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FORENSIC CHEMISTRY

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by

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P R E F A C E

THE subject of forensic chemistry is one which does not figure largely in the chemical literature so that there would seem to be room for a text book on the subject. The special characteristic of this one is that the subject matter is strictly confined to formally chemical theory and technique.

The object has been first to collect together information now widely diffused throughout the criminological literature, and secondly, to outline the manner in which the practice of forensic chemistry is conducted in a forensic chemical laboratory.

The author has had practical experience of most of the operations described in this book and he has thus tried to produce not merely a theoretical treatise, but a practical guide for those engaged in forensic chemistry and for chemists who are called upon from time to time to undertake work of this character.

For much of the information supplied in this book the author as well as the reader are indebted to the many research workers who have carried out investigations in this field. It contains, also, a certain amount of material of which no complete account has yet appeared in the literature. A paper on the oxidation of ferrous iron in ink on paper, prepared for the Institute of Criminalistics has not yet been published in full by reason of interruption in publication of the *Revue Internationale de Criminologie* owing to the war. A précis of the paper has, however, been published in this country in *Chemistry and Industry* by the courtesy of Dr. Stephen Miall the editor. The material appears for the first time in a text book here.

The author acknowledges the great help both direct and indirect which he has received from the workers named

throughout the text and in the references in this book. And in particular he must allude to Dr. Edmond Locard, Director of the Institute of Criminalistics of the University of Lyon, and of the Laboratories of Technical Police, under whose direction he has worked, and to whom he owes such proficiency as he has in the theory and practice of forensic chemistry.

HENRY T. F. RHODES.

CONTENTS

PREFACE	PAGE V
-------------------	-----------

PART ONE

APPLICATION OF CHEMICAL METHODS TO THE IDENTIFICATION OF THE PERSON

CHAPTER

I. THE DIRECT IDENTIFICATION OF THE PERSON	3
II. THE INDIRECT IDENTIFICATION OF THE PERSON	16

PART TWO

APPLICATION OF CHEMICAL METHODS TO THE PROOF OF *CORPUS DELICTI*

III. STAINS	53
IV. FIREARMS AND EXPLOSIVES	67
(a) Firearms, (b) Bullets, (c) Explosives and Explosions	
V. THE CHEMICAL EXAMINATION OF QUESTIONED DOCUMENTS	85
(a) Constitution of Inks, (b) Chemical Examination of Ink on Paper, (c) Maturing of Ink, (d) Examination of Pencil Writing, (e) Examination of Paper, (f) The Forged Document, (g) Sympathetic Inks, (h) Burnt Documents, (i) Subsidiary Materials, (j) The Development of Skin Prints on Documents.	
VI. THE CHEMICAL EXAMINATION OF COUNTERFEIT MONEY	145
(a) Counterfeit Banknotes, (b) Counterfeit Coin.	

VIII

CONTENTS

CHAPTER	PAGE
VII. THE EXAMINATION OF TOXIC AGENTS . . .	157
(a) Technique of Examination, (b) Detection of Abortifacients, (c) Detection of Inorganic Poisons, (d) Volatile Poisons, (e) Alkaloids, (f) Identification of Alkaloids, (g) Identification of Synthetic Drugs, (h) Organic Acids, (i) Gaseous Poisons	
REFERENCES	197
NAME INDEX	203
SUBJECT INDEX	206

PART I

APPLICATION OF CHEMICAL METHODS
TO THE IDENTIFICATION OF THE
PERSON

CHAPTER I

DIRECT IDENTIFICATION OF THE PERSON

SKIN PRINTS

As is well known, the discovery of the finger-print pattern as a means of identification of the person replaced the method of Bertillonage (measurement of the body). It has since been shown that other parts of the skin have characteristics which can be identified. Thus Locard (*Traité de Criminalistique*, I. 247) has found that the sweat pores of the fingers and palm are unique for the individual. Stirling (*Rev. Int. de Crim.* 350) has shown that the lines of the palmar surface are a means of identification. Claps (*Rev. Inter. de Crim.* 707) has studied impressions of the lips. Again, in an interesting note, Locard has reported that the lips of the vulva in females have a characteristic skin pattern. The spheres of identification of the human body have thus been considerably enlarged. Chemical or other methods of development are therefore applicable not only to the finger-print pattern but to skin impressions generally.

Development means the treatment of a skin impression by physical or chemical means. The object of the treatment is to make the latent print visible, or to define the details of it more clearly. Chemical methods of development have a restricted application, but they are important in their field.

COMPOSITION OF SWEAT

The skin impression is produced by the exudation from the sweat pores of the materials of perspiration. The composition of the sweat has been the subject of a number of investigations. Its composition has not been precisely determined. Classical

analyses made by Favre and Harnack are not concordant, and indeed show gross variations.

ANALYSIS OF SWEAT

<i>Favre</i>	<i>Harnack</i>
Water . . . 996.573	Water . . . 990.9
Albuminoids . . . traces	Urea . . . 1.2
Alkaline sudorates . . . 1.562	Organic Matter . . . 1.2
Urea . . . 0.042	Sodium chloride . . . 5.2
Alkaline lactates . . . 0.317	Calcium phosphate . . . 0.2
Fatty substances . . . 0.013	Magnesium phosphate . . . 0.1
Sodium chloride . . . 2.230	Sulphates . . . 0.6
Potassium chloride . . . 0.024	Potassium carbonate . . . 0.1
Alkaline sulphates . . . 0.011	
Alkaline phosphates . . . traces	

Perspiration is, in fact, of a very variable composition. Volatile fatty acids, traces of protein, perhaps urea (readily converted to ammonium carbonate), and fat appear, however, to be normal constituents of sweat. Sodium chloride is consistently present, and sulphates. The specific gravity varies from 1.001 to 1.010. Total solids from 4.4 to 22.6 (*Leung, Thèse de Lyon, 1931, 11.0 to 14.7*). Argutinski has found 1.24 to 1.61 of urea, but the presence of urea has not been confirmed by all investigators (Funke and others).

TYPES OF REACTION IN DEVELOPMENT

The chemical development of skin impressions depends upon the presence of certain constituents which affect the reagents in definite ways. The reactions are mainly of three types : (1) Reagents such as iodine vapour are absorbed by the fat and fatty acids present in the deposit ; (2) Reagents such as osmic acid which are reduced by substances to which they donate oxygen ; (3) Reagents such as silver nitrate which react with inorganic chlorides to produce silver chloride which is subsequently reduced by a photo-chemical effect.

There are some special cases which should also be noted. A skin impression may be produced by a surface soiled with some foreign substance. It may then become of importance

to determine its nature for two reasons : (1) The nature of the stain may be an indirect clue to the identity of the depositor of it and (2) The print may be incompletely visible in detail and a knowledge of the material composing it may make development possible. An imperfectly visible stain made, for example, with potassium ferrocyanide would in regard to (1) suggest that it was associated with a chemical worker, and in regard to (2) would make its development possible with such a reagent as an aqueous solution of a ferric salt. In this way a mere smudge might be revealed as a finger or other skin print.

SURFACES ON WHICH SKIN PRINTS ARE FOUND

The surfaces upon which skin prints may be found are very numerous. Polished surfaces of wood, metal, glass, or stone can retain the impressions. Paper also retains impressions, and it is upon this material that the true latent impressions are found. Prints upon paper are usually invisible until developed. It is thus particularly in connection with prints upon paper that chemical methods are used.

It is not, however, the case that paper is the only material which is amenable to chemical methods of development. The use of silver nitrate (*vide infra*) which has recently been developed is stated to have extended the range of materials upon which impressions can be sought. They are said to include unpolished wood, and textile materials. It has not previously been possible to develop skin impressions upon these materials.

PRINTS UPON PAPER

The substances exuded by the sweat pores are absorbed by paper, the speed of absorption depending upon the quality and nature of the surface. In glazed and loaded papers the absorption is slow, and it is at its maximum upon uncoated paper and blotting paper. The development of the impression is correspondingly affected since the diffusion of the material by absorption results in the loss of the identity of the impression. Mitchell (*Documents and their Scientific Examination*) has

stated that prints on highly-glazed paper can be developed after three years, highly-sized clayed paper retained impressions for several weeks ; tracing papers for three weeks, and ordinary unglazed paper such as is used for index cards for a few days only. For this reason it is essential that papers to be examined for fingerprints should be examined at the earliest possible stage in the enquiry.

PRINTS UPON WOOD

Two kinds of impressions have to be considered which are of an entirely different character. The print found upon polished wooden surfaces does not require development by chemical means. Unpolished wood, however, is not only chemically of the same nature as paper but in many respects physically comparable with it. Unpolished wood does not in all cases retain skin prints. If the surface is uneven no results can be obtained. Smooth wood is however comparable with paper. The rate of absorption would appear to be slower than in the case of inferior paper. No complete investigation, however, has been made.

REAGENTS USED IN PRACTICE

The chemical reagents most commonly used in practice for the development of prints are iodine, osmium tetroxide, and silver nitrate. It has not been conclusively shown that development of prints with any powder involved a chemical reaction of any importance. Their action is, in fact, of a physical type since the coloration of the print results from the mechanical adherence of the powder to the deposit, the powder being essentially unchanged chemically (*Rhodes, Rev. Inter. de Crim.* 1933, 328). It appears probable, however, that where metallic oxides, in particular oxides of the alkaline earths are used, a reaction may occur between the fatty acids of the print and the oxides. The greater efficiency of some powders appears not to depend only upon the particle size of the powder in question, and may be explained by a reaction of this kind.

METHODS OF DEVELOPMENT

ABSORPTION

Iodine.—Iodine or iodine vapour is absorbed by the fatty acid of which the print is partly composed. On exposing a finger or other print to this reagent it is accordingly coloured yellow or brown where the deposit is found. The paper is unchanged if the operation is carefully performed. Two methods can be used in practice. Stockis (*Arch. int. de med. leg. aôut*, 1912) deposits a thin layer of iodine by sublimation upon a sheet of celluloid. This prepared celluloid is then applied to the paper upon which the print is suspected to exist. In the hands of an experienced manipulator this method gives satisfactory results.

The application of the vapour of iodine is, however, more readily controlled. The classical method is to vapourize iodine with heat and to expose the paper to be tested to the vapours. Experience and skill in manipulation are necessary to obtain good results. If the process is not carefully carried out the whole surface of the paper becomes stained, so that the pattern of the print is destroyed. Iodine, is of course, fugitive, but it is not possible to repeat the developing process after the first charge of iodine has vapourized. The latent print will not reabsorb iodine a second time. The experiment will thus fail if these precautions are not observed.

Stockis (loc. cit.) has employed a method which utilizes iodine and aqueous vapours. A strong solution of iodine in potassium iodide is boiled in a shallow evaporating basin of large diameter. The paper is exposed in the same way as with the use of the dry vapour. Exposure must be rapid to avoid the staining of the paper, but latent prints are more sensitive to this treatment than to that with dry iodine vapour.

THE FIXATION OF THE IODINE PRINT

Iodine is generally recognised as the most satisfactory reagent for the development of skin prints on paper. One of its disadvantages is that the prints are difficult to photograph and

they are, of course, fugitive. Popp. (*Fixierung von mit Iod sichtbar gemachten Fingerspuren*, *Rev. Inter. de Crim.*, Nov., 1929, 492) has devised a method of fixation using palladium chloride. The reagent is prepared as follows :

Palladium chloride	..	..	0.10 gm.
Tannic acid	..	..	0.25 gm.
Alum	..	..	0.25 gm.
Hydrochloride acid (10%)	..	..	0.5 cc.
Water	..	..	100.0 cc.

The developed print is treated with this solution for slightly less than a minute. The paper is then thoroughly washed in a stream of water and dried. Under this treatment the developed print becomes dark brown and can readily be photographed.

EFFICIENCY OF THE METHOD

The results obtained by development with iodine vary between wide limits. Variations in the composition of the deposit forming the print influence the result. It would appear probable that a deposit rich in fat and fatty acid would produce a more satisfactory result than one deficient in these constituents. Since it has been shown that the total solids of perspiration vary between wide limits the substances which absorb iodine must show a corresponding variation. On the other hand, no systematic investigation has been carried out under standardized experimental conditions. The other variable is the method by which the test is performed.

REDUCTION

Osmium Tetroxide.—Charpy (1877) appears to have been the first to observe that the so-called osmic acid was coloured black by sweat. His method was applied to the development of finger-prints by Forgeot (1890). Locard (1906) also experimented with this reagent but with indifferent result. Ainsworth Mitchell, however (1920) has reported satisfactory results with the use of the vapour of an aqueous solution of osmium tetroxide.

Osmium tetroxide incorrectly described as osmic acid, the formula of which is H_2OsO_4 , is a colourless crystalline compound which is reduced by organic matter to produce metallic osmium grey-black in colour. The coloration is permanent. Mitchell recommends the application of a 1% aqueous solution of the reagent with a brush to the print to be developed. The paper is allowed to dry naturally. Sunlight hastens the reduction.

An alternative method is to boil a solution of osmium tetroxide and expose the surface with the print to be developed to the vapour.

Owing to the great readiness with which osmium tetroxide is reduced, this reagent tends to be too sensitive to produce well-defined results. The reaction can, however, be adjusted to develop prints showing sufficient detail. Mitchell has found that exposure of paper to the vapours of a boiling 1% solution of osmium tetroxide produced prints full of fine detail. This method of development can therefore be recommended if careful attention is given to the manipulative details. It is in general true, however, that this method is more difficult to control than that of iodine absorption.

Ruthenium Tetroxide.—This substance exists in the form of yellow crystals. It differs from osmium tetroxide in being only slightly soluble in water and it is less stable. Its behaviour in the presence of organic matter resembles that of osmium tetroxide, that is to say that it produces a black compound. The reaction taking place is not precisely known, but it appears probable that the tetroxide is reduced to the hemitrioxide Ru_2O_3 to which RuO_4 is readily degraded.

In practice the best results for the development of skin-prints are obtained by heating the crystals over a water bath at a temperature not exceeding 50°C . The tetroxide is decomposed at 100°C . at atmospheric pressure. In the writer's experience satisfactory results are not obtained by heating an aqueous solution of ruthenium tetroxide. First, the slight solubility of the oxide reduces the utility of the method, and secondly, the tetroxide is decomposed at boiling point so that it does not reach the organic material of the skin print

in this form. Since it is the tetroxide itself which reacts most energetically with organic matter, it seems important that the operation should be controlled in such a way as to ensure that the reaction is actually one between the tetroxide and the organic matter.

