidation of arsenite with permanganate or cerate. Another important condition is apt to be the pH of the solution in titrations, such as with oxygen-containing oxidants, where hydrogen ion enters into the reaction. Oxidations with permanganate, as is well known, proceed more or less rapidly, or to different extents, depending upon the pH of the medium. Other oxidants act similarly. Finally, it is sometimes necessary to exclude air from a reaction mixture in order to avoid oxidizing the reductant with oxygen. Nevertheless, the speed of the oxygen reaction may be so low in some titrations, e.g. in those involving ferrous ion, that exclusion of air is not necessary.

Types of Oxidation-reduction Titrations. A detailed consideration of the potentials developed during the course of oxidation-reduction titrations would be beyond the scope of this chapter. Particularly is this true since such reactions are much more complicated stoichiometrically than those previously considered. A few general conclusions applicable to some examples will, however, be mentioned without introducing the detailed arguments upon which those conclusions are based.

Ferrous and Ceric Ions. The simplest example might be the titration of ferrous ion with ceric ion in 1*M* sulfuric acid:

$$Fe^{++} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

This may be broken down into the two half-reactions with their standard potentials:

$$Fe^{3+} + e = Fe^{++} \qquad E^0 = +0.76 \text{ volt}$$
$$Ce^{4+} + e = Ce^{3+} \qquad E^0 = +1.61 \text{ volts}$$

This titration is typical of those in which an equal number of oxidant ions and reductant ions are involved (symmetrical reactions) and in which hydrogen ions do not participate. Provided that the original solution contains no ferric ion or cerous ion, the titration curve will be symmetrical about the end point and the point of inflection (a point of maximum change of potential with titrant volume) will be identical with the stoichiometric end point. Furthermore, the equivalence potential will be the mean of the standard potentials of the two electrode reactions concerned; in this case 1.19 volts = (1.61 + 0.76)/2 volts. The end-point potential will also be independent of the concentration of ferrous ion titrated. If ferric or cerous ion is originally present, these conclusions do not hold. In the former case the end point will be at a more positive (or oxidizing) potential, in the latter at a more negative (or reducing) potential.

Ferrous and Permanganate Ions. A more involved situation would be exemplified by the titration of ferrous ion with permanganate according to the following equation:

$$5\ Fe^{++} + MnO_4^- + 8\ H^+ \rightarrow 5\ Fe^{3+} + Mn^{++} + 4\ H_2O$$

The separate electrode reactions with their respective standard potentials are

$$Fe^{3+} + e = Fe^{++} \qquad E^0 = +0.76 \text{ volt}$$
$$MnO_4^- + 8\ H^+ + 5e = Mn^{++} + 4\ H_2O \qquad E^0 = +1.52 \text{ volts}$$

In titrations of this type the titration curve is not symmetrical about the end point, since the number of oxidant ions and reductant ions is unequal, and the potential value at the end point is influenced by the hydrogen-ion concentration. The potential at the end point is the weighted mean of the standard potentials of the electrode reactions, corrected for the hydrogen-ion concentration. For the example given, the end-point potential would be

$$\frac{0.76 + 5 \times 1.52}{6} + 0.079 \log [H^+]$$

The stoichiometric end point differs slightly from the inflection point, but the difference is negligible.

Iodide and Ceric Ions. With a titration such as that of iodide ion with ceric ion,

$$2I^- + 2Ce^{4+} \rightarrow I_2 + 2Ce^{3+}$$

calculation of the end-point potential becomes rather complicated and depends upon the equilibrium

$$I^- + I_2\,(aq.) = I_3^-$$

and upon the initial iodide concentration. If the latter is low enough, all the iodine formed in the titration remains in solution; otherwise some

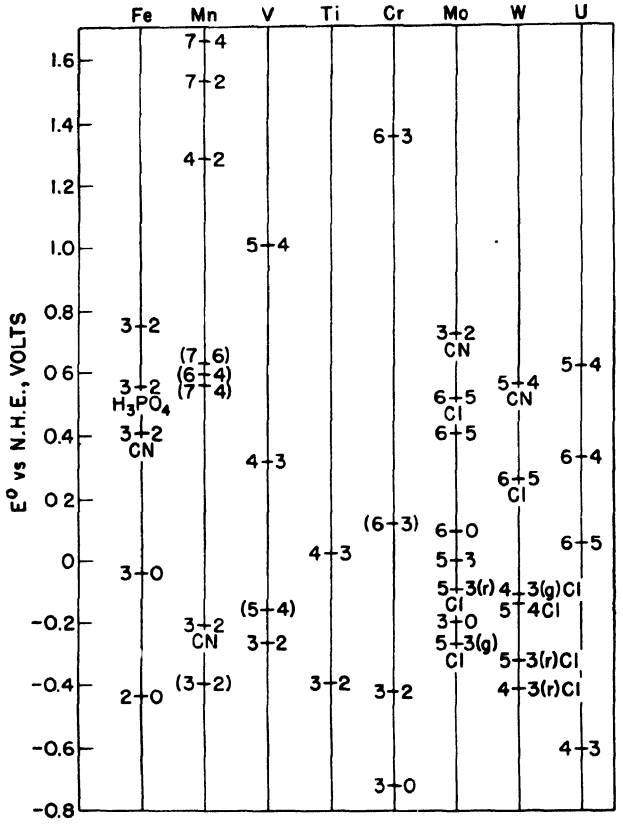


FIG. 11-6. Chart of oxidation potentials. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. VII-3. By permission of the publishers.*)

of it precipitates. Calculation of the end-point potential will follow a different equation depending upon which condition holds.

Successive Titrations of Two or More Oxidation States of One Substance or of Two or More Substances. This problem occurs not infre-

quently in analysis. Whether or not such a titration will give distinct breaks in the potentiometric-titration curve depends foremost upon the difference in potentials of the successive half-reactions. These must differ by 0.2 volt or more to make the titration a possible one. However, satisfaction of that condition alone is not sufficient. The reaction must also be rapid enough. If it is too slow, the titration will not be possible even with a marked difference in half-reaction potentials.

Figure 11-6 is a chart of oxidation potentials of various oxidation stages of a number of transitional elements. The pairs of numbers denote the oxidation stages of the element involved in a given half-reaction. Parenthesis indicate that the potential is that of the half-reaction in alkaline solution (1M in OH^-) and a compound, an element, or a radical below a pair of numbers indicates that the potential is that of a complex of the element with that substance.

By reference to the chart the feasibility could be predicted, for example, of successive titrations of V^{3+} in sulfuric acid with MnO_4^- to VO^{++} and of VO^{++} to VO_2^+, since E^0 for the first couple is about 0.3 on the chart and for the second about 1.0.

For titrations of two or more of the metals the same guiding principle will serve. Thus V^{3+} and Fe^{++} may be titrated with MnO_4^- to give three distinct inflections as predicted by the E^0 for the couple V^{3+}-VO^{++} of 0.3 volt, for Fe^{++}-Fe^{3+} of >0.7 volt, and for V^{4+}-V^{5+} of 1.0 volt. However, the prediction that U^{4+} could be titrated with Fe^{3+} because the U^{4+}-U^{6+} couple differs from that of Fe^{++}-Fe^{3+} by more than 0.3 volt is not borne out in practice since the reaction is too slow.

APPARATUS

Three types of apparatus should be considered for the measurement of potentials both for obtaining single potential measurements (as for pH determinations) and for titrations. The first type is the classical, nonelectronic type of apparatus; the second, manually operated electronic instruments; and the third, automatically or semiautomatically operating electronic instruments some of which are also automatically recording.

The relationship which it is sought to measure is that between the concentration of some ion or molecule and the emf of the galvanic cell which is involved. However, when an electrode reaction occurs, the concentrations involved change. Also, during the passage of current through a cell there is a potential drop equal to the product of the current (in amperes) and the resistance (in ohms) (an *IR* drop). If a voltmeter is connected across a galvanic cell, the emf which is read on the voltmeter will be higher than the true emf of the cell by an amount equal to this *IR* drop. For these reasons potentiometric measurements are always

made by compensation techniques which avoid the flow of more than a slight momentary current through the cell.

Nonelectronic Instruments. Two types of nonelectronic potentiometers are in use. The first, illustrated in Fig. 11-7,[39,87,88] is a direct-reading instrument which is quite simple and requires no standard cell or calibrated slide wire. AB is a slide wire or rheostat which need not be of uniform resistance. The battery D must have a voltage greater than that of the cell X which is being measured. It is arranged with its positive and negative electrodes connected to the corresponding electrodes of the cell so that the polarity of the cell opposes that of the battery. C is a sliding contact, G a galvanometer, and K a tapping key which closes the circuit momentarily when it is tapped. V is a voltmeter which is set in the circuit in such a manner that the current which actuates it does not pass through the galvanometer or the cell. To measure the emf of the cell X, K is tapped momentarily as C is moved until a position is found for C at which there is no deflection of the galvanometer needle. The reading on V will then be that of the cell X. The precision of the apparatus is limited by that of the voltmeter. With a 0- to 2-volt voltmeter a precision of about ± 5 mv may be obtained. This is good enough for most potentiometric titrations.

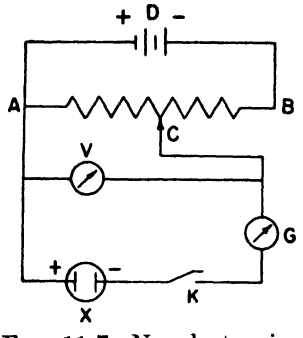


FIG. 11-7. Nonelectronic direct-reading potentiometer. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. II-1. By permission of the publishers.*)

More Precise Indirect Reading. For better precision an instrument such as that shown in Fig. 11-8 may be used.[88] This differs from that of Fig. 11-7 in the following respects: There is no voltmeter, but the resistance of the slide wire AB varies uniformly across its length, and the slide wire is provided with a linear scale which is used to indicate the position of C. A standard cell S, commonly the Weston cell (cadmium amalgam/cadmium sulfate/mercurous sulfate/mercury), may be thrown into the circuit alternately with the cell X, of which the emf is being measured, by means of the double pole–double throw switch L. The emf measurement is made by first putting X into the circuit and

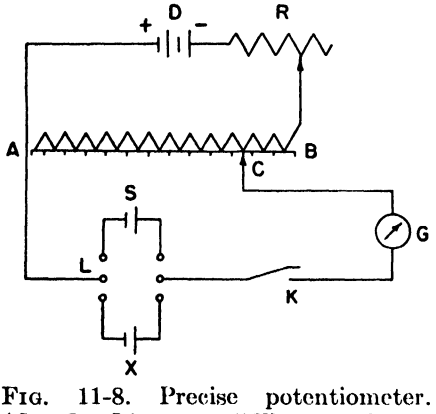


FIG. 11-8. Precise potentiometer. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. II-2. By permission of the publishers.*)

noting the position of C for no galvanometer deflection. Let the corresponding slide-wire length be AC_x. The standard cell is then put into the circuit and a similar null point AC_s is found. Let E_x and E_s be the potentials of X and S. E_x is then the only unknown in the equations

$$\frac{E_x}{E_s} = \frac{AC_x}{AC_s} \qquad \text{or} \qquad E_x = E_s \frac{AC_x}{AC_s}$$

and so may be calculated.

In order to have the scale reading on the slide wire correspond directly to emf, use is made of the rheostat R. The scale is divided into a number of equal units which will be convenient for the voltages to be determined. Thus for a 2-volt range, there may be 2,000 divisions, so that each division equals 1 mv. The standard cell is put into the circuit and the sliding contact is placed at a position on the scale which corresponds to the voltage of the cell. For the Weston cell the emf would be 1.0183 volts (at 20°C) and the setting would be 1,018.3 units on the scale. The setting of R is then adjusted for no deflection of G. The reading on the scale is then direct in millivolts. Commercial potentiometers are also based upon this principle, but with modifications to increase the accuracy. Thus the Leeds and Northrup student potentiometer has a slide wire which may be read directly to 1 mv and with which estimated readings may be made to ± 0.1 mv. The precision of about ± 0.5 mv is good enough for most electroanalytical work.

Simple Substitute for the Potentiometer. A simple instrument has been described which may be used instead of a potentiometer for most potentiometric titrations.[28] This consists of a high resistance and a tapping key in series with a sensitive galvanometer to form a high-resistance voltmeter. By using a box type of lamp-and-scale galvanometer with a 100-mm scale, a range of 0 to 1 volt may be obtained which can be read to 10 mv or better. With a galvanometer sensitive to 10^{-8} amp per division, a 100-division scale, and an internal resistance of 200 ohms, a voltmeter with a range from 0 to 1 volt can be constructed by placing a resistance of 999,800 ohms in series with the galvanometer. Although there is an IR drop through the cell being measured, and the electrode reaction takes place to reduce the concentration of the constituents being determined, both errors may be made negligibly small by normal potentiometric-titration techniques.

Manual Electronic Instruments. Electronic instruments are better than the above-described types in at least two respects. So little current is drawn by an electronic instrument that the current drain from the cell may be negligible in terms of the errors previously discussed even though the cell is left continuously in the circuit. This obviously is of great importance in continuous-reading automatic devices. However, even

for manual operation the low current drain is advantageous when the resistance of a cell is so large that ordinary galvanometers are not sensitive enough. This is true particularly with glass electrodes, which had to be used with the difficult electrostatic electrometers before the advent of electronic instruments.

Many so-called "pH meters" for use with glass electrodes and electronic voltmeters for pH measurements and potentiometric titrations are available commercially and have been described in the literature. There will be given here only a brief description of the first such application which was described, as an illustration of the principles involved. Figure 11-9 is a simplified schematic diagram of a circuit for a null-point detector in potentiometric titrations, using a vacuum triode.[35,89] The

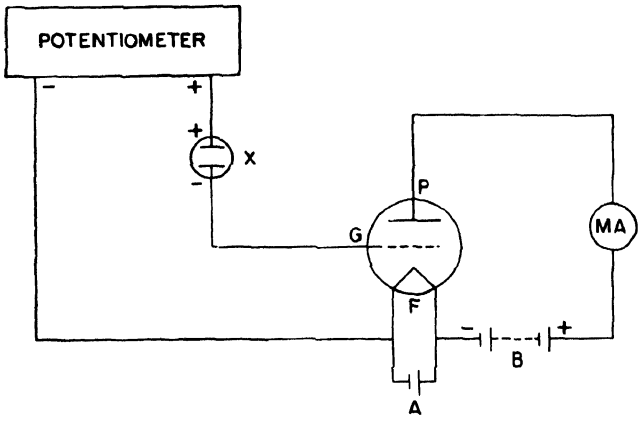


FIG. 11-9. Prototype vacuum-triode null-point detector. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. 11-3. By permission of the publishers.*)

triode is a vacuum tube containing a cathode F, a plate P, and a grid G. F, when heated by a source of low voltage A (one or more 1.5-volt A batteries in series), emits electrons which are attracted to the plate P by virtue of the positive charge on P produced by its being connected to the positive pole of the 45-volt B battery B. The small current which flows in the external plate circuit is indicated by the milliammeter MA. A negative charge impressed on the grid G repels the flow of electrons from the cathode to the plate and reduces the plate current indicated by MA. The negative electrode of the cell X, of which the potential is being measured, is connected to the grid so that any unbalance between the potential of X and the potentiometer will cause a deflection in MA. Restoration of the balance may be made by adjustment of the potentiometer. The extent of adjustment necessary to restore the milliammeter to the position corresponding to no charge on the grid is thus a measure of the potential drop in X. Within limits, the relationship between plate

current and potential applied to the grid is linear and is taken advantage of in constructing direct-reading vacuum-tube voltmeters.

Automatic Potentiometric Titration Instruments. The large number of routine repetitive titrations which are carried out in many laboratories has led to the development of a number of automatic titrators, some of which are available commercially. Such titrators may enable control analyses to be run by technicians, thus releasing skilled chemists for less routine work. They may also result in considerable saving of time if used under appropriate circumstances where the operator may take advantage of the time during which the titration is being run to prepare additional samples or to attend to other tasks. Ordinarily no improvement in precision or accuracy should be expected over carefully run manual titrations using the same volumetric measuring equipment and electrical equipment. Of course, errors due to human factors are minimized.

Types of Automatic Titrators. Two general types of automatic titrators are available. One type automatically draws a titration curve from which the end point may be calculated. The other type controls the addition of titrant in a manner similar to what would be done manually. In other words, it adds large increments at first, then smaller and smaller increments as the end point is approached, finally stopping the addition at the end point.

Precision-Dow Automatic Titrator. The Precision-Dow Recordomatic Titrator, manufactured by the Precision Scientific Company, Chicago, is an instrument of the first type. In its essentials it has been described by Robinson.[36] This instrument overcomes errors inherent in earlier instruments of this type which result from the fact that for slow reactions, or because of slow mixing, the curve is drawn too rapidly so that the inflection point may not correspond to the true end point. This instrument remedies this condition by having a control which stops delivery of an increment of titrant until equilibrium has been attained. When small increments are delivered under these conditions an accurate curve is drawn. However, this procedure causes a titration to be quite time-consuming. Furthermore, the precision of reading the inflection point is not so good as for careful manual titration.

Lingane Titrator. Several titrators of the second type have been described. In Lingane's apparatus[37] (Fig. 11-10) the titrant is delivered not by a burette but by a 50-ml motor-driven hypodermic syringe which introduces titrant by means of a capillary directly under the surface of the sample being titrated. The volume may be read with a precision of better than ± 0.005 ml by means of a revolution counter attached to the drive mechanism. There is an electrical anticipation circuit which is actuated by the potential between the indicator and reference electrodes.

When this potential reaches the previously set equivalence potential of the reaction, the motor drive stops. No more titrant is then added until upon continued stirring the potential departs from the equivalence value, when titrant delivery is resumed. Small increments are added in this fashion until the equivalence potential is reached and is not changed by further stirring. No further additions of titrant are made. The volume

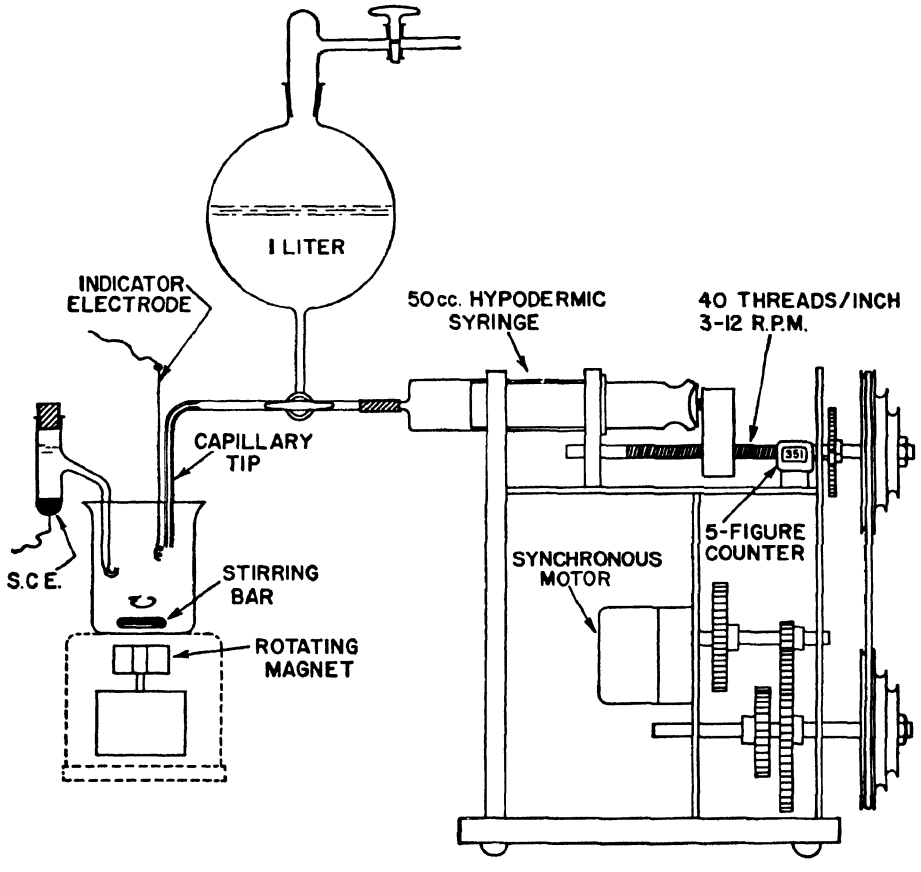


FIG. 11-10. Lingane autotitrator. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. VIII-1. By permission of the publishers.*)

of titrant delivered may be read from the revolution counter. The success of this anticipation technique is dependent upon proper positioning of the syringe delivery tip with respect to the indicator electrode. For rapid titration reactions the indicator electrode is placed closer to the delivery tip than for slow reactions. This allows more time for the reaction to proceed, for slow reactions, as the solution travels from the tip to the electrode.

This apparatus used with a synchronous motor delivers titrant at a fixed speed of about 1 to 2 ml per min so that a recorder may be attached

to record potential vs. time. Since volume is proportional to time, the record shows potential vs. volume of titrant.[38] To speed up the titration without loss of precision the synchronous motor may be replaced by a d-c motor, the speed of which varies according to the progress of the titration.[37] Titrant is added at from 5 to 7 ml per min up to within a few per cent of the end point, then at 0.5 to 1 ml per min, and finally near the end point in increments as small as 0.01 ml.

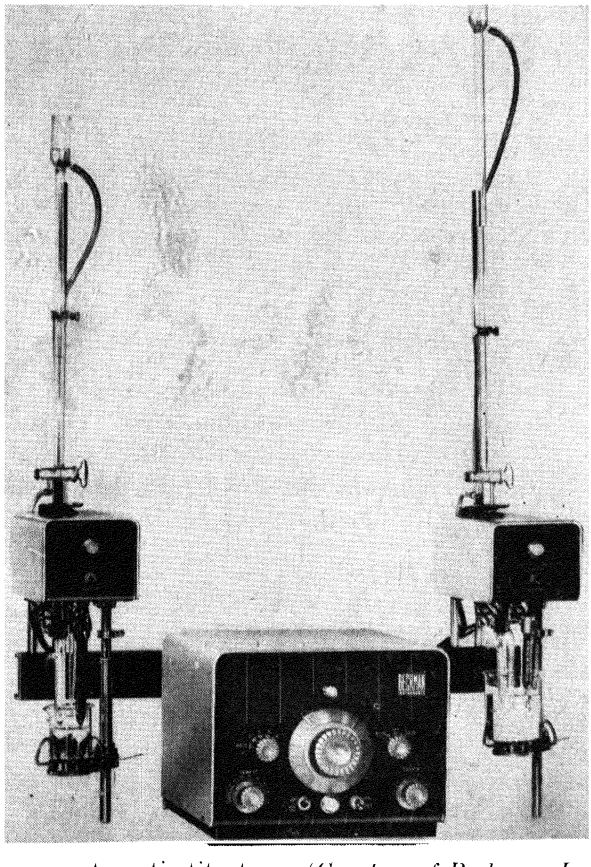


FIG. 11-11. Beckman automatic titrator. (*Courtesy of Beckman Instruments, Inc.*)

Beckman Titrator. A photograph of the Beckman automatic titrator, manufactured by the Beckman Instruments Company, South Pasadena, Calif., is shown in Fig. 11-11. This instrument does not use a syringe burette. It has an ordinary burette. Instead of opening and shutting the stopcock, there is a rubber diaphragm valve to control delivery. This valve is actuated by an anticipation circuit which is at the heart of the operation of the titrator. To carry out a titration, a setting is made on a potentiometer of the potential of the end point at which it is desired to have the titration stop. The burette valve closes when the cell potential reaches a value close to that set for the end point. As the reaction

proceeds, the potential changes and the anticipation circuit allows a further increment of titrant to be added. Each time this happens, the potential at the end of complete reaction with the increment of titrant becomes closer to that of the potential desired at the end point. When the difference is zero, no more titrant is added. The setting of the anticipator may be varied to suit the characteristics of the particular titration. It depends also upon the relative location of the burette tip with respect to the indicator electrode. By proper adjustment a titration may be carried out rapidly as precisely as the reading of the burette will permit and as accurately as the slope of the titration curve will allow.

APPLICATIONS

The applications of potentiometric titrations to analytical problems which have been reported are so numerous and diverse that no attempt can be made to present a complete list. The current literature and references given in the Bibliography and References should be consulted. Only a few references to specific titrations will be given here.

Nonaqueous Acid-Base Titrations. Application of potentiometric titration to aqueous acid-base systems is too commonplace to require examples. There has, however, been an upsurge in applications of acid-base titrations in nonaqueous media. In glacial acetic acid, titrations have been reported for salts of carboxylic acids; amines and their carboxylic acid salts;[40,41,42] amino alcohols;[41] amino acids;[43] chlorides, bromides, nitrates, and sulfates of alkali metals; ammonia and amines;[44] sulfonamides;[42] basic nitrogen in hydrocarbon oils and hydrogenated coal oils;[45,46] and salts of organic bases[47]. In G-H solvent (a 1:1 mixture of ethylene glycol, or propylene glycol, and isopropyl alcohol) titrations have been reported[48] for alkali-metal salts of monocarboxylic acids, amines, mixed acids, salts of inorganic acids, and boric acid. Titrations have also been reported in such solvents as methanol-benzene (1:1), monobutylamine and pyridine,[49] in chloroform,[50,51] alcohol-*p*-dioxane,[52] and ethylenediamine.[53]

Precipitation and Complex-formation Titrations. Potentiometric methods have been reported for a host of precipitation and complex-formation titrations. To mention only a few: titration of chromate with barium;[54] titration of cadmium,[55] cerium,[56] cobalt and nickel[57] and zinc[58,59] with ferrocyanide; lead with sulfide;[60] arsenate,[61,62] bromide in presence of chloride,[63] ferrocyanide[64] and phosphate[65] with silver nitrate; aluminum with fluoride;[66] and sulfite with mercuric chloride.[67]

Oxidation-reduction Titrations. Potentiometric oxidation-reduction titrations have been reported with ceric solutions for copper(I) and antimony(III)[68] and polyhydric alcohols;[69] with permanganate for iron,[70]

peroxides,[71] nitroprusside complexes,[72] and platinum;[73] with bichromate for barium,[74] chromium,[75] and glycerol;[76] with vanadic solutions for ferrous iron, tungsten, hydrazine, and sulfites;[77,78] with arsenite for lead dioxide;[79] with hydrazine for bichromate and vanadate;[80] with vanadyl sulfate for chromate;[81,82] with chromous solutions for copper,[83] iron, and molybdenum;[84] and with vanadous solutions for ceric ion[85] and cupric, ferric, silver, or bichromate ions.[86]

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CHAPTER TWELVE

Conductometric Analysis

One of the important milestones in the advance of modern chemistry was the study of the effects of acids, bases, and salts (electrolytes) on the ability of aqueous solutions to conduct the electrical current. Utilization of these effects for the purposes of chemical analysis has been extensively studied and forms the basis of a number of methods of analysis and automatic control. These have suffered in popularity over the years in comparison with other methods because of certain difficulties of technique and apparatus. A reappraisal of the proper place of conductimetric analysis would seem to be under way, however. As has been true for other instrumental techniques, this has been brought about to some extent by the progress of electronics, which has resulted in the development of more convenient measuring devices. Even more recently an offshoot of classical (low-frequency) conductometry has arisen in the form of high-frequency, or oscillometric, methods of analysis. These offer some features which broaden the scope of application of conductometry.

DEFINITIONS OF UNITS

If an electric current passes through a solution between two parallel electrodes of uniform area, A cm^2, with the distance between the electrodes equal to d cm, then the resistance R offered by the solution to the passage of the current is directly proportional to d and inversely proportional to A, or

$$R = \rho \frac{d}{A} \tag{12-1}$$

where ρ is a proportionality constant, known as the *specific resistance* of the solution. It is constant only for a specific solution at a definite temperature. By definition it is the resistance in ohms when $d = A$.

According to Ohm's law, $I = E/R$. If $E = 1$ volt, then I (in amperes) $= 1/R$. If R is equal to the specific resistance ρ, then

$$I = \frac{1}{\rho} = \kappa$$

and κ is the *specific conductance*, or the amount of current in amperes which passes through a body of solution of dimensions $d = A$ upon the application of a potential difference of 1 volt. Since it is easier to measure resistance than current, κ is usually calculated from the measured resistance and is expressed not in amperes but in a unit known as the *reciprocal ohm*, symbolized by mho or ohm^{-1}.

The *equivalent conductance* Λ_c of a solution of an electrolyte is the specific conductance of a hypothetical solution of that electrolyte containing 1 gram-equivalent per cubic centimeter, and is given by the expression

$$\Lambda_c = \frac{\kappa_c \times 1{,}000}{c}$$

where κ_c is the specific conductance of the solution which contains c equivalents per 1,000 cc (or practically per liter). Λ_c for a given electrolyte varies with c, increasing as c decreases. Λ_0, the equivalent conductance at zero concentration, or infinite dilution, is obtained by plotting Λ_c vs. $c^{1/2}$ at low values of c and extrapolating to zero c value. According to the Arrhenius theory of incomplete ionization (no longer accepted but still adequate for the study of conductometric titrations) the degree of ionization α may be calculated from

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \tag{12-2}$$

For an electrolyte AB, which dissociates according to the equilibrium $AB \rightleftarrows A^+ + B^-$, Kohlrausch's law of independent migration applies:

$$\Lambda_0 = \lambda_{A^+}{}^0 + \lambda_{B^-}{}^0 \tag{12-3}$$

$\lambda_{A^+}{}^0$ and $\lambda_{B^-}{}^0$ are the limiting equivalent conductances of the ions, which are calculated from their *ionic mobilities* (velocities) at infinite dilution. The equivalent conductances of ions may be considered to be independent of concentration for the purpose of predicting the course of conductometric titrations even though this is not rigidly true. By combining Eqs. (12-2) and (12-3)

$$\Lambda_c = \alpha(\lambda_{A^+}{}^0 + \lambda_{B^-}{}^0)$$

The equivalent conductance of a given ion is constant at a given concentration and temperature. At infinite dilution it is independent of the nature of the associated oppositely charged ions; thus λ^0 for Cl^- would be the same for barium chloride, potassium chloride, or sodium chloride. At finite concentrations λ varies only slightly with the nature of the oppositely charged ion. The values of λ^0 for Cl^- at 25°C in 0.1M solution for the following electrolytes indicate the extent of the differences caused by differences in the equivalent conductance of the cation: LiCl, 65.49; NaCl,

65.58; KCl, 65.79; HCl, 65.98. The extreme difference in the value of λ^0 for Cl^- caused by the difference between H^+ (of high equivalent conductance) and Li^+ (of low equivalent conductance) is only 0.7 per cent.