PHOTO-CHEMICAL METHODS OF DEVELOPMENT

Silver Nitrate.—The reaction involved in the development of skin prints with silver nitrate is of an entirely different kind. The sodium chloride present in all perspiration marks reacts with the silver nitrate to form silver chloride. The reaction, of course, takes place at the surfaces corresponding to the ridges, or other details, so that a film of silver chloride is produced in accordance with the pattern of the skin print.

This method of development is extremely sensitive because of the relatively high concentration of sodium chloride present in all types of perspiration. Further, the reduction of minute quantities of silver chloride produces a pronounced black stain. For this reason silver nitrate development is more sensitive a method than any of those previously described.

It is commonly stated that silver nitrate development is a recently devised method of developing skin prints. It is, however, an interesting fact that Aubert, a French surgeon, was the first to draw attention to the reaction between silver nitrate and perspiration products in 1878, some years before fingerprints were generally recognized as a means of identification of the person. Aubert was studying the reaction of the sweat glands and found that their products reacted with silver nitrate to produce silver chloride which upon reduction became visible as a black stain. The classic work of Forgeot in 1891 was concerned with the use of silver nitrate as a reagent for the development of finger-prints. Essentially his method does not differ from that used at present. He recognized the nature of the reaction as being one which involved the formation of silver chloride, the subsequent development being due to a photo-chemical effect upon the silver chloride. The nature of the latter reaction was, however, not well understood at that time, so that Forgeot's method was rudimentary (*vide infra*).

Silver nitrate can be used to develop skin impressions upon a variety of surfaces of which paper is the most satisfactory. The original deposit of sodium chloride, however, has been shown to retain the pattern corresponding to the skin print upon unpolished wood, and it is also claimed upon textile fabrics. This is of great importance forensically because theoretically at least skin impressions can be developed upon the inner surface of gloves, upon handkerchiefs, and other fabrics. It will also be recalled that in the Hauptmann trial in America, prints upon a step ladder were made visible in this way. By reason of the rapid diffusion of substances of fatty origin upon textile fabrics and also apparently upon unpolished wood, it is not possible to develop skin impressions on these materials by the methods previously described. Where the medium to be developed is sodium chloride, the case is different. Sodium chloride undergoes diffusion, but at a much slower rate than fatty materials. The reason for this is not clearly understood since it might be expected that the great solubility of sodium chloride would result in rapid diffusion where much moisture was present in the material with which it was incorporated. In the case of skin prints, however, there would appear to be present substances which retard its migration. This substratum of sodium chloride is thus particularly amenable to development in a variety of circumstances and under some conditions for long periods after the impressions have been made.

METHOD OF DEVELOPMENT WITH SILVER NITRATE

An aqueous solution of silver nitrate of about, and not in excess of, 5% should be used. If the surface upon which the print is to be developed is of suitable size, the most satisfactory method of treating it is immersion in a photographic developing dish. This operation must be performed in darkness or at least in diffused light to avoid photo-chemical reduction of the silver nitrate. The treatment should continue for about five minutes.

The treated surface must then be washed in running water until the washing gives no reaction for the silver ion with a

chloride. It is essential that this washing should be thorough, and it should be carried out in diffused light.

At this stage that part of the surface corresponding to the skin pattern is coated with silver chloride. It remains to reduce the silver chloride when the pattern will appear in black.

Forgeot's method was simply to expose the surface to the light. When the print had attained maximum intensity it was treated with sodium thiosulphate. The results, however, were not always consistent nor completely satisfactory. It seems now to be generally agreed that the photo-chemical reaction results in a reduction which produces the sub-chloride Ag_2Cl . Others, however, consider that metallic silver is produced. The object of fixation with sodium thiosulphate was further to reduce the sub-chloride to metallic silver with the formation also of silver chloride. Forgeot used the method to "fix" the print, but found that it sometimes reduced its intensity.

REDUCTION OF THE SILVER CHLORIDE .

A more recent and satisfactory method is energetically to reduce the silver chloride with a photographic developer. The disadvantage of utilizing the photo-chemical effect is that the reaction is not completely understood, and is thought by some authorities to leave a considerable proportion of the silver chloride unchanged. This may account for the inconsistent and unsatisfactory results obtained by Forgeot. In any case experiment has shown that a more pronounced coloration is produced by reduction with a developer. The present writer has found the solutions recommended by Locard (*Traité de Criminalistique* II, 864) for the development of spermatozoa stained with silver nitrate very suitable as a reducing agent. They are prepared as follows :—

Water	..	..	100 parts	or	Water	..	..	100 parts
Formaldehyde	..	..	5		Hydroquinone	..	..	1.6
Pyrogalllic acid	..	..	4		Sodium sulphite	..	..	10
Pyridine	..	..	8		Pyridine	..	..	8

The former of these is, in our view, the more efficient.

This operation should also be carried out in diffused light to

prevent photo-chemical interference. The development should be continued until the maximum intensity has been attained. The print should finally be washed and dried.

MODIFICATION OF THE PROCESS

Very satisfactory results can be obtained by this method if these precautions are carefully observed. In many cases it is not practicable to immerse the object in a developing dish. If this cannot be done, the silver nitrate must be painted on to the surface. The technique of washing a surface which cannot be completely immersed is also more difficult than in the example cited. It is, however, equally necessary to ensure that the silver nitrate is completely removed from the treated surface before the reduction is attempted. Development of the print must also be effected by application of the developer with a brush. The developed print must then be washed in running water.

METHOD OF FINN AND CORNISH

Finn and Cornish have reported (*Ind. Eng. Chem. News Ed.*, Feb., 1935, 73, 75) interesting results of development of prints on paper with silver nitrate. They recommend the use of a 0.2% solution of the salt. The material to be developed is soaked for two hours in the silver nitrate bath and is then thoroughly washed. The paper is then dried and developed with a solution of the M.G. type or with a mixture of sodium carbonate and formaldehyde. It is again washed and fixed with a solution of sodium thiosulphate.

These authors make some interesting observations concerning the migration of chloride ions of sweat under varying conditions of humidity and temperature. (*See also Bieger and Diesselhorst, Deut. Med. Wochschr.* 29, 1903). They suggest that, in fact, the age of the print can be approximately estimated by the sharpness of the print which, of course, depends upon the diffusion of the chloride. The authors, however, emphasize that extreme caution is necessary in interpreting the results. It is, however, always a fair inference

that if diffusion has taken place to an extent which makes the pattern of the print unrecognizable, its origin is not recent.

METHOD OF E. M. HUDSON

Dr. Hudson is director of the Technical Laboratory of Police of the city of New York. He recommends the use of a 10% solution of silver nitrate which has been acidified with acetic acid. In the alternative the surface to be developed may be treated with a 10% solution of acetic acid after treatment with silver nitrate. In other respects the process follows those described with the distinction that photo-chemical means are used for development. Hudson recommends the use of sunlight or preferably ultra-violet light. The print is finally fixed with sodium thiosulphate.

The presence of acetic acid decomposes carbonates and other substances if present which might interfere with the silver chloride reaction. The present writer has not found that the reaction in acid solution differs from the neutral reaction, but there can be no objection to acidification and it is correct on theoretical grounds.

Dr. Hudson has obtained remarkable results from prints upon handkerchiefs, collars, and other textiles. The method is also applicable to the treatment of latent prints upon wood. But both on theoretical grounds and in the experience of the present writer development of the print with a reducing agent is preferable to photo-chemical development.

APPLICATIONS

Development with silver nitrate has greatly increased the scope of the chemical development of skin prints. Chemical methods, formerly seldom employed except for the development of skin prints on paper, are now by reason of this new technique applicable to wood, textiles, and other materials upon which prints could not be developed. It is extremely sensitive which is in certain circumstances one of its disadvantages. Minute traces of chloride upon the surface carrying the print prevent

the successful application of the method. The variable diffusion rate of the chloride ions under different conditions of temperature and humidity also drastically influence the result. In circumstances quite frequently met with, the identity of the print may have disappeared in twenty-four hours.

It has, however, been applied to the development of prints on the inside of gloves, upon wooden instruments such as ladders, and the unpolished handles of tools or weapons after considerable periods of time. There is no objection as a rule to its experimental use since the method, except in the case of paper, is only applicable where other methods would be useless. In regard to paper it has been clearly shown that if the print can be developed at all, silver nitrate is in all cases a suitable reagent, and in many cases superior to others.

PRINTS PRODUCED BY FOREIGN MATERIALS

Skin prints formed by materials other than sweat are sometimes amenable to chemical development. If latent, however, the material forming them cannot be identified. If, however, a coloured stain suspected to be a skin print is observed, an attempt should be made to ascertain its composition. In many cases whilst the print may be visible it is not sufficiently distinct to ascertain its pattern. Development then becomes necessary. A micro-chemical examination of a small area of the print using Grey's reagents (*vide infra* page 21) may result in its identification. The colour may also be of assistance. Thus a yellow stain might be one of potassium ferrocyanide, one of blue a copper salt, or a brown stain an oxidized iron salt. If the composition can be ascertained development consists in treatment with a reagent which produces a highly-coloured or black compound. Since a high percentage of metallic sulphides is black H_2S , water, or ammonium sulphide are reagents likely to be effective for development.

If, however, the nature of the stain cannot be ascertained, it is preferable to resort to exposure to iodine vapour. Iodine will often mechanically adhere to the material producing the stain and thus reveal the details of its pattern.

CHAPTER II

INDIRECT IDENTIFICATION OF THE PERSON

STRICTLY the identification of the person means a definition of those characteristics which distinguish him from all other persons.

Locard (*Traité de Criminalistique*, III, I, 8) has said :—

Au sens précis, l'identité est la qualité d'une chose qui fait qu'elle est elle-même et se différencie de toute autre. C'est, en mathématiques, le fait qu'un terme (valeur, courbe, symbole algébrique) représente la même idée qu'un autre et se confond avec lui, avec, comme formule type, l'équation :

$$O=O$$

C'est, en logique, l'enveloppement en un même concept de deux entités, dont la comparaison demeure ainsi tautologique, suivant le principe d'identité : *quod est est*, ou le principe de contradiction : *quod non est non est*. C'est enfin, en criminalistique et en droit l'ensemble des caractères par lesquels un homme définit sa personnalité propre et se distingue de tout autre. Dans ce dernier ordre d'idées, établir l'identité d'un individu, est l'opération judiciaire ou médiocolégale appelée identification.

The last two sentences in this excellent definition to some extent justify our use of the term indirect identification. It is necessary to distinguish between those factors like finger and skin prints which are in themselves completely descriptive of the identity of the person, and those which are of themselves incompletely descriptive but which contribute in varying degrees to identification.

OCCUPATIONAL DUST

An example is the so-called occupational dust with which we shall first deal. Hans Gross (*Criminal Investigation*) quotes a

case of the discovery of glue and minute fragments of wood in clothing. The inference was that the owner of the coat was a cabinet maker, a conclusion which was afterwards confirmed. This is an example of indirect and partial identification. Such an observation does not serve to distinguish the wearer of the coat from all other persons, but it places him in an identifiable class and thus serves to distinguish him from the great majority of other persons. From the forensic chemical point of view, the identification of materials of this type is of great importance.

CLASSIFICATION OF DUSTS

The classical work of Locard, Popp, Icard, and others has resulted in a classification of occupational dusts which is of the greatest importance in criminalistics. The general classification divides them into organic and inorganic dusts, the particular classification into those associated with a given occupation or occupations. Theoretically, of course, all dusts are amenable to chemical examination, but in practice only certain dusts are identifiable by chemical methods.

Among the dusts classified as those of occupation (*Locard, Traité de Criminalistique, II*, 843-846) may be mentioned coal dust, starch, metallic oxides and metallic powders, calcium sulphate (gypsum), drugs and related compounds, sugar, and dyes. These are materials of a type which can be examined chemically and in many cases positively identified. It is not, of course, possible to deal with the technique to be followed in every case, but only to describe the scheme which must be followed in the analysis of dust.

THE COLLECTION OF DUST

The classical method of collecting dust from clothing or other material was to enclose it in a strong bag of brown paper which was then beaten and the dust collected. This method has now been replaced by the use of a special vacuum cleaner designed by Söderman (*Rev. Inter. de Crim.*, 373, 1931). Essentially the apparatus does not differ from the ordinary vacuum cleaner. It is, however, fitted with three filters with screens of different

mesh. This triple screening is of great value since it secures a differential sampling of the dust in terms of particle size.

By the use of nozzles of different sizes it is possible to regulate the pressure according to the material from which dust is to be extracted. It has not been found possible to extract dust from material more closely woven than silk. For cotton materials and for flannel less pressure is required ; from the extraction of dust from pockets a very light pressure should be used.

OTHER SOURCES OF OCCUPATIONAL DUST

Dusts are also found in the hair including the hair of the eyebrows and in the wax of the ears.

Hair.—No special method has been devised for the removal of dust from the hair. A brush must on no account be used owing to its tendency to retain dust in general or dusts of a particular type more readily than others. The most convenient instrument is a hair comb, care being taken when using it to avoid contact with the epidermis or epithelium as far as possible.

Ears.—Great care is necessary in removing wax from the ears or the ear-drum may be injured. It is advisable to request the services of a medical man who is able to remove a much larger quantity of wax with less danger of injury to the subject. It is important that as much wax as possible should be removed since dusts deeply imbedded in the wax may be equally or even more important from an evidential point of view than those found at the surface.

THE PRELIMINARY TREATMENT OF DUST

Extracted Dusts.—It is not proposed to deal with the microscopic examination as such. An examination should, however, be made with a lens with which it may be possible to detect the presence of crystals, coloured substances not recognizable with the naked eye, and other substances which may have some characteristic appearance. Whilst it is never possible to arrive at a positive decision by means of an examination of this

kind, it may be a useful guide in the subsequent investigation.

Every precaution must be taken to conserve the material examined. The quantity of dust available seldom exceeds 0.5 gm. in the case of clothing. In many instances, the quantity available will be of the order of milligrammes. If, however, sufficient dust is available the following preliminary tests should be made. (1) A small quantity should be treated with a drop of water upon a cupped spotting tile ; (2) A second lot should be treated with one drop of 0.1 N HCl and (3) A drop of ethyl alcohol should be applied to a third quantity.