Table 12-1 contains values for the ionic conductances at infinite dilution of a number of common cations and anions. The values for hydrogen ion and hydroxyl ion are strikingly high, a fact which is utilized in acidimetry and alkalimetry.

TABLE 12-1. IONIC CONDUCTANCES AT INFINITE DILUTION

Cations	18°C	25°C	Anions	18°C	25°C
H^+	316.6	349 7	OH^-	175	196
Li^+	33.3	38 7	Cl^-	65 5	76.6
Na^+	43.5	50.1	Br^-	67 6	77.7
K^+	64.4	73.5	I^-	66.1	
NH_4^+	64.4	74.8	CNS^-	56 5	
Ag^+	54 4	61.9	NO_3^-	61.8	71.4
$\frac{1}{2}$ Ca^{++}	51	61	$\frac{1}{2}$ $SO_4^=$	68	80
$\frac{1}{2}$ Sr^{++}	51	61	$\frac{1}{2}$ $C_2O_4^=$	63 0	73.5
$\frac{1}{2}$ Ba^{++}	55	65	$\frac{1}{2}$ $CO_3^=$	70.0	83 3
$\frac{1}{2}$ Pb^{++}	60.8	71.2	HCO_3^-	40 5	47.0
$\frac{1}{2}$ Mg^{++}	45	53	CH_3COO^-	35 0	40 8
$\frac{1}{2}$ Zn^{++}	46	54	$\frac{1}{2}$ $CrO_4^=$	72	

CONDUCTOMETRIC TITRATIONS

Acid-Base Titrations. (In the following discussion what is said about titration of acids applies with obvious changes to titration of bases.) The specific conductance of a solution of an electrolyte is a linear function of the concentration closely enough for practical purposes.

Strong Acid, Strong Base. If a strong acid is titrated with a strong base, e.g.,

$$H^+ + Cl^- \xrightarrow{Na^+ + OH^-} Na^+ + Cl^- + H_2O$$

highly conducting H^+ is replaced by much less conducting Na^+ and the specific conductance of the solution drops until it is equal to that of NaCl at the end point. Continued titration causes a rise in the specific conductance because of the presence of highly mobile OH^- ions. A plot of the specific conductances would consist of two straight lines AB and BC (Fig. 12-1) intersecting, with some rounding off, at the end point B *provided that there was no change in volume.* Actually the volume increases because of the added alkali and this causes the lines to deviate from linearity. To minimize the effect of dilution, conductometric titrations are always performed with titrants which are much more concentrated

(at least ten times so) than the solution being titrated. Under these conditions each observed conductance value may be multiplied, before plotting, by the correction factor:

$$\frac{\text{Volume of titrant + original volume of solution titrated}}{\text{Original volume of solution titrated}}$$

in order to correct for the effect of dilution and thus produce essentially straight lines. In actual practice at least two points which are not close to each other or to the end point are determined on *AB* and *BC*. Straight lines are drawn through these points and their intersection is taken as the end point.

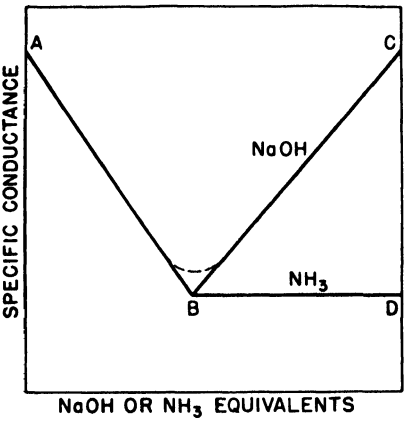


FIG. 12-1. Titration curves for strong and moderately strong acids. (*After W. G. Berl, "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, 1950, vol. II, p. 65, Fig. 7. By permission of the publishers.*)

Strong Acid, Weak Base. If a strong acid is titrated with a weak base, e.g., HCl with NH_3 according to

$$H^+ + Cl^- \xrightarrow{NH_3} NH_4^+ + Cl^-$$

the conductance plot up to the end point is similar to that for the titration with a strong base, but NH_4^+ replaces H^+. Beyond the end point, the weak hydrolysis of the base to form hydroxyl ion:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

is suppressed by the NH_4^+ ions already present, so that no increase in conductance occurs and the line of constant conductance *BD* is formed.

That part of the curve of Fig. 12-1 corresponding to *AB* will be followed by strong acids and moderately strong acids, such as trichloroacetic and dichloroacetic acids, down to a dissociation constant of about 10^{-2} but with decreasing slope and an increasing, but small, departure from linearity for *AB*.

Weak Acids. For weaker acids with dissociation constants ranging down from about 10^{-3} to about 10^{-9}, for example, in order of decreasing dissociation, monochloroacetic, formic, and acetic acids and para-nitrophenol, curves such as that shown in Fig. 12-2 are obtained. The weaker the acid is, the greater is the proportion of *AB* (*A'B*, *A''B*, etc.) which is straight. By reference to the following equations for dissociation and neutralization of a weak acid:

$$HA \rightleftharpoons H^+ + A^- \qquad (12\text{-}4)$$

and

$$H^+ + A^- + M^+ + OH^- \rightarrow H_2O + M^+ + A^- \qquad (12\text{-}5)$$

the behavior of the curves before the end point may be explained. Equation (12-5) indicates the loss of H^+ by neutralization, with a drop in conductivity. At the same time A^- is being formed and by its mass effect it suppresses the ionization indicated in Eq. (12-4), thus reinforcing the drop in conductivity. At the same time slightly ionized HA is being replaced by completely ionized MA with a tendency to increase the conductivity. When the two trends balance, a minimum is formed. At a point beyond the minimum the increase becomes linear. The point at which the increase becomes linear is closer to the end point, the stronger the acid. The linear part of the curve is the *salt line* which represents the increase in conductivity due to MA alone.

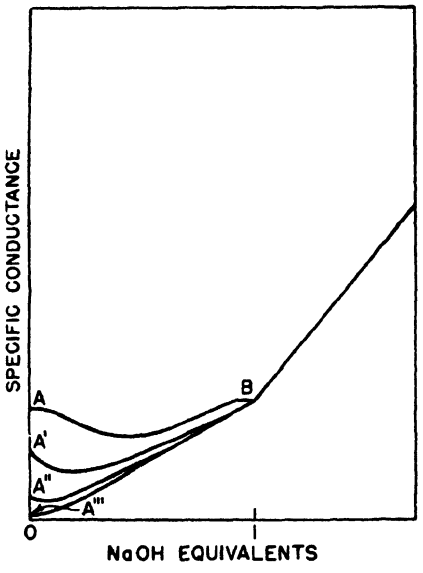


FIG. 12-2. Titration curves for weak acids. (*After W. G. Berl, "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, 1950, vol. II, p. 70, Fig. 8. By permission of the publishers.*)

When some acids with dissociation constants about 10^{-3}, e.g., salicylic acid, are titrated with a strong base such as sodium hydroxide, the curve (Fig. 12-2) is so rounded before the end point as to make its exact location difficult. One method of overcoming this difficulty[1] is to carry out one titration with a strong base and another with ammonia. The end point is located by the intersection of the oblique strong-base line with the straight line of ammonia parallel to the NH_3-equivalents axis.

For very weak acids, with their dissociation constants lower than about 10^{-9}, such as boric acid and arsenious acid, too few hydrogen ions are produced to affect the conductance. A straight line is therefore formed from the beginning of the titration and the neutralization curve coincides with the salt line when such acids are titrated with strong bases. When, however, such very weak acids are titrated with weak bases, such as ammonia, the curve is so rounded near the end point, because of hydrolysis, that an accurate end point cannot be located.

Mixed and Polybasic Acids. The titration behavior of mixtures of acids depends upon the difference in their dissociation constants and their concentrations. The behavior may be understood by consideration of the trends shown in Figs. 12-1 and 12-2 and by the small but real differences in mobilities of the various anions. Mixtures of a strong acid (such as hydrochloric acid) and an acid such as acetic acid can be titrated more

accurately conductometrically than potentiometrically. Figure 12-3 illustrates the curves for such a titration with sodium hydroxide and with ammonia. Point 1 is the end point for the neutralization of the strong acid and point 2 for the weak acid. Polybasic acids may be considered as mixtures of acids of different strengths corresponding to the several stages of ionization. A complication which exists is that, in a mixture of stronger and weaker acids, the weaker acid may begin to be neutralized before the stronger acid has been completely neutralized. The idea that the conductometric-titration curve of a mixture of acids is merely a succession of the curves of the separate acids is too simple to fit the facts.

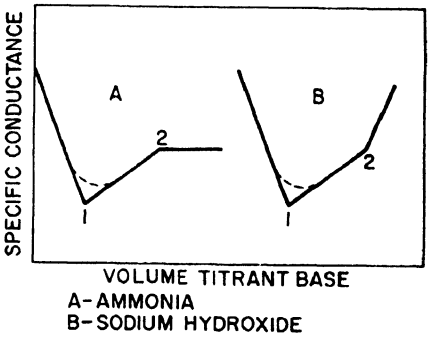


FIG. 12-3. Titration curves for mixed strong and weak acids. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. IX-5. By permission of the publishers.*)

Salts. Weak acids (or similarly bases) may be titrated by replacement from their salts by strong acids (or bases), respectively, rather than by direct titration with bases (or acids). Sharper breaks may sometimes be obtained than by titration of the acids (or bases) directly with bases (or acids). With salts of polybasic acids, such as, for example, Na_3PO_4, titration with hydrochloric acid leads to replacement of the weakest stage first followed by the next weakest and so on with the formation of more than one break.

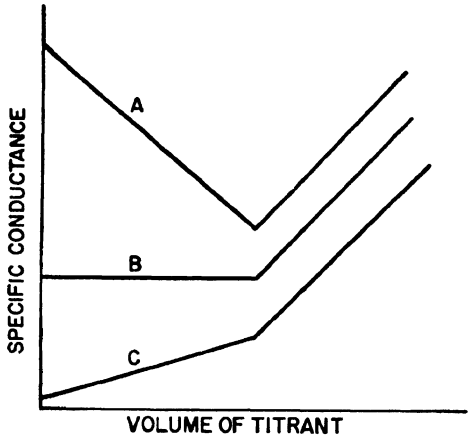


FIG. 12-4. Precipitation-titration curves.

Precipitation Titrations. In precipitation titrations in which a salt MA is being titrated with a salt NB to precipitate MB:

$$M^+ + A^- \xrightarrow{N^+ + B^-} MB\downarrow + N^+ + A^-$$

any change in conductivity up to the end point is caused by the substitution of N^+ for M^+, and beyond the end point by excess NB. Depending upon whether the mobility of M^+ is greater than, equal to, or less than that of N^+, curves such as *A*, *B*, or *C*, respectively, in Fig. 12-4 will be obtained. For a precise end point a curve of type *A* is most desirable. One should, therefore, if it is possible, choose as a precipitant a salt which will cause such a break. For example, in precipitating AgCl by the action

of a chloride upon silver nitrate it is better to use LiCl than NaCl and NaCl than KCl, for although the mobilities of all three ions are less than that of Ag^+, Li^+ has the lowest mobility and Na^+ the next lowest.

Appreciable solubility of the compound being precipitated, or supersaturation of the solution with the precipitant, causes rounding of the curve near the end point with resulting indistinctness. This can be particularly serious if dilute solutions are used. Addition of a nonaqueous solvent such as alcohol, or cooling, may help by decreasing the solubility.

Conductometric titrations have been carried out with silver nitrate for the precipitation of silver chloride, bromide, and iodide,[3,4] cyanide,[2] cyanate, thiocyanate, chromate, oxalate, ferricyanide, molybdate, tungstate, vanadates,[5] tartrate, succinate, citrate, and salicylate for the determination of either silver or the acid radicals. Lead nitrate has been used for conductometric-precipitation titration of iodide, ferrocyanide, sulfate, thiosulfate, oxalate, tartrate, succinate, and malate. Barium acetate or chloride has been used to titrate sulfates, chromates, carbonates, oxalates, tartrates, and citrates.

Lithium sulfate has been used to titrate barium and lead salt solutions; lithium oxalate for calcium, strontium, barium, silver, lead, copper, nickel, and cobalt salts; lithium chromate for barium and strontium; and sodium chromate for barium, lead, thallium, and strontium.[6] Potassium ferrocyanide has been used, under strictly controlled conditions, to precipitate zinc ferrocyanide[7] and potassium ferricyanide or potassium lithium ferricyanide for silver, copper, cadmium, cobalt, and nickel. Sodium sulfide has been used for the accurate titration of lead, cadmium, bismuth, zinc,[8] and ferrous iron.

Titrations with Mercuric Perchlorate. Mercuric perchlorate is a useful reagent for conductometric titrations even though it does not form precipitates with most metallic salts. Certain mercuric salts such as $HgCl_2$, $HgBr_2$, $Hg(SCN)_2$, and $Hg(CN)_2$ are for all practical purposes nonelectrolytes. The specific conductances of a wide range of concentrations of their solutions are of the same order as those of aqueous solutions in equilibrium with ordinary so-called "insoluble salts."[14] However, certain other mercuric salts, the nitrate, sulfate, and perchlorate, are strong electrolytes in solution. They are, unfortunately, also strongly hydrolyzed, with the precipitation of basic salts, unless excess free acid is present. The perchlorate can, however, be prepared in a satisfactory state for conductometric titrations by saturating perchloric acid with mercuric oxide.[15]

With mercuric perchlorate soluble chlorides, bromides, thiocyanates, and cyanides can be titrated.[16] With potassium bromide an ill-defined break due to the formation of K_2HgBr_4 occurs before the final break

which is due to the formation of $HgBr_2$. Iodides react by precipitation of mercuric iodide with preliminary formation of K_2HgI_4. Mercuric salts of the weaker monobasic acids such as nitrous, acetic, butyric, valeric, and lactic acids are poor electrolytes and the alkali salts of these acids may be titrated conductometrically.

Miscellaneous Titrations. Ammonia obtained by distillation in the Kjeldahl nitrogen determination is determined by reference to a calibration curve.[9] Soap, free fatty and resin acids, or free alkali are determined in admixture by conductometric titration[10] and also in the presence of rubber latexes.[11] Alkaline thioglycolate- and sulfite-containing solutions are analyzed conductometrically for free bases and for thioglycolates and sulfites.[12] Iron in iron ores is determined by conductometric titration with sulfosalicylic acid or its ammonium salt.[13]

DETERMINATION OF WATER

The water content of some water-miscible organic solvents such as alcohol and acetone may be determined by taking advantage of the increased solubility of most inorganic salts or the increased dissociation of weak acids in the presence of small amounts of water.[17] Thus sparingly soluble calcium sulfate increases in solubility and the conductivity of ethanol rises as the water content increases. The rise in conductivity is not linear and so the water determination must be carried out by means of empirical calibration curves.

ANALYSIS OF SALT SOLUTIONS

The conductometric standardization of electrolyte solutions[18] has been recommended with the use of a fairly simple apparatus which measures conductance with a precision of ± 0.1 per cent. There have been described many empirical applications of conductivity based upon a single measured value rather than upon a titration.[19] Of interest is the determination of the solubility of slightly soluble ionic compounds and the critical micelle concentrations of soaps, detergents, and other electrolyte-forming colloids. Conductivity measurements are also utilized for industrial control of water purification and other operations.

MEASUREMENT OF CONDUCTANCE

Measurements with Alternating Current. *Wheatstone Bridges.* Accurate measurement of conductance with direct current is not a straightforward process. Changes in ionic concentrations of electrolyte due to the electrode reactions cause changes in resistance. Conductivity meas-

urements are therefore commonly carried out not with direct current but with alternating current (at a frequency of 1,000 to 10,000 cycles per sec and at an applied potential of 6 to 10 volts). This avoids interfering electrode reactions. The Wheatstone bridge, in the general arrangement illustrated in Fig. 12-5, is most commonly used. R_1 and R_2 are usually matched fixed resistors (but may be precision variable resistors) and R_3 is a precision variable resistor. R_c is the conductivity cell. ABC is sometimes made up of a uniform slide wire with a movable contact at B so that the ratio R_1/R_2 is equal to the ratio of the lengths of wire (in terms of scale divisions) AB/BC or $AB/(AC-AB)$. A pure sine-wave alternating current is applied across A and C and a null detector Det. is placed across B and D. In classical conductometry the null detector was a telephone but in recent years this has been superseded by electronic null devices[20] such as the cathode-ray tube.

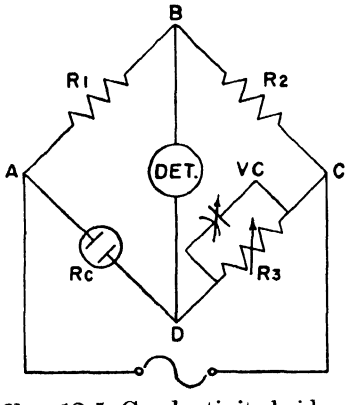


FIG. 12-5. Conductivity bridge. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. IX-1. By permission of the publishers.*)

When a conductivity measurement is to be made, R_3 is varied until no current passes through Det. (With variable resistors R_1 and R_2, these are also adjusted. A setting such that $R_1 = R_2$ makes for the best precision.) When the null setting has been attained, B and D will be at the same potential. If i_{ABC} is the current across ABC and i_{ADC} the current across ADC, then, if there is no capacitance or inductance in the system,

$$i_{ABC}R_1 = i_{ADC}R_c$$

and

$$i_{ABC}R_2 = i_{ADC}R_3$$

Therefore

$$R_c = R_1\frac{R_3}{R_2} \qquad (12\text{-}6)$$

For a-c current in a Wheatstone bridge the R terms in (12-6) should be replaced by corresponding Z terms, where Z, the impedance, is a function of the resistance and reactance. The reactance may be caused by either inductance or capacitance, or both. The inductive reactance of the resistors and the cell may be made negligibly small by proper mechanical design, but the capacitance of the cell itself can never be eliminated, even though it can be minimized by proper cell design. Cell capacitance causes a broadening of the null-point signal with a resulting drop in precision. The variable condenser V.C. is therefore inserted for precise measurements across R_3 to balance the cell capacitance, and is adjusted to give the sharpest signal when balancing R_3.

Commercially available bridges may be obtained which will make measurements precise to 0.001 per cent, such as a bridge described by Jones and Josephs[21] and manufactured by Leeds and Northrup Company,

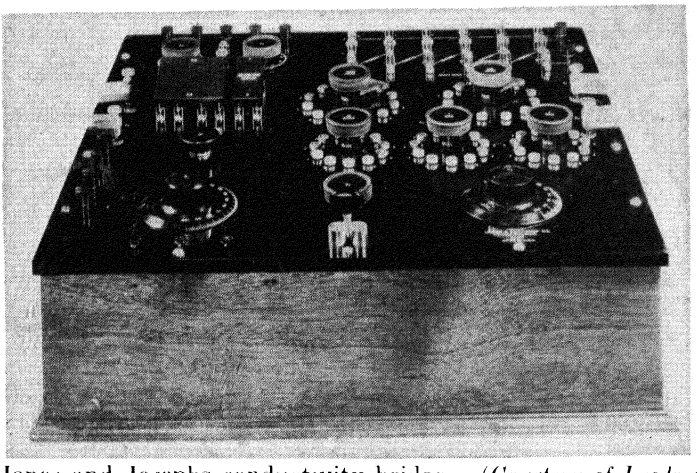


FIG. 12-6. Jones and Josephs conductivity bridge. (*Courtesy of Leeds and Northrup Company.*)

Philadelphia, Pa. (see Fig. 12-6). Shedlovsky[31] has described a bridge which can yield measurements precise to 0.01 per cent. However, such precision is not needed for ordinary analytical work. Industrial Instruments Inc., Cedar Grove, N.J., manufactures a simple, easy to operate bridge (see Fig. 12-7) with which a precision of ± 1 per cent is attainable. The Serfass bridge (see Fig. 12-8) sold by A. H. Thomas Company, Philadelphia, Pa., is direct reading in reciprocal ohms and so is convenient for conductometric titrations.

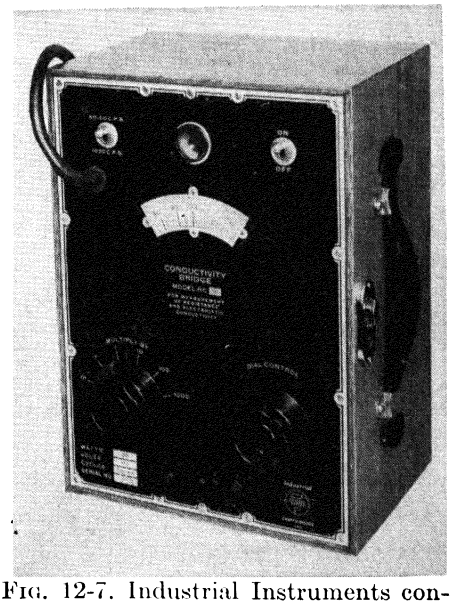


FIG. 12-7. Industrial Instruments conductivity bridge. (*Courtesy of Industrial Instruments, Inc.*)

Measurements with Direct Current. Conductometric measurements may be made with good accuracy with direct current by using nonpolarizable electrodes such as

$$Ag/AgCl \text{ or } Hg/Hg_2SO_4.^{22-24}$$

For very dilute solutions of high resistance, platinum electrodes may be used by applying about 150 volts across the cell so that the back potential at the electrodes is negligibly small in comparison with the potential drop through the

solution.[25–27] Taylor and Furman[28] have described a method for determining conductivity by direct constant current. The latter is obtained by using a 540-volt battery (twelve 45-volt radio *B* batteries in series) across a high resistance. The constant current passes through the solution through a pair of platinum primary electrodes. The voltage drop across a pair of secondary tungsten electrodes is then inversely proportional to the conductance of the solution. This arrangement makes it possible to get conventional conductometric-titration curves by using a



FIG. 12-8. Serfass conductivity bridge. (*Courtesy of A. H. Thomas Company.*)

pH meter to measure conductance instead of the specialized or inconvenient apparatus of a-c conductometry. This method is reported additionally not to have the disadvantages of other d-c methods described. For example, with some other methods there is the necessity of using a small current to prevent electrode polarization and at the same time having the *IR* drop across the secondary electrodes sufficiently high for convenient measurement. This requires cumbersome long cells in which it is difficult to stir the solution, so that titrations are practically impossible. Another difficulty which is avoided is the necessity in other methods of using nonpolarizable electrodes which are less convenient than ordinary electrodes and must be changed to conform to the solution being measured.

Conductivity Cells and Electrodes. Conductivity cells should be made of an insoluble glass such as Pyrex. The platinum electrodes should be about 1 sq cm in area and should be rigidly fixed in the vessel. To

exists with ordinary cells. The necessity for such measurements is avoided in practice, given a cell with rigidly fixed electrodes, by measuring in the cell the resistance of a potassium chloride solution of known composition. Extremely accurate specific-conductance values have been reported for such solutions by Kohlrausch and others.[32,33] The specific conductance of the standard solution should be of the same order of magnitude as that of the solutions to be measured.

From Eq. (12-1), one may derive the relation

$$\frac{d}{A}\frac{1}{R} = \frac{1}{\rho}$$

But $1/\rho = \kappa$ and $d/A = C$, a constant for the particular cell, the cell constant, so that

$$\kappa = C\frac{1}{R}$$

By measuring a solution of known R, C may be calculated for a given cell. Thereafter, in making a measurement with that cell, the reciprocal of the observed resistance may be multiplied by C to give the true specific conductance of the solution. This is not needed for mere end-point determinations in a titration but will be necessary for interpretation of the precise conductivities occurring during the course of a titration. [For titrations, instead of plotting specific conductance against volume, one may plot the ratio of the lengths of slide wire $(AC\text{-}AB)/AB$ (Fig. 12-5) if a slide wire is used, or R_2/R_1 otherwise.]

Table 12-2 gives some specific conductances of potassium chloride solutions which are useful for all but the most precise work.[60]

TABLE 12-2. SPECIFIC CONDUCTANCES OF POTASSIUM CHLORIDE SOLUTIONS

°C	Specific conductance		
	1*N*	0.1*N*	0.01*N*
0	0 06543	0.007154	0.0007751
18	0 09820	0.011192	0.0012227
20	0 10202	0 011667	0 0012757
25	0.11173	0 012886	0.0014114

Temperature Control. Since conductance varies about 2 per cent per degree centigrade, for conductivity measurements to be precise to ± 0.1 per cent, the temperature of the cell must be controlled to ± 0.05°C. For ordinary purposes one may use a water thermostat, but for more precise work an oil thermostat should be used to prevent current leakage

to ground. For ordinary titrations no thermostat is needed, but merely a water bath at room temperature to prevent temperature changes during the titration. Omission of the water bath is not recommended since heat of reaction may change the temperature of the contents of the cell even if the titration is done rapidly enough to prevent heat transfer to and from the cell. Müller and Vogel[18] have devised a bridge with an automatic temperature compensator which makes a thermostat unnecessary for work with a precision of ± 0.1 per cent.

Effect of Conductivity of Water. The specific conductance of the highest-purity conductivity water is less than 0.1×10^{-6} mho at 25°C. Ordinary distilled water containing carbon dioxide, ammonia, and traces of impurities from the containers has a κ value of about 2×10^{-6} mho. For most analytical work the solutions will have a κ value greater than 10^{-3} mho and so the κ of the water may be neglected. For work of the highest precision, the water should be purified to a negligible conductivity since application of solvent corrections is not a simple matter.[34–36]

HIGH-FREQUENCY (OSCILLOMETRIC) METHODS

Conventional conductometry utilizes alternating current at a frequency of about 1,000 to 10,000 cycles per sec. Blake[37–42] and Jensen and Parrack[43,44] independently reported on the use of high-frequency current—of the order of several megacycles per second to several tens of megacycles per second—in analytical chemistry (oscillometric or high-frequency methods) for the determination of conductivity (and dielectric constant) without the use of internal electrodes. The sample solution in a suitable cell is placed in the oscillating circuit (e.g., within the coil) of an oscillator operating in the frequency range indicated. The frequency, the current, or the voltage, depending upon the particular instrumentation, varies with changes in the composition of the solution being tested. The method may thus be used for titrations, for the determination of the composition of binary mixtures from calibration curves, or for such applications as the location of bands in a chromatographic column.

The concept of conductivity with respect to high frequency and external electrodes is not the same as with conventional d-c or low-frequency a-c conductivity methods with internal electrodes. Electrolytic effects are absent or negligible. Furthermore, conductivity really becomes a matter of energy loss from the oscillating system to the sample because of the rapid motion of molecules relative to neighboring molecules in the sample. It is sometimes described as "dielectric loss." Blake has used the term "Q metrics," using Q in a sense familiar to adepts in electronics. In deference to convention, however, the term conductivity will be used

here. High-frequency methods also involve measurement of a property other than conductivity, namely, the dielectric constant, which is concerned with the storage of energy, as conductivity is concerned with its loss. At lower frequencies, for ordinary a-c conductometry, the dielectric effect may be minimized, as indicated in our previous discussion, by use of a variable condenser, but not at higher frequencies. The interpretation of oscillometric curves is therefore more complicated than that of conventional conductometric curves and the applications are highly empirical.

One type of instrument measures changes in frequency caused by the sample. Such instruments produce S-shaped curves of frequency plotted against concentration. The concentration at which an inflection occurs depends on the electrolyte being tested. Another type of instrument measures the change in oscillator current at constant frequency. This type of instrument produces a curve of current vs. concentration which goes through a maximum at a concentration which again is a characteristic of the particular electrolyte. Thus the shape of a titration curve depends upon the nature of the specific electrolyte being titrated, on its concentration, and on the type of instrument being used. Hall[45] thus found, with an instrument measuring current at constant frequency, that titration of 0.005M hydrochloric acid with 0.05M sodium hydroxide gave a V-shaped curve, whereas the titration of 0.02M hydrochloric acid with 0.2M sodium hydroxide gave an inverted V-shaped curve. Both had rounded rather than straight titration lines. Blaedel and coworkers[46] found curved V-shaped lines for the same titration with a frequency-measuring instrument. The curvature was dependent upon the concentration of the acid being titrated.

Applications. Many of the titrimetric applications which have been reported for oscillometry are such that other techniques, including those of low-frequency conductometry, would be as good or better. For some purposes, however, oscillometry does offer some advantages. The avoidance of internal electrodes is occasionally useful, although generally in conductometric titrations such electrodes offer no difficulties. For example, in the oscillometric titration of sulfate with barium[47] the freedom from the disturbance caused by the deposition of barium sulfate on internal electrodes is a real gain.

Other titrations not involving this feature would seem on occasion to give more precise end points than with some other methods, as witness the reported mercurimetric determination of chloride by Blaedel and Malmstadt.[48] However, there are some instrumental limitations in this method to the concentration range which can be titrated. The same authors have also carried out a number of other titrations oscillometrically.[49,50] Anderson and Revinson[51] titrated beryllium with sodium

hydroxide, thus achieving oscillometrically a titrimetric determination which has not been carried out successfully by other more usual titration methods. In general, however, oscillometric titration curves are rather complex and suffer the disadvantage of usually being rounded so that measurements must be made close to the equivalence point. The effect of foreign electrolytes is also a complex one.

It would seem that the field in which oscillometry holds the greatest promise is not in titrimetry but in the analysis of mixtures, particularly of organic substances, by direct measurement. In so far as changes in composition are accompanied by dielectric changes, high-frequency

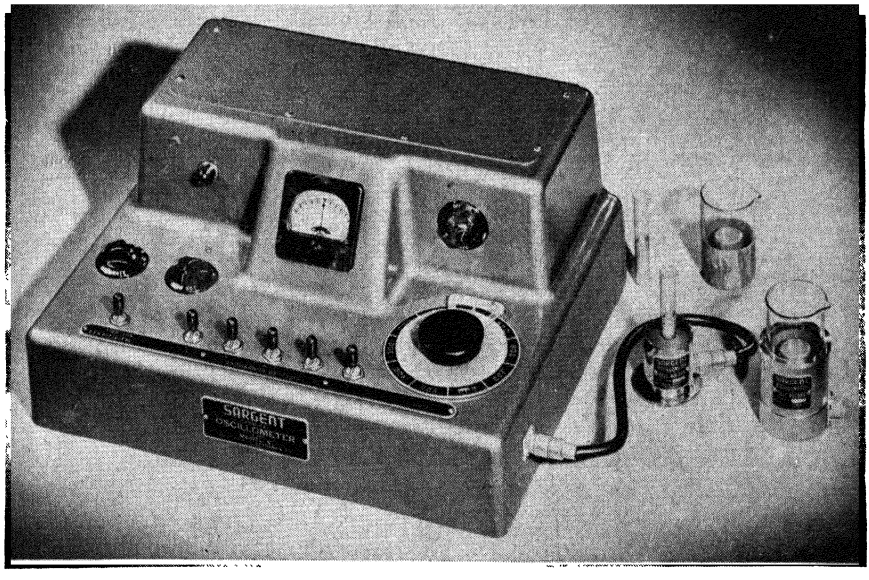


FIG. 12-10. Sargent chemical oscillometer, model V. (*Courtesy of E. H. Sargent and Company.*)

methods may be used. The method in principle has long been used for the determination of moisture in substances such as grains and seeds. The analysis of mixtures of organic liquids has been reported by West and his coworkers.[52,53] They have also reported[54] the analysis of the system water–benzene–methyl ethyl ketone by measuring frequency before and after dehydration. The change in frequency gives a value for water. The ratio of benzene to methyl ethyl ketone is obtained from the frequency after dehydration by reference to a working curve for mixtures of those two substances.

The location of chromatographic zones in a column[55] illustrates one of the unique uses of electrodeless oscillometry. There would seem to be the possibility of applying oscillometry to the control of composition in continuous industrial processes, which would make unnecessary the withdrawal of samples for analysis in the laboratory. In this direction

a continuously recording dielectric-constant apparatus has been used for direct concentration measurement.[56] An electrodeless oscillometer could have been used to advantage.

Finally there should be mentioned the application of oscillometry in kinetic studies by the use of a dielectric-constant meter[57] and by electrodeless methods.[58] Complexation studies have also been carried out oscillometrically.[59]

Instrumentation. There has been considerable work on a variety of instruments for use in high-frequency studies. A consideration of these would lead far afield from the interests of the analytical chemist who is not circuit-minded. Three commercial instruments are available: the Sargent model V oscillometer (Fig. 12-10), the Beckman high-frequency conductometer, and a twin-T impedance bridge (General Radio Co., Cambridge, Mass.) which is claimed to be suitable for high-frequency titrations.

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CHAPTER THIRTEEN

Coulometric Analysis

Coulometric analysis is an application of Faraday's law of electrochemical equivalence which states that the extent of a chemical reaction which takes place at an electrode is directly proportional to the quantity of electricity passing through the electrode. For each equivalent of chemical reaction 1 faraday (96,494 coulombs of electricity) is required. A coulomb is that quantity of electric current represented by a flow of current of 1 ampere for 1 second. An equivalent of chemical reaction is the amount of reaction corresponding to that fraction of a gram-atom or mole of reactant which is conventionally represented by e in the equation for the reaction. Thus the reaction $Fe^{3+} + e = Fe^{++}$ would require 1 faraday, $Cu^{++} + 2e = Cu$ 2 faradays, and $2H_2O = O_2 + 4H^+ + 4e$ 4 faradays.

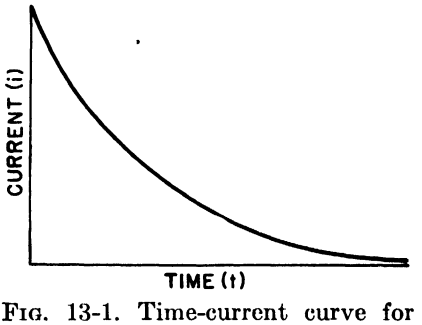


FIG. 13-1. Time-current curve for coulometric analysis at controlled potential.

It follows from Faraday's law that, if a substance can be made to undergo an electrode reaction, it can be determined quantitatively by the amount of current used. This is so, provided that either the current is used with 100 per cent efficiency for that reaction or else the efficiency, if less than 100 per cent, is known and constant during the course of the electrolysis. Coulometric analysis is that branch of quantitative analysis which utilizes this principle.

Two different general techniques have been used, coulometric analysis with controlled potential and coulometric analysis with controlled current.

Controlled Potential. In the first method by suitably controlling the potential of an electrolysis electrode only the substance (or group of substances) being analyzed will undergo oxidation or reduction. Furthermore, as the concentration decreases, the current will finally decrease to substantially zero or to the background current (Fig. 13-1). By meas-

uring the quantity of electricity utilized (by methods to be discussed) and applying Faraday's law, a quantitative determination may be made.

It has been shown[2] that in a controlled-potential coulometric analysis the current usually follows the relationship

$$i_t = i_0 10^{-kt} \tag{13-1}$$

where i_t and i_0 are, respectively, the current at time t and at zero time, and k is a constant. The magnitude of k is directly proportional to the diffusion constant of the reacting substance (which is a measure of its tendency to diffuse to the electrode from the solution) and to the electrode area, and inversely proportional to the volume of solution and to the thickness of the layer from which diffusion occurs. From Eq. (13-1) it follows that, as indicated in Fig. 13-1, i_t approaches zero asymptotically. Thus, strictly speaking, the reaction is never complete. Nevertheless, when the ratio i_t/i_0 reaches a sufficiently low value, the analysis may be ended. This ratio is equal to the ratio of the concentration of the ingredient at time t to that at zero time, so that a "sufficiently low value" of i_t/i_0 may be chosen on that basis. A further complication occurs when there is an appreciable background current, so that i_t finally drops no lower than to the background value, for which a correction may be applied. Such a background current, for cathodic reactions, is usually due to hydrogen evolution and indicates less than 100 per cent current efficiency. This, of course, limits the accuracy of the determination.

Controlled Current. In coulometric analysis with controlled current the current is kept constant (or nearly so) while the potential varies. The end point of the determination must then be signaled, as in any ordinary titration, by an indicator—visual, potentiometric, amperometric, or of any other suitable kind. At the end point the circuit is broken. The amount of constituent being determined is then calculated from the amount of electricity used.

In both the controlled-potential and the controlled-current techniques, the substance may be determined by either primary or secondary coulometric analysis. In the former it undergoes reaction directly at one of the electrodes, whereas in the latter it reacts in solution with some other substance which has been generated by an electrode reaction.

MEASUREMENT OF QUANTITY OF ELECTRICITY CONSUMED

The quantity of electricity Q passing through a coulometric circuit in which the current i is kept quite constant with time t is

$$Q = it \tag{13-2}$$

When the current is held constant enough (in a manner which will be

described) in constant-current coulometric analysis, consideration of Eq. (13-2) leads to a simple means of calculating Q, namely, by the use of a precise clock. When i varies as in the controlled-potential technique, or as in the controlled-current technique when carried out with inadequate control, Eq. (13-2) no longer applies but becomes

$$Q = \int i \, dt \tag{13-3}$$

Q may then be measured by the area under the current-time curve, which may, of course, be obtained either manually or with an automatic recorder. The area may be measured graphically, but this obviously is not a convenient procedure.

It would be more convenient to integrate Eq. (13-3) automatically and to record directly the value of Q thus obtained. Electromechanical integrators have been described for this purpose,[1,3,4] but none of these is sufficiently precise. They are therefore not to be recommended for coulometric analysis unless one is prepared to sacrifice precision for convenience and speed. An electrical integrator has recently appeared on the market which makes possible precise integration of current and time in a simple and inexpensive manner.[82]

Chemical Coulometers. The instrument which is generally used for measuring Q is the chemical coulometer. Several types have been described, but they are all based on a common principle. This is to insert in series with the electrolysis cell a cell at which a known chemical reaction may be carried out with 100 per cent current efficiency. By measuring, in any suitable manner, the products of the reaction which have arisen during the exact period of the coulometric analysis, and applying Faraday's law, the value of Q for the coulometric analysis is obtained. Several standard types have been used for a long time. The silver coulometer[5,6] consists of a platinum cathode upon which silver is deposited from a silver nitrate solution. The iodine coulometer consists of either a platinum anode at which iodine is deposited by oxidation of iodide ion, or a platinum cathode at which iodine is reduced. The reaction is measured by titration with standard arsenious acid solution.[7] These coulometers are of high precision but rather inconvenient for practical analysis. More recently a vanadyl-ion coulometer[8] has been proposed; and a study of the oxalate-ion coulometer has revealed it to be highly accurate.[9] The hydrogen-oxygen coulometer[10,2] is convenient and capable of yielding an accuracy of ± 0.1 per cent or better. Figure 13-2[2] represents such a coulometer. The electrolysis tube (about 100 ml in volume above the platinum electrodes) is immersed in a water bath containing a 0.1° thermometer and is connected to a burette. The electrolyte, which may be 0.5M potassium sulfate, must be completely free of impurities such as iron salts. Such impurities may be repeatedly oxidized

and reduced at the electrodes, thus decreasing the volume of hydrogen and oxygen produced by a given amount of electricity. Instead of the theoretical value of 0.1741 ml of gas per coulomb at standard conditions, the experimentally determined value of 0.17394 ml is used for 0.5*M* potassium sulfate with the simple coulometer described.

Microcoulometer. The coulometer shown in Fig. 13-2 is not recommended for measuring quantities of electricity less than about 10 coulombs (corresponding to about 1.7 ml of gas). For such analyses a titration coulometer may be used which can measure as little as 1 coulomb with an accuracy of ± 1 per cent and 10 coulombs or more with an accuracy of ± 0.1 per cent. It consists of a platinum cathode located within a helical silver wire anode or a cylindrical platinum gauze plated with silver. The electrolyte consists of a solution of potassium bromide and potassium sulfate (the latter for good conductance). The net coulometer reaction is

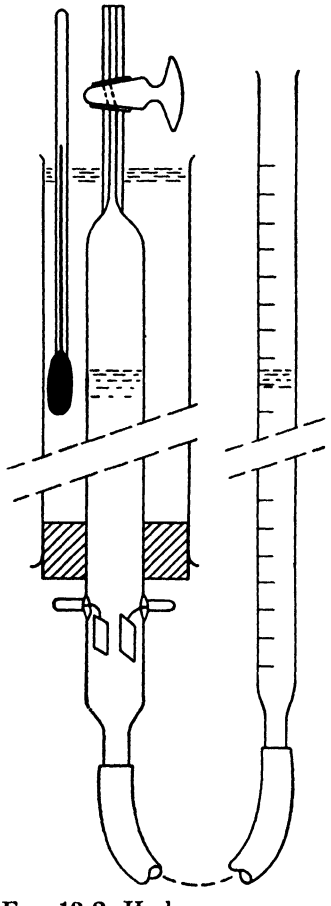


FIG. 13-2. Hydrogen-oxygen coulometer. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. XVII-1. By permission of the publishers.*)

$$2Ag + 2Br^- + 2H_2O = 2AgBr + H_2 + 2OH^-$$

The hydroxyl ion is titrated with standard acid in an atmosphere of carbon dioxide–free air using a glass electrode[11].

COULOMETRIC ANALYSIS AT CONTROLLED POTENTIALS

Instrumentation

The three instrumental units in controlled-potential coulometric analysis are the current supply together with a means for controlling its potential, the electrolysis cell, and the coulometer or other means for measuring quantity of electricity. Measurement has been discussed. The form of electrolysis cell depends upon the specific application and will be discussed in connection with specific applications. Some discussion of current supply and its potential control will be given at this point.

Manual Control. Manual potential control in coulometric analysis is quite feasible. It is naturally not so convenient as automatic control

but will serve adequately for an occasional analysis, or where for other reasons the expense of an instrument for automatic control is felt not to be justified.

A generalized circuit is given schematically in Fig. 13-3, but the coulometer or other device for measuring the quantity of electricity is not included. The d-c source provides the current. This is adjusted manually at the voltage adjuster during the course of the analysis so as to provide a voltage across the entire electrolysis cell which will maintain the potential between E', the working electrode, and R.E., the reference electrode, at the desired value for the oxidation or reduction concerned in the coulometric analysis. This potential is indicated on the potential-measuring device. The meter M indicates the electrolysis current. This drops to zero or to some constant small value (see Fig. 13-1) upon completion of the electrolysis.

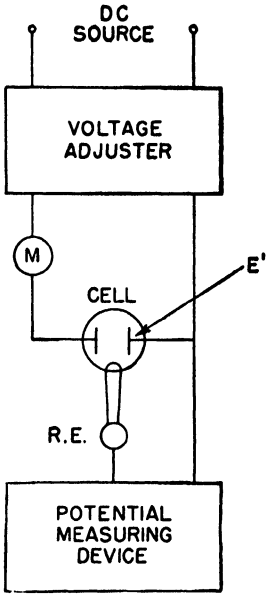


FIG. 13-3. Circuit for controlled-potential electrolysis. (*J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, 1953, Fig. XI-1. By permission of the publishers.*)

For the current and voltage requirements of coulometric analysis one or two lead storage batteries in series will suffice. Dry batteries do not have sufficient capacity. If a central d-c supply is available this may be used, with the introduction into the circuit of a resistor if necessary to cut down the voltage. Selenium rectifier units are commercially available too which are convenient to use and inexpensive. These produce a pulsating current which is smoothed out by the instrument, so that one must be certain that the variations in voltage (residual ripple voltage) produced by a particular apparatus are tolerably small.

A selenium rectifier unit includes a voltage-adjusting feature so that no additional voltage adjuster, as shown in Fig. 13-3, is necessary. With other d-c current sources voltage adjustment may be attained by placing a variable power resistor across the current supply and adjusting a moving contact to furnish the electrolysis cell with the desired emf.

The ammeter M is used merely to follow the progress of the electrolytic reaction and not to measure the current consumed. It need therefore not be an expensive meter of high precision. Either an ammeter with two ranges (0 to 5 amp and 0 to 0.1 amp) may be used or two instruments of the desired ranges may be combined in series together with a switch to short out the lower-range meter when higher currents are being used, in order to prevent damage to the lower-range meter.

The potential-measuring device is used to measure the potential of the working electrode, be it either the cathode or the anode. This potential is measured against a reference electrode, usually a saturated calomel electrode. In order not to cause a change in this potential (which it is sought to keep constant) appreciable current must not be drawn by the potential-measuring device. The latter must therefore be either a potentiometer or a high-resistance voltmeter. A pH meter such as is conventionally used with the glass electrode, and which has a voltage scale in addition to the pH scale, is suitable. Another type of potentiometer may be the well-known Leeds and Northrup student potentiometer. Self-contained portable potentiometers which are generally available may be used. For most purposes a range of 0 to 1 volt with a precision of ± 0.01 volt will be satisfactory. (Occasionally up to 1.5 or 2 volts may be needed.) If none of these instruments is available, a potentiometer may be constructed using a 1.5-volt dry cell.[1] For greater convenience than is afforded by a potentiometer, one may use a high-resistance voltmeter.[12,13,14]

Automatic Control by Potentiostats. Although controlled-potential coulometric analysis with manual control is feasible, it is unquestionably time-consuming and tedious. A considerable number of instruments for automatic control of potential have therefore been described to relieve the analyst of the chore of manual control. The term potentiostat applied to the first of these instruments is now used generally. The original potentiostat[15] is based upon an all-electronic circuit. It requires a d-c source of about 200 volts potential and can furnish no more than about 300 ma of electrolysis current. This is sufficient for most coulometric analysis.

For microcoulometry an all-electronic potentiostat has been reported.[16] Since it is limited to electrolysis currents of less than 1.5 ma, it cannot be recommended for more general use.

Another potentiostat[17,18] includes a selenium rectifier unit and may be operated from the 110-volt a-c line. It is not completely electronic but depends upon the use of a motor which changes the setting of a Variac transformer in response to an unbalance between the potential of the working electrode and the controlled potential setting. The instrument will handle electrolysis currents up to 8 amp, but such large currents, while useful for controlled-potential electrogravimetric analysis and for the electrolytic preparation of chemicals, are not needed for coulometric analysis. It is, moreover, rather complex and requires considerable adjustment before use. Another limitation is that it controls the potential in only one direction; i.e., it prevents a cathode potential from becoming more negative or an anode potential from becoming more positive than the control setting. It does not control a drift in the opposite direction.

Still another potentiostat[19,20] is also not completely electronic. It too employs a selenium rectifier unit and uses a motor to adjust a Variac transformer to restore the preset potential in response to an off balance between that potential and the potential of the working electrode. The off-balance detector is a sensitive galvanometer relay. This potentiostat operates from the 110-volt a-c line but has in addition one 1.5-volt dry cell, which has practically shelf life. The instrument has only a few simple controls and no preliminary adjustments or calibrations are required. It controls potential drift in both directions to within ± 0.01 volt of the preset value and furnishes a continuous maximum current of 5 amp. Up to 7 or 8 amp may be drawn for short periods.

An electroanalytical instrument has also been reported[21] which serves as a potentiostat in addition to performing other functions. It may be assembled from commercially available units and thus does not require expert knowledge for its construction. It is operated from the 110-volt a-c line. The potential may be set at a number of values between 10 mv and 10 volts. For the range 0 to 1 volt, the precision is ± 5 mv.

A number of other potentiostats have been described.[22–30] An excellent discussion appears in ref. 1.

Applications

The applications of coulometric analysis at controlled potential have not yet been extensive. The method was first reported[15] for the determination of cupric ion by measurement of the quantity of electricity required to plate out metallic copper at a platinum cathode and for the determination of iodide by anodic oxidation to elemental iodine at a platinum anode. It was then extended by introducing a mercury cathode.[2] This has an advantage over the platinum cathode in having a higher hydrogen overvoltage so that it is possible to carry out cathodic reactions over a wider range of potentials without reducing the current efficiency below 100 per cent because of hydrogen evolution. On the other hand, anodic reactions are limited to potentials more negative than $+0.2$ volt (or even lower in the presence of ions which precipitate or which form complexes with mercury) because of the relative ease of oxidation of mercury at these potentials. With the mercury cathode optimum control potentials may be established by reference to polarograms made with the dropping-mercury electrode.

Halide Determinations. Chloride, bromide, and iodide ions may be determined separately, or in mixtures with each other[11] by the reaction at a silver anode of halide ion (X^-) to form silver halide with the liberation of one electron ($Ag + X^- = Ag\,X + e$).

The relationship between the optimum potential for determining each halide and the activity of the ions involved is indicated in Fig. 13-4. The ordinate indicates emf vs. the saturated calomel electrode of the silver–

silver halide electrode and pX the negative logarithm of the halide concentration. The dashed line shows a similar relationship for pAg of the silver ion and the emf of the silver–silver ion couple. The intersections of the Ag^+ line with the halide lines, where the activities of silver ion and halide ions are equal (which condition corresponds to the solubility of silver halide in water) represent the optimum potentials for the coulometric determination of the halides. At more positive potentials there is an excess of silver ion over halide in solution, and vice versa at more negative potentials.

The limits within which the potential must be controlled for any of the halides are narrower, the more soluble the silver halide. (It should be remembered that each pX unit represents a tenfold change in activity.) For chloride, the potential is controlled at +0.25 volt vs. S.C.E. (±0.01 volt); for bromide, regulation within the range +0.12 to +0.25 volt is satisfactory; and for iodide within the range −0.10 to +0.25 volt. A potentiostat is used for automatic voltage control.

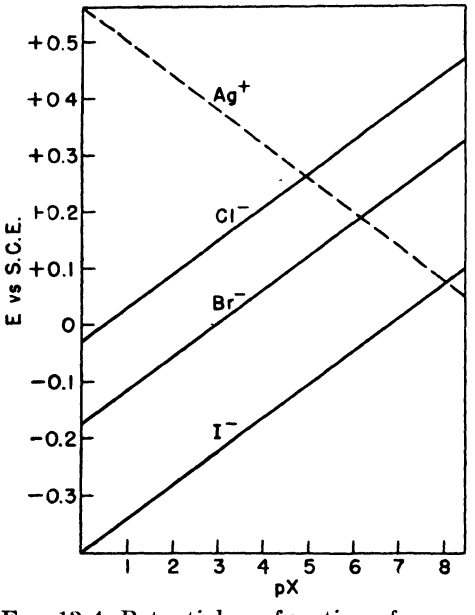


FIG. 13-4. Potentials as function of negative logarithm of halide (or silver) ion activity. [*J. J. Lingane and L. A. Small, Anal. Chem.*, **21**: *1119 (1949) Fig. 1.*]

A cell such as shown in Fig. 13-5 is used. Its size depends upon whether macro or semimicro samples are being analyzed. The cell consists of a 250-ml beaker (for macro samples) which is placed over a rotating magnet which rotates the magnetic stirrer. The cathode consists of a cylinder of platinum gauze which is placed within an outer cylinder of platinum gauze plated with silver. The tip of the salt bridge from the saturated calomel electrode is placed close to the anode. Its potential drop to the anode is utilized by the potentiostat to control the potential of the working anode.

The electrolysis is continued until the current decreases to a negligibly small value, usually below 1 ma. The quantity of current is measured with the hydrogen-oxygen coulometer for macro determinations and with the acidimetric-titration coulometer for semimicro determinations.

Chlorides. For determining chlorides an acetic acid–sodium acetate buffer is added in order to prevent the formation of hydroxyl ion at the platinum cathode, with the resulting deposition of silver oxide on the

anode. Somewhat low values are obtained when strongly acid solutions are used.

Iodides. In determining iodide, in an acetic acid–acetate buffer, values were obtained with 25- to 100-mg samples of iodide which were low by 0.3 to 0.5 mg. This was caused by the oxidation of iodide to iodine by dissolved oxygen in the acid medium, and the subsequent formation of silver iodide at the silver anode by a nonelectrolytic process. By removing air from the solution this error could be avoided. Another approach to this problem was to carry out the determination in an ammoniacal medium.

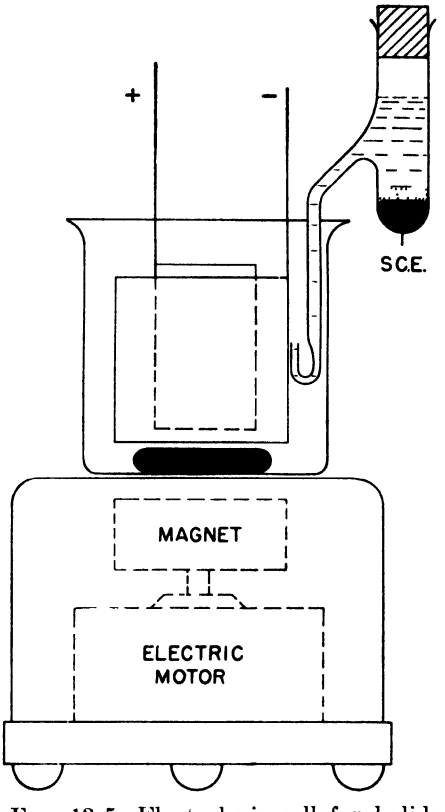


FIG. 13-5. Electrolysis cell for halide determinations. [*J. J. Lingane, Anal. Chim. Acta*, **2**: *592 (1948), Fig. 3.*]

Mixtures of Halides. Neither bromide nor chloride reacts at the silver anode under the conditions prevalent for the iodide determination. Either may therefore be determined together with iodide by first using an ammoniacal medium in which to determine iodide, then acidifying to pH 5 with acetic acid, adjusting the voltage suitably, and determining bromide or chloride. The accuracy is better in the coulometric determination of these mixtures than in the corresponding potentiometric determinations,[32,33] apparently because of a lesser tendency for coprecipitation under the conditions of the coulometric determination.

The coulometric determination of bromide and chloride in mixtures of the two should be feasible as far as the potentials are concerned. Actually high bromide values and low chloride values are obtained because of coprecipitation of chloride with silver bromide.[34] This problem has been solved by a so-called "coulogravimetric analysis."[35] Chloride and bromide ion in admixture are determined together coulometrically in a sodium acetate–acetic acid buffer first at +0.22 volt vs. S.C.E. and finally at 0.25 volt. The increase in weight of the silver anode is also determined. Two simultaneous equations are thus obtained:

$$\Delta W = W_{Cl} + W_{Br} \qquad (13\text{-}4)$$

in which ΔW is the increase in weight of the silver anode and W_{Cl} and W_{Br} are the weights of chloride and bromide ions deposited, respectively; and

$$\frac{Q}{96{,}500} = \frac{W_{Cl}}{35.46} + \frac{W_{Br}}{79.92} \tag{13-5}$$

in which Q is the number of coulombs of electricity passed and 35.46 and 79.92 are the atomic weights of chloride and bromide ions, respectively. Q is first corrected for a small amount of electricity used in depositing a little silver on the platinum cathode at +0.25 volt (see Fig. 13-4) which is determined from the increase in weight of the platinum cathode. Solution of the simultaneous equations (13-4) and (13-5) leads to a value for chloride and bromide.

Determination of Iron and Arsenic. Fe(II) and As(III) are determined by oxidation in acid solution at a platinum anode.[36,37] The electrolysis cell, shown in Fig. 13-6, consists of two beakers joined together by wide-bore tubing in which is placed a fritted glass disk separating the anode and cathode compartments. The separation is necessary in order to prevent reduction of the oxidized ions at the cylindrical platinum gauze cathode. The anode is also a cylinder of platinum gauze. A magnetic stirrer is used. The total quantity of electricity is determined either with the hydrogen-oxygen coulometer or by integrating the current-time curve. The integration is simplified by taking advantage of the fact that a straight line is obtained when the log of current is plotted against time of electrolysis. It is therefore possible to calculate total current by getting only two points, thus obviating the necessity for running the electrolysis to completion.

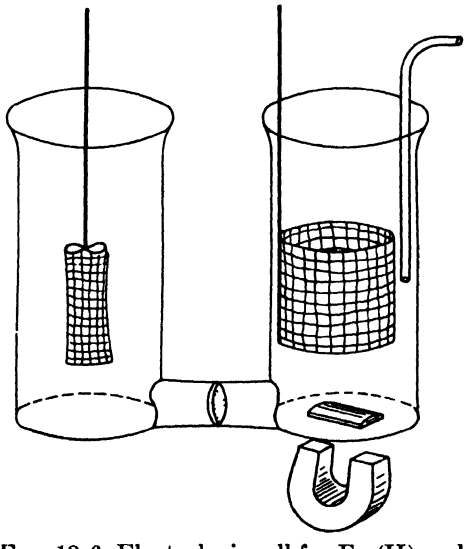


FIG. 13-6. Electrolysis cell for Fe (II) and As (III) determinations. [*W. M. MacNevin and B. B. Baker, Anal. Chem.*, **24**: *986 (1952), Fig. 2.*]

Determination of Metals. The cell shown in Fig. 13-7 may be used to determine various metals. It has a pool of mercury as the cathode and a helical silver wire as the anode. Nitrogen or other inert gas is used to sweep out dissolved air through a tube in the Bakelite cover. Oxygen is reduced at the cathode at about −0.05 volt vs. S.C.E. and so would decrease the current efficiency.

Chloride is added to the solution to furnish anions for the anode reaction,

$Ag + Cl^- = AgCl + e$, equivalent to the metal reduced at the mercury cathode. In cases where the metal ion is not reducible by hydrazine, a platinum anode may be used with hydrazine being added to the solution. The hydrazine is oxidized at the anode and thus prevents the undesired evolution of oxygen at the same time that the nitrogen which is formed by the oxidation of the hydrazine serves to sweep dissolved air from the solution.

With this apparatus and technique lead, copper, and bismuth have been determined, and the possibility has been suggested of successive determinations of several metals in a mixture.

Tin-iron alloy may be determined[38] in tin plate by stripping off the metals by anodic oxidation and then determining them coulometrically.

Submicrogram quantities of silver may be determined[39] in solution in volumes from 20 to 25 ml by electrodeposition onto a smooth platinum cathode followed by a coulometric determination involving stripping the silver at an anode. Submicrogram quantities of cadmium and zinc may be determined[40] similarly but with a mercury-plated platinum cathode instead of the smooth platinum cathode.

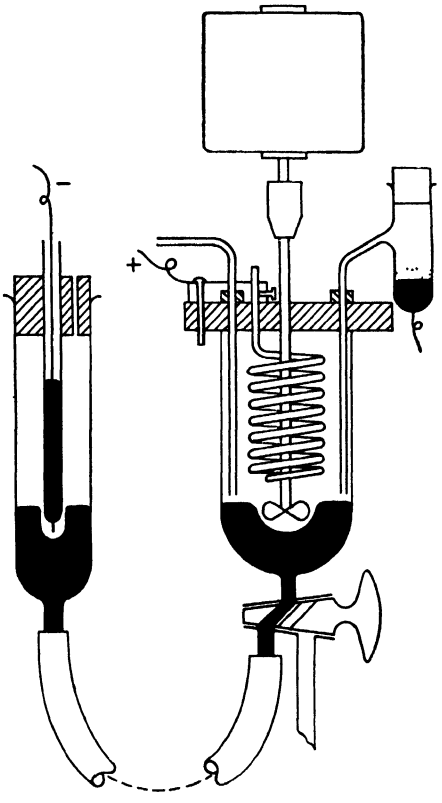


FIG. 13-7. Mercury-cathode cell for controlled-potential coulometric analysis. [*J. J. Lingane, J. Am. Chem. Soc.*, **67**: *1916 (1945), Fig. 1.*]

Miscellaneous Applications. One-thousandth of a monomolecular layer of oxygen or oxide may be determined[41] on a metal surface coulometrically. The metal surface serves as the cathode and a cadmium rod as anode. No external source of current is needed.

The gamma isomer of benzene hexachloride may be determined[42] coulometrically.

The number of electrons n involved in the Ilkovic equation (see page 168) is difficult to determine when there is a lack of precise diffusion coefficients (see page 169) particularly for electrode reactions involving more than three or four electrons. This can be done[2] by carrying out a controlled-potential coulometric analysis with a mercury-pool cathode on a solution corresponding to that used in the polarographic determination,

and at a potential corresponding to the plateau of the polarographic wave. This has been applied to the polarography of many organic compounds[43] and of selenium, tellurium,[44] tungsten,[45] and perrhenate.[46]

By the use of a small volume of solution, about 0.3 ml, n values may be determined coulometrically with the dropping-mercury electrode.[4] In such a small volume there is a sufficiently large decrease, over a period of an hour or more, in the concentration of the reactant at the electrode so that a correlation may be made between the current passed (measured by an electromechanical integrator[47]) and the decrease in concentration. This makes possible the calculation of an n value.