(1) All examinations must be made with a lens. (a) The colour, if any, of the aqueous drop should be noted. (b) It should be noted what proportion of the solid matter remains in suspension, and what proportion settles rapidly. (c) A minute quantity of the aqueous drop should be drawn up with a fine capillary and transferred to sensitive neutral litmus paper. The reaction acid, alkaline, or neutral must be noted.

(2) (a) When the drop of acid is added which must be delivered very cautiously from a fine capillary, the reaction, if any, must be noted. (b) Bubbles of gas may be evolved or (c) a precipitate formed. (d) Any change in colour in the drop must be noted. (e) Material dissolved by the acid must be noted.

(3) (a) The colour of the alcoholic drop must be noted. (b) It must be compared with the colour of drops (1) and (2). (c) Any other change such as the quantity of solid matter dissolved must be noted.

(4) A further small portion of the dust should be ignited. This operation should not be done in a crucible but on a thin disc of porcelain. The colour and other characteristics of the residue are more readily perceptible if this method of incineration is used. (a) The smell on ignition should be carefully noted. (b) The colour of the ash must be observed.

Spectroscopic examination is not within the scope of this book. It should be noted, however, in connection with the ignition of dust that a spectroscopic examination can be made and in many cases is very useful. The reader is, however, referred to the appropriate literature (*S. Judd Lewis, Analyst*, 60 (1935), 10-17).

THE CHEMICAL EXAMINATION OF DUST

It is important to observe first, that a quantitative examination of dust is seldom practicable, and if practicable is of little use except in special cases. (*vide supra*.) From a criminalistic point of view the identification of the substances present is sufficient. Secondly, substances present in dust cannot, of course, readily be identified as such. In regard to inorganic constituents bases and acid radicles can be recognized. Organic compounds can also in some cases be identified as such. The nature of dusts, however, requires the application of special methods in particular cases. It is not possible to deal with special cases in detail. A systematic scheme of procedure should, however, be followed whenever the quantity of material makes it possible. In the micro-chemical examination of dust, as in other micro-chemical operations, the procedure depends upon the quantity of material available.

DETECTION OF COMMON METALS

Micro-chemical methods devised by Grey (*Practical Chemistry by Micro-methods, Cambridge, 1925*) can be used for the detection of metals. Three drops of the ash of the dust which has been brought into solution are treated with drops of ammonium carbonate, potassium iodide, and ammonium sulphide. The reactions appear in the table given on the opposite page.

In the author's experience this scheme of analysis is of great value in many cases. The test is simple to apply and rapid. Since it can be applied to a very small quantity of the substance to be tested it is always useful as a preliminary test.

The tests may give confusing results where more than one metal is present, but this is not always the case. It frequently happens that in occupational dusts a particular metal is present in considerable excess of other bases. In these circumstances the reaction given by this metal may mask that of others and thus make the test specific.

On the other hand, where the concentration of the metallic constituent is feeble the results must be interpreted with great

MICRO-CHEMICAL REACTIONS OF THE COMMON METALS

(E. C. GREY. *Practical Chemistry by Micro-Methods.*)

	Ammonium Carbonate	Ammonium Sulphide	Potass. Iodide
Silver . . .	White	Black	White
Lead . . .	White	Black	Bright yellow
Mercury (ous) . . .	Black	White	Olive
Mercury (ic) . . .	White	Black	Red
Bismuth . . .	White	Black	*Dark brown
Copper . . .	Blue	Brown	Light brown
Cadmium . . .	White	Yellow	—
Arsenic . . .	—	*Yellow	—
Tin . . .	White	*Yellow	—
Antimony . . .	White	*Orange	—
Iron (ous) . . .	Dirty white	Black	—
Iron (ic) . . .	Brown	Black	—
Aluminium . . .	White	White	—
Chromium . . .	Green	Green	—
Zinc . . .	White	*White	—
Manganese (ous) . . .	White	Yellow	—
Manganese (ic) . . .	Brown	Brown	—
Nickel . . .	Green	Black	—
Cobalt . . .	Amethyst	Black	—
Barium . . .	White	—	—
Strontium . . .	White	—	—
Calcium . . .	White	—	—
Magnesium . . .	White	—	—

Asterisk indicates that the precipitate is soluble in excess of the reagent.

caution. The reaction of manganese, cadmium, and arsenic can be confused if the reactions are feeble. Chromium and iron may also give colour reactions which are difficult to distinguish in weak concentration. Further certain mixtures of metals may give colour reactions which appear to indicate the presence of a single metal which is not in fact a constituent of the mixture.

GROUP SEPARATION

In these circumstances it is necessary to resort to separation by means of a micro-modification of the classical methods. In this connection it should be noted that it is rarely practicable to make the separation unless 5 to 10 mgms. are available for each metal sought. Miniature apparatus suitable for performing the separation is described by Grey (*loc. cit.*). In micro determinations of all kinds it is very important to consider each step carefully before it is taken. The amount of reagent used and the order of concentration must be controlled and standardized as far as possible.

METHODS OF ICARD, LOCARD, AND POPP

These investigators recommend a method, the principle of which is the production of crystals of a definite form, specific in the given conditions for a given metal. The crystalline form is identified by microscopic examination.

Aluminium.—This method relies upon the formation of the caesium-alum. The material is treated with sulphuric acid and then with caesium chloride. The mixture is heated and then cooled. The crystals formed are octahedra.

Antimony.—This metal is identified in the form of the pyro-antimonate of sodium. The crystals are of lenticular form.

Arsenic.—If arsenic is suspected, the material is tested with silver nitrate and ammonia is added. Crystals of arsenite of silver are produced. They are rhombic, needle-like in form and yellow in colour.

Barium.—The crystalline form of barium sulphate is rhombic. It produces small plates and in some circumstances clusters in the form of a cross.

Cadmium.—The oxalate of cadmium produces rhombic crystals and prisms of some length. They frequently resemble those of lead chloride.

Calcium.—This metal is also examined in the form of the oxalate. The salt produces octahedra and star-like structures in the cold. Warm solutions produce cubes and prisms.

Cobalt.—This metal is detected in the form of the purpureo cobaltic chloride. Excess of ammonia is first added and then potassium permanganate in very slight excess. The solution is then boiled and cooled, and finally neutralized with a slight excess of hydrochloric acid. On cooling the solution deposits purple crystals of the purpureo chloride. They are octahedra. This test is inapplicable to small quantities of cobalt. It also requires experience and careful manipulation.

Tin.—The stannous oxalate shows a rhombic form and prisms. The crystals are often leaf-like in a cruciform shape or in that of an H.

Magnesium.—Magnesium ammonium phosphate if carefully prepared produces prisms of various types, and groups of cruciform shape.

A drop of the solution to be tested is placed upon a microscopic slide and a drop of ammonium chloride is added. A second drop of sodium phosphate is placed close to the first. The slide is then carefully heated over a water bath. A drop of ammonia is then used to unite the two drops. The drop is then rapidly cooled and allowed to stand until the crystalline precipitate has settled. Crystals of the rhombic type, plates, cruciform formations, stars, and other patterns are observed.

Potassium.—The chloro-platinate of potassium produces cubes and rhombic forms of a yellow colour.

Lead.—This metal is examined in the form of lead chloride. It produces plates and prisms. These sometimes

show triangular shaped cavities at their extremities with the apex directed inwards.

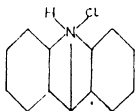
Strontium.—Both the sulphate and the oxalate produce rhombic crystals which, however, often have the appearance of octahedra. On heating and recooling the rhombic form becomes apparent. The oxalate crystals often show a leaf-like appearance.

These methods are founded upon the classical procedure of crystallographic identification. Theoretically, they are sound, but in practice they suffer from certain disadvantages. In the first place, it is extremely difficult to achieve standardization of procedure with this type of operation on a micro-scale. Secondly, the crystalline formations described are not in all, or even in the majority of cases, specific. In the hands of highly experienced investigators, however, the metals and bases described can in most cases be identified. Considerable difficulties, of course, arise if more than one base are present.

THE USE OF ORGANIC “SPOT” REAGENTS

Recently a wide range of organic reagents have been utilized for the detection of minute quantities of basic and certain acid radicles. The use of these reagents marks a notable advance in the technique of micro-chemical analysis. First, these reagents produce for the most part bulky precipitates of high molecular weight, a great advantage in quantitative work, or in the alternative colorations of a much greater intensity than those produced with classical reagents. Secondly, a very high percentage of the tests are specific, and the presence of constituents other than those sought does not generally interfere with the reaction. Thirdly, a number of bases not readily identifiable by classical micro-methods are detectable by the “spot” reaction.

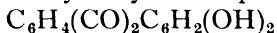
In dealing with these reactions it is more convenient to describe the reagents themselves in conjunction with the method of their employment in particular tests.

Chromium, Zinc and Iron**Acridine Hydrochloride**

In 1% solution this reagent will detect cobalt, iron, and zinc. A drop of the solution to be tested, which should be very slightly acid, is mixed on a microscopic slide with a drop of 1% solution of ammonium thiocyanate, and a drop of 1% solution of the reagent. The mixture should be allowed to crystallize spontaneously at a moderate temperature and it should be dilute. Well formed isolated crystals are produced in this way. If the crystallization is rapid the crystals clump. The crystals of cobalt are green. Those of ferric iron are red; those of zinc yellow. The presence of other bases does not seriously interfere with the reaction.

Aluminium**Alizarin**

1 : 2 Dihydroxy-anthraquinone



This reagent is a typical example of the uses of the “spot” reaction. As is well known, alizarin produces lakes with a number of metallic hydroxides. The chief of these are aluminium, iron, chromium, uranium, thorium, titanium, and manganese. The last six of these metals therefore interfere with the reactions for aluminium. These metals, however, form insoluble ferrocyanides which is a method by which they can be separated from aluminium and zinc.

The procedure is as follows :—

(1) A piece of filter paper is impregnated with a 10% solution of potassium ferrocyanide which should be made very slightly acid. The paper is then allowed to dry. A drop of the liquid to be tested is applied to the paper. The ferrocyanide of iron, chromium, uranium, thorium, titanium and manganese are

precipitated but the outer zone of the drop will contain the soluble aluminium.

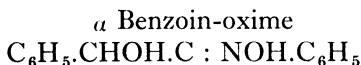
(2) A drop of an alcoholic solution of alizarin is now added to the spot. The paper is then exposed to ammonia vapour when it turns violet owing to the formation of aluminium alizarinate.

(3) On drying the violet colour is discharged and the red aluminium lake remains unchanged.

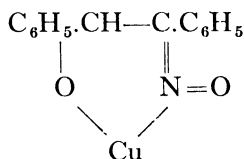
This is a general example of the manner in which separations in "spots" can be applied upon filter paper. It represents one of the principal advantages of this type of reaction.

Zirconium which also forms a lake with alizarin can also be detected by the use of this reagent. The test is specific in strongly acid solution since other lakes are soluble in an acid medium. Zirconium is not, however, of much importance in criminalistic practice whilst aluminium may be found in a variety of circumstances.

Copper

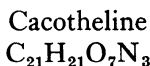


With copper salts in neutral solution this reagent forms a compound for which the following formula has been suggested :



As a spot reagent, however, a drop of the solution to be tested is treated with a drop of a 2% alcoholic solution of benzoïn-oxime which is then exposed to ammonia vapour and dried. A green coloration indicates copper. The sensitivity is of the order of 0.17γ.

Tin



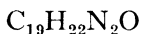
This substance is an alkaloid and a derivative of brucine. It

is reduced by stannous ions producing a violet compound of unknown composition.

Before the test is made the solution to be tested must be reduced with nascent hydrogen, using zinc dust in acid solution. The reduced solution is then spotted on filter paper which has been saturated with the reagent and dried. A violet coloration indicates the presence of tin. The sensitivity is of the order of 2γ . Silver, copper, chromium, mercury, cobalt, nickel, molybdenum, vanadium, and ferric iron interfere with the reaction.

Bismuth

Cinchonine



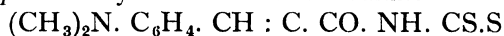
The use of this reagent for the detection of bismuth is another example of the manner in which capillary separation can be utilized in spot reactions. This alkaloid gives an orange-red coloration with salts of bismuth in the presence of potassium iodide.

The test reagent consists of a mixture of 1 gram of cinchonine and 2 grams of potassium iodide dissolved in 100 cc. of warm water acidulated with nitric acid. A drop of the solution to be tested if added to a piece of filter paper impregnated with the reagent produces an orange-red spot in the presence of bismuth.

Mercury, lead, and cuprous ions interfere with the reaction. But the performance of the test on filter paper results in capillary separation. The innermost ring is white produced by mercury. The second ring is orange-red due to bismuth. The third is a yellow ring formed by lead (lead iodide). The fourth is a brown ring produced by liberation of the iodine by the cuprous ion. The test can thus be made specific for bismuth. Its sensitivity is of the order of 0.16γ .

Silver

p Dimethylamino-benzal-rhodanine



This reagent is dissolved in acetone 0.03 gram in 100 cc. When added to a solution containing silver, whether in acid or

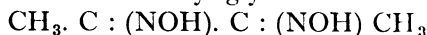
alkaline solution a reddish brown precipitate is formed. The reaction can be spotted on filter paper. It should, however, in this case be carried out in the presence of nitric acid to decolorize the reagent which is yellow.

Mercury interferes. If this metal is present a drop of potassium cyanide should be added. This inhibits the reaction of the reagent with mercury.

The reagent can also be used for the detection of mercury if cyanides, hydrochloric acid, or sulphates are not present. A purple coloration is produced in a solution containing mercury. It should be acidulated with nitric acid.

Nickel

Dimethyl-glyoxime



This reagent is used for the detection of nickel. It is prepared by dissolving 1 gram of the reagent in 100 cc. of alcohol.

The solution suspected to contain nickel is boiled and treated with the reagent in slight excess on filter paper. A drop of ammonia is then added. A red coloration indicates the presence of nickel. The sensitivity is about 0.16γ in one drop of solution.

Cadmium, Magnesium and Chromium

Diphenyl-carbazide



This reagent will detect cadmium, magnesium, and chromates.