Finally reference should be made to the utility of controlled-potential techniques in the electrolytic preparation of organic compounds by oxidation or reduction.[48]

COULOMETRIC ANALYSIS WITH CONSTANT CURRENT

In coulometric analysis at controlled potentials the determination is self-indicating. That is to say, its completion is signaled by the current's dropping to zero or to a minimum background value. In coulometric analysis with constant current this, of course, does not happen. As a given electrode reaction reaches completion, the potential rises to that at which another constituent of the solution is electrolyzed. The current remains constant, by definition. The end of the particular reaction of analytical interest must thus be pointed out by an indicator—optical, electrical, or of any other suitable type. The circuit may then be broken, either manually or automatically, at the end point, and the quantity of electricity determined, or the end point may be overrun and a correction applied. The originators of this type of method[49] determined the quantity of electricity with a coulometer. However, this method is used most advantageously by measuring the quantity of electricity not directly but indirectly through the time consumed in the determination. Time is obviously directly proportional to quantity of electricity since constant current is another way of saying constant quantity of electricity per unit of time.

Primary Coulometry

In principle, it is possible to employ primary coulometric methods, whereby the substance being determined is electrolyzed directly. In practice, this cannot often be accomplished for reasons best indicated by an example. Ferrous ion can be oxidized directly at a platinum anode to ferric ion. However, as the electrolytic reaction proceeds, the concentration of ferric ions increases at the anode surface, where they are produced by oxidation of the ferrous ions. At the same time the concentration of ferrous ions decreases at the anode surface since they are

supplied by diffusion from the main body of the solution and the rate of diffusion decreases as the concentration decreases. As a result of the increasing ratio of ferric to ferrous ions at the anode surface, the anode potential becomes more and more positive as the determination proceeds—in accordance with the Nernst equation. Ultimately, and before all the ferrous ion in the solution has been oxidized, the anode potential becomes positive enough so that the oxidation of water begins:

$$2H_2O = O_2 + 4H^+ + 4e$$

The oxidation of ferrous ion thus proceeds at an efficiency which becomes progressively lower than 100 per cent, and the determination is spoiled.

Secondary Coulometry

Oxidation of ferrous ion is possible[50] by secondary coulometry by adding cerous ion in considerable excess to the ferrous-ion solution. When the potential starts rising, as just described, cerous ion is oxidized to ceric ion, instead of water to oxygen. The last part of the oxidation of the ferrous ion is thus accomplished by means of the ceric ion rather than by direct electrolytic oxidation. However, the net result is stoichiometrically the same when the end point is reached as though the ferrous ion had been oxidized directly, but there is no oxygen evolution and the efficiency remains at 100 per cent.

Secondary coulometric titrations at constant current may be carried out, as in the example cited, by generation of reagent directly in the solution or alternatively by external generation of reagent.[51] This technique is analogous to ordinary titrimetric analysis except that time measurements are substituted for volume measurements. The advantage over internal-generation methods is that reactions which interfere with the generating reaction may be avoided.

These methods are advantageous from several points of view. Since small increments of current may be more easily and conveniently measured than small volumes of standard solutions, the methods are peculiarly adaptable to precise microtitrations. The troublesome preparation and standardization of sensitive reagents such as titanous and cuprous solutions and bromine solutions may be avoided by generating them electrolytically. In fact, it has been proposed[52] that the coulomb be adopted as the primary standard for titrimetry in place of the present chemical standards. Furthermore, coulometric titrations are easily adaptable to automatic operation.

Instrumentation

The components necessary for constant-current coulometric titrations are a source of constant current, a current-measuring device, an electrolytic cell, a current-integrating device such as a coulometer (already

described) or preferably a time-measuring device, and a means of end-point indication. For automatic operation special devices are necessary, including a means for breaking the electrolytic circuit and stopping the timer simultaneously.

The recent development of a precise but simple device for integrating current and time[82] has resulted in considerable simplification of constant-current coulometry. This device is a low-friction motor, the speed of which varies linearly with voltage. If a fixed precision resistor is put in the circuit, the speed may be made to vary linearly with the current passing through a coulometric cell. The integrated time-current value is indicated by a revolution counter which may be calibrated in terms of faradays or chemical equivalents. No timer is necessary, nor is there need for a well-controlled constant-current supply. A selenium rectifier is sufficient at higher current levels, or dry cells at low current levels for microtitrations.

Constant-current Sources. *A manually controlled constant-current source*, consisting of a battery with a variable resistance in series, may be used if the attention required in occasionally adjusting the resistor is not considered a drawback. A 6-volt lead storage battery with a relatively small resistance in series[54] or a 45-volt *B* battery of dry cells with a larger resistance in series[53] may be used to furnish currents up to 100 ma. The usual range of currents used is 1 to 20 ma. With the 45-volt battery the current changes by no more than about 0.5 per cent during the course of an analysis taking several minutes. It has been suggested that the use of several *B* batteries in parallel would keep the current decrease to less than 0.1 per cent for a 5-min period and that a dummy resistor be switched into the circuit between titrations in place of the cell in order to maintain the resistors in thermal equilibrium and to keep the battery "conditioned."[1]

Rectifiers are available commercially which may be used instead of a battery. These furnish d-c output voltages which do not vary with the load, by regulation of the input a-c current.

Automatic control of current may be achieved in several ways. A potentiostat, such as those discussed above, may be used to deliver current of constant voltage to the electrolytic cell across a precision resistor which is placed in series with the cell. By actuating the control element of the potentiostat from the output across this resistor, the current delivered to the cell will be maintained at a constant value. The multipurpose potentiostat[21] can be used to regulate currents from a few milliamperes to an ampere or more with a precision of ± 0.2 per cent.

Several electronic current regulators have been described. One battery-operated regulator[55] delivers a current up to 15 ma which decreases linearly by about 0.1 per cent in 4 min when two 45-volt *B* bat-

teries are used and by 0.1 per cent in 20 min when lead storage cells are used. Another[51] maintains currents up to 500 ma constant to about ±0.05 per cent.

An a-c line-operated regulator[56] maintains currents of from 0.5 to 20 ma constant to about ±0.1 per cent for periods of ½ hr.

An electronic a-c line-operated regulator[57] can be used to supply currents up to about 150 ma which are constant to ±0.01 per cent. By some modifications[58] the range of this regulator can be extended up to 450 ma.

Current-measuring Devices. The obvious means for measuring the current is a milliammeter. A more precise method is to determine with a potentiometer the voltage drop across a precision resistor in series with the electrolysis cell and to calculate the current from the voltage and resistance.

Time Measurement. The time-measuring device must be of high precision in order to avoid large errors in the relatively short time period usually required for a coulometric titration. It is generally necessary to start and stop the current more than once during the course of a titration and the timer should also start and stop simultaneously. For good precision this cannot be accomplished with a manually controlled stop watch. An electric timer controlled by the same switch which starts and stops the electrolysis current is needed.

Variations in frequency of current from a poorly controlled 110-volt a-c line can cause serious errors in time measurement with the ordinary synchronous motor clock or timer.[59] By providing controlled-frequency current from a supply controlled by a tuning fork[58] this error may be avoided. However, the motor has sufficient inertia to cause an error in time measurement because it does not start and stop exactly simultaneously with the starting and stopping of the current. The Standard Electric Time Company of Springfield, Mass. manufactures precise stop clocks with magnetic brakes, which do not have this drawback. The Model S-10 has a capacity of 1,000 sec and a precision of ±0.01 sec and the S-1, with a capacity of 60 sec, a precision of ±0.002 sec.

End-point Indication. Any of the methods of end-point indication applicable to the usual volumetric titrations may be used with coulometric titrations. The decolorization of methyl orange may be used to detect the end point in the titration of hydroxylamine, hydrazine, and other substances with bromine generated at a platinum anode[49]. However, electrometric, and particularly potentiometric, methods are better suited to take advantage of the utmost in precision of which coulometric titration is capable. A discussion of potentiometric end points given in the chapter on Potentiometric Titrations applies here but brief reference will be made here to some of the special points connected with coulometric titration. **Amperometric end-point determination** (see chapter on

Polarography) has been more frequently applied than the potentiometric and the latter cannot be used where no reversible indicator electrode is available. Where such an electrode is available, the potentiometric end point is better. The titration may be stopped exactly at the end point and the end-point potential is independent of a number of factors which are critical in the amperometric method, such as speed of stirring and the size and shape of the cell and the electrodes.

Furthermore, in both the potentiometric and amperometric methods, the positioning of the indicator electrode relative to the point of entry of the generated reagent is important.[60] By controlling this it is possible to obtain an "anticipatory approach" to the end point, so that there is a continual and repeated local overshooting of the end point and opening and closing of the generating circuit. This may be used to prevent addition of an amount of reagent in excess of that required to attain the true end point. However, the amperometric end point is not suited to take advantage of this in stopping the titration precisely at the end point as the potentiometric is thus suited. With the amperometric end point it is usually better to overstep the end point and measure and correct for the excess of reagent. Examples of the use of both end points will be pointed out in the applications which follow.

Applications

Visible End Point. Titrations[49] to a visible end point with electrolytically generated bromine have been mentioned. The cell consists of two platinum electrodes immersed in the solution of the sample to which bromide ion has been added. The reaction at the cathode is $2H^+ + 2e = H_2$ and at the anode $2Br^- = Br_2 + 2e$. A visible end point has also been used in determining sulfuric and hydrochloric acid by direct reaction of the hydrogen ion at a platinum cathode. The cathode reaction is $2H^+ + 2e = H_2$. The anode is silver and the anode reaction is $Ag + Cl^- = AgCl + e$. For sulfuric acid solutions chloride ion is added. A precision of better than 0.1 per cent was reported for macrotitrations.

Potentiometric End Point. *Nitric–Acetic Acid Mixtures.* The glass electrode may be used for the coulometric titration with potentiometric end-point detection of weak organic acids for analysis in the presence of mineral acid.[61] To cite an example, mixtures of nitric and acetic acids in 70 per cent isopropanol containing lithium chloride may be titrated with a platinum wire cathode, a glass electrode, and a silver–silver chloride reference electrode. The platinum anode, in a compartment containing potassium chloride solution, is separated by a saturated potassium chloride–agar bridge from the cathode compartment. A curve of pH against generation time is plotted to locate the two inflection points in the titration curve.

Electrolytically Generated Ferrous and Ceric Ions. The potentiometric end point has been used for a number of coulometric titrations with electrolytically generated ferrous and ceric ions and the indicator circuit shown in Fig. 13-8.[62] The indicator electrode is immersed in the titration solution containing the generator electrodes (not shown). The potentiometer is set to the known end-point voltage and the indicating circuit is kept closed. The off-balance current is indicated by the galvanometer and decreases to zero at the end point. By allowing the circuit to remain closed throughout the titration, with a resulting slight continuous electrolysis at the indicator electrode, the usual sluggish behavior near the end point of a potentiometric oxidation-reduction titration is avoided.

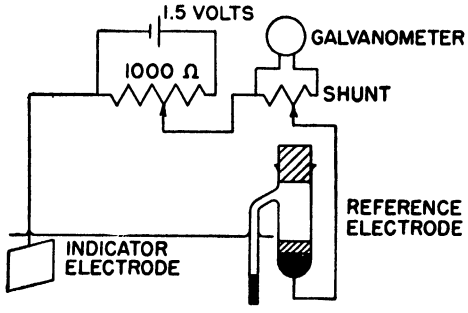


FIG. 13-8. Indicator circuit for ferrous and ceric ions. [*W. D. Cooke et al., Anal. Chem.*, **23**: *1662 (1951), Fig. 1.*]

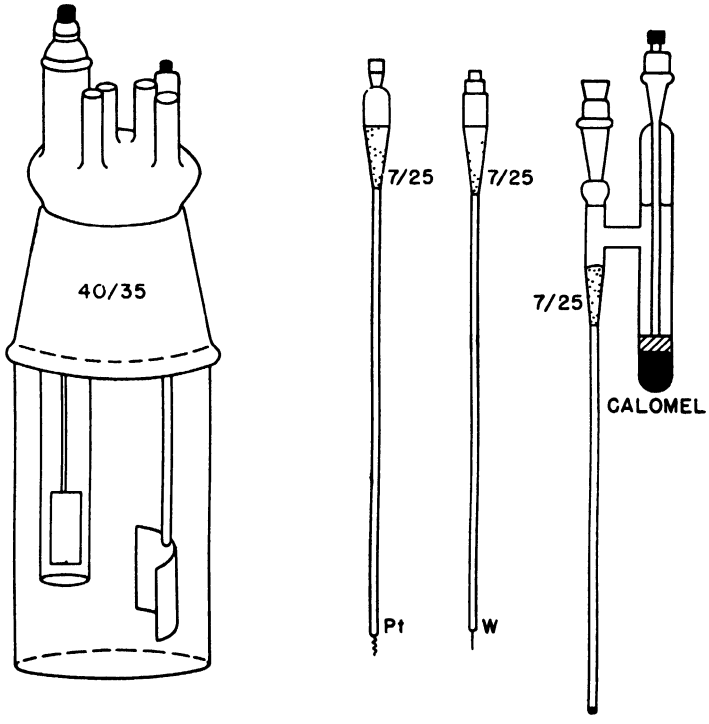


FIG. 13-9. Titration cell and replaceable electrodes. [*N. H. Furman et al., Anal Chem.*, **23**: *945 (1951), Fig. 2.*]

The cell and electrodes shown in Fig. 13-9[50] may be used to generate ceric ion for the titration of ferrous ion. The platinum anode at which

the ceric ion is generated is separated from the platinum cathode by a glass tube with a sintered glass disk. The ammonium sulfate cathode solution is above the level of the sample solution in order to minimize diffusion errors. Ceric ion is generated from cerous sulfate in sulfuric acid with the exclusion of air by means of carbon dioxide. For microgram quantities a platinum indicator electrode of large area is used to hasten attainment of equilibrium.[62] Traces of reducing impurities are removed before adding the sample by generating ceric ion in the supporting electrolyte until the equivalence-point potential is reached.

Using a cell which is similar to that of Fig. 13-9, but without ground-glass connections, and with the indicated tungsten reference electrode instead of the calomel cell, ferrous ion may be generated from acidified ferric ammonium sulfate and may be used as a titrant.[63] Because of the use of tungsten as the reference electrode the end point is indicated by an abrupt drop in voltage. Dichromate ion may be titrated with equally good results.

Using a somewhat less elaborate cell, but with the same end-point technique, as little as 22 micrograms of vanadium+5 may be titrated[64] by reduction to vanadium+4 with electrolytically generated ferrous ion even in the presence of considerable uranium+6. By titration with electrolytically generated ferrous ion[62] in a smaller cell but with a similar technique to that used for titrating vanadium, submicrogram quantities of permanganate may be determined.

Electrolytically Generated Titanous Ion. Titanous ion may be generated from titanic chloride for the titration of ferric ion to a potentiometric end point[65] with a platinum-foil generator cathode which has been gold-plated to increase the hydrogen overvoltage. A mercury-pool generating cathode[66] is less troublesome than the gold-plated platinum cathode, which requires very frequent conditioning. By using an external-generation procedure[51,67] with the generator cell modified for use with a mercury pool,[66] reducible dyestuffs, such as azo dyes, may be titrated.[66]

Film Thickness. The coulometric-titration principle may be used in determining the thickness of thin films of silver iodide on silver and of oxide and sulfide films on iron, copper, and silver.[68,69,70,71] By one technique[71] a constant current is applied to the sample in air-free potassium chloride solution and successive readings of the potential, measured against a calomel reference electrode, are taken. A potential-time curve is obtained which is similar to an ordinary potentiometric curve. From the current consumed to the time of inflection, and other data, the thickness of the film may be calculated. Cuprous oxide films on copper as thin as 10 A may be determined.

Amperometric End Point. *Electrolytically Generated Bromine.* Amperometric end-point detection has been used for a number of coulometric

titrations starting with a method for using electrolytically generated bromine.[53] A cell and circuit for the electrolytic generation of bromine and its use in amperometric titrations[72] are shown in Figs. 13-10 and 13-11. Bromide and sulfuric acid react to form hydrogen at the generator cathode, $2H^+ + 2e = H_2$, and bromine at the generator anode, $2Br^- = Br + 2e$. A voltage is impressed across the indicator electrodes which is below the decomposition voltage of the supporting electrolyte itself but is close to, or above, the decomposition voltage of the supporting electrolyte containing free bromine. Very little current passes, therefore, until the titration has been completed and there is present an excess of bromine. Since, under the conditions of the titration, the indicator current is diffusion-controlled, it increases linearly with increasing excess of bromine.

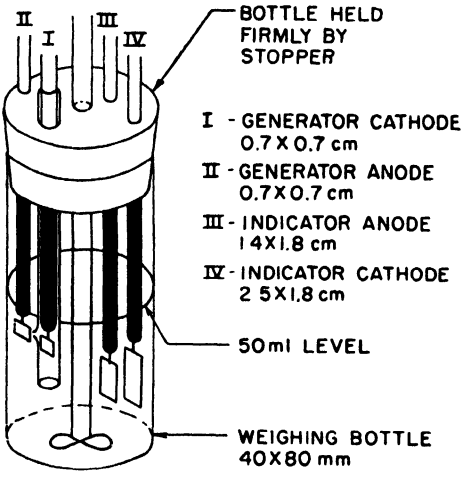


FIG. 13-10. Titration cell for bromometric titrations with amperometric end-point detection. [*R. J. Meyers and E. H. Swift, J. Am. Chem. Soc.*, **70**: *1047 (1948), Fig. 1.*]

In performing a titration with electrolytically generated bromine the circuit is broken after the current reading indicates the presence of excess

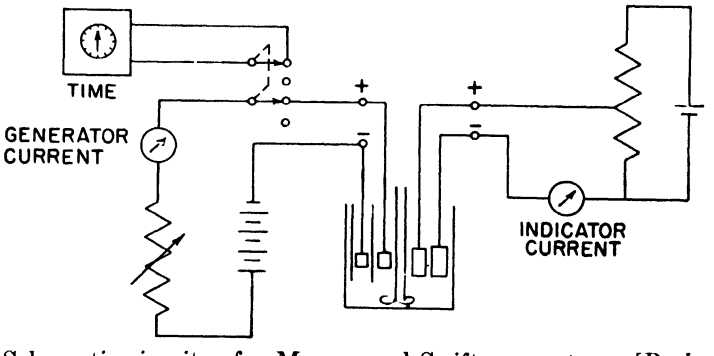


FIG. 13-11. Schematic circuitry for Meyers and Swift apparatus. [*R. J. Meyers and E. H. Swift, J. Am. Chem. Soc.*, **70**: *1047 (1948), Fig. 2.*]

bromine. The current is directly proportional to the excess of bromine, which in turn is proportional to time of generation, so that $i = kt$. The value of k is established by generating bromine for various periods of time in the medium used and with the same conditions of temperature and stirring as in an actual titration but without any sample being present to consume the generated bromine. Having established the value of k, and knowing the current at the end of the titration, the total time con-

sumed in the titration may be corrected for the time used in generating excess bromine.

It has been suggested[1] that the excess time could be calculated directly from the value of i at two time periods after the end point has been reached, by extrapolating back to zero current. Obtained in this manner the correction would not require close duplication of conditions, particularly of stirring and temperature, between the calibration run and the titration run.

Effect of Dissolved Hydrogen. The guard tube in Fig. 13-10 which is placed around the generator cathode serves to lead off most of the hydrogen formed at the cathode. If this is not done, the dissolved hydrogen causes the current after the end point to decrease before rising again in the normal manner. The small amount of hydrogen which is dissolved in the presence of the guard tube merely causes a slight momentary dip in the current which serves as an indication that the end point is being approached.

Platinum Electrode with Calomel Reference Cell. Instead of two platinum indicator electrodes a platinum indicator anode may be used with a calomel reference cell as the indicator cathode joined to the cell by a salt bridge.[56] This avoids the evolution of hydrogen. It has an additional advantage over the two-electrode indicating system. Exact duplication of the state of activity of the two polarizable electrodes is difficult (but not impossible) to attain. If it is not accomplished, by proper preconditioning of the electrodes, the slope of the current-time curve after the end point will not be reproducible.

Titrations with Electrolytically Generated Bromine. Using the amperometric end-point technique, micro quantities of thiodiglycol (produced by the hydrolysis of mustard gas) may be titrated[53] with bromine to form thiodiglycolsulfoxide. Arsenic+3 may be determined amperometrically with bromine by oxidation to arsenic+5.[72] In a similar manner antimony+3 may be determined.[73] Since, in the hydrochloric acid solution used, the antimony+3 would be reduced to the metal at the generator cathode, the latter is enclosed in a glass tube with a sintered glass disk at the bottom and the level of the solution in the tube is kept above the level in the rest of the cell. A method similar to that used for antimony may be used[74] to determine iodide by the reaction $I^- + Br_2 \rightarrow IBr_2 + e$.

Electrolytically generated bromine may be used[56] to titrate 8-hydroxyquinoline to an amperometric end point with good agreement with the conventional bromide-bromate titration. Thallium+1[75] may be titrated to an amperometric end point by oxidizing it to thallium+3 with bromine (or chlorine).

Aniline is titrated[76] amperometrically with bromine by generating the latter in excess in a solution which also contains cupric ion. The polarity

of the generator electrodes is reversed after the end point has been reached and cuprous ion is generated at the cathode. This is used to titrate the excess bromine amperometrically.

Electrolytically generated iodine may be used[77] to oxidize arsenic+3 to arsenic+5 amperometrically. A similar titration may be performed[78] with electrolytically generated chlorine.

Dichromate ion may be reduced to chromium+3 and vanadate to vanadium+4 by means of *electrolytically generated cuprous ion* in the presence of hydrochloric acid.[55]

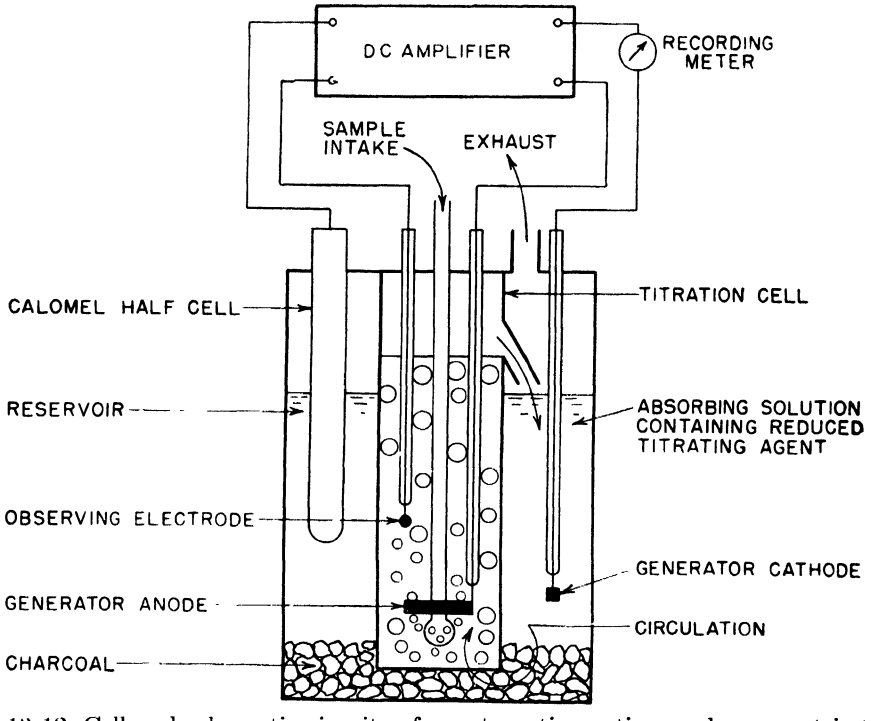


FIG. 13-12. Cell and schematic circuitry for automatic continuous bromometric titration apparatus. [*P. A. Shaffer et al., Anal. Chem.*, **20**: *1008 (1948), Fig. 2.*]

Automatic Coulometric Titration. An apparatus for the continuous automatic determination of mustard gas, hydrogen sulfide, sulfur dioxide, and acrolein in air in concentrations above 0.1 ppm by means of electrolytically generated bromine has been described.[79,80] (The Titrilog manufactured by the Consolidated Engineering Corporation, Pasadena, Calif., utilizes a similar principle.) Figure 13-12 is a schematic drawing of the cell and circuit.

The sample (e.g., metered air) is pumped through the bromide–sulfuric acid electrolyte where it reacts with the bromine generated at the generator anode. The potential of the platinum observing electrode against the calomel half-cell is dependent upon the excess bromine present.

This potential is presented to the d-c amplifier, the output of which goes to the generator electrodes. The instrument is adjusted so that the generating current has a low value when there is no reactant in the air. This current is sufficient to generate just enough bromine to compensate for losses by circulation to the outer compartment where the excess bromine is absorbed in the charcoal. When the mustard gas, or other bromine-consuming constituents of the sample, causes consumption of bromine, the drop in potential of the observing electrode causes a large increase in generating current which maintains the concentration of free bromine at a fixed small value. The generator current shown on the recording meter serves to measure the concentration of reactant in the air at any moment. By placing a current integrator in the amplifier output the content of mustard gas (or other bromine-consuming constituents) may be determined in a measured volume of air for a definite time period. A portable unit for field use is available.

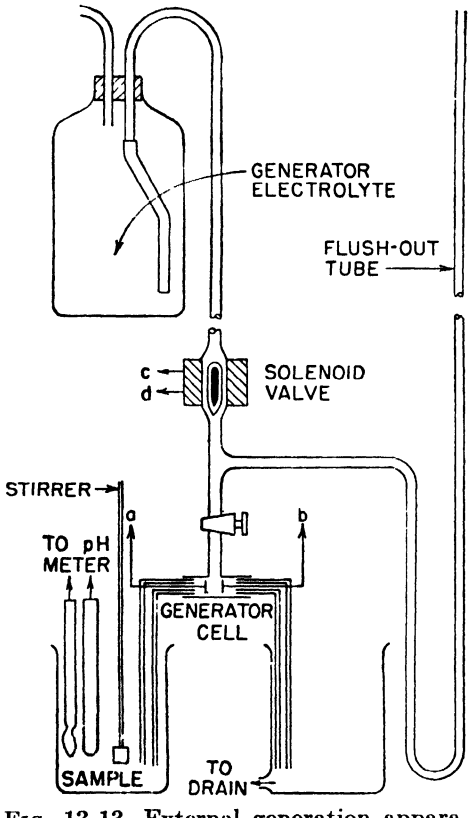


FIG. 13-13. External generation apparatus. [*D. D. DeFord et al., Anal. Chem.*, **23**: *941 (1951), Fig. 3.*]

The apparatus shown in Fig. 13-13 provides for titration with externally generated reagent to an automatic cessation of titration at the end point. The electrodes *a* and *b* are connected in such a way as to make *a* the cathode or the anode depending upon the reagent being generated. Thus for titration of acids *a* serves as the cathode and the generator electrolyte is a sodium sulfate solution. The reaction $2H_2O + 2e = 2OH^- + H_2$ generates hydroxyl ion which flows into the sample beaker while the oxygen and hydrogen ion generated by the anode reaction,

$$2H_2O = O_2 + 4H^+ + 4e$$

are swept out into the drain. The generator electrolyte flows by gravity through the open solenoid valve until the preset end-point potential between the glass electrode and the calomel reference electrode is attained. The electrodes are connected with a Beckman model G pH meter the

output of which actuates a galvanometer-photo relay. At the end point this simultaneously interrupts the electrolysis current, closes the solenoid valve, and stops an electric timer. Proper relative positioning of the indicator electrode and reagent delivery is important to obtain anticipatory approach to the end point and thus prevent overtitration.[60]

Requirements have been discussed for the design of titrator components for automatic coulometric titrations with potentiometric end-point detection, including a trigger circuit and an end-point anticipation circuit.[81]

It has been suggested that the Beckman automatic titrator may be adapted to automatic coulometric titration by disconnecting the solenoid burette valve and connecting in its place a double-pole double-throw relay, one side of which controls the generating current and the other an electric stop clock.[1]

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CHAPTER FOURTEEN

Radioactivity

The use of radioactivity in analytical chemistry is intrinsically instrumental since the radiations are not evident to man's senses and can be detected only by suitable instruments. Natural radioactivity has been studied since the days of Becquerel and the Curies at about the turn of the century but the use of natural radioisotopes as tracers was first studied by Hevesy in 1920. However, not much tracer work was done with natural radioisotopes. Artificial radioactivity was discovered in 1933 by I. Curie and F. Joliot, but the main impetus for the use of artificial radioisotopes had to await the availability of an abundant supply of a great variety of isotopes at reasonable prices. This came about with the release in 1946 by the Atomic Energy Commission for general nongovernmental use of radioisotopes produced in the nuclear chain reactor ("atomic pile") at Oak Ridge, Tenn.

There are two classes of uses for radioisotopes. They are used for some purposes because of certain properties of the radiation which they emit, without regard to the chemical nature of the radiating atoms. For other purposes the radiation serves merely to identify the radiating atom and the chemical properties of the isotopes are important. Among the first class are such applications as measurement of thickness, of liquid levels, and of flow of liquids; detection of leaks in gas systems; medical treatment of tumors; and inspection of castings and welds for flaws by radiography with a radioisotopic source instead of with X rays. These nonanalytical applications will be referred to only briefly.

The second class of use, in which the chemical nature of the radioisotope is of primary importance, is of most interest for chemical research and analytical chemistry. It includes studies of mechanism of reactions, determination of efficiency of separation processes, measurement of diffusion coefficients, of limited solubilities and of vapor pressures, studies of adsorption and coprecipitation, of aging of precipitates, detection and determination of trace elements, quantitative analysis of complex mixtures without quantitative isolation of the constituent being determined, and a large number of miscellaneous applications. In general, the possi-

bility of using methods involving radioisotopes should always be considered if there is no effective or simple means available for solving a given problem. Occasionally these methods should be considered as preferable to cumbersome or expensive conventional methods.

ATOMIC AND NUCLEAR STRUCTURE AND RADIATION

A thorough understanding of radioactivity is beyond the grasp of most chemists, involving as it does a mastery of intricate nuclear physics and mathematics. Fortunately, the chemist can use radioisotopes without such a grasp of the subject. In the following a brief description will be given of the main points necessary for the intelligent use of radioisotopes.

A very simplified picture of the atom would be the following: The atom contains a nucleus with a cloud of electrons, revolving in definite orbits about it. The electrons determine the chemical behavior of the atom but the nucleus is the seat of radioactivity. The nucleus consists of two main types of particles—neutrons and protons, both collectively called *nucleons*. These may be arranged in a system of shells and may be held together by a continuous exchange between them of particles known as mesons. Neutrons and protons each have a relative mass of about 1, but the neutron has no electrical charge and the proton has one positive charge. Since the electron, which has a negative charge of 1, has a relative mass of 0.0005486, it is obvious that most of the mass of the atom is concentrated in the nucleus. The nucleus is, moreover, much more compact than the electron cloud. The latter is about 10^{-8} cm in diameter and the former is about 10^{-13} cm in diameter. Consequently, the density of matter in the nucleus is in the neighborhood of 10^{14} grams per cm^3 or 10^8 tons per cm^3.

In the ordinary neutral atom there are as many negative electrons as there are positive protons. The electrons are arranged in shells which are called K, L, M, and N shells in order of increasing distance from the nucleus. In the lighter elements the number of protons generally approximately equals the number of neutrons. In the heavier elements the number of neutrons exceeds the number of protons.

A shorthand notation is used to indicate the nuclear and electronic make-up of atoms. Let Z be the number of protons in the nucleus (the atomic number, also equal to the number of electrons about the nucleus). Z determines the chemical properties of the atom. Let A be the number of nucleons (neutrons plus protons) in the nucleus. A is the whole number nearest the atomic weight of the particular atom and is known as the mass number. The A and Z values of an atom fix its identity. These are accordingly written together with the symbol of the atom. The mass number is written as a superscript, usually to the right of the symbol, and

the atomic number as a subscript to its left, e.g., $_{2}He^{4}$, $_{27}Co^{59}$, $_{92}U^{235}$. The atomic number is frequently omitted since the chemical symbol determines it without any question. Thus Co^{59} and Co^{60} would represent cobalt isotopes with masses 59 and 60, each with the (understood) atomic number 27.

TABLE 14-1

Particle		Charge*	Mass†
Symbol	Name		
e^- or β^-	Electron or beta ray	−1	0 0005486
e^+ or β^+	Positron	+1	0 0005486
γ	Photon or gamma ray	0	0
ν	Neutrino	0	<0 00002
n	Neutron	0	1 008982
μ	μ meson	+1, −1	0.115
π	π meson	+1, −1(0)	0 151
H^1 or p	Proton	+1	1 008142‡

* In units of $e = 4.8025 \times 10^{-10}$ esu (electrostatic units).

† Mass of the particle at rest.

‡ Mass of the neutral atom.

Nuclear Particles. Table 14-1 gives a list of the main particles, with their masses and electrical charges, which are involved in one way or another in the structure of nuclei. Actually, the types of radioactive particles which the user of artificial radioisotopes for tracer purposes will encounter are considerably fewer in number. They are negative electrons (beta particles), positive electrons or positrons (which suffer immediate annihilation by combination with negative electrons, with the liberation of gamma rays), gamma rays (which are like X rays, except that they originate in the nucleus and are of shorter wavelength), and rarely alpha particles (He^4 nuclei). Still another source of activity is K-electron capture (K-or orbital-electron capture). In this process an electron from the K level of the electron cloud is captured by the nucleus. This converts a proton in the nucleus into a neutron. An electron from a higher energy level then falls into the position vacated by the K electron and an X ray is emitted. Still another not uncommon type of radioactive particle is the internal-conversion electron. This is produced by a gamma ray from the nucleus of an atom causing an electron to be driven out of one of the electron shells surrounding the gamma-emitting nucleus. Internal conversion leaves a vacancy in one of the inner electron shells and is therefore always accompanied by the emission of X rays and so-called Auger electrons.

Emission of Particles. A single radioisotope may emit only one type of particle or a sequence or combination of two or more. Figure 14-1 gives several typical so-called β-ray decay schemes which indicate the simultaneous or consecutive emission of β or γ rays from an active atom. The horizontal lines represent energy levels which the atom reaches as a result of the emission of beta particles or gamma rays. The diagonal lines indicate emission of beta particles, and the vertical lines the emission of gamma rays. It may be seen that a given atom may sometimes exist at several energy levels, but usually successive emissions of energy in the form of γ rays bring all the intermediate products of disintegration down to the same energy level.

During the process of emission of radioactivity changes occur in the atoms to produce new atoms. Since a γ ray has neither charge nor mass, an atom does not change in either mass or chemical characteristics when

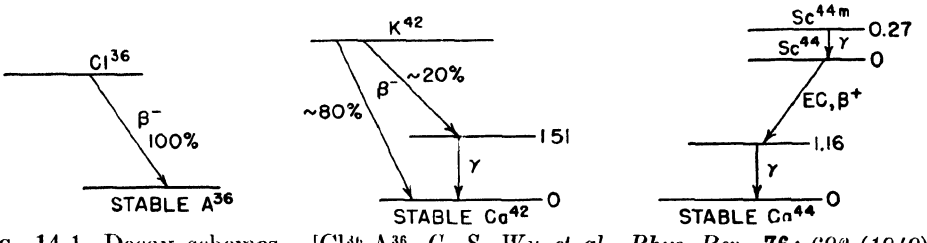
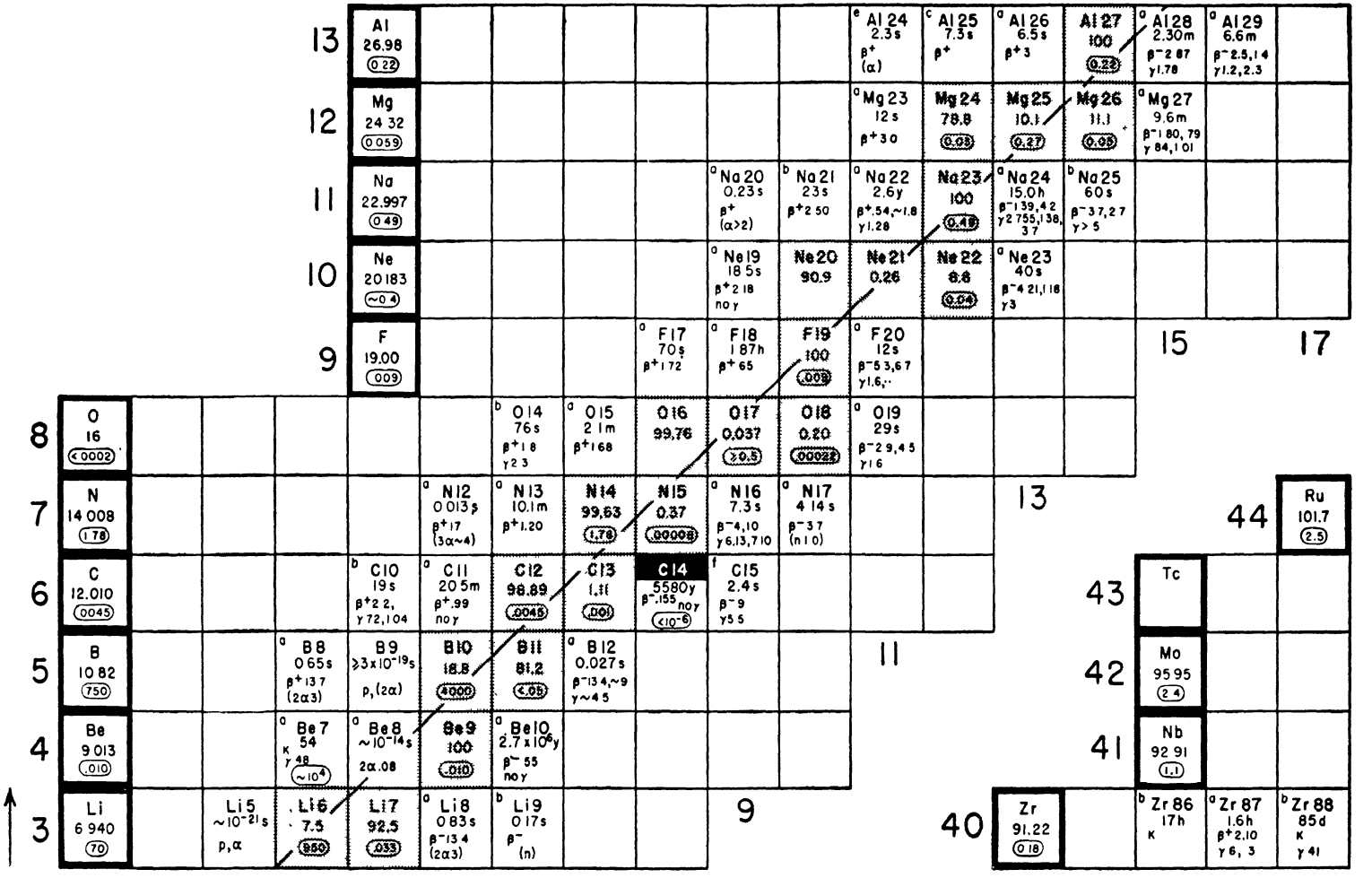


FIG. 14-1. Decay schemes. [Cl^{36}-A^{36}, *C. S. Wu et al., Phys. Rev.*, **76**: *692 (1949);* K^{42}-Ca^{42}, *J. M. Hollander et al., Revs. Modern Phys.*, **25**: *488 (1953);* Sc^{44}-Ca^{44}, *M. Goldhaber and R. D. Hill, Revs. Modern Phys.*, **24**: *179 (1952).*]

it loses γ rays. The change is merely one of energy level. However, β^- and β^+ rays have a charge but practically no mass. When they are emitted, the atom accordingly changes over to another atom having the same weight but different chemical properties (isobars). Thus, for example, when $_7N^{17}$ loses a β^- ray, a neutron in its nucleus thereby acquires a positive charge, becoming a proton. This increases the atomic number from 7 to 8. The atom becomes $_8O^{17}$ which is a stable isotope of oxygen. When $_{19}K^{38}$ loses a positron (β^+ ray) from its nucleus, a proton loses its charge and is converted to an uncharged neutron, thus decreasing the atomic number and causing the atom to change to $_{18}A^{38}$.

Nuclides. Because of the great number of atomic species which have been recognized with increasing knowledge of radioactive and inactive isotopes, natural and artificial, a new term, *nuclide*, has been proposed. A nuclide is a species of atom with a characteristic number of neutrons and protons in its nucleus. An isotope would then be one of a group of two or more nuclides characterized by having the same number of protons.

Several charts have been devised in which the nuclides are arranged in a systematic manner. These charts give information concerning some of the properties of the individual nuclides and indicate their relationships


13
12
11
10
9
8
7
6
5
4
3
Al 26.98 (0.22)
Mg 24.32 (0.059)
Na 22.997 (0.49)
Ne 20.183 (~0.4)
F 19.00 (0.09)
O 16 (<0.002)
N 14.008 (1.78)
C 12.010 (0.045)
B 10.82 (750)
Be 9.013 (0.010)
Li 6.940 (70)
Al24 2.3s β+ (α)
Al25 7.3s β+
Al26 6.5s β+3
Al27 100 (0.22)
Al28 2.30m β−2.87 γ1.78
Al29 6.6m β−2.5,1.4 γ1.2,2.3
Mg23 12s β+3.0
Mg24 78.8 (0.08)
Mg25 10.1 (0.27)
Mg26 11.1 (0.05)
Mg27 9.6m β−1.80,.79 γ.84,1.01
Na20 0.23s β+ (α>2)
Na21 23s β+2.50
Na22 2.6y β+.54,~1.8 γ1.28
Na23 100 (0.48)
Na24 15.0h β−1.39,.42 γ2.75,5.13,8.37
Na25 60s β−3.7,2.7 γ>5
Ne19 18.5s β+2.18 no γ
Ne20 90.9
Ne21 0.26
Ne22 8.8 (0.64)
Ne23 40s β−4.21,1.18 γ3
F17 70s β+1.72
F18 1.87h β+.65
F19 100 (0.009)
F20 12s β−5.3,6.7 γ1.6,..
O14 76s β+1.8 γ2.3
O15 2.1m β+1.68
O16 99.76
O17 0.037 (≥0.5)
O18 0.20 (0.0025)
O19 29s β−2.9,4.5 γ1.6
N12 0.013s β+17 (3α~4)
N13 10.1m β+1.20
N14 99.63 (1.78)
N15 0.37 (0.0008)
N16 7.3s β−4.10 γ6.13,7.10
N17 4.14s β−3.7 (n 1.0)
C10 19s β+2.2, γ.72,1.04
C11 20.5m β+.99 no γ
C12 98.89 (0.045)
C13 1.11 (0.01)
C14 5580y β−.155 no γ (<10−6)
C15 2.4s β−9 γ5.5
B8 0.65s β+13.7 (2α3)
B9 ≥3x10−19s p,(2α)
B10 18.8 (4000)
B11 81.2 (<0.05)
B12 0.027s β−13.4,~9 γ~4.5
Be7 54 K γ.48 (~10−4)
Be8 ~10−14s 2α.08
Be9 100 (0.10)
Be10 2.7x10^6y β− .55 no γ
Li5 ~10−21s p,α
Li6 7.5 (950)
Li7 92.5 (0.033)
Li8 0.83s β−13.4 (2α3)
Li9 0.17s β− (n)
9
11
13
15
17
40
41
42
43
44
Zr 91.22 (0.18)
Nb 92.91 (1.1)
Mo 95.95 (2.4)
Tc
Ru 101.7 (2.5)
Zr86 17h K
Zr87 1.6h β+2.10 γ.6,.3
Zr88 85d K γ.41

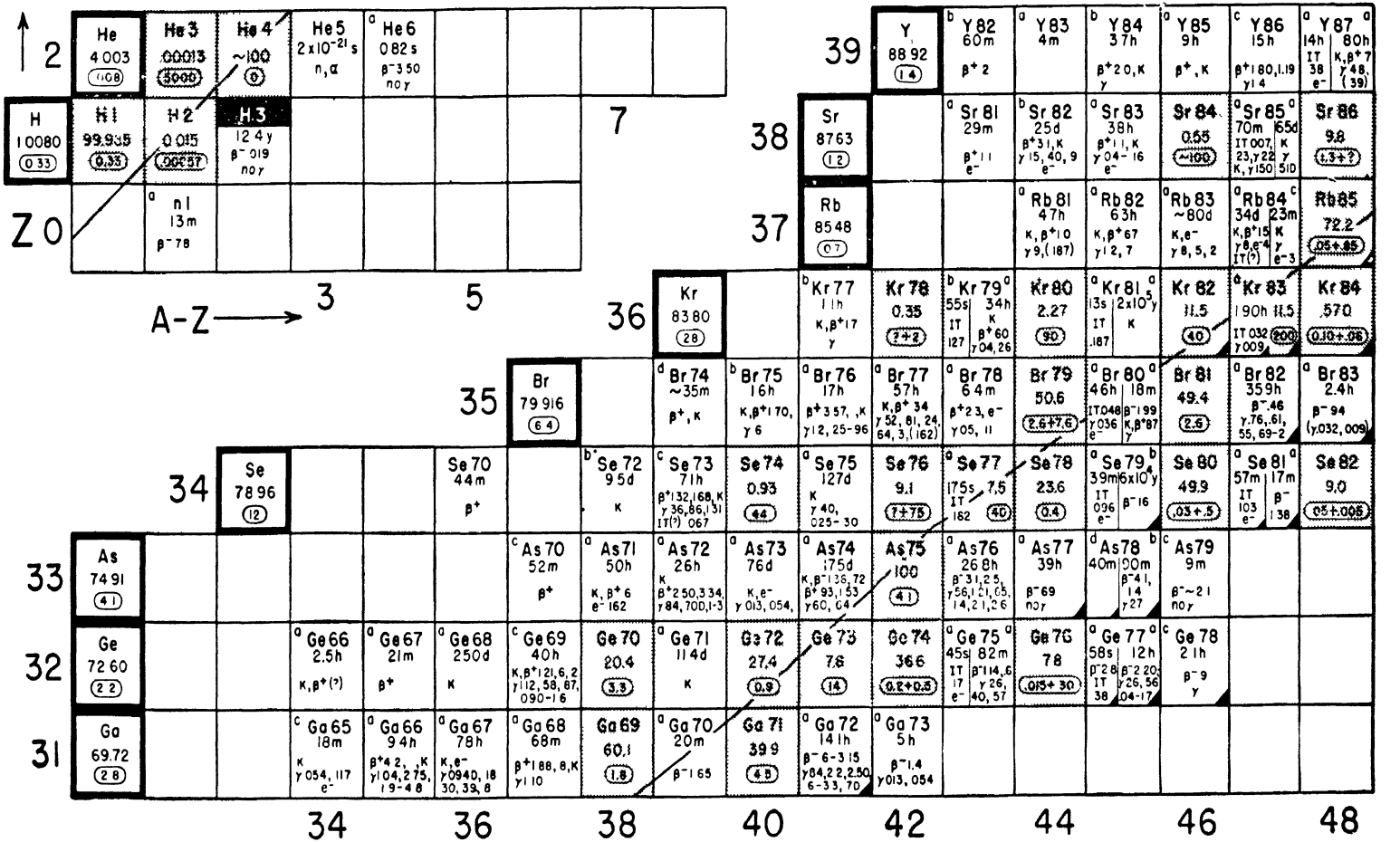


FIG. 14-2. Section of General Electric chart of the nuclides. (*Courtesy of General Electric Company.*)

to one another. The best known of these charts are the Segrè "Isotope Chart," the General Electric "Chart of the Nuclides," Sullivan's "Trilinear Chart of Nuclear Species," and the Harshaw-Bradford "Chart of the Isotopes." Figure 14-2 gives a section of the General Electric chart.

PROPERTIES OF RADIOACTIVITY

Radioisotopes are characterized and identified by the usual chemical and physical properties by which the stable atomic species are characterized and identified. In addition, they are also characterized and identified by the properties of the radiation which they emit. The user of radioisotopes must be familiar with these properties in order to utilize the isotopes properly.

The first fact which must be known about a radioisotope is what radiation it produces—alpha or beta particles, gamma rays, or X rays from K capture. This information is available in charts such as have been mentioned and in other places in the literature.

Penetration of Matter and Energy of Radiation. All radioactivity has in common the property, when it penetrates matter, of losing energy which (for alpha and beta rays and usually for gamma rays) it imparts to the electrons of the atoms which it meets. The electrons may be removed completely from their parent atoms, in which case the atoms become ionized and acquire positive charges. If the electron which receives the energy from the radiation is not removed from the atom, it may merely be raised to a higher energy level. The atom is thus put into a state of excitation, and when the electron falls back to its originally lower energy state, the atom loses the absorbed energy by thermal processes, chemical reaction, or otherwise.

The distance to which a given radiation can penetrate matter depends upon the kind of radiation, its energy, and the density of the substance being penetrated. Alpha particles are the least penetrating; they have the shortest range. Beta particles have a longer range. Gamma rays are the most penetrating. Figure 14-3 shows a comparison of the ranges of the three types of radiation in air in relation to their energy. For gamma rays, for reasons which will appear later, the distance at which half of the activity is absorbed, or the half-range, is given. The energy of radioactive particles and rays is usually expressed in terms of million electron volts (mev). A million electron volts is the energy acquired by any charged particle carrying a unit (electronic) charge when it falls through a potential drop of one million volts.

In practice the energy of radiation is determined by interposing between the source of radiation and the detector known thicknesses of aluminum, for beta particles, and of lead, for gamma rays, and calculating the energy

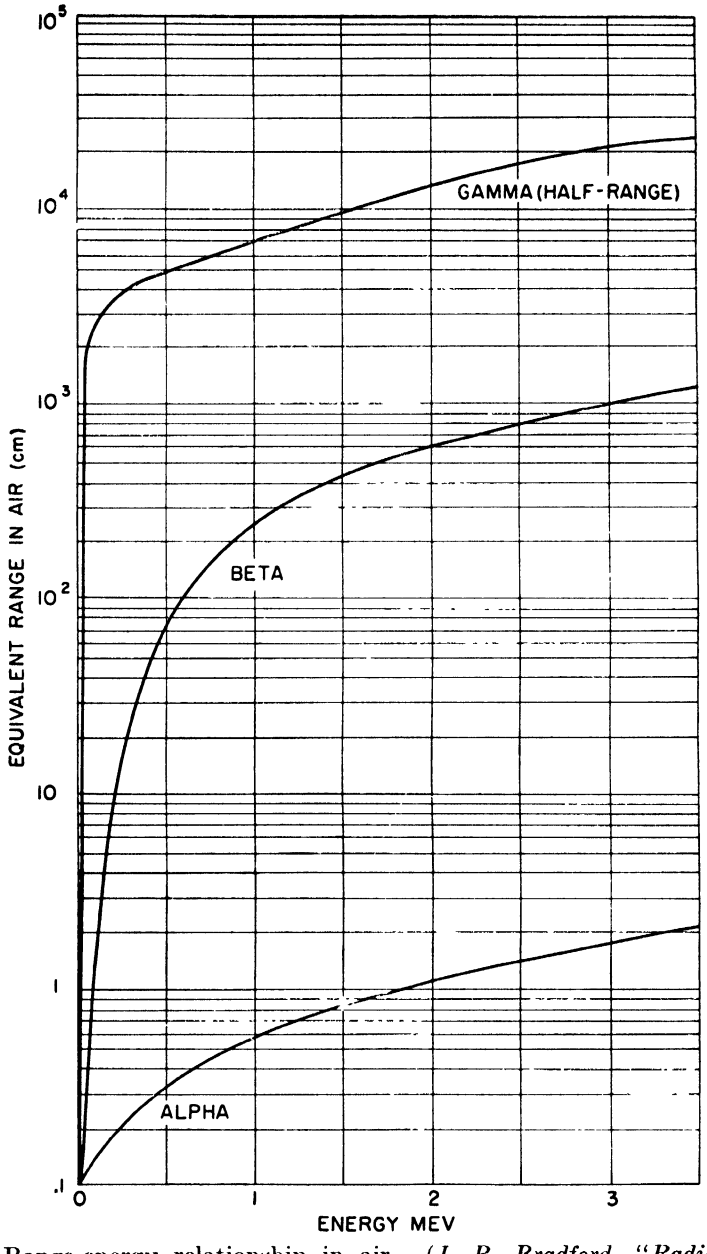


FIG. 14-3. Range-energy relationship in air. (*J. R. Bradford, "Radioisotopes in Industry," Reinhold Publishing Corporation, New York, 1953, p. 44, Fig. 3.13. By permission of the publishers.*)

from the values thus obtained. It is a convenient fact in such absorption studies that (with certain limitations) the kind of material used as an absorber is of no consequence, except as a matter of convenience. The *thickness* of the absorber is expressed as mass per unit area, e.g., grams per square centimeter (g/cm^2) or milligrams per square centimeter

(mg/cm^2). This value is obtained from the weight of the absorber and the area of the surface which the rays strike.

Alpha Particles. All alpha particles from a given isotope have essentially the same energy. Consequently they are (for all practical purposes) all stopped by the same thickness of matter, the range R in the given medium.

Beta Particles. Beta particles, on the contrary, are not monoenergetic but those from a given radioisotope cover a wide spectrum of energies. The energy usually given is understood to be the maximum energy. The absorption of beta rays is too complicated for theoretical analysis. However, quite by chance, the absorption of beta particles of a given maximum energy follows an exponential law.

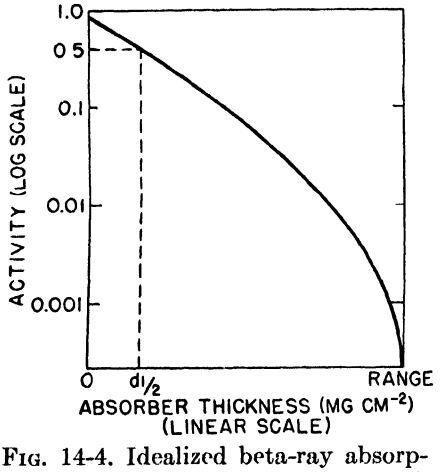


FIG. 14-4. Idealized beta-ray absorption curve. (*G. Friedlander and J. Kennedy, "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York, 1955, Fig. 7-5. By permission of the publishers.*)

Consequently, as shown in the idealized curve in Fig. 14-4, if the activity is plotted on a logarithmic scale as ordinate against absorber thickness (mg/cm^2) on a linear scale as abscissa, a straight line is obtained for a considerable portion of the curve. If the energy of beta radiation from an isotope is known, the range calculated from the energy may be used in a practical way to indicate the amount of shielding which may be required to protect a worker from the radiation. Conversely, the range may be used to determine the energy for the purpose of partially identifying the isotope emitting the radiation. Figure 14-5 is a curve which gives the relationship between the range in aluminum (mg/cm^2) vs. the energy (mev) for beta particles and monoenergetic electrons.

Gamma Rays. Gamma rays are (like X rays) extremely penetrating. Their effective range depends upon their energy, but in general they will penetrate considerable thicknesses of even heavy metals like lead before losing enough of their energy to make their detection difficult. Gamma rays lose energy mainly by three processes: The first, which is the most prevalent process for low-energy gamma rays, is the *photoelectric effect.* This process involves knocking electrons out of their orbits to form ionized atoms. The second process is the *Compton effect.* In this process the gamma ray collides with a loosely bound electron, which removes some, but not all, of the energy of the gamma ray. The latter is scattered and may suffer a series of collisions before its energy is so reduced that it is

no longer detectable. The Compton effect is a major one for absorbers made up of material of low atomic weight and for radiation energies of intermediate magnitude. The third process is important for gamma rays of high energy where the first two effects are not so important, especially in elements of high atomic weight. This process is known as *pair production* and involves the formation of a positive and a negative electron. The positive electron (positron) suffers rapid annihilation by combination with a negative electron to produce energy similar to gamma rays.

Homogeneous gamma rays consisting of radiation of a single frequency are absorbed in such a manner that, if the activities or intensities are plotted on a logarithmic ordinate against thickness of absorber on a linear

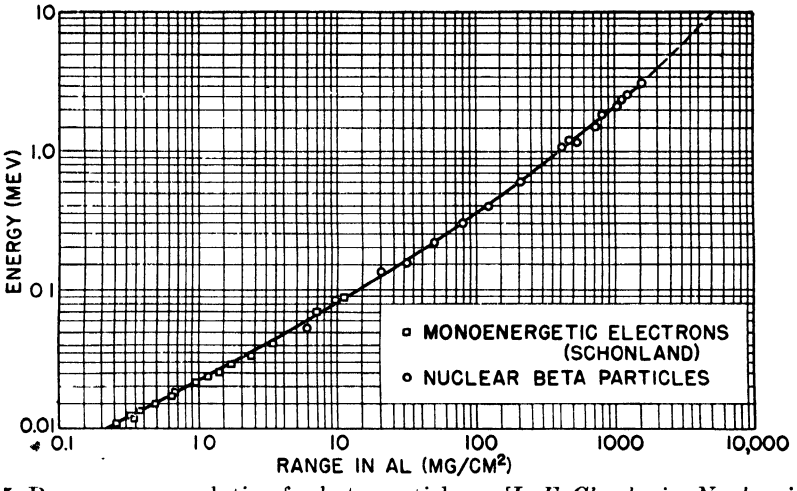


FIG. 14-5. Range-energy relation for beta particles. [*L. E. Glendenin, Nucleonics*, **2**(*1*): *26 (1948)*.]

abscissa, a linear plot is obtained. (For several rays of different energies, several successive straight lines are formed.) Expressed mathematically,

$$I = I_0 e^{-\mu x} \tag{14-1}$$

where e is the base of natural logarithms, μ is the *linear absorption coefficient*, which is characteristic of the given gamma ray, and I is the intensity of the gamma ray after passing through a distance x of the absorber, when the intensity of the gamma ray with no absorber is I_0.

It follows from the exponential absorption of gamma rays that theoretically their intensities can never be reduced quite to zero. Nevertheless, for all practical purposes this is attained when the radiation is too weak to be detected.

Half-thickness and Mass Absorption Coefficient. A modification of the absorption coefficient which is frequently encountered in practice is the *half-thickness*. This is the thickness of absorber necessary to reduce

the gamma-ray intensity to one-half of its initial value. Equation (14-1) may be written

$$\log_e \frac{I}{I_0} = -\mu x \tag{14-2}$$

or when converted to common logarithms

$$\log \frac{I}{I_0} = -0.4343\ \mu x \tag{14-3}$$

At the half-thickness $I/I_0 = \frac{1}{2}$ and

$$\log \tfrac{1}{2} = -0.4343\ \mu x_{\frac{1}{2}} \tag{14-4}$$

where $x_{\frac{1}{2}}$ is the half-thickness. Transposing (14-4), and substituting the value for $\log \frac{1}{2}$,

$$\mu = \frac{0.693}{x_{\frac{1}{2}}} \tag{14-5}$$

If the half-thickness is determined in centimeters, μ can be calculated in reciprocal centimeters.

Another convenient quantity is derived from the linear absorption coefficient μ by dividing by the density of the absorber. This is the *mass absorption coefficient.* Since μ is expressed as cm^{-1} and density as $gram/cm^3$, μ/density is expressed as $cm^2/gram$. This quantity is almost independent of the nature of the absorber for low gamma-ray energies. It increases somewhat for elements of high atomic weight.

Still another variation is the *mass half-thickness.* This too does not vary much with the absorber. It is equal to $x_{\frac{1}{2}}$ multiplied by the density and is expressed in units of $gram/cm^2$ which are used for alpha- and beta-particle absorption.

Figure 14-6 gives curves for half-thickness (symbolized by $d_{\frac{1}{2}}$) vs. energy for photons (gamma rays).

Radioactive Decay. The emission of radioactive particles involves the decay of one species of atom (and the consequent formation of another species). It is an experimentally ascertained fact that the activity of a given radioactive species diminishes in an exponential (or logarithmic) manner. This means that the rate of decay (or the number of atoms disintegrating per unit of time) is proportional to the number of active atoms present at any given time. Since the number of active atoms is decreasing as a result of the decay process, the rate of disintegration is also changing. In mathematical terms

$$-\frac{dN}{dt} = \lambda N \tag{14-6}$$

where dN is the change in the number N of atoms of a given radioactive species in an infinitesimal time period dt. The left-hand side of the equation is negative because N is decreasing. λ is known variously as the *radioactive constant*, the *disintegration constant*, or the *decay constant* of the radioactive element. It is the fraction of the total number of atoms which disintegrates in unit time.