Cadmium.—An alcoholic solution of the reagent is used. Filter paper is impregnated with it and allowed to dry. The solution to be tested is made slightly acid with acetic acid and spotted on the test paper. On exposure to ammonia vapour a red-violet coloration develops on the presence of cadmium.

In the presence of copper the reagent must be prepared as follows :—A saturated solution of diphenyl-carbazide in alcohol is saturated with potassium thiocyanate and a small quantity of potassium iodide is added. This solution reduces the copper

to the cuprous state which prevents its reaction with the reagent.

Magnesium.—For the detection of this metal the solution suspected to contain it must be made alkaline. A drop is then applied to the test paper as before. A pink coloration indicates magnesium.

Chromium.—Chromium in the form of chromates forms a magenta coloured compound with diphenyl-carbazide. The reagent is prepared by making a 2% solution of the reagent in one part of glacial acetic acid and nine parts of alcohol.

If chromium salts are present they must first be oxidized to chromates in acid solution with bromine excess of sodium hydrate then being added. The excess of bromine is then removed with a trace of phenol. Whilst the solution is still alkaline the reagent is added and the mixture is then made very slightly acid with sulphuric acid. This test can be performed on spotting paper, but care must be taken in manipulation. A magenta colour develops in the presence of chromium.

Mercury



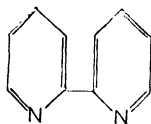
This reagent produces a violet coloration with mercuric ions.

Excess of acid reduces the sensitivity of the test. The solution to be tested must be very faintly acid (pH 6).

The reagent is prepared as a saturated solution of diphenyl-carbazone in alcohol. The spot test with a solution containing mercury produces a violet coloration.

Ferrous Iron

a a' Dipyridyl



This reagent is exceptional since it reacts with ferrous but not with ferric ions. It is specific although copper produces a faint blue tint if in great excess. In practice it does not interfere with the reaction. A rose coloration is produced with ferrous ion.

The test is operative between wide limits of pH 3.5—8.5. It is desirable, however, to adjust the pH between 4 and 6. The reagent consists of a 0.1% solution of $\alpha\alpha'$ dipyridyl in 0.1N HCl. The test gives satisfactory results on paper.

Ferric ions, can also be detected by this method since the iron can be reduced with sodium sulphite, a trace of mercuric chloride is then added and the test carried out as before. If ferrous and ferric iron are present together an increase in intensity of the colour reaction will be observed if reduced and unreduced solutions are tested.

Other metals do not seriously interfere. If other heavy metals are present, however, excess of the reagent should be used.

Manganese

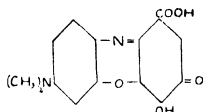
Formaldoxime

$\text{H} \cdot \text{CH} = \text{N} \cdot \text{OH}$.

This reagent produces a wine-red coloration with manganese in alkaline solution. Neither the heavy metals nor the alkaline earths interfere. If the test solution contains copper, however, it must be treated with an alkaline cyanide which suppresses the blue colour produced by copper.

The test solution should be made faintly alkaline with 4N sodium hydroxide after the addition of a small quantity of the reagent. The test is extremely sensitive.

Iron if present in the solution should be removed. Zinc oxide is added to the solution which is afterwards filtered. The manganese can then be determined in the filtrate. The test cannot so readily be performed by spotting on paper if this procedure is necessary.

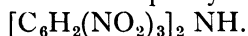
Lead**Gallocyanine**

An aqueous solution of this reagent produces an intense blue precipitate in solutions containing lead. The reaction has not been fully studied and the composition of the compound is not known. The reaction should preferably be carried out in neutral solution (pH 7) but if alkaline the solution should be ammoniacal.

The test should be carried out as follows :—The solution to be tested should be spotted on filter paper. A drop of aqueous pyridine 1% should then be added. It is essential that excess of the reagent should be removed. This is done by the addition of drops of aqueous pyridine which are absorbed by pieces of filter paper placed beneath the test paper, the addition of pyridine being continued until the liquid is colourless. When the excess of reagent is removed a deep violet colour indicates lead.

If silver, copper, bismuth, or cadmium is present the spot must first be treated with a drop of dilute sulphuric acid to remove these metals, and then washed with alcohol to remove the acid. The paper is then dried and the test applied.

Whilst this is a sensitive test for lead it requires considerable manipulation and experience before satisfactory results are obtained. This is specially true in cases where other metals have to be removed with sulphuric acid. Every trace of the acid must be removed. This presents some difficulties in practice.

Potassium**Hexanitro-diphenylamine**

This reagent is of great value since it produces a colour reaction with potassium. The reagent is prepared by adding

0.2 gram of the compound to 20 cc. of a boiling 0.1 N solution of sodium carbonate. The solution is then cooled and filtered.

The test solution must be neutral. It is spotted on filter paper with one drop of the reagent. An orange-red streak is produced. If on the addition of one drop of 0.1 N HCl the colour is unchanged potassium is present. If the colour fades to yellow the test is negative.

The alkaline earths do not interfere, but ammonium salts must be removed.

Ferric Iron

7-Iodo-8-hydroxyquinoline-5-sulphonic Acid $C_8H_4N.OH.I.SO_2OH.$

This is the most useful of all organic reagents for the detection of ferric iron. Neither coloured nor colourless ions interfere unless present in high concentration. Ferrous iron gives no reaction with the reagent.

The pH of the test solution should, however, be regulated at about 2.5 by suitable buffering, a phalate hydrochloric acid buffer being recommended. A drop of the reagent is added to the buffered test solution on filter paper. A permanent green colour develops in the presence of ferric iron. The concentration of the reagent should be 0.2% in aqueous solution. After it has been added to the test solution on the paper, the mixture should be diluted with a drop of water.

Calcium

Picrolonic Acid

1 p Nitrophenyl-3-methyl-4-nitro-5-pyrazolone $NO_2.C_6H_4.N.N : C(CH_3).C(NO_2) : C(OH)$

In a neutral solution or one slightly acidified with acetic acid this reagent produces a crystalline precipitate of a characteristic type.

The reagent consists of a cold saturated solution of picrolonic acid in 1% acetic acid. A microscopic slide is gently warmed and a drop of the reagent placed upon it and a drop of the solution to be tested. Characteristic rectangular crystals are

produced in the presence of calcium which can be identified microscopically.

Both barium and strontium produce crystalline salts with picrolonic acid. They are, however, readily distinguishable from the crystals of calcium picrolonate. Barium forms needles in clusters, and strontium rod-shaped crystals.

UTILITY OF THE SPOT REACTION

These reagents are in our experience the most useful in criminalistic practice for the detection of metals and bases present in dusts. Many other reagents of the same type are, of course, in use and their number is always increasing. For more detailed information the reader is referred to the appropriate literature. (*See References pp. 198-202*).

Many of the tests described are specific. These reagents therefore avoid the necessity of group separation which may be impracticable where small quantities of material are concerned. At the same time, the term specific is applied to these reactions advisedly. Owing to the great sensitivity of these reagents, and to the fact that the reactions involved are not always understood the conclusion that they are, in fact, specific in all circumstances must be accepted with reserve. It must not be supposed that the spot reactions have superseded the classical methods of micro-analysis. Strictly, they ought in all cases to be regarded as confirmatory tests. In this connection, however, it should be noted that the inorganic constituents of dusts are not usually of a complex nature. The evidential value of the analyses generally depends upon the presence in relatively large quantities of a single constituent. A complete qualitative analysis is rarely possible. With the proviso, therefore, that the results must be interpreted with caution, the spot method is one of great value.

THE DETECTION OF ACID RADICLES IN DUST

The identification of bases in dust analysis is not necessarily of much evidential value. For example, the presence of large

quantities of calcium in an occupational dust gives no indication of the ultimate composition of the compound with which it is associated. If, however, it is further shown that the dust contains sulphates, the presence of calcium sulphate in the dust might be assumed. Such a dust might be associated with plasterers or those working with plaster casts. The detection of bases (unless present in the dust in metallic form) must therefore be supplemented by the identification of acid radicles.

CLASSICAL METHODS

It is not necessary to describe these in detail since they are to be found in any text book dealing with qualitative analysis. There are, however, certain points which should be noted. The tests made should be as few as possible and should be carefully chosen. They should be carried out in the same order.

The preliminary tests (*see pp. 18 and 19*) may give an indication as to the acid radicle present. For example, effervescence with acid indicates the presence of a carbonate.

Tests which involve the formation of white precipitates (SO_4 and Cl) should be carried out on a sheet of glass resting on a piece of black paper. Traces of precipitate are more readily observed against a black background. On the other hand, a white spotting tile should be used for tests of the type of the black ring test for nitrates. For the micro reaction solid ferrous sulphate must not be used as it often is in the macro method. A drop of ferrous sulphate solution is added to a drop of the test solution, followed by a very cautious addition of dilute sulphuric acid.

Yellow precipitates such as those of ammonium phosphomolybdate (test for phosphates) are best observed upon a white tile.

In the decolorization of iodine (sulphurous or hyposulphurous acids) the test solution should be added to the iodine delivered from a fine drawn capillary pipette. The decolorization effect is much more readily observed if this procedure is followed. In general it is always necessary to bear in mind that owing to lack of material, it may be impossible to repeat a test. For this reason every possible precaution must be taken to perform the

test in such a way that the possibility of a failure or an indeterminate result is reduced to a minimum.

THE SPOT REACTIONS

Unfortunately the range of reagents available for the detection of acid radicles is much smaller than in the case of bases. Reagents exist, however, for the detection of nitrates, fluorides, phosphates, boric acid, and bromides.

Nitrates

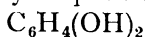
Brucine

In 1863, Kersting found (*Annalen* 125.254) that nitrates and nitric acid produced a red colour with this alkaloid. For many years this test was employed, and is still employed, for the detection of brucine. More recently, however, the method has been adapted to the detection of nitrates. This is an interesting example of the early use of micro-analysis.

An alcoholic solution of brucine is added to the test solution. A blood-red coloration indicates the presence of nitrates. Nitrites give a similar reaction. If present they must be decomposed with sodium azide in acid solution. The excess of hydrazoic acid must be removed by boiling and the solution cooled before the test is applied.

Phosphates

Hydroquinone



This reagent gives a satisfactory colour reaction for phosphates in the presence of ammonium molybdate.

The following solutions are required: (1) a 5% solution of ammonium molybdate in 5N sulphuric acid, (2) a 20% aqueous solution of sodium sulphite, (3) a 0.5% aqueous solution of hydroquinone acidified with 1% sulphuric acid.

Three drops of each reagent mixed are used. A drop of the mixture is added to a drop of the test solution. A blue colour develops which attains its maximum intensity in about half an hour.

Bromides*m* Phenylene-Diamine
 $\text{C}_6\text{H}_4(\text{NH}_2)_2$

This substance can be brominated to produce 2 : 4 : 6-tribromo-*m*-phenylene-diamine. The compound is insoluble in water. The reaction in concentrated solution produces an amorphous precipitate. In dilute solutions, however, it is in the form of needles.

For the detection of bromides, a drop of the aqueous solution of the reagent is placed upon a microscopic slide. This is inverted over a small crucible containing a drop of the test solution, acidulated, to which has been added a little lead dioxide. On warming the bromide is reduced and bromine evolved. On examination of the slide microscopic clumps of needles of the tribromo derivative are observed.

INTERPRETATION OF RESULTS

The interpretation of the results of an inorganic analysis of dust requires considerable experience. It calls also for discretion. All analysts are familiar with the method of interpretation commonly called "the most probable composition." It is applicable only when a complete analysis of all bases and acid radicles has been made quantitatively, and therefore cannot generally be applied in the case of dust.

This does not prevent valid interpretations being made within limits which must be clearly recognized. If, for example, carbonates and chlorides are found associated with calcium and sodium it is clear that the dust contains either sodium chloride and calcium carbonate or calcium chloride and sodium carbonate. The physical appearance of the dust when examined microscopically may sometimes assist in the interpretation. Crystals of a certain form may be recognized or the deliquescent or efflorescent nature of substances present in the dust may be observed. Again, if copper were found associated with potassium, sulphates and chlorides the microscope might reveal which acid radicles and which bases were associated. Even in the many cases where this is not practicable, if the acid

radicles and bases present are known, the results can be provisionally interpreted in such a way as to produce useful results. Inferences which go beyond the facts, however, must be avoided.

In certain cases positive inferences can be drawn. These generally belong to that exceptional category in which quantitative results are available and can be interpreted. Thus Locard (*Manuel de Technique Policière*, 87) quotes a case of a quantity of occupational dust found in the clothing of suspected coiners. The dust was abundant and proved to be of a metallic type. An analysis by classical methods was practicable. The dust was found to consist of lead, antimony and tin in certain proportions. Those proportions were later found to agree substantially with the composition of an alloy of which certain counterfeit coins were found to be composed. The inference was that the suspects had manufactured the coins in question. This conclusion was ultimately confirmed.

To return to a typical illustration, however, if traces of these metals were identified without quantitative estimation, this would be presumptive evidence that it was a counterfeiter's occupational dust, although the inference would be less positive than in the former case.

These illustrations are examples of the attitude which should be adopted to facts of this type. We are not here concerned with definitions of the nature of scientific and judicial proof. It is merely necessary to indicate that the interpretations of laboratory results in criminalistic practice are not useless because they lack the precision which the ideal type of investigation achieves.

THE EXAMINATION OF ORGANIC DUSTS

Whilst the chemical examination of the organic constituents of dust is in some respects more limited than that of the inorganic constituents, the results are in many cases more precise. The reason for this is that numerous organic compounds are identifiable as entities and it is thus possible to demonstrate their precise composition as they exist in the material examined.

Examples of such substances are alkaloids, aniline dyes, certain drugs, starches and sugars. These materials are often to be found associated with occupational dusts.

It must, on the other hand, be remembered that many of the organic constituents of dust are not amenable to chemical examination. This must be emphasized. A failure to realize the importance of this fact has frequently led chemists to attempt investigations they are not qualified to perform. No chemist, for example, without specialized practice should attempt the bacteriological examination of dusts containing bacteria, yeasts, or moulds. Seeds and vegetable debris should be passed on to the botanist. Physiological debris such as hairs should be dealt with by the medico-legist. The chemist, however, should be in a position to identify those materials and make a general report upon them before handing them over for detailed examination to the appropriate expert.

PRELIMINARY EXAMINATION OF ORGANIC DUST

The preliminary tests already described (*p.18 et seq.*) should be carried out with special reference to the detection of organic materials. The aqueous and alcoholic extracts of the dust should be carefully examined for colour and for finely divided particles which may remain in suspension. The insoluble matter both in water and alcohol should also be examined. It is also desirable to make an ether extract of the dust for the purpose of recovering fatty substances which may be contained in it.

As large a portion of the dust as is practicable should be gently ignited and the smell carefully noted. The manner in which the material ignites should also be observed. It is important to note, for instance, if the dust burns quickly, or if it chars and swells.

The behaviour on heating may give a clue to the presence of one of the simpler organic acids. Formic and acetic acids are recognized by their smell. Oxalic acid evolves gas but does not char, succinic acid does not char, whilst tartaric and citric acids char rapidly and slowly respectively. Owing to the mixed nature of most dusts it is not ordinarily possible to

observe these reactions but they illustrate the necessity for close observation of the results of these preliminary tests.

SUBSTANCES AMENABLE TO EXAMINATION

Starch.—Starch is found as an occupational dust on the person and in the clothing of bakers, millers, and other workers with starch.

Dried Blood and Fatty Substances.—These materials are associated with butchers and slaughterers.

Perfume, Fatty Substances, and Hair.—Hairdressers' clothing is associated with dusts of this type.

Sugar.—Sugar is found often in large quantities in the clothing of confectioners, pastry cooks, and workers in sugar factories.

Dyes.—Dyes are found among workers in dye works, dry-cleaners, and dyers.

Shellac.—French polishers and others working with furniture are associated with shellac.

Organic Compounds.—Chemists, pharmacists, chemical workers, and those handling drugs are associated with drugs and organic chemicals of various kinds.

Tannins and tannic acid.—These compounds are found in the clothing of workers in tan yards.

These are typical examples of the organic materials associated with occupational dust of the organic type. The list could obviously be greatly extended. It is not, however, possible to deal here with special cases in detail. To a great extent every case has to be considered individually. A systematic procedure can, however, be followed which is applicable in all cases.

Aqueous Extract.—If the extract contains finely divided matter which remains in suspension a microscopic examination

should be made of it. A small quantity should be treated with iodine and any change noted in its appearance. A blue colour indicates the presence of starch. The microscopic examination will reveal the presence of starch granules whose origin can be identified by their form. If the microscopical appearance of the suspended matter is amorphous, it is seldom possible to form any conclusion which might lead to further tests, but any special characteristic should be noted.

The aqueous drop should then be evaporated to dryness and the nature of the deposit noted. This residue should be tested with Fehling's solution. If this reagent is reduced it indicates most probably the presence of invert sugar, dextrin, or certain forms of cellulose. It must be borne in mind, however, that there are many other compounds which reduce Fehling's solution.

If the aqueous solution is strongly coloured it is probable that an aniline or other dye is present. Its shade can best be determined by immersing a piece of wool in the extract. This in itself may give some indication of its character. If sufficient material is available its reaction to acids, oxidizing, and reducing agents may make it possible to identify the dyestuff. For full details the reader is referred to textbooks dealing with the subject.

Alcoholic Extract.—Most of the organic constituents which are soluble in water will also dissolve in alcohol, and others will be included which are insoluble in water. The alcoholic extract is evaporated to dryness and the residue carefully examined. Its general form, whether crystalline or amorphous, should be noted, and if amorphous whether it is of a gummy or scaley nature. The smell should be very carefully noted since odorous substances can sometimes be directly detected.

If as much as three drops of the extract are available they should be treated as follows : (1) With a drop of sodium phospho-molybdate 10% solution in 10% nitric acid, (2) Sulphuric acid and a drop of iodine solution, (3) Sulphuric acid and a drop of Mayer's reagent (solution of potassium iodide added to one of mercuric chloride until the precipitate first formed is just dissolved).

If alkaloids are present (1) gives a yellow amorphous precipitate which turns blue on standing, (2) Produces a chocolate coloured precipitate, (3) Gives a white or yellowish precipitate. If a choice has to be made between the tests owing to lack of material (1) should be applied. These tests, however, are not specific, but if the reactions do not take place alkaloids are absent.

There is often insufficient material available to make systematic confirmatory tests for alkaloids possible. But if the preliminary tests are positive, confirmatory tests should be applied. On page 42 is a table indicating the reactions of alkaloids to certain reagents.

In the alcoholic extract drugs other than alkaloids may be identified by specific tests. Owing, however, to the very large variety of organic materials which may be present in dust it is obviously not possible to provide for every case. It is the business of the investigator to acquaint himself with the circumstances and then use his discretion as to the method of attacking the problem. But the tests now being described are ones which can be applied either *in toto* or in modified forms in every case. The principle of them is that they supply the maximum amount of information without wastage of material. No test of a general kind can supply precise information. To quote, however, specific examples, it is of value to determine that a particular dust contains a sugar, a substance reducing Fehling's solution, or an alkaloid even if the nature of the reducing substance or the alkaloid cannot be determined.

Ethereal Extract.—An ether extract of the dust should also be made. Fats or fatty acids are substances which should particularly be examined in this extract. The smell should be noted and compared with that of the alcoholic extract with a view to determining if any odorous substances not extracted by alcohol have been removed by the ether. The extract should, of course, be allowed to evaporate spontaneously.

Since a comparatively small quantity is required for the test, it may be practicable to take the refractive index in a refractometer. It must, of course, be borne in mind that the refractive index is not necessarily of great value since a mixture of fats

IDENTIFICATION OF ALKALOIDS (Locard)

Alkaloid	Sulphuric Acid	Fröhde's Reagent	Mandelin's Reagent	Ammonium Tellurate	Nitric Acid	Potassium Ferrocyanide
Aconitine	Yellow-brown then violet					
Atropine	Brown (warm)	Brown-green then brown			Yellow-green (cold)	
Berberine	Olive-green	Red then yellow	Yellowish red			
Brucine	—	—			Bright red	
Caffeine	—	—				Orange
Cinchonine	—	—		Green		
Chelidonium	Pale green then brown and red	—				
Cocaine	—	Dirty green then blue	Blue-green			
Codeine	Dark brown-green	Yellow-green then brown red-violet	Olive-green then brown			
Colchicine	Yellow	Cherry-red			Violet then brown	
Curarine	Red then red-violet	Red then green	Brown		Purple	
Emetine	Greenish-brown	Violet, green, brown, yellow, blue-violet	Reddish		Orange	White becoming blue
Morphine	Red then violet	Green (cold)			Yellow	
Narceine	Yellow then red	Red (warm)	Violet then red-orange	Yellow then dirty green, violet		White
Narcotine	Yellow then red (warm)	Green then yellow and red	Red	Rose	Yellow	
Nicotine	—	Yellow then red				
Papaverine	Blue-violet	Red-violet then blue yellow and de-colored	Bluish-green			
Piperine	Yellow then brown, green-brown	Yellow, brown and black	Dark blood red			
Quinine	—	Green				Green
Strychnine	—	—	Violet then rose on dilution		Light yellow	Bluish
Thebaine	Red then orange	—	Red-orange		Yellow	
Veratrine	Yellow then orange and red	—	Yellow then orange and red, violet		Yellow	
Yohimbine (Quebrachine)	—	—	Violet			

may be present. But the figure obtained may exclude a number of fats and oils.

PARTICULAR CASES

There are certain special cases which are important from a forensic chemical point of view. Where the dust is abundant a careful examination of it should be made with a lens with a view to the separation of certain constituents which may be identifiable by direct inspection. In some cases these can be mechanically separated from other constituents. In other cases the coarse screen effects this separation to a great extent since it is only the large particles which can be recognized and separated.

Tobacco.—This is a constituent of a type which can often be recognized and separated. A determination of the class of tobacco may often be of great evidential value. Although tobacco is mainly of organic origin an examination of the inorganic constituents may serve to identify it.

Thorpe quotes the following figures for certain classes of tobacco.

TOBACCO ASH

Thorpe's Dictionary of Applied Chemistry.

Kind of tobacco (a)	Total Ash	Potassium Chloride	Lime	Magnesia	Potash	Sand
	%	% (b)	% (b)	% (b)	% (b)	% (b)
China . .	14.8	3.7	31.1	12.7	14.4	2.1
German . .	25.9	25.0	35.7	6.5	—	0.9
Havana . .	21.4	12.7	33.1	5.3	11.8	1.8
Java . .	18.8	19.6	22.3	8.5	14.1	1.7
Kentucky . .	18.0	2.4	29.5	6.8	16.8	5.3
Latakia . .	18.2	4.1	34.7	5.5	19.6	0.9
Manila . .	21.4	6.5	33.3	7.2	16.3	0.6
Turkey . .	12.9	19.3	22.5	9.2	14.5	1.8
Virginia (ripe) .	15.0	2.5	18.9	6.7	34.2	1.0
Virginia (bright)	12.3	7.0	21.7	12.4	22.2	1.3

(a) The tobacco was dried at 100 degrees c. before being analysed.

(b) Calculated on the ash.

A quantitative analysis is necessary if definite conclusions are to be drawn. Even when the material is abundant micro methods of analysis must be employed. Many of the methods previously described (*page 25 et seq.*) can be applied quantitatively.

Textile Fabrics.—In dust from clothing, fibres due to the cloth itself are always found, but a careful search should be made for foreign fibres. Their colour should be noted and if white they can be tested with such reagents as iodized zinc chloride, iodine in sulphuric acid, and cuprammonium sulphate. Certain textile fibres can be identified in this way. The tests, however, require experience in interpretation, particularly if small fibres are under examination.

If the fibres are coloured the nature of the dye can also be determined. In this connection, however, it must be borne in mind that the actual isolation of a fibre of a definite colour is often of greater value as evidence in itself than is a determination of the nature of the dye staining it. A portion of such fibres must always be preserved untouched, so that they can be compared with others found upon the scene of the crime, associated with the clothing of a victim, or in other circumstances.

These are examples of materials of large particle size which in our experience can be dealt with in this way.

Gome.—The fingernails should not be neglected as a source of occupational dust. It is always to be found in the form of what is known as gome, that is to say a mixture of dusts with fatty materials. As much as possible should be removed and the material examined for general appearance and colour.

Blood.—In the case of butchers and slaughterers the gome is generally dark red or brown, and the consistency will be remarkably greasy. It should be tested for blood using Adler's method as modified by Medinger (*Rev. Inter. de Crim.*, 1931, 7, 493, *also Rhodes, Manufacturing Chemist*, 1937, VIII, 9, 287). This is among the most sensitive of all tests known for blood. The colourless leuco-base of malachite green dissolved in

dilute acetic acid produces a green and then a dark blue-green coloration with blood. The test does not, of course, distinguish between human and animal blood.

Metals.—Those who carry quantities of gome in their fingernails are generally mechanical workers of some kind. Traces of metallic dust are not infrequently found in deposits of this type. The gome must be treated with ether to remove the fatty substances. It is then often possible to identify metallic fragments by inspection. Where this is not the case the metal is dissolved in acid and its nature determined. It is of interest to note here that in a case of coining investigated at the laboratories of technical police at Lyon, metallic dust was discernible with the naked eye in certain parts of the clothing of the suspected man. These metals were identified, namely, as lead, antimony and tin.

SUMMARY

It is seldom possible to make a complete examination of dust and determine its precise nature by chemical or any other means. What the forensic chemist must aim to do is to make a general systematic study of the sample and then investigate its outstanding characteristics in detail. It is not possible to devise methods of particular treatment in advance, for each case has to be considered on its merits.

It is important to bear in mind that there are other methods of investigation besides chemical methods which throw light on the composition of dust. These are beyond the scope of this book, but a word must be said concerning the responsibility of the individual who first examines the sample. In many cases the chemist undertakes this important preliminary operation. He must therefore acquaint himself with the general nature of dusts and be able to recognize the evidential importance of constituents which he may not be able to examine himself. Dusts may and often do contain vegetable debris, seeds, spores, parasites, and bacteria to which chemical methods cannot be applied. Human secretions may be mixed with it which are not amenable to examination by chemical methods. There are

many other substances also whose examination requires the co-operation of the physician, the botanist, and the bacteriologist. It is the responsibility of the preliminary examiner to decide the types of investigation which are necessary, their relative importance, and thus in what order they should be carried out. It is for this reason that so much depends upon the preliminary examination.

THE EXAMINATION OF BLOOD GROUPS

An increasingly important aspect of the indirect identification of the person is the determination of blood groups. It is questionable how far the technique of examination can be appropriately called a chemical problem. Without special training and experience the chemist should not undertake the examination, but some description of blood groups and their identification seems to be appropriate here.

The fact that human blood is known to fall into four groups which can be identified is of great forensic importance from the point of indirect identification. Whilst it is clearly not possible to distinguish individuals in this way groups can be distinguished from other groups. In a negative sense the evidence supplied may be definite. If, for example, a blood stain found upon a weapon is of a different group from the blood of the alleged victim of the weapon, the crime could not have been committed with that weapon. On the other hand, evidence of a positive kind exists if a blood group of a more uncommon type is found upon a weapon or elsewhere since it may presumptively connect it with a particular person.

A further use of the group test is the example in which a suspected person declares that a blood stain upon his clothing originated from his own blood from a cut finger or bleeding nose. If the blood group differs, identification is clearly disproved, whilst agreement may indicate but does not, of course, establish identity.

Classification and Nature of Groups.—There still exist differences in nomenclature but the international classification of Landsteiner is now generally accepted, namely the groups

O, A, B and AB. The characteristics of these groups are determined by the presence in the blood and serum of substances which have been described as agglutinogens and agglutinins. The agglutinogens exist in the red corpuscles, whilst the agglutinins are found in the serum. Agglutinogens are designated A and B, and the agglutinins a and b. This explains the classification. Group A contains agglutinogen A only ; B contains B only ; whilst AB contains both. In group O, both are absent. In regard to the agglutinins, b is associated with A ; a with B ; O with ab ; whilst AB is not associated with an agglutinin.