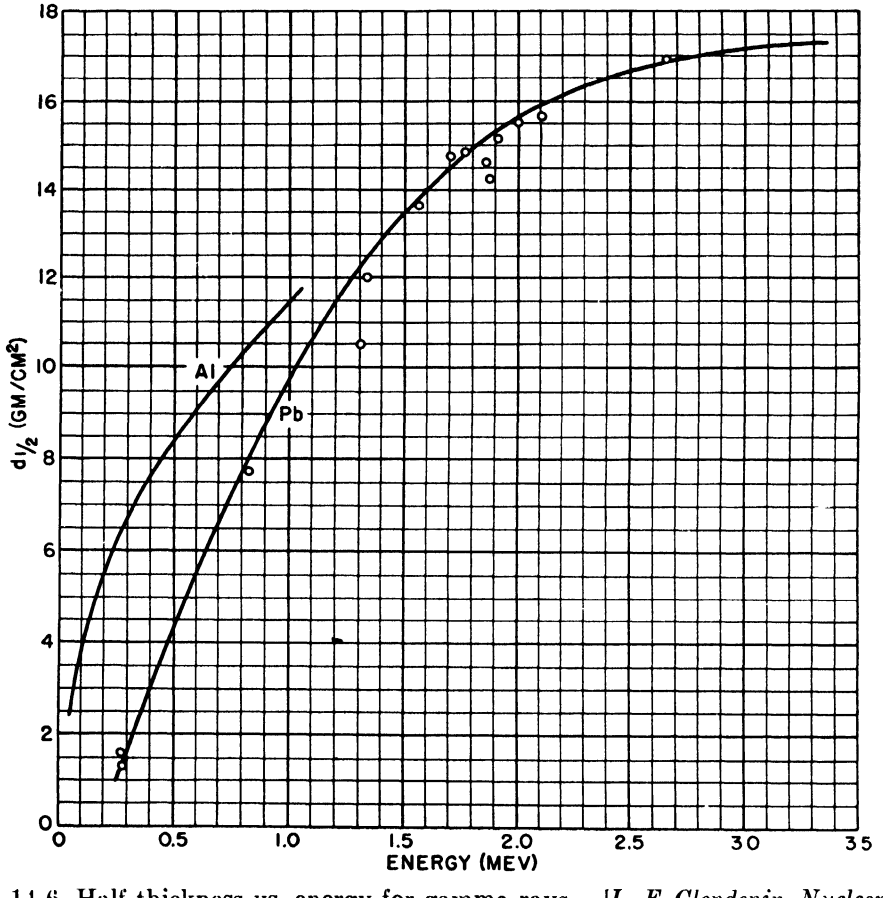


FIG. 14-6. Half-thickness vs. energy for gamma rays. [*L. E. Glendenin, Nucleonics*, **2**(*1*):*29* (*1948*).]

The decay constant is a specific property of a given radioelement. Together with the energy of the radiation (or conversely the range or half-range) and the decay scheme, it is a means of identification and characterization.

Integration of Eq. (14-6) leads to

$$\ln \frac{N_t}{N_0} = -\lambda t \tag{14-7}$$

or

$$N_t = N_0 e^{-\lambda t} \tag{14-8}$$

where N_t is the number of radioactive atoms left after time t and N_0 is the number present at zero time. Conversion to common logarithms changes Eq. (14-7) to

$$\log \frac{N_t}{N_0} = -0.4343\lambda t \tag{14-9}$$

or

$$\log N_t = \log N_0 - 0.4343\ \lambda t \tag{14-10}$$

For N_0 and N_t the activities I_0 and I_t, as measured by suitable instruments, may be substituted. Graphically the logarithm of activities may be plotted against time, or more simply activities on a logarithmic scale may be plotted against time on a linear scale, against an arbitrary zero reference time, with a resulting straight line. The slope of this line will be equal to $-0.4343\lambda t$ and so can be used to calculate λ.

Half-life. A perhaps more commonly used constant than the decay constant is the *half-life.* This is the time necessary for a given number of atoms, or for the corresponding activity, to decay to one-half the initial value. It may be derived from the decay constant by the following process: In Eq. (14-9) at the time corresponding to the half-life, N_t/N_0 will be $\frac{1}{2}$. Substituting $\frac{1}{2}$ in Eq. (14-9) for N_t/N_0 and T (the half-life) for t:

$$\log \tfrac{1}{2} = -0.4343\ \lambda T \tag{14-11}$$

or

$$T = \frac{0.693}{\lambda} \tag{14-12}$$

If then λ is known, the half-life may be calculated, or vice versa. For some purposes the half-life may be adequately determined by plotting activity on a logarithmic scale against time on a linear scale and reading from the straight line so obtained the time which corresponds to an activity of 50 per cent of the original activity.

Randomness of Decay Process. An important property of radioactive decay is the exponential nature of the process. This indicates that there is a definite probability, depending upon the magnitude of λ, that any particular atom will disintegrate at any given moment. The process is strictly random; it is impossible to predict whether a given atom will disintegrate at any given time. Its lifetime may be any period from zero time to a time of great magnitude. It can, however, be predicted, from the constant λ, how many of a *large number* of atoms will decay in a certain time period. The random statistical nature of radioactive disintegration places a limit on the precision with which activity may be measured. In order to get more precise measurements, larger numbers of disintegrations must be counted.

Counting Errors. Two classes of errors must be considered in counting radioactive disintegrations: fluctuations in the counting rate caused by the random nature of the disintegration process and errors brought about

by the limitations of the instruments used and of the techniques of sample preparation.

Because of the random nature of the disintegration process, the individual values in a series of determinations of the counting rate of a sample will differ from each other. They will be randomly distributed about the mean value of the series. The greater the number of counts used in computing the average counting rate, the closer will that average agree with another such independently observed average counting rate.

Standard Deviation. For all except a very small number of counts the probability of an observed number of counts differing from the true number of counts may be calculated from the standard deviation. If n is the total number of observed counts, $n^{1/2}$ is the standard deviation of n. The probability of observing an error as large as, or larger than, the standard deviation is 0.3173. In other words, there are about 32 chances out of 100 that an error as large as, or larger than, $n^{1/2}$ would occur because of the random nature of the disintegration process, or 68 out of 100 that the error will be smaller. The value 1.645 $n^{1/2}$ would represent the so-called nine-tenths error. There are 9 chances out of 10 that the random error will be smaller. The value 1.96 $n^{1/2}$ is the ninety-five hundredths error. There are 95 chances out of 100 that the random error would be smaller than this. This error is most commonly used as the level at which deviations are considered to exceed chance variation and so are considered to be due (in part) to other than random fluctuations.

It is more customary to deal with counting rates, rather than with the number of counts. If n particles are counted in t min, the counting rate is $N = n/t$. Since $n = Nt$, $n^{1/2}$ (the standard deviation) is equal to $(Nt)^{1/2}$ and the standard deviation of N is $(Nt)^{1/2}/t = (N/t)^{1/2}$.

Standard Deviation of Net Count. The true counting rate of a radioactive sample is the difference between the counting rate which includes the background, and that of the background. Since each counting rate has its own random error, the random error of the difference will include that of both counts. If $(N_s/t_s)^{1/2}$ is the standard deviation of the rate for sample plus background and $(N_b/t_b)^{1/2}$ is the standard deviation of the rate for the background, then the standard deviation for the difference is $\sqrt{[(N_s/t_s)^{1/2}]^2 + [(N_b/t_b)^{1/2}]^2}$ or $(N_s/t_s + N_b/t_b)^{1/2}$.

Having calculated the standard deviation, one may decide from the particular problem whether the nine-tenths error or the ninety-five hundredths error (or any other level of significance) represents the chance which one wishes to take in deciding upon the error of a counting rate. If one wishes to obtain a counting rate with an error of no more than a definite magnitude, one must then arrange to count for a long enough period of time to reduce the deviation to the desired magnitude.

Nonrandom Errors. Errors other than random errors of counting

include the normally recognized errors associated with chemical manipulations, plus errors associated with the techniques of preparing and mounting samples, plus errors due to limitations of radiometric instruments. For example, a Geiger tube has a dead time (or recovery time or resolving time) during which it is insensitive to incoming radiation. As the counting rate increases, a higher and higher percentage of the counts is not recorded. A correction, which depends upon the counting rate and the characteristics of the tube, must be applied for these coincidence losses if the counting rate is high enough to make the magnitude of these coincidence losses material to the experiment. There are other errors caused by possible lack of stability of the counting circuit and then there are, of course, the errors caused by loss of activity due to absorption, back scattering, and unreproducible positioning of the mount. These errors do not, however, enter into consideration in ordinary tracer work in which the relative count against a standard is desired rather than an absolute count. The only such error of any consequence would then be that caused by lack of reproducibility of mounting and positioning the sample (erratic geometry). There are statistical methods for testing whether successive counting-rate determinations on a sample differ from each other by an amount greater than could be ascribed to random fluctuation errors.

AVAILABILITY AND PROCUREMENT OF RADIOISOTOPES

The user of radioisotopes has at his disposal naturally occurring and artificially produced radioelements. The natural radioelements such as radium, thorium, uranium, and others are available without governmental restrictions but they are less generally useful than the artificial radioelements.

The artificial radioelements furnish the main source of supply of materials for the uses to be discussed. Practically all these elements are produced in nuclear chain reactors, the so-called "atomic piles." A minor source is the particle accelerator such as the cyclotron. The distribution of all artificial radioisotopes is governed by regulations of the Isotopes Extension, Division of Civilian Application of the U.S. Atomic Energy Commission. The Commission is authorized by the Atomic Energy Act of 1954 (amending that of 1946) to distribute radioisotopes to applicants seeking such materials for research or development activity, medical therapy, industrial uses, or such other useful applications as may be developed. The Atomic Energy Act also places upon the Commission the responsibility for making certain that radioisotopes are used in a manner which will be safe to the user and to those about him. It is also the Commission's duty to withhold isotopes from those not properly

equipped or trained to carry out safe practices and to withdraw such permission, and if necessary, call for the return of purchased isotopes, from those who do not observe safe practices or who use authorized materials for unauthorized purposes.

This description of the Isotopes Extension's functions sounds more formidable than the regulations have worked out to be in actual practice. Aside from ensuring adequate safety provisions, the Isotopes Extension has no official interest in nonmilitary uses to which isotopes are put. It will not interpose its own judgment into the question of the scientific or technical adequacy or validity of the use being authorized. That decision is entirely up to the user.

A person who desires to purchase artificial radioelements (except for less than certain specified extremely small quantities, the purchase of which requires no authorization) must fill out Form AEC-313 in triplicate and forward two copies to the Isotopes Extension, Division of Civilian Application, U.S. Atomic Energy Commission, P.O. Box E, Oak Ridge, Tenn. The Isotopes Extension does not lay down any definite training requirements needed to satisfy it of the competence of the person who plans to use radioisotopes. The extent of training and experience needed will depend upon the nature of the use of, and the degree of hazard attached to, the isotope requested. A good way to acquire the requisite foundation for this type of work is to attend one of the 4-week sessions offered by the Oak Ridge Institute of Nuclear Studies at Oak Ridge, Tenn. A number of universities also offer courses in these studies.

The Isotopes Extension will review the application and, if it approves it, will forward to the applicant an AEC Byproduct Material License, AEC-374. This authorizes the applicant to purchase a specific isotope or isotopes, in such amounts that he will have on hand no more than a definite maximum quantity of each isotope at any one time. The applicant must use this authorization to order radioisotopes. The supplier may be the management of the Oak Ridge or Brookhaven or Argonne Laboratory chain reactors or any one of a number of commercial suppliers, depending upon the availability of the material desired. Sometimes materials are purchased from foreign sources, particularly Canadian or British. Nevertheless, an AEC authorization is required just as for purchase from domestic sources.

Table 14-2 gives a list of radioisotopes which are available from nuclear reactors, with their half-lives, and the types of radiation produced, as well as the energy of the radiation. Table 14-3 is a similar list of cyclotron-produced radioisotopes. Isotopes are available in a number of chemical combinations. Carbon 14 particularly has been synthesized into a great variety of organic compounds which are available from several commercial suppliers.

TABLE 14-2. USEFUL RADIOACTIVE ISOTOPES (PILE PRODUCED)*

Isotope	Half-life	Beta particles, mev		Gamma rays, mev	
Antimony 122	2.8 days	1.36	1 94	0 568	
Antimony 124	60 days	0 57	2.24	0.60	1.69
Antimony 125	2 7 years	0 128	0 299	0 035	0.465
		0 616		0.425	0.637
Argon 37	34 1 days	K, L		No γ	
Arsenic 74	17 5 days	0 69	1.36	0.596	0.635
Arsenic 76	27 6 hr	0.40	2.56	0 58	1.76
		1 40	3.12	1 20	2 02
Arsenic 77	40 hr	0.68		No γ	
Barium 131	13 days	K		0 122	0 372
				0.206	0 494
Barium 140	12 8 days	0.480	1 022	0 160	0 306
				0 54	
Bismuth 210	Long	1.17		No γ	
Bromine 82	35 7 hr	0.465		0 547	1 35
				0.787	1 70
Cadmium 115	2 33 days	0 46	1.1	0.52	
	43 days	1.41		1.10	
Calcium 45	152 days	0 255		No γ	
Carbon 14	5,700 years	0 155		No γ	
Cerium 141	32.5 days	0.41	0 56	0 141	0 315
Cerium 144	290 days	0 35		0 03	0 134
Cesium 134	2 3 years	0.09	0 66	0 57	1 35
				0 79	1 96
Cesium 137	33 years	0.52	1 17	0.663	
Molybdenum 99	67 hr	0 445	1.23	0 367	0 740
				0 780	
Niobium 95	35 days	0.163		0 771	
Neodymium 147	11.6 days	0.35	0 78	0 091	0 520
Nickel 59	750,000 years	K			
Nickel 63	85 years	0.067		No γ	
Osmium 191	16 days	0.14		0 039	0 128
Phosphorus 32	14 3 days	1.718		No γ	
Potassium 42	12.4 hr	2.04	3.60	1.5	
Praseodymium 142	19.1 hr	0.636	2 154	0 135	1.576
Praseodymium 143	13.8 days	0.93		No γ	
Promethium 147	3.7 years	0.223		No γ	
Rhenium 186	91 hr	1 07		0.14	0 21
Rubidium 86	19.5 hr	0.716	1.822	1.08	
Ruthenium 97	2 8 days	K		0 217	
Ruthenium 103	39.8 days	0.222	0.684	0.040	0 494
Ruthenium 106	1 year	0.041			
Samarium 153	47 hr	0.78		0 07	0 11
				0 60	
Chlorine 36	400,000 years	0.716			
Chromium 51	26 days	K		0.32	0.267

TABLE 14-2. USEFUL RADIOACTIVE ISOTOPES (PILE PRODUCED)* (*Continued*)

Isotope	Half-life	Beta particles, mev			Gamma rays, mev		
Cobalt 60	5.25 years		0.31		1 17		1.33
Copper 64	12.8 hr		0 57			1.34	
Europium 152	5.3 years	0.7		1.6	0.12		1.4
Europium 154	5.4 years	0.3		0.7		1 1	
			1.6				
Gallium 72	14.25 hr	0.64		1 48	0.63		2 21
		0.96		3.15	0.84		2.51
Gold 198	2.69 days		0.96			0 411	
Gold 199	3.3 days		0.32		0.16		0.21
Hafnium 181	46 days		0 42		0 34		0.48
Hydrogen 3	12.5 years		0.018			No γ	
Indium 114	50 days		2.05		0 55		0.72
						1.27	
Iodine 131	8.04 days	0.32		0.60	0 080		0 364
					0 284		0 638
Iridium 192	70 days		0.67		0 14		0.65
Iridium 194	19 hr		2.1		0 38		1 65
Iron 55	2.94 years		K			No γ	
Iron 59	46 days	0.26		0.46	1 1		1 3
Lanthanum 140	40 hr	1.32		1.67	0 33		1 65
			1 67		0 87		2 30
Mercury 197	23 hr		K		0 13		0.16
	64 hr		K			0 08	
Mercury 203	51 days		0.21			0 28	
Scandium 46	85 days	0.36		1 49	0 89		1 12
Selenium 75	128 days		K		0 025		0 402
Silver 110	270 days	0 09		2 12	0.65		0 91
		0.57		2 86	0 90		1 52
Silver 111	7.5 days		1 06			0 34	
Sodium 24	14.9 hr		1.39		1.38		2 758
Strontium 89	54 days		1.5			No γ	
Sulfur 35	87.1 days		0 167				
Tantalum 182	117 days		0.53		0.3		1 1
					•	1 2	
Technetium 99	212,000 years		0 292				
Thallium 204	3 years		0 77			No γ	
Tin 113	112 days		K			No γ	
Tungsten 185	73 days		0.43			No γ	
Tungsten 187	24 hr	0 6		1.33	0 2		0 7
Yttrium 90	65 hr		2 24			No γ	
Yttrium 91	57 days		1 56				
Zinc 65	250 days		0.32		0.201		1.14
Zinc 69	14 hr		0 86			0.439	
Zirconium 95	65 days	0.39		1.0	0.23		0.73
						0.92	

* J. R. Bradford, "Radioisotopes in Industry," Appendix I, Reinhold Publishing Corporation, New York, 1953. By permission of the publishers.

TABLE 14-3. USEFUL RADIOACTIVE ISOTOPES (CYCLOTRON PRODUCED)*

Isotope	Half-life	Beta particles, mev			Gamma rays, mev		
Arsenic 73	76 days		K			0.052	
Beryllium 7	54 5 days		K			0.479	
Cobalt 57	270 days	β^+		0.26	0.014		0.119
						0.131	
Iodine 125	56 days		K			0.035	
Iron 59 (free of Fe 55)	46 days	0.26		0.46	1.1		1.3
Manganese 54	310 days		1.0			0.835	
Sodium 22	2.6 years	β^+	0.54	1.8		1.28	
Zinc 65 (free of Zn 69)	250 days	β^+		0.32	1.14		0.201

* J. R. Bradford, "Radioisotopes in Industry," Appendix II, Reinhold Publishing Corporation, New York, 1953. By permission of the publishers.

UNITS OF RADIATION AND RADIATION DOSAGE

Before going on to a treatment of the important matter of the safe handling of radioelements, it is necessary to discuss units of measurement and instruments required to make suitable measurements.

In the discussion on properties of radioactivity two broad concepts were introduced which must be clearly differentiated. The first concept is that of the *disintegration* or *decay constant*, which is related to the half-life, of a radioelement. This indicates the fraction of the total number of radioactive atoms which will decay in a given time. The unit of radioactive decay is the *curie*. Originally it referred to the quantity of radon (a radioactive gas) in equilibrium with 1 gram of radium. Now it refers to the rate of disintegration of a radioelement. One curie is that quantity of any radioelement which undergoes 3.7×10^{10} disintegrations per second (d/sec). The millicurie (mc) 3.7×10^7 d/sec and the microcurie (μc) 3.7×10^4 d/sec are smaller units of radioactivity which are more applicable to work at the tracer and intermediate levels.

It is obvious from the definition of the curie that it makes no distinction between radioelements which emit various kinds of particles. Yet the kinds of particles and their energies are of great importance in a consideration of the effect on human and animal tissue. It has been pointed out that, when radiation penetrates matter, it loses its energy, and the penetration ceases when all the energy of the radiation has been dissipated in the absorber. It has also been pointed out (Fig. 14-3) that different types of radiation have different penetrating power. Furthermore, the penetrating power of a given type of radiation varies with its energy. Injury to body tissue is caused mainly by ionization produced by the energy released during absorption. The unit of radiation dosage accord-

ingly takes into account the energy of the radiation and the *specific ionization*. The *specific ionization* is the number of ion pairs formed per centimeter of path. For particles of equal mass the specific ionization increases with the magnitude of the charge. For particles of the same energy the specific ionization increases with the mass, i.e., with decreasing speed. The unit of radiation dosage is the *roentgen* (r). This is defined as the quantity of X rays or gamma rays which will produce by absorption in 1 cc of dry air at 0°C and standard atmospheric pressure ionization sufficient to form 1 electrostatic unit of electricity, either positive or negative. Calculated in other terms, 1 roentgen (r) produces in 1 cc of dry air 2.08×10^9 positive or negative ions or 1.61×10^{12} ion pairs in 1 gram of air. The average energy expended in producing one ion pair in air is about 32.5 electron volts (ev) and the energy for 1.61×10^{12} ion pairs is 5.23×10^{13} ev. Since 1 ev is equivalent to 1.60×10^{-12} erg, the energy gained by the absorption of 1 r of X rays or gamma rays in 1 gram of air is 84 ergs.

Since particles such as alpha and beta particles, protons, and neutrons cause biological effects upon absorption in tissue which are similar to the effects of X rays and gamma rays, the roentgen unit has been extended to such particles. To make this extension, a new unit, the *roentgen equivalent physical* (rep), has been defined as the dose which produces energy absorption of 93 ergs per gram of tissue. The actual energy absorption depends upon the kind of tissue and the wavelength of the radiation, and ranges between 60 and 100 ergs per gram. This difference is usually ignored in calculating permissible exposures to radiation. A beta-ray dose of 1 rep is taken to be physically equivalent to an X-ray or gamma-ray dose of 1 r at any given point in the body.

The absorption of quantities of ionizing radiations from several sources which provide the same amounts of energy may nevertheless cause different biological effects in the human (or animal) body. To give recognition to these differences the unit *roentgen equivalent man* (*or mammal*) (rem) has been devised. This is defined as that quantity of radiation which produces the same biological damage in man as that resulting from the absorption of 1 r of X rays or gamma rays. Table 14-4 gives

TABLE 14-4. RELATIONSHIPS AMONG RADIATION DOSAGE UNITS

Type of radiation	r	rep	rem
X rays and gamma rays	1	1	1
Beta rays	...	1	1
Fast neutrons	...	1	10
Slow neutrons	...	1	5
Alpha rays	...	1	10–20

some equivalent dosage values for various types of radiation. The figures 10 to 20 rem for alpha rays as equivalent to 1 rep are based on the assumption that the radioactive *substance is fixed at some point within the body.*

PERMISSIBLE RADIATION DOSAGE

Exposure of humans to radiation is not something new or unnatural. We are being bombarded constantly by cosmic rays from outer space. The earth contains radium and other radionuclides which give off radium and thorium emanations to the atmosphere. The body contains enough carbon 14 to produce about 100,000 beta particles per minute in the average adult and enough potassium 40 to produce more than 150,000 beta particles per minute. The average luminous watch dial emits more than a negligible amount of radiation. This normal exposure is evidently harmless. What we must carefully guard against is overexposure.

The U.S. National Committee on Radiation Protection has recommended that the tolerance dose or the *permissible dose* for X rays and gamma rays be set at 0.3 r (300 mr) per week for absorption over the whole body. To extend this concept to other types of radiation, use is made of the biological equivalence given in Table 14-4 between dosages of 1 r and 1 rem. The permissible whole-body exposure for any type of radiation is thus taken as 0.3 rem (300 mrem) per week from the combined radiation of all types of particles, taking into account the nature of the radiations.

Several points must be remembered regarding the 0.3-rem tolerance dose. First, this is for exposure over the whole body. Certain small areas, particularly hard tissues, may get higher exposure without danger. Secondly, the exposure must be spread over a period of a week. A dosage of a given magnitude may have much more serious effects if received rapidly than if it is spread over a long period of time. Thus exposure to the permissible dose of 0.3 rem per week for 10 years would be equivalent arithmetically to exposure to 156 rem per min for 1 min, but the latter exposure would be extremely more harmful than the former. The reason probably is that the slower exposure gives body tissue time for repair before irreparable damage has been done.

The above discussion refers to external radiation. In addition one must consider the possibility of ingestion or inhalation of radioactivity. The total tolerance dosage, from both external and internal sources, is taken as 0.3 rem per week. However, additional facts must be considered in assessing the hazards of internal exposure. These include such matters as whether the isotope is distributed over the whole body, or whether it concentrates in a given organ, the half-life, the energies, and the *biological half-life.* The biological half-life is the time taken for the activity in the

body to fall to half its initial value as the result of elimination and radioactive decay. The biological half-life may be equal to, or less than, the radioactive half-life.

The measurement of dosages is an important matter, but its considerations will be deferred until the general subject of instrumentation for radioactivity measurements has been taken up. This will be done because instruments for safety monitoring have fundamentals in common with instruments for measuring activity for scientific and technical purposes.

RADIOACTIVITY INSTRUMENTS

A number of methods for the detection and measurement of radioactivity have been employed since radioactivity was discovered. All these are based on the fact that radioactivity causes ionization of matter. They differ from each other in the selection of the means by which the ionization is made evident and measurable. The most currently prevalent class of such methods is that in which electrical effects produced by the ionization are measured. This class of methods will be considered first and will be followed by a briefer reference to some which are of less current interest.

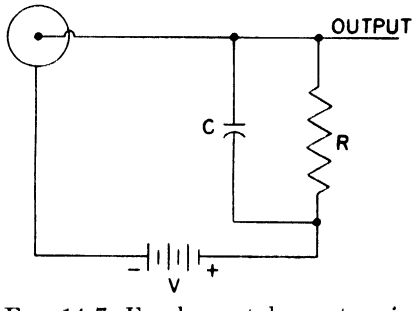


FIG. 14-7. Fundamental counter circuit. (*Serge A. Korff, "Electron and Nuclear Counters," D. Van Nostrand Company, Inc., New York, 1955, Fig. 1-1. By permission of the publishers.*)

Let us consider an arrangement, such as is indicated schematically in Fig. 14-7, which is ordinarily used in measuring radioactivity. This consists of a cylindrical metallic chamber which acts as a cathode and in which is contained a central wire which acts as an anode. These electrodes are insulated from each other and are connected to a source of potential. A resistance R is inserted in the circuit in order to pass a voltage pulse to the detecting instrument. A condenser C is understood to include all the capacity in the circuit. The wire serves to collect negative changes which are discharged as a pulse. The air or other gas in the chamber cannot normally conduct electricity unless a very high voltage (several thousand volts) is impressed across the electrodes. The current will then be evidenced by a spark across the electrode gap. If, in the absence of a high voltage, radioactivity is introduced into the chamber, positive and negative ions are formed in the gas. These move toward the electrodes and can carry a current. (This behavior is somewhat analogous to that in a liquid electrolyte which also does not conduct a current unless ions are present.)

Saturation Current. If one starts with zero potential and gradually increases it up to several thousand volts, the current produced may be observed to behave in the manner indicated in Fig. 14-8. When the voltage is low, the ions formed travel very slowly toward the electrodes and so have a considerable chance of recombining, thus neutralizing each other. The current pulses formed by the so-called ionizing events (the radioactivity) are consequently small. As the voltage is increased, more and more ion pairs escape recombination. The size of the pulse accordingly increases (see region I of the curve) until the voltage is high enough to accelerate the ions sufficiently so that virtually all of them reach the electrodes without recombination. At that point an increase in voltage does not increase the size of the pulses and the current reaches a constant value which is called the *saturation current.* This condition is indicated by region II. The actual potential range for voltage region II depends on a number of factors such as the shape and size of the electrodes, the distance between them, the kind of gas in the chamber, and its pressure. Generally speaking, it is between 100 and 500 volts. The type of instrument which makes use of the behavior exemplified by region II is known as an ionization chamber.

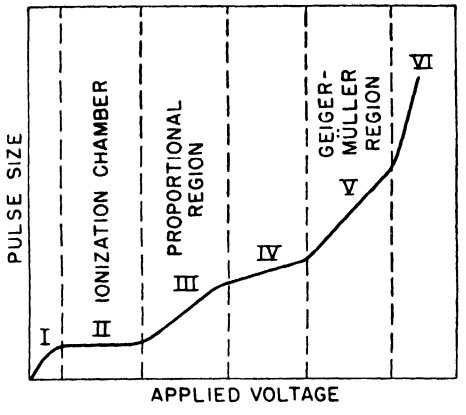


FIG. 14-8. Variation of pulse size with applied voltage. (*S. Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York, 1950, Fig. 6.2. By permission of the publishers.*)

Multiplicative Region. At voltages higher than those for region II a new phenomenon occurs. The increased voltage gradient becomes larger and larger, with the result that the electrons move toward the anode with higher speed. They thus have more energy to impart to the gas and so they cause ionization of other atoms and molecules of the gas. The electrons thus produced will themselves give up energy to ionize additional atoms and molecules of the gas, and so on. The regions beyond region II are thus known collectively as the *multiplicative region.* It is a more sensitive region than the ionization-chamber region, but at the same time it is subject to many experimental variables.

The total number of ion pairs produced by a single primary ion pair is called the *gas-amplification factor.* This factor is unity in region II. In region III it may be as high as 10^5 to 10^6, depending upon the particular voltage employed. This region is known as the proportional region since the size of the pulse is proportional to the number of primary ion pairs

produced by the entering radioactive particle. The number of primary ion pairs is in turn dependent upon the energy of the entering radioactive particle. Instruments operated in this region, called *proportional counters*, will accordingly differentiate between radiation of different energies.

With further increases in voltage, region IV is traversed. This is not made use of for instrumentation. We then enter region V, the Geiger-Müller region. Here the gas-amplification factor may be as high as 10^8 and is so great that the size of the pulse is almost independent of the number of primary ion pairs. Discrimination between radiation of various energies is thus not possible, but very little amplification of the current is needed. The instruments used in this region are known as Geiger-Müller counters or tubes; or briefly Geiger or G-M counters or tubes. They are the most common counters in radiochemical work.

Finally, beyond region V, in region VI, the potential is so high that a continuous discharge occurs, rendering this region useless for counting.

Pulse Counters and Counting-rate Meters. Radiation detecting and measuring instruments may be operated in one or the other of two ways. In one type of instrument each pulse produced by discharge of the anode is counted individually. In another type, the counting-rate meter, the effect of a number of pulses is integrated over a definite period of time. The current produced increases with an increase in the rate at which pulses reach the instrument and is recorded on a meter. This in turn is calibrated to read in terms of counting rate or dosage.

Instruments arranged to count individual pulses have a vacuum-tube amplifier which amplifies the pulses so that they may be recorded on a mechanical register or counter. However, such registers generally cannot count faster than about 30 to 50 counts per second. To make it possible to count pulses from samples containing activity which causes a greater number of counts per second, a *scaler* is used. This is an electronic device which allows only a predetermined proportion of the counts to actuate the register. Only one pulse in every 2, 4, 8, 16, 32, or 64 is registered. Some scalers go as high as 128, 256 or higher. (These numbers are all factors of 2.) Scalers based on factors of 10 are also available. The number of counts on the register is multiplied by the scaling factor to get the total number of registered counts. To this number is added the number of counts indicated by the lights on the scaler. Figure 14-9 is a photograph of a typical scaler set for a scaling factor of 32. To read this, suppose the register read 50 and the lights were on for 2, 4, and 32. The total number of counts would be $(50 \times 32) + 2 + 4 + 32 = 1{,}638$. A timer used in conjunction with the register makes possible the calculation of counts per unit time (seconds or minutes usually).

In a counting-rate meter (such as is shown in Fig. 14-10) the meter is calibrated to read in terms of counts per unit time. A separate timer is

not needed. For most counting purposes for analysis, the scaler and register are used, since this combination is more flexible and can give better precision than the ratemeter. Ratemeters are mostly used for surveying and monitoring for radioactive contamination, but sometimes

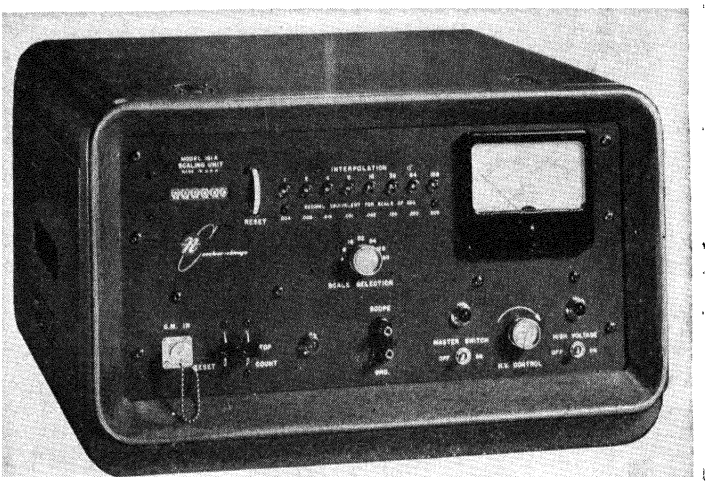


FIG. 14-9. Scaling unit. (*Courtesy of Nuclear Instrument and Chemical Corporation.*)

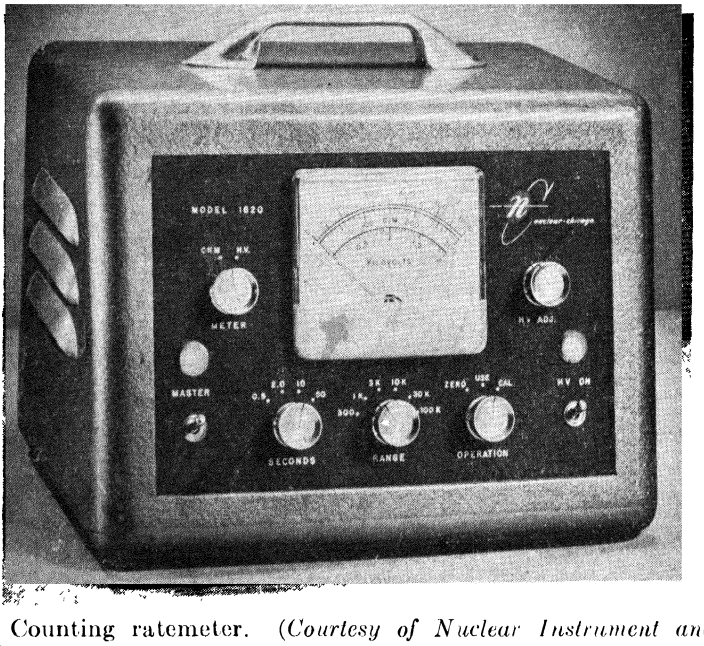


FIG. 14-10. Counting ratemeter. (*Courtesy of Nuclear Instrument and Chemical Corporation.*)

also for analytical purposes where their convenience outweighs a possible loss in precision.

The Ionization Chamber. Ionization chambers are operated at a voltage corresponding to about the middle of region II (Fig. 14-8) so that a

small change in the voltage will not affect the pulse size. Each radioactive particle entering the ionization chamber ionizes the gas contained therein (air, carbon dioxide, argon, methane, or others) and should produce a pulse. However, the specific ionization of beta and gamma particles is so small that the pulses formed by them are too feeble for counting. Alpha particles have a high specific ionization and produce strong pulses. Ionization chambers arranged for counting are therefore especially useful for alpha particles. For counting alpha particles the ionization chamber has parallel-plate electrodes arranged about 1 cm apart, rather than a cylinder and central-wire arrangement. The sample is sometimes placed on the lower plate in the chamber. If it is desired to place the sample outside the chamber, the latter is provided with a thin window of mica, nylon, or pliofilm which allows a reasonable proportion of the alpha particles to penetrate into the chamber.

For measuring beta and gamma activity (as well as alpha) ionization chambers are arranged to determine the total ionization rather than to count the number of individual particles. There are two main forms of such instruments. One kind is the electrostatic type, exemplified by the Lauritzen quartz-fiber electroscope. This contains a metal-coated quartz fiber parallel to, and connected with, a rigid metal wire. This is enclosed in a cylindrical aluminum case, from which it is insulated. The case acts as a chamber and as an electrode. When the device is charged by a 100- to 200-volt battery, the quartz fiber is deflected. Its position may be read by means of a microscope with a scale on its eyepiece. Ionizing particles cause the fiber to discharge and the deflection to decrease. The rate of movement of the fiber is roughly proportional to the activity. This device is less subject to breakdown than counters and scalers and is accurate. It is not used very much for general counting work because it is time-consuming and otherwise not convenient.

Another type of ionization chamber for measuring alpha, beta, and gamma radiation is arranged as in Fig. 14-7. The weak continuous output flow of current is measured directly by a sensitive electrometer or by a less sensitive meter after high amplification by a suitable vacuum-tube amplifier. The current strength is directly proportional to the rate at which radiation enters the chamber. Ionization chambers such as these have been found useful in measuring low-energy radiation such as from carbon 14 and sulfur 35.

The Proportional Counter. The ionization chamber, although essentially a simple instrument, produces only relatively feeble pulses. It therefore requires a sensitive electrometer or a powerful vacuum-tube amplifier. If counting is done in the proportional region (region III of Fig. 14-8), with a gas mixture which generally consists of methane and argon, the gas-amplification factor is 10^5 to 10^6 and so the pulses obtained

are larger. Less powerful amplification is needed than with the ionization chamber. Nevertheless, the size of pulse is still proportional to the number of primary ion pairs produced by the radioactive particle, as with the ionization chamber. It is thus possible to count alpha particles and ignore betas and gammas by means of a *pulse analyzer,* sometimes known as a *kicksorter.* This device rejects pulses below a certain size and passes those above that size. To count beta particles in the presence of alpha particles, a thin aluminum window is used to absorb the latter. Gamma rays will, of course, also penetrate. If it is desired to count only gamma rays, a thin sheet of lead will prevent the passage of alpha and beta particles. (The use of differential absorbers is not, however, limited to counting with proportional counters.) One disadvantage of the proportional counter is the necessity for controlling the applied voltage very exactly since the gas-amplification factor, as may be seen from Fig. 14-8, depends on the voltage.

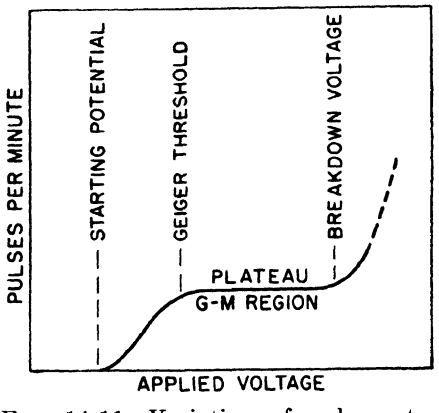


FIG. 14-11. Variation of pulse rate with applied voltage. (*S. Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York, 1950, Fig. 6.4. By permission of the publishers.*)

The Geiger-Müller Counter. Counters operating in the Geiger-Müller region (region V of Fig. 14-8) are the most common. They give the same pulse size for practically all ionizing particles so that they will not distinguish between alpha, beta, and gamma rays. They are rarely used to count alpha particles and are more efficient for beta particles than for gamma rays. Since the specific ionization of gamma rays is small, most of them pass through a Geiger counter with only about 1 per cent loss in total energy and therefore with about only 1 per cent counting efficiency.

G-M tubes comprise essentially the same arrangements as given in Fig. 14-7. The central wire is the positive electrode (anode) which attracts electrons, and the outer tube is the negative electrode (cathode) which attracts the positive ions. The electrodes are attached to a scaling device which indicates only relatively large pulses, but not small ones. Consequently, as the applied voltage is increased, the number of pulses indicated per minute for a source of radioactivity will follow the curve given in Fig. 14-11. Below the *starting potential* no count is obtained since the pulses are too small. Beyond the starting potential, the number of counts increases up to a maximum known as the Geiger threshold, which is the beginning of region V in Fig. 14-8. Over the voltage range

corresponding to the horizontal portion of the curve the number of counts per minute is practically constant. In this voltage range, known as the Geiger *plateau*, there is actually a slight increase in count. For a good counter, however, the increase is so small that with any reasonable regulation of the voltage the count rate remains practically constant. The plateau region is somewhere between 800 and 1,500 volts and extends over a range of about 200 to 300 volts. The *operating voltage* is usually taken at a point somewhat lower than the middle of the range. Beyond the plateau, at the *breakdown voltage*, discharge is continuous and counting is impossible.

Multiple Discharges. A troublesome phenomenon which occurs in G-M tubes is that of multiple discharges. This is connected with the so-called *avalanche* which occurs during gas amplification, whereby the multiplication of ionizations from a single ionizing particle spreads electrons over the whole center wire. If another ionizing particle enters the tube before the preceding avalanche has been discharged, another avalanche is formed. The separate pulses are therefore not *resolved* and counting is made impossible. An avalanche once started will continue to perpetuate itself, presumably because of the action of the positive ions. When these reach the cathode wall of the G-M tube, electrons are liberated which rush toward the center wire and perpetuate the discharge.

Two methods may be used to stop or *quench* the discharge. One method, used with G-M tubes containing argon of 98 per cent purity to provide high specific ionization and a low starting potential, involves an external resistance or a vacuum-tube circuit. These automatically reduce the voltage below the starting potential after each pulse, thus preventing additional avalanches from the one initial ionizing event. The circuit restores the potential in time for the next ionizing event.

A more convenient and more widely used method for quenching the discharge is the use of *self-quenching* or internally quenched Geiger counters. Some are filled with argon containing a few per cent of an organic vapor or gas such as methane, ethane, or ethyl alcohol. The organic molecules ionize more readily than argon so that the positive argon ions formed at first transfer their charges to the organic molecules. These are practically the only ions which reach the walls of the tube and they spend their energy in dissociating organic molecules rather than in causing emission of electrons from the walls. After about 10^8 to 10^9 counts the quencher is largely used up and decomposition products have deposited on the walls and central wire of the tube, so that for further use the tube has to be opened up, cleaned, and refilled. Furthermore, these tubes are spoiled if the voltage should accidentally be set above the plateau region, in the region of continuous discharge. These troublesome features of tubes quenched with organic substances are obviated by the

more recently devised self-quenching tubes which contain chlorine or bromine as the quenching agent. The halogen atoms formed by dissociation of the halogen molecules in the quenching process recombine to form the original molecules. These tubes thus have an unlimited life. Their counting efficiency is not quite so high as that of the organically quenched tubes but the difference is not usually serious. Another type of internally quenched tube has been patented which contains argon with small amounts of xenon, oxygen, and nitrogen.

Shapes and Types of Geiger Counters. Geiger-Müller counters come in a variety of types and shapes for a number of uses. The basic form is

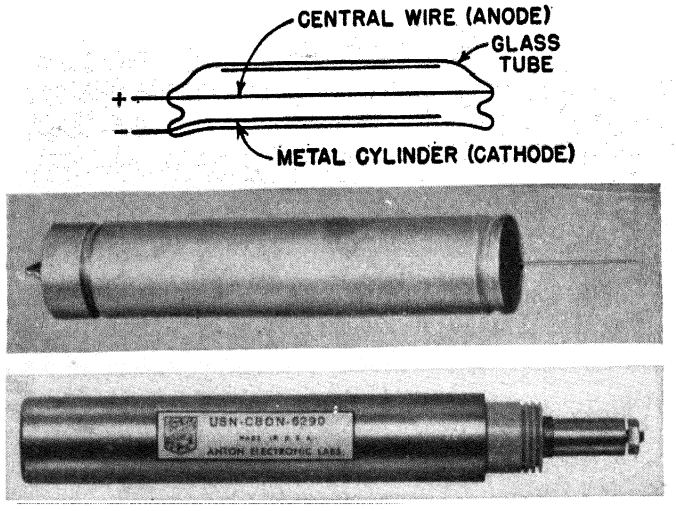
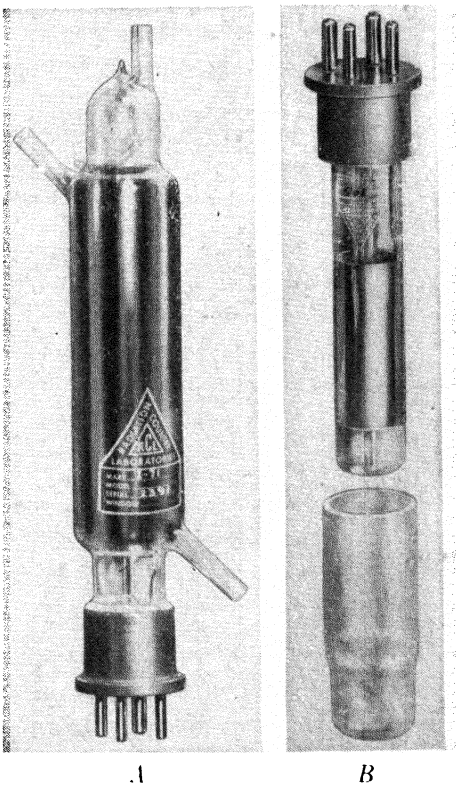


FIG. 14-12. Simple Geiger-Müller tube. (*Drawing from S. Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York, 1950, Fig. 6.5. By permission of the publishers. Photographs courtesy of Amperex Electronic Corporation and Anton Electronic Laboratories, Inc.*)

illustrated in Fig. 14-12. It consists of a glass tube containing gas at less than atmospheric pressure, with a central wire anode, usually of tungsten, 0.08 to 0.10 mm thick, and a cylinder of a metal such as copper within the glass tube to act as the cathode. The walls may also be of metal without a glass envelope or, in place of a metal tube, a thin layer of an electrical conductor such as silver or graphite may be deposited on the interior of the glass. The walls of the tube may vary in thickness depending upon the use for which the tube is to be applied. For gamma-ray counting the wall may be fairly thick but for beta rays thinner walls may be necessary. Figure 14-13 shows photographs of two modifications of G-M tubes adapted for purposes such as dipping into a liquid and allowing a liquid to flow around the counter. Counters may be made in a variety of sizes and have varied from 1 cm to 1 meter in length and from 0.3 to 10 cm in diameter.

For counting low-energy beta particles, such as those from carbon 14 or sulfur 35, extremely thin windows may be needed. For this purpose, as well as for the purpose of obtaining more easily reproducible location of the sample with respect to the tube, end-window counters are commonly employed. Such a counter is illustrated in Fig. 14-14. This type of counter is essentially the same as that of Fig. 14-12 except that radiation is received through a thin window of glass or mica which is placed at one end of the tube. These windows come in various thicknesses. Those for low-energy particle counting may be only slightly thicker than 1 mg per cm^2. Such tubes are usually mounted in a cylindrical lead shield, to cut down background radiation. They are attached rigidly to a set of shelves, made of plastic or metal, so that trays containing suitably mounted samples may be placed at a reproducible distance from the window and in a fixed geometrical relation to the window.



A *B*

FIG. 14-13. *A*. Thin-wall jacketed counter. *B*. Thin-wall dipping counter. (*Courtesy of Radiation Counter Laboratories.*)

Still another type of G-M counter is the so-called windowless flow counter which has found some use particularly for samples of low activity, emitting low-energy particles, such as carbon 14 and sulfur 35. In this type of counter the mounted sample is placed within the counter and a gas of suitable composition, such as a mixture of helium and isobutane or helium saturated with ethanol or xylene, is made to flow through the counter while it is in operation. By this means loss of activity by absorption in a window is avoided and a more efficient spatial arrangement is attained which is referred to either as 2π or 50 per cent geometry. This means that, if the sample is considered as a point source, with rays radiating from it in all directions to strike the surface of a sphere, such a counter would intercept a hemispherical segment of rays or 50 per cent of the rays. With end-window counters, the angle intercepted would be considerably less, depending upon the arrangement of sample and window.

Scintillation Counters. Mention must be made of a counting method which is becoming of increasing interest—scintillation counting. When beta or gamma rays are absorbed in certain solids such as calcium tungstate or alkali halides activated with traces of thallium, or organic solids such as naphthalene, anthracene, chrysene, and stilbene, scintillations of light are produced. If these impinge on the cathode of an electron photomultiplier tube, the scintillations of light, which would be too feeble to measure directly, release many electrons. These build up by multiplication to a measurable current pulse which can be counted in the manner previously described. Scintillation counters are particularly useful for counting gamma rays, since the density of the solids used leads to a much higher absorption than is attained when gamma rays enter the rarefied gas in a Geiger-Müller tube. In still another modification of this method

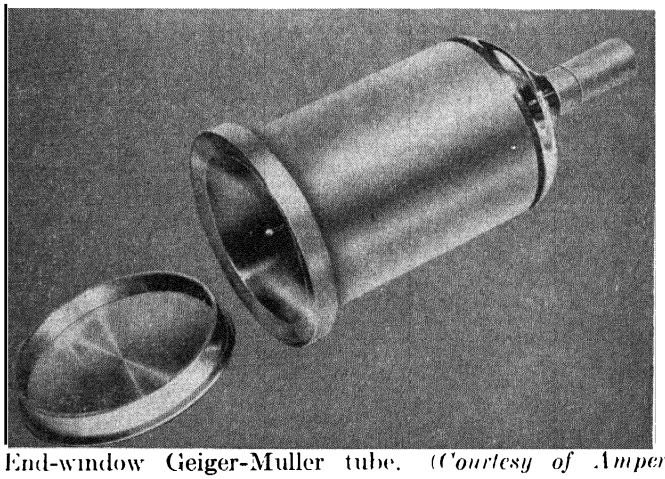


FIG. 14-14. End-window Geiger-Muller tube. (*Courtesy of Amperex Electronic Corporation.*)

the radioactive sample is dissolved in a solvent in which a scintillating substance such as, for example, terphenyl, is also dissolved. This method is advantageous for counting low-energy beta rays.

Photographic Methods. Radioactivity was discovered by the ability of radiation to blacken a photographic plate, but little use was made of such methods until recently. Now photographic detection methods are used for two purposes. For health protection, those working with radioactivity wear badges containing photographic film. When these are developed and the blackening is compared with standards, a measurement of the dosage which the worker has received may be obtained.

For determining the distribution of radioactive substances on a surface, so-called *autoradiographic or radioautographic methods* are used. In the method of detail radioautography, sections of tissue or other materials containing radioactivity are held in contact for a suitable length of time with a photographic emulsion. After development of the plate, the loca-

tion of the radioactive particles may be seen under the microscope. In gross radioautography, specimens are held in contact with a photographic plate and, after development of the plate, the distribution of radioactivity is examined without magnification. For example, the location of radioactive phosphorus in a leaf of a plant or in a section of bone may be studied. Another example is the paper chromatography of radioactive samples, such as biological fluids of experimental animals. It is sometimes better to expose the paper to a photographic plate than to spray it with color-forming reagents or to expose it to ultraviolet light for the observation of fluorescent bands.

RADIOACTIVITY LABORATORY SAFETY PRACTICES

In designing and equipping a laboratory for radiochemical work, two considerations must be kept to the fore. The first is to prevent exposure of those in and about the laboratory to hazardous dosages of radiation.

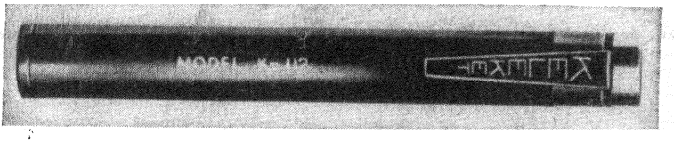


FIG. 14-15. *Pocket dosimeter.* (*Courtesy of Tracerlab, Inc.*)

The second is to avoid contaminating the laboratory with radioactivity, thus producing a high background count and causing contamination of equipment and reagents which may subsequently prevent the carrying out of accurate experimental work.

Personnel Monitoring Meters. These safety requirements cannot be met satisfactorily without suitable instruments for monitoring and surveying personnel and equipment. The instruments used for these purposes are specialized forms of ionization chambers, Geiger-Müller counters, and photographic film described previously. Pocket ionization chambers or so-called dosemeters (or dosimeters) which are clipped in the pocket like a fountain pen (see Fig. 14-15) or photographic-film meters, so-called film badges (see Fig. 14-16), or a combination of these should be worn whenever there is exposure to gamma rays. There are two types of pocket ionization chambers. One, the self-reading type, has a self-contained scale from which the user can read his accumulated exposure in milliroentgens by holding the meter up to the light and looking into it. The other type, not self-reading, requires a separate electroscope or electrometer for reading the cumulative dosage. The film badge, which is worn for both beta- and gamma- or X-ray exposure, consists of a piece of photographic film. Part of the film is shielded with about 1 mm of a suitable metal to prevent response to beta radiation, thus allowing only

gamma and X rays to enter. Part of the film has only the usual paper wrapping, thus allowing both gamma rays and beta rays of all but the lowest energy to enter. These films are processed, usually at weekly intervals, together with standards and controls, and indicate the dosage to which the wearer has been exposed during the time when the badge was worn.

Survey Meters. The above are known as personnel-monitoring meters and either inform the worker of the dosage he is receiving or furnish a record of the dosage he has received. Another class of so-called health-physics meters is designed to give information concerning the intensity of radiation from radioactive sources which is present either in the form

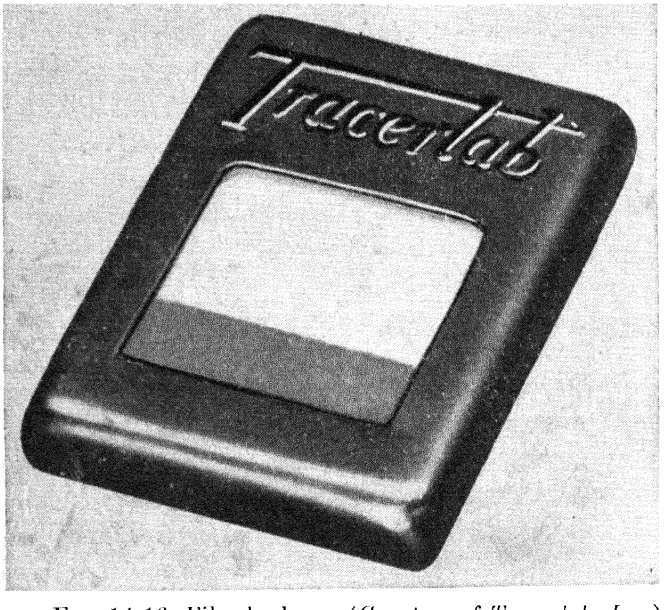


FIG. 14-16. Film badge. (*Courtesy of Tracerlab, Inc.*)

of active samples which are being handled or in the form of contamination on laboratory benches or equipment or on the clothes or hands of the worker Figure 14-17 shows photographs of two such instruments, and Table 14-5 gives some of their characteristics.

Other Radioactivity Meters. A minimum requirement in work with radioactivity is availability of a portable Geiger-Müller instrument. If low-energy beta particles are being handled, the instrument should be equipped with a thin-window tube. With this type of meter, activity which is present above the background intensity may be detected. However, no quantitative significance should be attached to the readings unless the meter has been calibrated against the same radioisotope. The calibration furnished with such an instrument is usually made against radium and is not correct for other radioelements. An additional pre-

caution in using a G-M tube meter is to approach activity from the least active region. If the tube is suddenly brought into a region of activity greater than that corresponding to its maximum capacity, the meter may register zero activity.

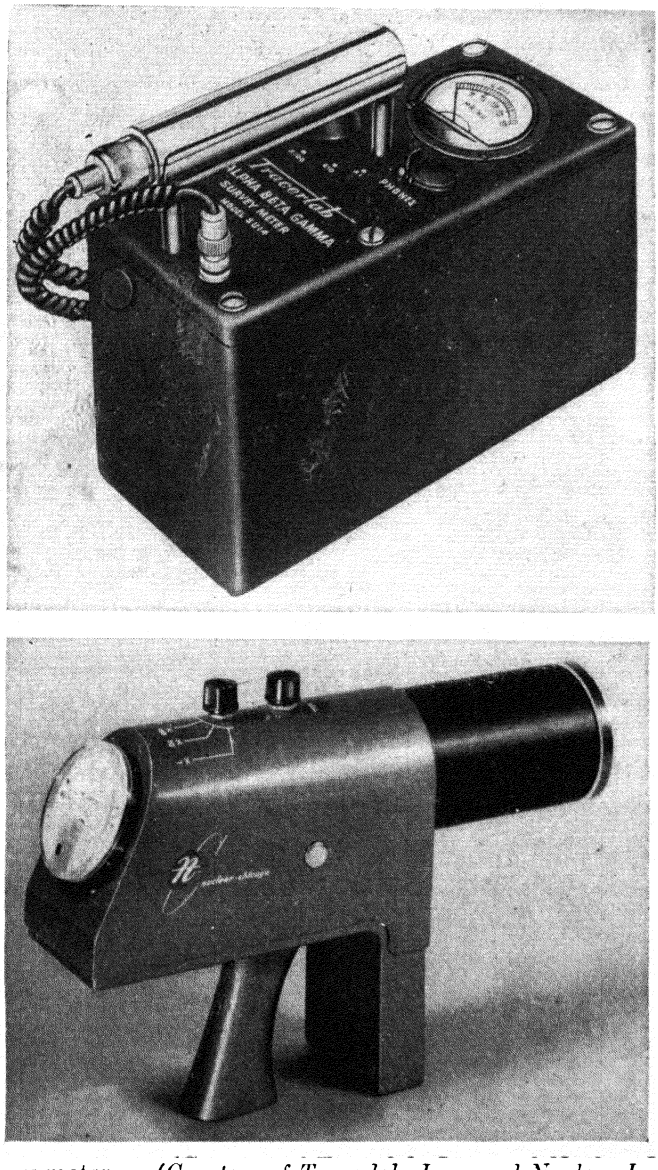


FIG. 14-17. Survey meters. (*Courtesy of Tracerlab, Inc., and Nuclear Instrument and Chemical Corporation.*)

If shipments of radioelements are to be handled which have activity beyond the range of the G-M meter an electroscope or ionization chamber meter should be available, such as those in Table 14-5, which have higher ranges. The readings on these instruments are not so dependent upon

the energy of the activity as are the G-M meters. They can therefore be used to read dosage rates without the need for recalibration.

TABLE 14-5. SOME HEALTH PHYSICS SURVEY METERS*

Instrument	Weight, lb.	Size, in.	Radiation detected	Usual accurate sensitive range, mr/hr†	Most useful purpose
Lauritzen electroscope	8	8 × 3 × 14	Beta, gamma	<0 1–1,000	Measuring dosage rates. Instrument response too slow for measuring low-activity contamination
Portable Geiger-Muller instruments	2–15	7 × 5 × 4 (avg)	Beta, gamma	<0 1–15 to 20	Detecting surface contamination (low-energy beta particles can be detected with suitable thin-walled tubes)
Cutie Pie meter.	4	12 × 3 × 8	Beta, gamma	10–5,000	Measuring dosage rates
Zeus .	10	12½ × 6½ × 5	Beta, gamma	5–5,000	Measuring dosage rates
Commercial model of Zeuto	6	9½ × 5 × 6	Beta (alpha)	<0.1 -40	Measuring dosage rates. Detecting surface contamination
Juno meter. . .	5	9 × 5¼ × 4	Beta, gamma (alpha)	5–4,000	Measuring dosage rates
Scaler (G-M tube on cable)	40–100	21 × 15 × 10½	Beta, gamma	<0.1–15 to 20	Detecting surface contamination (low-energy beta particles can be detected with suitable thin-walled tubes)

* Taken from G. W. Morgan, Surveying and Monitoring of Radiation from Radioisotopes, *Nucleonics*, 4(3): 24 (1949). The inclusion or exclusion of specific instruments in this table does not necessarily endorse or disapprove their use.

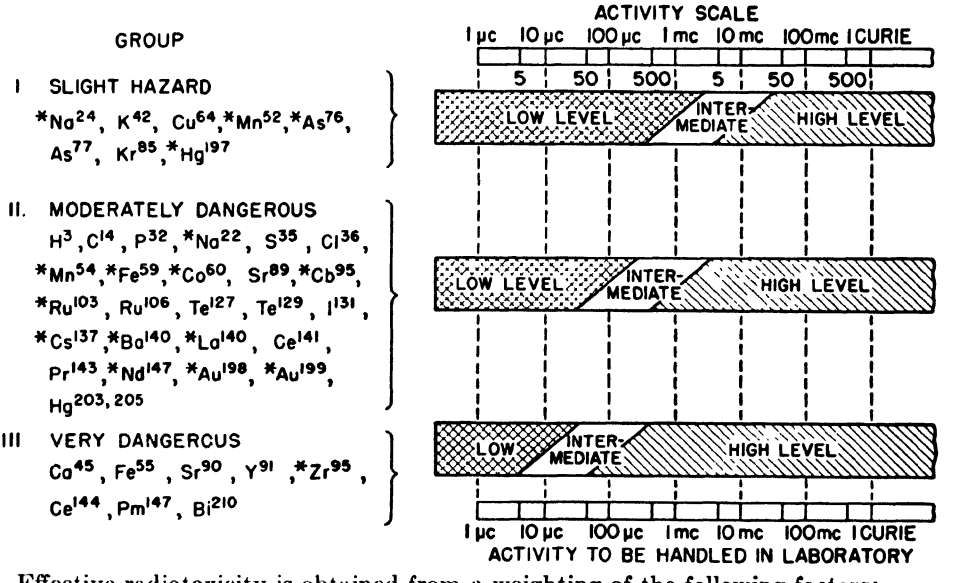
† D. M. Davis, "Health Physics Instrument Manual," Health Physics Department, O.R.N.L.