Principles of the Test.—The principle of the test is that bloods of corresponding groups cannot agglutinate with each other. Landsteiner's definition states that : " In a given blood containing a given agglutinogen, the serum will also contain agglutinins which are incapable of acting upon the said agglutinogen and thus bring about agglutination." On the other hand, unlike agglutinogens and agglutinins bring about agglutination if the bloods containing them are mixed. It is thus possible with a pair of serums and one confirmatory test to determine into which group the blood falls. For example, A and B will both agglutinate AB, B will agglutinate A and A,B. Thus if both results are positive the group is AB. If A is negative and B is positive, the group is A ; and if A is positive and B is negative the group is B. O, on the other hand, is negative to all other groups. The negative result can be confirmed by treating the serum of the unknown blood with the corpuscles of Group A and B. Since the serum of Group O is unique in containing both agglutinins a and b, the reaction is positive in both cases.

Method of Determination.—The serum of the blood to be tested may be mixed with the corpuscles of known groups or sera of known groups may be used to test the blood under examination. The second procedure is generally the most convenient.

Two drops of the sera of Groups A and B are placed on a microscopic slide. A small drop of the blood to be tested is then intimately mixed with the two drops. A fresh rod should be

used for each test. If the test is being made upon an individual, the blood should be freshly drawn and transferred to the serum before coagulation.

The clumping of the corpuscles can be seen with the naked eye but it is preferable to examine the mixture with a lens.

In order to increase the reactivity of the blood, Martley (*Analyst*, 53, 1928, 15) recommends the removal of the serum by treatment with physiological saline.

In dealing with stains the same author (*Trans. Med. Leg. Soc.*, 18, 1923-24, 77-9) places the stained material in a small test tube with distilled water and incubates it, after sealing, for twenty-four hours. A clear solution is obtained from this extract by suction into a small pipette packed at the nozzle with fibres of filter paper. The solution contains the serum and must thus be tested with blood corpuscles.

The following tables make the reactions clear :—

Using Serum of

	<i>Corpuscles</i>			
	Group AB	Group A	Group B	Group O
Group AB	—	—	—	—
Group A	+	—	+	—
Group B	+	+	—	—
Group O	+	+	+	—

Using Corpuscles of

	<i>Serum</i>			
	Group AB	Group A	Group B	Group O
Group AB	—	+	+	+
Group A	—	—	+	+
Group B	—	+	—	+
Group O	—	—	—	—

+ = Positive reaction

— = Negative reaction

In the hands of an experienced manipulator the test is extremely sensitive and can give positive results using very small quantities of blood. It must be borne in mind, as we have stated, that serious errors can arise if the technique of the test is not fully understood. Those performing the test must be fully experienced in biological and bio-chemical tests.

Developments of the Group Test.—The classic work of Landsteiner and his collaborators has established that blood can be further differentiated into sub-groups. Thus they have identified Group A as being divisible into A_1 and A_2 . (See also Harvey, *Indian Journ. of Med. Research*, 17, 1936, 1307–11.) Substances described as P and Q, M, and N have been identified. Locard indeed considers (*Traité de Crim.*, IV, 558) that eighteen groups can now be identified, namely OM, ON, O MN, A_1M , A_1N , A_1MN , A_1A_2M , A_1A_2MN , BM, BN, B MN, $A_1B M$, $A_1B N$, $A_1B MN$, $A_1A_2 BM$, $A_1A_2 BN$, $A_1A_2 B MN$.

Locard, however, points out that whilst under carefully regulated experimental conditions reliable results may be obtainable, that in practice the classic four groups can alone be verified in ordinary laboratory work.

From a theoretical point of view, however, the investigation is of great importance. Whilst it seems improbable that tests will be devised which will make possible the individual identification of blood, the multiplication of identifiable groups makes a closer approximation to personal identification possible.

SEMINAL STAINS

The semen of the individual is of the same agglutinative group as the blood of the same individual. The tests described suitably modified can also be applied to the examination of seminal stains. Dervieux (*Le Diagnostic des Taches en Médecine Légale*, Paris, 1912) and others have described tests using a serum prepared from rabbits which have been injected with human sperm. This serum reacts with blood and with sperm. Dervieux has stated that the sperm taken from the individual from which the serum was prepared reacts more strongly with the serum than the sperm of other individuals. This interesting observation has not been confirmed. Tests of this kind are very difficult to interpret, and it is doubtful if they could be applied in ordinary practice to the diagnosis of individual seminal stains.

PART II

APPLICATION OF CHEMICAL
METHODS TO THE PROOF OF
CORPUS DELICTI

CHAPTER III

STAINS

IT is not necessary to discuss the definition of the term *corpus delicti* in detail. The term, which cannot literally be translated, means the "corpus" (content) of the act. It is often wrongly interpreted as the body of the victim. This misconception arises from the fact that in certain special circumstances the body of a victim may be *corpus delicti* as, for example, when the discovery of the body depends upon proof of the commission of the crime. In general, however, the term means the existence and therefore demonstration of a fact or facts which establish that a crime has been committed.

It can thus be assumed in general that any material clue which is to be interpreted not for the purpose of identifying the person but primarily for the purpose of determining the nature of the crime or the manner of its commission can be classed as *corpus delicti*.

Into this class fall stains, weapons, documents, poisons, counterfeit money, dusts circumstantially associated with crimes, and in fact traces of every kind found on the scene of the crime or elsewhere which throw light upon its commission. We shall, of course, deal only with those materials which are amenable to chemical examination.

GENERAL EXAMINATION OF AND SEARCH FOR STAINS

Clothing.—First it is necessary to consider the actual location of the stain. Stains upon fabric are not necessarily visible. A search should be made for these with an ultra-violet lamp which by reason of fluorescence of the stains or the fluorescence of the background reveals their presence. When

their position is located in this way. a pin can be placed close to the margin of the stain to indicate where it can be found. The use of the ultra-violet lamp will also often differentiate one stain from another by reason of a different type of fluorescence or the absence of fluorescence. Differences of this kind should be noted so that some general indication as to the nature of the stain may be secured.

A physical examination of the stain should also be made and it should be examined with a lens. It should be noted if any crystals are present or amorphous particles. The physical examination will often give an indication as to the nature of the stain. Substances of an oily or fatty nature can be recognized, stains due to dyestuffs may be recognizable; tar and paints and varnishes may also be detected. At the same time no definite conclusion can be drawn from the physical examination alone. Bloodstains (*vide infra*) may be confused with those of paint or even oil. Further, the stain may be of a mixed nature as when blood is associated with oil and dust. On the other hand, stains may in some cases be recognized as having been produced by material of a certain class.

Weapons.—Certain special considerations apply to stains upon weapons. In the first place, when examining a knife for bloodstains it is not sufficient merely to examine the blade. Traces of blood, for example, may be found in the crevices where the blade is connected with the hilt even if the blade itself has been carefully cleaned. Secondly, stains upon metal often have an entirely different character from that of the same type of stain upon fabric. Bloodstains may produce a mere blackening and by inspection alone, it is not possible to distinguish between a bloodstain and one made, for example, by fruit juice.

General Tests.—It is advisable to determine the reaction of the stain with litmus paper to decide if it is neutral, acid or alkaline. If the stain is not minute a small portion should be mixed with a drop of water. Any coloration or obvious characteristics of the drop should be noted. Similar tests should be made with alcohol and ether. In the case of these solvents

the residue after spontaneous evaporation should be examined. The physical characteristics of the residue, whether crystalline or amorphous, and if amorphous whether gummy, or oily, may assist in identification.

As with dust, it is necessary to ignite a small portion of the stain preferably in a small porcelain crucible or on a thin sheet of porcelain. If the stain is mixed with cloth when clothing is the matrix, the smell will not be a guide to the composition, but where the material is free from foreign matter the smell should be noted. The appearance of the residue must be observed since its colour or other physical characteristics, may assist in the recognition of its composition.

THE CHEMICAL EXAMINATION OF BLOODSTAINS

Stains upon clothing and elsewhere if suspected to be those of blood must be tested. It is important to note that bloodstains cannot necessarily be recognized by their appearance. They may be black, green, or brown in colour. For the preliminary tests very small quantities of the stain should be used. It should be mutilated as little as possible in securing the sample to be tested. A general method is to moisten a piece of filter paper with distilled water and apply it to the stain.

The Benzidine Reaction.—The reagent is prepared by filtering a saturated solution of benzidine in acetic acid to which a few drops of an O.I N solution of sodium perborate have been added. The reagent should be freshly made up in small quantities for each test. A few drops of the solution are added to the aqueous extract of the stain on the filter paper. If blood is present a blue or green colour develops. The test, however, is not specific.

The Guaiac Resin Reaction.—The reagent consists of a filtered solution of the resin in alcohol to which have been added a few drops of ozonized turpentine. The test is carried out on blotting paper in the same way as for the benzidine

reaction. A blue colour develops after a few seconds if blood is present.

The Leuco Malachite Reaction.—This test already noted (*Medinger. Rev. Inter. de Crim.*, 493, 1931) is the most delicate known for blood. One gram of the leuco base of malachite green is dissolved in 100 cc. of glacial acetic acid and 150 cc. of water. The stock solution must be kept in a dark brown bottle and it must be tightly sealed. It will then keep indefinitely. For the actual test a mixture in the ratio of 4 to 1 is made with the reagent and a 1% solution of hydrogen peroxide.

The most suitable method of performing the test is to add a small fragment of the stain to a drop of the reagent on a porcelain tile. The mixture should then be macerated with a glass rod. A dark green coloration will develop at once if blood is present. On standing for a minute the coloration becomes bluish-green. Another method is to transfer the fragment to a piece of filter paper and add a drop of the reagent on one side so that it comes in contact with the fragment as it spreads.

For very minute stains, moistened filter paper can be applied and a drop of the reagent added. The test is, in fact, so sensitive that it will detect the presence of blood in circumstances where no stain is visible. In the case of motor accidents it is quite common to find no visible traces in the supposed origin of impact. In these circumstances pieces of filter paper moistened with the reagent are applied to the surface to be tested at all suspected points. If the minutest trace of blood is present the reaction will be positive.

The extreme delicacy of this test makes it necessary to ensure that all apparatus is chemically clean. Minute traces of blood from previous tests may otherwise lead to error. The reaction should be definitely positive and should in all cases show the colour change on standing.

Teichmann's Reaction.—This relies upon the microscopical identification of haemin crystals. A portion of the stain is mounted with water upon a microscopic slide and the liquid evaporated over a water bath. A cover slip is then placed over the residue and a drop of glacial acetic acid run in under

the slip. The mixture is again evaporated to dryness. This operation is repeated three times. The residue is then examined microscopically. Coffee-coloured crystals of haemin will be observed if blood is present.

Strzyzowski Reaction.—This relies upon the formation of the bromo- or iodo-hydrate of haematin, the formation of the iodo-hydrate being a modification which has been devised by Locard. Locard's method is to mix the sodium bromide or iodide with the aqueous extract of the suspected stain on a microscopic slide and evaporate the mixture to dryness with very gentle heat. The cover slip is then placed in position and a drop of a mixture of alcohol, water and glacial acetic acid in the proportions of 1 : 1 : 1 is run in beneath the slip. The extract is again evaporated slowly. Large crystals of the bromo- or iodo-hydrate of haematin are observed if blood is present.

The classical method is to treat the stain with the following mixture :—

	<i>Parts</i>
Alcohol	1
Distilled water	1
Glacial acetic acid	1
Hydriodic acid	3

The method of performing the test is the same as that of Teichmann's reaction.

CONFIRMATION OF RESULTS

In so important a matter as the identification of blood, it is essential that confirmation of all results should be obtained. It is extremely unsafe to rely upon unconfirmed results. Lucas (*Forensic Chemistry and Scientific Criminal Investigation*) recommends the benzidine reaction as the most useful preliminary test. He has stated (*p.* 32) that "in no case has the presence of blood ever been found after a negative benzidine reaction." In our experience the same is true in regard to the leuco-malachite reaction. In regard to confirmation, if the benzidine and leuco-malachite reactions are positive, one of the micro-chemical tests, Strzyzowski's reaction as modified by

Locard, should be applied. If this is also positive it may be safely assumed that the stain is one of or actually contains blood.

METHOD OF BEAM AND FREAK

This is a modification of the haemin test strongly recommended by Lucas (*loc. cit.*, p. 36), who has wide experience in the examination of blood. These authors (*Bio-Chemical Jour.* 9 (1915), 161-70) describe the test as follows:—

A small quantity of the suspected material is placed at the bottom of a flat arsenic sublimation tube about 6 by 3 mm. and 35 mm. long. A thin round ignition tube will answer if no flat tube is procurable, but for examination under the microscope the flat form is obviously better. A few drops of acetic acid containing from 0.01 to 0.1 per cent sodium chloride are added and a very fine cotton thread adjusted so that its upper end is near the top of the tube and the lower end reaches to the bottom of the liquid. The thread should be everywhere in contact with the tube, to which it adheres readily by being moistened with the liquid. The adjustment is readily made by means of a glass rod one end of which is drawn out for the purpose. The tube is now placed in a rack, or supported by forcing its base into a small blob of plasticine, and allowed to remain until crystallization has taken place.

Before placing the thread into position, the solution of the blood may be aided, if desired, by cautiously heating the tube over a small flame, loss of the liquid by explosive boiling being prevented by holding the finger tightly over the mouth of the tube.

While such heating appears rarely to be essential, the long contact with the acid in the cold sufficing for solution in practically all cases, it is nevertheless advisable in that it gives at once an indication of the strength of blood solution obtained. For the best results this should be quite weak.

The clear liquid, filtered by its passage through and along the thread, is slowly drawn up, by capillary action, to the mouth of the tube. Under these conditions evaporation takes place so slowly that, even when the temperature of the atmosphere is above 38°C., it is complete (if the tube is held in an upright position) only after 12 to 24 hours or more. The rate of evaporation is readily controlled, within wide limits, by altering the dimensions of the tube and the angle at which it is supported.

The crystals usually begin to appear, on or near the upper half of the thread, and of sufficient size to be distinguished with a

power of 75 diameters, in about an hour ; and they ultimately become so large that, in place of requiring a magnification of 250 to 300 diameters, as usually recommended, they may readily be seen with one of 25 diameters or even, in many cases, with a good hand lens. The crystals are best viewed against a dull white background. A piece of white paper is suitable.

The extraordinarily large size of the crystals is due, in great part, to the slow evaporation of the liquid ; but it is also a result of the removal, by the thread, of the interfering action of the blood albumin on crystallization. Examination of the thread at the end of the experiment shows that the soluble, non-crystallizable constituents of the blood are carried to its upper end, and that the maximum growth of haemin crystals is found lower down.

If the solution is sufficiently weak, the first crystals form at the point of greatest concentration—the upper end of the thread ; but as the albuminous matter accumulates these cease to grow and the largest and most numerous crystals are found, later, about midway down the tube.

For the best results the following precautions should be observed :

The tube should be thoroughly clean and dry. It is best cleaned by swabbing out successively with acetic acid, water, and alcoholic soda, followed by thorough rinsing with distilled water and drying on a hot plate.

The thread should be clean and as fine as can be obtained. A good plan is to take No. 80, "six-cord sewing machine cotton" and to untwist it, using one of the "cords" for the test.

The solution of the blood in acetic acid should not be concentrated, but very weak. The liquid should only be faintly pink. This ensures large crystals and clean fields.

If the method is to be applied experimentally to fresh blood, the latter must be completely dried before the addition of the acid, and especial care should be taken to work with very dilute solutions.

The large-sized crystals found in this test to which the authors allude make the results particularly easy to interpret. The disadvantage is that it takes some time to carry out. It is a very valuable confirmatory test which should not be neglected if opportunity exists to make use of it.

INTERFERING AGENTS

It is important to ensure that the crystals formed in the haemin and haematin reactions are of a brown colour. Inorganic

salts may assume a form which will be confused with those of the true blood reaction. They are, however, colourless. Indigo, often associated with textile fabrics on which stains are found, forms crystals somewhat resembling haemin or haematin crystals. They are, however, blue. Iron and calcium salts interfere with Teichmann and Strzyzowski's reactions. Very old bloodstains, and those which have been treated with soap or alkalis sometimes give uncertain results.

THE EXAMINATION OF SPERM

Sperm stains are recognizable by the starched appearance which they give to fabric and to the geographical formation of the borders of the stain. The appearance, however, is not specific, and does not serve to identify the origin of the stain. Fresh stains have a characteristic smell which can be readily identified. The dry stain has as a rule no smell, or if it has, it is characteristic of urine.

Florence Reaction.—There is no specific chemical test for seminal fluid or stains. The Florence reaction must be applied. 1.5 grams of potassium iodide and 2.5 grams of iodine are dissolved in 30 cc. of distilled water. This must, of course, be done with the usual precaution of dissolving the iodine first in a concentrated solution of the potassium iodide. A small portion of the stain is mixed with the reagent on a microscopic slide and the reaction watched under the microscope. The formation of brown rhombic crystals occurs in the presence of sperm. Pus, blood, urine, and saliva also respond to the Florence reaction.

The only specific test for sperm is the microscopic detection of spermatozoa. The identification of spermatozoa should, however, on no account be attempted by a chemist who has not specialized in such work. Several cases are on record where vaginal fluids containing flagellate protozoa have been reported to contain spermatozoa. A physician specialized in such examinations must make the report.

It is, however, often desirable to stain the preparation. Spermatozoa if treated with silver nitrate which is afterwards

reduced are stained black by the reduced silver salt. A portion of the stain is soaked in a 3% solution of silver nitrate for six hours at a temperature of 50 C. The stain is then washed thoroughly in one of the following solutions. (*See p. 12*).

Water	100	Water	100
Formalin	5	Hydroquinine	1.6
Pyrogalllic acid	4	Sodium sulphate	10
Pyridine	8	Pyridine	8

The stain is then again washed for half an hour in water. A portion of the stain is then carefully transferred to a microscopic slide and mounted in the ordinary way. Spermatozoa are much more readily identified when stained in this way than when they are unstained.

OTHER STAINS

Stains are often of sufficient size to make a more or less complete analysis possible. It is important, however, to distinguish between those amenable to chemical analysis and those which require other examination. Obstetrical stains, those made by urine, or faeces are not amenable to chemical examination. It is for this reason that as complete a preliminary examination as possible should be made before any systematic tests of a more specialized nature are carried out. The need for avoiding any wastage of the material examined must be emphasized. It applies to all forensic chemical operations. The rule should be to use as little of the sample as possible, and where it is practicable sufficient of the sample should be left for independent confirmation of the results. It is not possible, of course, to lay down any general rules for chemical examination other than those already described. On the other hand, there are certain types of stain of which a systematic examination can be made.

Wax Stains.—Stains made by candle grease are generally recognizable as such. In certain circumstances it may be of great importance to determine if the wax agrees in composition with that of a given candle. This type of examination was, for

example, required in the inquiry into the murder of Vera Page (*Rhodes, Garda Review, April, 1935, 496*).

In order to ensure a sufficient removal of the wax stain it should, if upon cloth, be extracted with ether in a Soxhlet apparatus. In cases where the stain is large and can readily be detached from the surface to which it adheres, this procedure is not necessary.

There are three general tests which should be applied to stains of wax. (1) Melting Point, (2) Specific gravity, (3) Acidity.

The melting point is determined in the usual way, the wax being contained in a closed capillary strapped to the thermometer bulb. The impure stearic acid of which candles are made has a melting point of between 51° and 58° C.

The density of the wax is of the order of 0.850 (water = 1).

Acidity is determined by treatment of the wax with neutral alcohol (95°). The mixture is heated over a water bath, agitated, and allowed to cool. The acid is then titrated with 0.1 or 0.01 N sodium hydroxide, according to the quantity of wax taken. The result may be expressed as an acid number or as acetic acid.

Dangl (*C. r. Academie Inter. de Crim. Vienna, Oct., 1930*) makes use of an interesting crystallographic method for the identification of candle wax. He has shown that if the wax is melted under carefully controlled conditions of temperature and then cooled, it shows a characteristic structure which is clearly shown microscopically under polarized light.

In practice a small quantity of the wax is melted exactly at the temperature of fusion upon a microscopic slide, the preparation being protected by a cover slip. On cooling the wax is examined with polarized illumination. As a result of the treatment, highly characteristic crystalline structures are observed which serve to distinguish different samples of wax.

The author points out that this method is particularly successful with the cheaper forms of paraffin wax which contain derivatives of fatty acids which raise the melting point of the wax. The treatment produces conditions analogous to those which obtain when a metallic alloy is cooled and passes from the dystectic to the eutectic state. As with metallic alloys, well defined structures which can be identified result.

The method is of great value particularly when small quantities of wax have to be examined. It is essential, however, that the temperature is carefully controlled by means of a thermopile and that the samples are cooled under identical conditions. Strictly, this involves comparison of samples of identical volume and weight. The test can be carried out on a few milligrams of the sample and thus in circumstances in which classical methods are not applicable.

Stains of Oil or Grease.—Stains of oil or grease should be extracted with chloroform. The solvent is then evaporated. If the residue is sufficient the iodine number should be determined, 0.2 to 0.3 gm. is necessary. Hubl's method (*Locard, Traité de Criminalistique, II, 857*) is convenient. The iodine number must, however, be interpreted with caution since the stain may consist of a mixture of oils. On the other hand, conclusions of a general nature which are of value can frequently be drawn. A very high iodine number, for example, will exclude butter, margarine, beef and mutton fats, and others of a similar class. A very low iodine number indicates a number of waxes such as Carnauba, Japan, and China waxes and stearic acid. The physical state of the fat should also be noted, *i.e.*, if it is liquid or solid at normal temperature. If solid, the melting point should be determined. In general, the waxes have high melting point. The true fats melt at a lower temperature.

Paint Stains.—The composition of these stains can usually be more precisely determined than those of any other type. White paints may consist of compounds of lead, zinc, or barium. Blue paints usually consist of Prussian or Turnbull's blue. The lighter blue paints contain copper salts.

In general the stain should be dissolved in nitric acid. The usual tests can be applied for the identification of the base present. If the presence of lead sulphate is suspected the stain must be treated with ammonium acetate. The lead is then identified by the formation of the yellow lead iodide on treatment with potassium iodide.

The table below sets out the more common mineral pigments :

<i>White</i>	<i>Blue</i>	<i>Red and Yellow</i>	<i>Red</i>
Lead Hydrocar- bonate $2\text{PbCO}_3 \text{ Pb(OH)}_2$	Prussian blue	Chromates and diochromates of lead	Lead oxide Pb_3O_4
Lead Sulphate Pb SO_4	Turnbull's blue		
Zinc oxide Zn O	Basic Car- bonate of copper		Mercurice sulphide Hg S
Lithophone ZnS Ba SO_4			
Barium Sulphate Ba SO_4			

Mud Stains.—It is often of great assistance to make a complete examination of mud stains, whether found upon clothing, boots, or elsewhere. In the case of stains upon boots the quantity of the sample available is often sufficient to make a full analysis, by classical methods, possible. This may also hold good in other cases. Even if the quantity is small as complete an examination as possible should be made.

The sample should be treated with hydrochloric acid and evaporated to dryness, the acid treatment and evaporation being repeated a second time. The insoluble residue which will consist mainly or entirely of silica is filtered off and washed with hot water.

The filtrate contains metals and bases which can be identified by the methods already described (*see page 20*). The main constituents will generally be found to be iron, aluminium, magnesium, and silica. Traces of other bases may, however, establish the individuality of the mud and identify it with a given locality.

A quantitative estimation of the sample should also be made if the amount of material permits of it. It is, in fact, generally

impossible to identify the material if quantitative comparison cannot be made.

For the analysis of mud and soil, Beroud (*Rev. Inter. de Crim.* 3, 1933, 158) recommends the following method.

About two grams of the sample are treated after being finely ground in a mortar with 10% hydrochloric acid. The mixture is boiled and then filtered. The residue is washed free from chlorides, ignited and weighed. The result is expressed as matter insoluble in hydrochloric acid.

The Filtrate.—The filtrate is diluted, an aliquot part is taken and a colorimetric determination of iron made using ammonium thiocyanate. The result represents the quantity of ferric iron present in the filtrate.

For the estimation of calcium the solution is boiled to remove excess of hydrochloric acid. It is then made alkaline with ammonia and a slight excess of acetic acid is added. A saturated solution of ammonium oxalate is then added after bringing the acidified solution to boiling. The precipitated calcium oxalate is left to settle for some hours, and is then filtered. The precipitate is filtered off and washed with hot water. It is then strongly ignited and weighed as calcium oxide.

For the purposes of comparison of one sample of mud or soil with another Beroud considers that these three estimations are sufficient. In our experience, it is preferable to carry out a more complete analysis. It is in any case advisable to separate aluminium and iron. Matter insoluble in hydrochloric acid can be treated with strong hydrochloric acid, evaporated to dryness and baked to render all the silica insoluble. The determination of moisture will not give comparative results of any value other than in exceptional cases. The loss on ignition of the dried sample should, however, be determined. The loss will represent mainly organic matter and dehydration of silicates. This figure is of value in comparing the results of different analyses.

It is of great importance to make an examination of mud stains with a view to the identification of individual constituents imbedded in them. The present writer recalls a case in which the mud on a pair of boots was found to consist of two layers separated by a whitish layer of foreign material. On

examination this proved to be starch. The identification of this substance between two layers of mud represented in this case entry into a flour mill and a return. A very careful examination should therefore always be made of a section of the mud. Any stones or other particles imbedded in it should be removed and if possible identified by chemical or other means.

For this purpose a portion of the mud (if necessary with preliminary drying) should be powdered and carefully examined for foreign particles. Many of these will not be amenable to chemical examination but may be recognizable on inspection. In special cases where such bodies as grass seed are found the co-operation of an expert should be sought. Minerals may be present of a type which can be identified by a mineralogist. The chemist must confine himself to the examination of materials amenable to chemical examination, but he should put himself in a position of being able to seek the co-operation of the appropriate expert when necessary.

CHAPTER IV

FIREARMS AND EXPLOSIVES

(a) The Chemical Examination of Firearms

General.—The chemical examination of the products of explosion in the barrels of firearms frequently produces evidence of considerable value from a forensic point of view. In cases of shooting, therefore, when the discovery of the firearm places it in the category of *corpus delicti*, a chemical examination of the contents of the barrel must always be made. In this connection, however, as in many others, the results must be interpreted with caution. Hans Gross, for example (*Criminal Investigation*) in discussing the interpretation of the results suggests that the period at which the gun was fired can be determined within very narrow limits if the products of explosion have been identified. His conclusions, however, require modification, and positive conclusions should not be founded upon facts which experience has shown do not in all cases admit of precise interpretation. On the other hand, the presence or absence of certain substances can be correlated with the time factor within certain limits.

Types of Powder.—There are two forms of powder commonly used in cartridges, namely, black and smokeless. They are of very different composition and the products of their decomposition vary greatly. It is therefore of importance to know the type of powder which has been used in the case under examination. In the absence of other evidence it may be possible to decide this from the chemical examination of the residues.

Military rifle ammunition usually contains smokeless powder. Sporting ammunition either black or smokeless powder.

Automatic pistols and revolvers are generally loaded with smokeless powder, but the ammunition may contain a mixture of black and smokeless powder.

Composition of Black Powder.—Black powder is essentially the classical gunpowder which does not vary in composition from early types. It consists of charcoal 15%, potassium or sodium nitrate 75%, sulphur 10%. These proportions are approximate, but in good powder should not vary more than $\pm 1\%$. Modern gunpowder is very uniform in composition, but the purity of the constituents varies as do the proportions of the ingredients within narrow limits.

Products of Explosive Decomposition.—As is generally known every explosion results in the formation of large quantities of gas. The gases produced by the explosion of black powder are carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen, and sulphuretted hydrogen. The following solid substances are also decomposition products. Potassium carbonate, potassium sulphate, potassium sulphide, potassium thiocyanate. With the exception of the sulphuretted hydrogen the gases formed have little forensic importance. It is the identification of the solids which provides evidence of value.

As Fleury, Silveira and others have noted, explosive decomposition is never complete. Traces of free sulphur remain and small quantities of unburnt charcoal. Chavigny has stated that traces of potassium nitrate may remain undecomposed. Lucas, however (*Forensic Chemistry*, p. 202), does not confirm this observation. The present author has never discovered nitrates among the decomposition products of explosion of black powder.

From a forensic point of view only those products of decomposition are important which, if identified, serve to indicate the time at which the shot was fired. The substances for which tests should be made are sulphides, sulphates, thiosulphates, thiocyanates, iron (ferrous and ferric), nitrates, nitrites and alkalinity.