Laboratory Design and Practice. Beyond the basic need for personnel monitoring instruments and other health-physics instruments, what are the requirements for a radioactivity laboratory? The answer is involved largely with the question of the amounts and kinds of activity to be handled. Table 14-6 tabulates three groups of radioelements according to the hazard from absorption into the body—slight hazard, moderately dangerous, and very dangerous. For each group the amount of activity is given which comprises the low, intermediate, and high levels. Table 14-7 gives an arrangement of isotopes classified according to hazard from external radiation.

It does not seem desirable here to go into a detailed discussion of laboratory design and practice. References are given in the Bibliography to literature which covers this subject thoroughly. Only some general principles will be covered here.

Most analytical work with radioisotopes involves handling less than 1 millicurie of activity. At that level laboratory arrangements such as

TABLE 14-6. HAZARD FROM ABSORPTION INTO THE BODY*



Effective radiotoxicity is obtained from a weighting of the following factors:

Half-life
Energy and character of radiations
Degree of selective localization in the body
Rates of elimination
Quantities involved and modes of handling in typical experiments

The slant boundaries between levels indicate borderline zones, and emphasize that there is no sharp transition between the levels and the associated protection techniques.

The principal gamma emitters are indicated by asterisk (e.g., *Na^{24}). The above level system does not apply to the hazards of external irradiation.

* Safe Handling of Radioactive Isotopes," National Bureau of Standards, Handbook 42, Table 2.

are found in any orderly analytical laboratory will suffice except for some easily observed additional precautions and a few special techniques. By the use of survey instruments, one can determine what the exposure will be at any given distance from the source. At levels of 1 millicurie or less it should be possible to carry out manipulations with tongs and tweezers so as to stay within the maximum tolerable dosage level. In addition, precautions should be taken to avoid undesirable consequences from accidental spillage, by working over a surface covered with absorbent paper with an impermeable backing and by having other surfaces of a nonporous nature so that spills may be washed off. One exception to this rule of simplicity at low levels would occur when isotopes in the very dangerous category are being handled. For such substances the use of a gloved box, such as is shown in Fig. 14-18, is imperative so that there will be no chance of breathing active dusts. In all work with radio-

TABLE 14-7. ISOTOPES CLASSIFIED ACCORDING TO HAZARD FROM EXTERNAL RADIATION*

Increasingly hazardous ↓	Pure beta-ray emitters:	
	Subclass I (primarily 0 ~ 0.5 mev)	H^3, C^{14}, S^{35}, A^{37}, Ca^{45}, Fe^{55}, Ni^{59}, Ni^{63}, Tc^{99}, Pd^{103}, Ru^{106}, Cd^{109}, Sn^{121}, Ce^{144}, Pm^{147}, W^{185}
	Subclass II (primarily 0.5 ~ 1.0 mev)	Cl^{36}, As^{77}, Sr^{90}, Pr^{143}, Pt^{197}, Tl^{204}
	Subclass III (primarily 1.0 mev and over)	P^{32}, Ge^{77}, Sr^{89}, Y^{90}, Y^{91}, Pd^{109}, Ag^{111}, Bi^{210}
Increasingly hazardous ↓	Gamma (and beta)-ray emitters:	
	Subclass I (primarily 0 ~ 0.5 mev)	Cr^{51}, Se^{75}, Ru^{97}, Tc^{97}, Rh^{105}, Sn^{113}, In^{114}, Te^{127}, Te^{131}, Cs^{131}, Ce^{141}, Pm^{149}, Sn^{153}, Eu^{155}, Ir^{192}, Os^{193}, Hg^{197}, Au^{198}, Au^{199}, Hg^{203}
	Subclass II (primarily 0.5 ~ 1.0 mev)	Zn^{69}, Ge^{71}, Cb^{95}, Zr^{95}, Zr^{97}, Mo^{99}, Ru^{103}, Rh^{106}, Ag^{110}, Cd^{115}, Sb^{122}, Sb^{125}, Te^{129}, I^{131}, Ba^{131}, Cs^{134}, Cs^{137}, Ba^{140}, Ce^{143}, Nd^{147}, Eu^{152}, Hf^{181}, Os^{185}, W^{187}
	Subclass III (primarily 1.0 mev and over)	Na^{24}, K^{42}, Sc^{46}, Ti^{51}, Fe^{59}, Co^{60}, Zn^{65}, Ga^{72}, As^{76}, Br^{82}, Rb^{86}, Sb^{124}, La^{140}, Pr^{142}, Pr^{144}, Eu^{154}, Ta^{182}, Re^{188}, Os^{191}, Ir^{194}

* George G. Manov, Isotopes Division, Atomic Energy Commission, "Protection in Use of Radioisotopes—Low and Intermediate Levels."

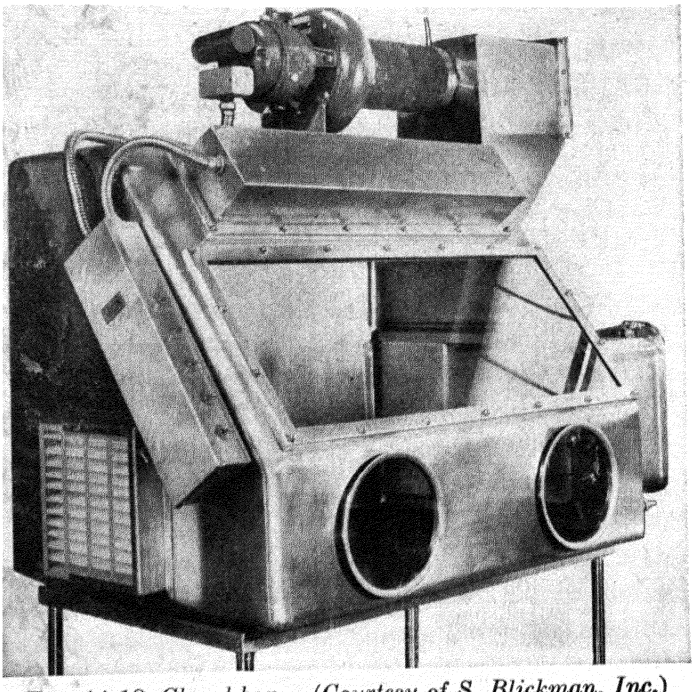


FIG. 14-18. *Gloved box.* (*Courtesy of S. Blickman, Inc.*)

activity, practice runs with inactive materials should always be made before the true runs are made.

Sometimes work at a low level involves previous handling of a considerably higher level of activity which must be diluted for subsequent low-level work. In such a situation the handling of the higher level of activity may have to be done with the use of lead or iron shielding, for gamma emitters, or plastic shielding for beta emitters. It will also be necessary

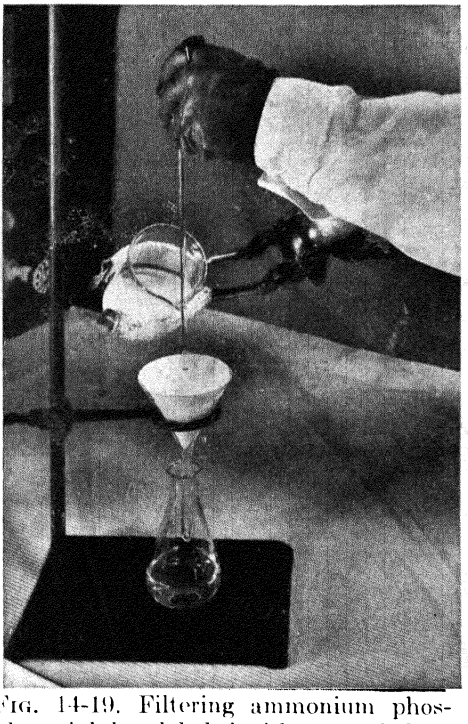


FIG. 14-19. Filtering ammonium phosphomolybdate labeled with 10 μc of phosphorus 32 (maximum beta energy 1.7 mev, no gammas). (*Oscar M. Bizzell, Isotopics, p. 21, April, 1951, Fig. 1. Courtesy of Isotopes Extension, Division of Civilian Application, U.S. Atomic Energy Commission.*)

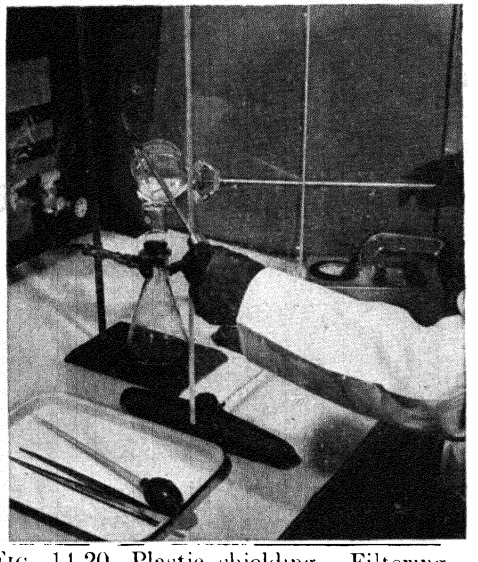


FIG. 14-20. Plastic shielding. Filtering ammonium phosphomolybdate labeled with 10 mc of phosphorus 32 (maximum beta energy 1.7 mev, no gammas). (*Oscar M. Bizzell, Isotopics, p. 21, April, 1951, Fig. 2. Courtesy of Isotopes Extension, Division of Civilian Application, U.S. Atomic Energy Commission.*)

to use simple remote-handling equipment. Figures 14-19 to 14-22 give examples of typical handling procedures at several levels of activity. The presence of activity near counting equipment is undesirable for obvious reasons. It is thus desirable in arranging a laboratory to segregate the area in which activity is stored and handled from that in which counting is done. It is also desirable to keep the counting room separated from the low-activity area. Figure 14-23 gives a diagrammatic arrangement of space for a low-activity radiochemical laboratory. With the exercise of constant vigilance, a one-room laboratory may be adequate for handling

several millicuries of very weak beta-ray emitters (below 0.3 mev) or microcurie quantities of either energetic beta-ray emitters or gamma-ray emitters.

APPLICATIONS

The usefulness of radioisotopes in scientific and technical work is based either on the utilization of the energy of the activity without regard to the chemical nature of the radioelement or on the chemical nature of the radioelement (the usual tracer applications). In tracer techniques the radioactivity serves merely to indicate the presence of a particular atom or to measure its quantity. The special utility of radioisotopes in this connection is enhanced by the extremely small quantities which may be detected. The exact quantities detectable will vary, of course, with the nature and specific activity of the radioelement and with the instruments and techniques used, but in general they may be put at from 10^{-10} to 10^{-14} gram or even less. Radioactivity methods are nevertheless apt to be somewhat inconvenient in view of the necessary procurement procedures and of the special precautions which must be taken in work with radioisotopes. One therefore would not ordinarily use a radioisotopic method where another more convenient and equally adequate procedure is available. However, in many applications radioisotopic methods are the only ones which can provide adequate answers or simplify otherwise complex problems, and in those instances they are invaluable.

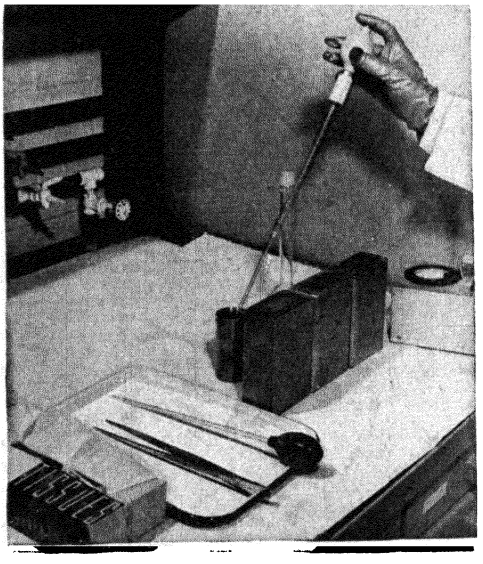


FIG. 14-21. Lead brick shielding. Preparing a 10-μc dilution of iodine 131 (betas up to 0.815 mev, gammas up to 0.722 mev). *(Oscar M. Bizzell, Isotopics, p. 21, April, 1951, Fig. 4. Courtesy of Isotopes Extension, Division of Civilian Application, U.S. Atomic Energy Commission.)*

Applications of Energy from Radioisotopes. Perhaps the most prominent industrial uses of radioactivity depend upon the penetrating power of radiation. This makes it possible to locate a radioelement in a system even through walls of sometimes considerable thickness. In the petroleum industry a gamma-ray emitter such as Ba^{140} is placed in a pipeline at the end of one type or grade of oil and before another grade or type. By suitable detection instruments the location of the boundary between the two grades may be determined from outside the pipeline without

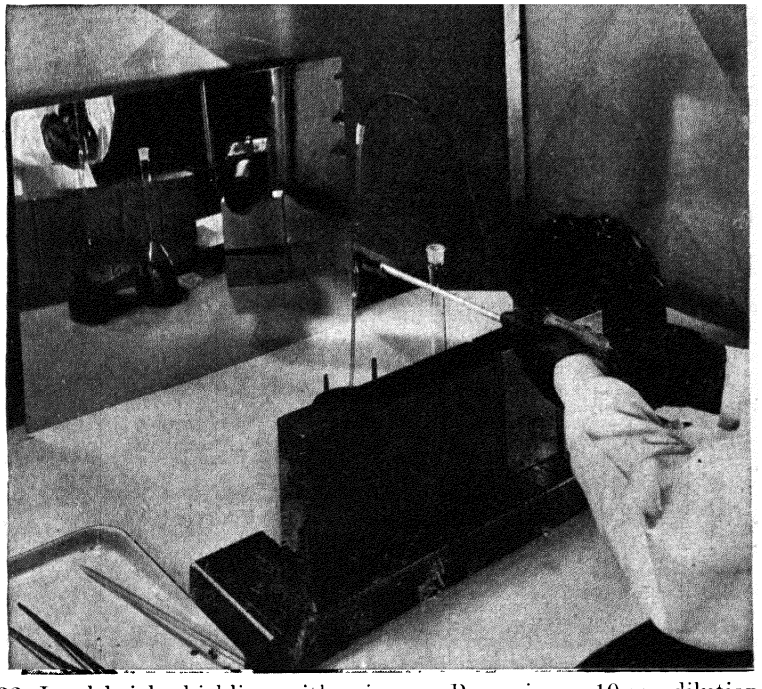


FIG. 14-22. Lead brick shielding with mirror. Preparing a 10-mc dilution of iodine 131 (betas up to 0.815 mev, gammas up to 0.722 mev). (*Oscar M. Bizzell, Isotopics, p. 21, April, 1951, Fig. 5. Courtesy of Isotopes Extension, Division of Civilian Application, U.S. Atomic Energy Commission.*)

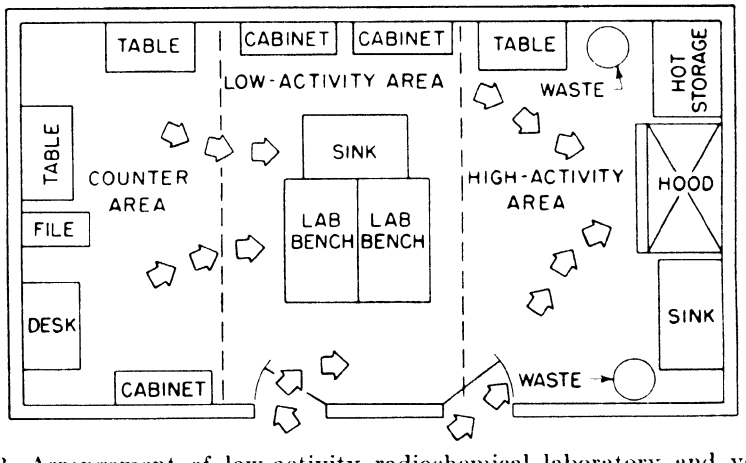


FIG. 14-23. Arrangement of low-activity radiochemical laboratory and ventilation pattern. (*D. R. Ward, "Design of Laboratories for Safe Use of Radioisotopes," Isotopes Division, Atomic Energy Commission.*)

sampling the oil. Many grades of oil may thus be transported in one pipeline and diverted and separated from one another with no difficulty. (This application, incidentally, could be considered a special type of tracer technique in which the tracer need not be related chemically to the material being traced.)

By taking advantage of the fact that absorption of radiation is related to mass it is possible to measure the thickness of rapidly moving sheets of paper, metals, plastics, textiles, and other materials without physical contact with the sheet. This is done by alpha- and beta-ray gauges. It may also be done by utilizing the differences in back scattering of beta rays caused by variations in thickness of a given material. Sr^{90} and Ru^{106} are common sources for such instruments.

Another industrial application of the penetrability of radiation is the measurement of liquid levels in tanks or autoclaves. A source of gamma rays such as Co^{60} rides on a float on the surface of the liquid and is kept centered by guide wires running vertically through the tank. The readings of a radiation-detection instrument on top of the tank depend upon the free space above the surface of the liquid. Another type of level gauge is based upon the fact that absorption of radiation by the material in the tank is greater than that of the air above it.

Gamma rays from isotopes such as Co^{60}, Ra, and Ta^{182} are used instead of X rays to detect flaws in molds or castings and in metallic equipment. By placing a gamma-ray source on one side of the object and a photographic plate on the other, a fissure or blowhole may be detected in the radiograph. Such a defect absorbs less radiation than the surrounding denser areas and shows up as a darker region on the developed photographic plate.

One application of radiation which is still in its infancy is its use as a source of energy to promote chemical reactions. Work has been done to indicate that reactions such as chlorination of benzene to form hexachlorobenzene can be promoted more efficiently by gamma rays than by the use of ultraviolet energy. Sulfur dioxide has been oxidized by oxygen to sulfur trioxide without a catalyst. Cross linkages have been produced in polymers to form polymers with special properties. Work is being done on the use of radiation for sterilizing foods and drugs. However, thus far the main use of radiation energy (neglecting of course, energy from fission, exemplified by the atom bomb) has been in the field of medical diagnosis and to some degree, in therapy.

Tracer Applications. Isotopic tracing usually involves first synthesizing, or otherwise obtaining, some of the material to be traced which is tagged with a radioisotope of an element of the molecule. The labeled compound is then introduced into the mixture to be studied, the experiment is carried out, and the products of the experiment are analyzed radiochemically.

The tracer must obviously be exactly the same as the material being traced except for the substitution of one or more of the normal inactive elements by radioactive isotopes of the elements. With organic substances this means carrying out a synthesis of the organic compound with

a radioactive intermediate. Thus, for example, $C^{14}O_2$, liberated from Ba $C^{14}O_3$, which may be obtained from the Oak Ridge neutron reactor, may be used in a Grignard reaction to produce C^{14}-labeled carboxylic acids. Sulfur 35 in the form of $H_2S^{35}O_4$ may be used to sulfonate organic molecules to form S^{35}-labeled sulfonic acids. Many labeled organic and inorganic compounds are available commercially. For work with a number of inorganic ions material obtained from Oak Ridge may be used without synthesis. For some problems it may not be possible to introduce a labeled compound in a representative manner into the material under study. For example, this would be true in studying automobile piston-ring wear. One, then, resorts to irradiation of the object, the piston ring in this case, in a neutron reactor so as to produce radioisotopes of the material (active iron) *in situ*. Unfortunately this cannot ordinarily be done with organic compounds without disrupting the molecule. Still another method is to expose the material to be studied to a solution containing ions of the radioisotope to be introduced. After a sufficient length of time, by a process of exchange, some of the inactive atoms may be exchanged for active atoms.

General Principle of Tracer Methods. The kinds of experiments in which tracers may be used are practically limitless, and there are several classes of specialized techniques. However, the general principle of an isotopic tracer experiment is a simple one. If the assumption is made that the labeled compound behaves exactly like the unlabeled compound in every way, then whatever information, qualitative or quantitative, is obtained concerning the labeled compound applies also to the unlabeled compound. (The truth of this assumption must be scrutinized carefully for radioisotopes of low mass number, such as tritium, H^3, since molecules containing them may undergo some reactions at a different rate from that of molecules containing the normal isotopes. This is known as the *isotope effect.*) Quantitative information concerning the labeled compound is derived from the ratio of its activity before introduction into the experimental mixture to that in the samples obtained from the experiment. For example, suppose a substance A is mixed with a substance B and it is desired to determine the efficiency of a process used to separate A from B. Some radioisotopically labeled A (designated as A^*) is added to the mixture. Let us say A^* has an activity indicated by a counting rate of 20,000 counts per minute (cpm). If now, after the separation experiment, it is found that the total activity of the separated A is 10,000 cpm, then it is evident that the separation process has been only 50 per cent efficient for separating A. If B had also been tagged, then similar information could be obtained for B, provided that the activities of A and B could be distinguished by radiometric methods, or by a quantitative separation of A and B before counting.

Isotope-dilution Method. Tracer methods have been used to study adsorption and coprecipitation, aging of precipitates, efficiency of extractions, precipitations, and filtrations, and numerous other phenomena. However, probably the most important analytical application is the *isotope-dilution method.* This method is particularly useful for the determination of a constituent in a mixture of such complexity that it is either impossible or difficult to separate the desired constituent from interfering substances quantitatively and without loss. By this method a value for the constituent to be determined may be obtained if only a fraction of it can be isolated in pure condition. The method may be outlined as follows: Suppose it is desired to determine the weight x of a substance a which is contained in a definite weight of a sample. Prepare some of this substance with a radioactive indicator atom. Add to the weight of sample containing x grams of a a small weight y of the tracer, which has been determined to have a specific activity S_0 (counts per minute per gram). After mixing the tracer with the sample, isolate a small amount of pure a (containing some of the tracer, of course) and determine its specific activity S_f. The total activity of the tracer is yS_0 (counts per minute). S_f, the specific activity of the isolated pure a, is also the specific activity of the mixture of $x + y$, since the proportion of tracer to inactive a does not change during the process of isolating a pure sample. Therefore the activity of $(x + y)$ grams of the mixture is $(x + y)S_f$. Since the activity of the mixture equals that of the original weight of tracer,

$$(x + y)S_f = yS_0$$

and

$$x = y\left(\frac{S_0}{S_f} - 1\right) \tag{14-13}$$

Thus, by determining the specific activity and the weight of the tracer to be added and the specific activity of the isolated pure material, the weight of the latter in the sample may be determined without the need for a quantitative method of isolation. This method has been applied in many problems, e.g., the determination of dibenzyl sulfide, dibenzylsulfoxide, and dibenzylsulfone, each tagged with S^{35}, and the determination of naphthalene in crude oils, using naphthalene tagged with C^{14}.

In some analyses it is necessary to work with tracer material of unknown specific activity. Suppose it is desired to determine the number of grams x of a compound in a complex mixture and we have a tracer of unknown specific activity but containing a known total activity equal to A cpm. This quantity, which is negligible in weight compared with the weight of x, is added to the sample and z grams of the pure compound are isolated with an activity equal to B cpm. The amount of compound in the mixture is given by the equation

$$x = z\frac{A}{B} \tag{14-14}$$

This method is referred to as the *radiometric-correction* method. Equation (14-14) holds only if the added weight of tracer is negligibly small compared with x. Equation (14-14) can be shown to be a limiting case of Eq. (14-13) as follows: The specific activity of the mixture of x and the (unknown but negligible weight of) tracer y is $A/(x + y)$. This is also equal to the specific activity of z. Therefore,

$$\frac{A}{x + y} = \frac{B}{z}$$

If $y \ll x$, this reduces to $A/x = B/z$ or

$$x = z\frac{A}{B}$$

This method was used originally by G. Hevesy and R. Hobbie* in analyzing rocks for lead, and recently by A. J. Freedman and D. N. Hume† in determining cerium.

The isotope-dilution method may be varied in other ways. The *reverse-isotope-dilution* method is used to determine the amount of a radioactive constituent (e.g., in a body fluid of an experimental animal) by adding a known weight of the inactive compound and then proceeding in the usual manner. Another variation of the isotope-dilution method, the *isotope-derivative method*, employs a radioactive reagent of known specific activity to form an active derivative with the inactive substance which is to be determined. When an inactive substance is determined by treatment with an active reagent, but without the addition of carrier, the method is known as *radiometric analysis*. An example is the determination of silver ion by precipitation with radio-iodide ion.

Other Analytical Uses of Radioisotopes. A number of other variations of the use of radioisotopes for qualitative and quantitative analysis have been reported. One in particular will be mentioned, namely, *activation analysis*. It involves exposing the samples to deuterons in a cyclotron or, more conveniently, to neutrons produced in a nuclear reactor or by a Ra-Be source. Many elements absorb neutrons to form radioactive isotopes which can be detected by radiometric methods. If standard samples are irradiated along with the unknown sample, a quantitative analysis may be obtained. Interfering elements may have to be separated chemically or their effects may be negated by application of radiometric techniques. Depending upon the nature of the element, quantities of many elements as low as 10^{-6} to 10^{-11} gram may be determined. Chemists do not ordinarily have neutron sources available, but arrange-

* *Z. anal. Chem.*, **88**: 1 (1932).
† *Anal. Chem.*, **22**: 932 (1950).

ments may be made to have analyses performed at the Oak Ridge nuclear reactor for a moderate fee.

Miscellaneous Applications. There are available many tracer applications which may not be considered strictly analytical. Much valuable information has been obtained of the behavior of compounds in biological systems by means of radioisotopes. The chemist can study diffusion processes; determine low vapor pressures; and study surface layers, crystal impurities, and many other phenomena not easily accessible to other techniques. Reaction mechanisms are particularly suitable for study by radioisotopes. In fact, there are few areas of physical science where radioisotopes may not be used to advantage.

Example of Isotope-dilution Analysis. A good example of the use of the isotope-dilution method in an involved analytical problem was reported by F. C. Henriques, Jr. and Charles Margnetti.* The problem was to determine dibenzyl sulfide, sulfoxide, and sulfone in a mixture of the three.

Synthesis of Active Compounds. The three compounds were synthesized to contain radioactive sulfur^{35} by means of the following reactions with Na_2S^{35}:

$$C_6H_5CH_2Cl + Na_2S^{35} \rightarrow (C_6H_5CH_2)_2S^{35}$$
$$(C_6H_5CH_2)_2S^{35} + H_2O_2 \rightarrow (C_6H_5CH_2)_2S^{35}O$$
$$(C_6H_5CH_2)_2S^{35}O + CrO_3 \rightarrow (C_6H_5CH_2)_2S^{35}O_2$$

The tagged Na_2S^{35} had previously been obtained by heating 200 mg of $BaS^{35}O_4$, containing 30 μc of S^{35}, in a stream of hydrogen to form BaS^{35}. This was then converted to H_2S by means of phosphoric acid, the H_2S condensed with liquid nitrogen and converted to Na_2S as needed by distilling it into a benzyl chloride reaction mixture containing sodium hydroxide. By means of this synthesis about 45 mg of each compound were prepared each of which contained about 10 μc of S^{35}. This quantity would suffice for the analysis in triplicate of at least 100 unknown mixtures of the three dibenzyl compounds.

Radioactivity Standardization. Approximately 1 mg of each of the three active compounds was weighed on a microbalance. The samples were oxidized to sulfate by the Carius method, and each digestion mixture was diluted to 100 ml in a volumetric flask. The specific activity of 3-ml aliquots was then determined in triplicate for each solution by the method described by F. C. Henriques, Jr., G. B. Kistiakowsky, Charles Margnetti, and W. G. Schneider.† According to this method, the aliquots were transferred to 30-ml beakers and the sulfate was precipitated as benzidine sulfate. This was then washed onto a weighed filter paper which had

* *Ind. Eng. Chem., Anal. Ed.*, **18**: 476 (1946).

† *Ind. Eng. Chem., Anal. Ed.*, **18**: 349 (1946).

been fitted over a coarse fritted glass filtering disk, and finally washed with 95 per cent alcohol. After being dried in a desiccator, the paper and precipitate were weighed and then mounted on a 19-mm-diameter brass disk on which the paper was firmly attached with a snug brass ring. The mounted sample was then placed inside an electroscope and the activity determined. (An end-window Geiger counter, or windowless counter and scaler could have been used.) From the weights of the benzidine sulfate samples and their activity, the specific activities of the standard solutions, and so of the tagged compounds, were calculated:

$$\text{Activity} = \left[\left(\frac{d}{t}\right)_s - \left(\frac{d}{t}\right)_b\right]\frac{10^2}{f}$$

where d = number (10) of scale divisions traversed by the electroscope fiber in t sec (with a counter and scaler, d would be counts in t sec), s and b denote sample and background, respectively, and f is the beta-ray self-absorption correction factor due to the weight of the benzidine sulfate precipitate. With the electroscope used, one unit of activity represented about 10^{-3} μc of S^{35}.

Preparation of Radioactive Standard Solution. About 15 mg of each of the radioactive compounds were weighed out to within 0.05 mg. The weighed compounds were placed in a 100-ml volumetric flask and diluted to the mark with 95 per cent ethanol. Thus a definite volume contained known weights of the three compounds. As an additional check, triplicate determinations of the activity were made on 1-ml aliquots. The average of the activities was found to be within 0.4 per cent of that computed from the radioactivity standardizations of the individual components.

Isolation of Pure Compounds from Mixture. To an acetone solution containing the mixture of the three inactive compounds to be analyzed, there were added exactly 10 ml of the radioactive standard solution. The acetone and alcohol were evaporated, and from the dried mixture there were isolated pure portions of each of the three compounds by a procedure based on their relative solubility in petroleum ether followed by recrystallizations from alcohol and petroleum ether. The purifications were followed by melting-point determinations, and recrystallizations were continued until the melting behavior indicated constant purity. The specific activities of the isolated pure samples were determined (as described above) on triplicate weighed portions (~6 mg) of each purified component. Since 200 mg was the minimum amount of any of the dibenzyl compounds in the original mixture and since 20 mg sufficed for the radioactivity analysis, it was not difficult to obtain the three substances in a highly purified state.

Calculations. Let P refer to the nonradioactive compound, P^* to the

active compound, $P.P^*$ to the isolated mixture, and R to the ratio of specific activities $(\text{activity/mg})_{p^*}/(\text{activity/mg})_{p.p^*}$, then

$$\text{mg } P = \text{mg } P^*(R - 1)$$

Results. Six different mixtures containing various known amounts of the three dibenzyl compounds were analyzed. The average percentage deviation between the value found by an individual analysis and the amount of compound added was 1.4 per cent. The maximum and average percentage deviations between the average of triplicate analyses and the amounts added were, respectively, 1.8 and 0.7 per cent.

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