Lucas (*Forensic Chemistry*, p. 205, *et seq.*) has carried out an interesting series of experiments relating to the composition

of the products of explosions in the barrels of firearms at known periods after firing.

He has found that sulphuretted hydrogen will persist in the barrel of a weapon of which the breech has been closed for two to three hours ; if the breech is open, however, the gas disappears in from one to five minutes.

The greater part of the sulphides has decomposed in from four to five hours, but traces have been observed to remain for ten hours.

Sulphates are present at all periods but they increase in quantity with time owing to the oxidation of the sulphides.

Thiosulphates are one of the decomposition products of the sulphides. Thus they appear only when the sulphides have decomposed. It would appear that they result from the oxidation of the potassium sulphide.

Thiocyanates are occasionally found present.

Ferrous iron is always present in the residue, but it undergoes slow oxidation. It would appear that ferric iron is first found after twenty-eight hours. It is not, however, found in a soluble form earlier than after thirty-three days. Varying conditions such as those of atmospheric moisture influence these reactions.

Nitrites are never found less than four hours after the shot was fired. The presence of sulphides interferes with the formation of nitrites so that their appearance is contemporaneous with the decomposition of the sulphides.

These interesting experimental results confirm and considerably supplement the findings of Chavigny (*L'expertise des plaies par armes à feu, Paris, 1913*).

Smokeless Powders.—These powders consist essentially of nitro-cellulose which may exist as the sole ingredient or mixed with nitro-glycerin. Other varieties contain vehicles such as mineral jelly with the addition of potassium or barium nitrate. Macerated wood is also an occasional ingredient.

The products of explosive decomposition are gaseous and solid, the gases being mainly carbon dioxide, carbon monoxide, nitrogen and hydrogen. The solid products are nitrites, nitrates, and sulphates. Sulphides are generally absent.

The condition of the barrel from which a cartridge containing

smokeless powder has been ejected differs greatly from that produced by black powder. In the first place the fouling of the barrel is less marked and is much lighter in colour.

An aqueous solution of the contents of the barrel is either colourless or slightly brown. Nitrites may be and generally are present. Black powder on the other hand produces a much darker solution in which nitrites are never found. The reaction of the aqueous solution of the residuum of smokeless powder is neutral whilst that of black powder is alkaline.

Variations in Composition.—Smokeless powders vary greatly in composition so that the products of their explosion also vary. It is not, however, generally possible to base any conclusions of a precise nature upon such variations. The quantity of nitrate found, however, is much greater in some cases than in others. This might exclude certain powders known to produce only small quantities of nitrates on explosion. More specific evidence is supplied by the presence of barium or chromium in the residues. These more unusual constituents may give an indication concerning the type of powders used.

Examination of the Barrel Residue.—The appearance and smell must be noted as soon as the firearm is received. Before the breech is opened a test should be made for sulphuretted hydrogen with lead test paper in the usual way. With the breech closed the paper will naturally be applied at the muzzle as close as possible and should be retained there for not less than a minute.

If the reaction is negative, the breech should be opened and a current of air should be blown through the barrel. The breath should not be used. A rubber bulb with a short nozzle is the simplest method of injecting air.

The barrel is then rinsed with boiling distilled water. This can best be done with a wash bottle fitted with a very fine jet. The firearm should be supported with the barrel in a slanting position and with the muzzle placed over a small beaker to catch the liquid. Small washing should be used and a rotary motion given to the nozzle of the wash bottle. The total volume should not exceed 25 cc. After this first washing the

washings should be returned through the barrel pouring through the whole volume as quickly as possible. This operation should be repeated a second time. By this means an efficient washing of the barrel is assured.

The colour, appearance, and smell of the solution must be noted. The reaction to phenolphthalein should also be examined. Alternatively, the approximate hydrogen ion concentration may be determined by means of a universal indicator.

The solution is then filtered and the appearance of the residue noted. The filtrate is treated as follows: (1) If alkaline, a portion of the filtrate should be neutralized, (2) A further portion should be acidified with hydrochloric acid free from iron.

(1) **Sulphides.**—Solution (1) should be tested for sulphides with lead acetate.

(2) **Ferrous and Ferric Iron.**—The most satisfactory test for ferrous in the presence of ferric iron is the $\alpha \alpha'$ dipyridyl reaction (*see p.29*). The pH of the solution should be slightly on the acid side (up to 3.5). The reagent is used in aqueous solution.

Potassium thiocyanate may be used for the identification of ferric iron. If a more delicate test is required the 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) in aqueous solution may be used. It has been stated (Yoe, *J. Amer. Chem. Soc.*, 1932, 54, 4139) that this reagent will detect concentrations of ferric iron of the order of 1 in 10,000,000. It is in any case more sensitive than the classical test with potassium thiocyanate. The test solution should not exceed pH 3. The thiocyanate test is, however, generally sufficient.

Sulphates.—The classical test with barium chloride should be used. The portion used should be that faintly acidified with hydrochloric acid.

Nitrates.—Lucas (*Forensic Chemistry*, 211) has pointed out that the tests with brucine or the 1-4 diphenyl-3-5 endanilo-4-5 dihydro-1-2-4 triazole are unsatisfactory owing to the

interference of ferric salts, nitrites, and other substances which may be present in the residues of powder. This author recommends the classical "black ring" test or that with phenolsulphonic acid and ammonium hydroxide.

The diphenyl-benzidine test is, in our experience also satisfactory. A 0.02% solution of the reagent is used in pure sulphuric acid. 2 cc. of pure sulphuric acid are added to every 1 cc. of the solution to be tested. 1 cc. of the reagent is then added. After standing 24 hours a blue colour develops in the presence of nitrates. It should be borne in mind, however, that the "black ring" test is, with careful manipulation, very sensitive, and it can be carried out on a very small quantity of solution.

Nitrites.—Nitrites may be identified as follows. A solution of sulphanilic acid is prepared by dissolving 0.8 gram of the acid in 100 cc. of distilled water. The second reagent consists of a solution of 0.5 gram of naphthylamine hydrochloride in a 0.8% solution of hydrochloric acid. To 10 cc. of the solution 0.2 cc. of the solution of sulphanilic acid are added followed by 0.2 cc. of the solution of naphthylamine hydrochloride. The mixture should be stirred and let stand for half an hour. A pink coloration indicates the presence of nitrites. (*Lucas and Barral.*)

Potassium.—A 1% solution of hexanitro-diphenylamine in 0.1 N sodium carbonate may be used to identify potassium (*see p. 31*). Other substances likely to be present do not interfere, but if ammonium salts are present they must be removed.

Interpretation of the Results.—It is necessary to repeat that the results of the analysis must be interpreted with great caution. In preparing the report, the chemist should state the findings of the analysis precisely and he should then indicate the probable conclusions to be drawn. On no account should any dogmatic statement be made. If the examiner is in doubt it is preferable to withhold judgment altogether than to draw too positive an inference from the evidence supplied by the analysis. The following points, however, will serve as a guide.

Smell.—If the smell is marked it is probable that the firearm has been very recently fired. It is not generally possible to identify the smell as positively resembling sulphuretted hydrogen although some examiners profess to be able to detect this in a recently fired firearm. The smell differs with black and smokeless powder and the odours can be distinguished by an experienced nose. (*Chavigny, Supra.*)

Appearance of the Deposit.—This requires guarded interpretation. In general the deposit left by black powder is much darker than that of smokeless powder. Söderman and Gerard have noted that whilst a black powder freshly fired is black or dark grey in colour, it may become light grey or even white with the lapse of time. If therefore the deposit smells very faintly, and is white, the charge may have been one of black powder. On the other hand, a strong smelling white deposit is most probably smokeless powder. It is not possible to identify a mixed powder residue by inspection and/or smell.

Sulphuretted Hydrogen and Sulphides.—If the smell of the residue resembles that of this gas, the firearm (a) has been very recently fired and (b) the charge consisted of or contained black powder. If an abundance of sulphide is observed, the gun was recently fired. If traces are present it was probably discharged more than five hours before examination. This, however, refers to black powder only. Sulphides are not found in the residue of smokeless powder.

Alkalinity.—An alkaline residue indicates that the original charge was one of black powder. The alkalinity varies inversely as the time, but no conclusion as to the time of firing can be drawn from this fact.

Sulphates.—Sulphates are always present in black powder residues and may be present in smokeless residues. Sulphides vary inversely and sulphates directly as the time. They are present at all stages in the residue. Although their quantity increases with time at the expense of the sulphides no positive conclusion can be drawn as to the time of firing.

Thiosulphates.—Thiosulphates are occasionally found in the residues of black powder but not in those of smokeless powder. Being formed by the oxidation of potassium sulphide they are not present in the early stages. No conclusion as to the time of firing can, however, be drawn from their presence.

Thiocyanates.—Lucas states that thiocyanates are occasionally found in the residues. No conclusion can be drawn from their presence.

Nitrates.—Nitrates if present to a very marked degree indicate that the residue is one of smokeless powder. Nitrates are seldom if ever present in the residue of black powder. The quantity may vary from a trace to that sufficient to produce a marked reaction.

Potassium and Sodium.—The presence of potassium does not directly indicate what type of powder was contained in the charge. Its absence, however, shows that the charge must have been one of smokeless powder since potassium is normally invariably present in black powder. But it must be noted that black powder is sometimes made with sodium nitrate. The absence of both sodium and potassium shows that smokeless powder was used.

Other Bases.—Barium, strontium and chromium are sometimes found in the residues of smokeless powder. The presence of constituents of this type may be a useful guide to the identity of the powder, and may provide important evidence of a negative character. It will, for example, explicitly exclude a number of powders known not to contain the constituents found.

These notes will make it evident that much useful information can be gathered from the examination of the residues found in the barrels of firearms provided due care is taken not to exaggerate the evidential significance of the facts. It will be clear, however, that the residue of smokeless can be distinguished from that of black powder, and that in certain circumstances chemical tests supply evidence of the time at which the shot was fired. Special types of smokeless powder

may be identified by reason of the presence of special constituents. These general inferences, often of value in themselves, can in most cases legitimately be drawn.

(b) The Chemical Examination of Bullets

The examination of bullets may give important information as to their identity and origin. Bullets are of two general types. (1) Those of uncoated lead and (2) those sheathed with a harder metal which covers a lead core. Both the lead itself and the coating material may vary considerably. Whilst the lead is of the ordinary commercial type, the impurities found in it, such as arsenic, antimony, and tin, vary often to a sufficient extent to make identification possible.

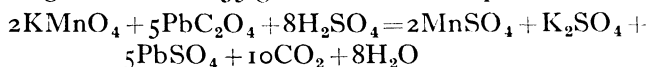
Coatings are of various types. They may consist of cupr-nickel, soft steel, copper-zinc or copper alone. British rifle bullets are coated with an alloy of 80% of copper and 20% of lead. American coating consists of 90% of copper, 8% of zinc, and 2% of tin. French bullets are frequently copper sheathed. An analysis of the bullet will thus give a clue to its origin. In any case, comparison of the analysis with that of unfired ammunition may be the means of tracing the bullet to its source.

Preliminary Examination.—The first and most important operation is to weigh the bullet accurately. Bullets show great variations in weight but the weight of the bullets of the same type are constant within fairly narrow limits. Variations of the order of ± 0.4 gram may be found in bullets of the same type, so that small differences are not of much evidential value.

When the weight has been determined, reference should be made to the manufacturers' catalogues. These generally record the maximum and minimum weights of the bullets so that an indication of the origin of the bullet may be obtained from the weight alone. On the other hand, the weights of bullets of different makes often lie close together and caution must be observed in interpreting evidence of weight. As a sorting test it may, however, be of great value.

Analysis.—Determination of Lead.—The lead can be estimated in the form of sulphate by solution of a weighed portion of the bullet in sulphuric acid to which has been added ammonium sulphate to avoid the precipitation of the tin. The disadvantage of this method is that the results tend to be too high if tin is present owing to the formation of the insoluble stannic sulphate. If tin is absent, the method is satisfactory.

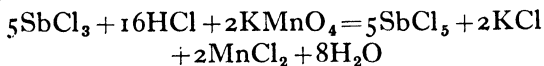
In the author's experience the volumetric estimation of the lead oxalate is the most convenient. The weighed portion is dissolved in nitric acid. It is then exactly neutralized with sodium hydrate. Oxalic acid is then added in excess (ammonium oxalate must not be used). The precipitated lead oxalate should be allowed to stand for two hours. It is then filtered. The precipitate is washed with hot water and dissolved in very dilute nitric acid. Sulphuric acid is then added and the solution titrated with 0.1 N potassium permanganate. 1 cc. of potassium permanganate = 0.01035 gm. Pb. and the equation is :



Antimony.—If antimony is present without tin the weighed sample should be dissolved in strong nitric acid and the solution diluted with water. The antimony remains as an insoluble residue of hydrated Sb_2O_3 . The oxide is filtered off, ignited after separation from the filter paper. Before ignition it should be moistened with nitric acid and gently heated before burning.

Antimony and Tin.—If these metals are present together the solution from which the lead has been removed should be treated with sulphuretted hydrogen. Both antimony and tin are precipitated. The precipitates are dissolved in a 10% solution of hydrochloric acid which must be heated until the mixed sulphides are dissolved and the sulphuretted hydrogen completely expelled. Boiling must be avoided or antimony will be lost.

The solution is then diluted so as to reduce the acidity to about 1%. It is then titrated with 0.05 N potassium permanganate.



To estimate the tin, the same solution should be evaporated to about 150 cc. The solution is then reduced by the addition of about 50 cc. of strong HCl and some fragments of pure iron and a trace of metallic antimony. It is essential that the tin should be completely reduced to stannous chloride. To ensure this the solution should be transferred to a second flask containing iron and a little hydrochloric acid, the reaction having been first allowed to continue for two minutes. The solution is then boiled until the iron is dissolved and while cooling the flask must be connected with a carbon dioxide generator. The titration must also be carried out in an atmosphere of CO₂. It is effected with 0.1 N iodine solution using starch as indicator.



Iron, lead, and antimony do not interfere with this estimation. Copper is unobjectionable if less than 3% is present (*Scott*). Arsenic, however, must be removed. The separation can be effected by distillation owing to the volatility of arsenic trichloride.

Nickel.—This metal can be conveniently determined with dimethyl-glyoxime. Lead, copper, and tin must, however, first be removed with sulphuretted hydrogen. The filtrate from which the sulphuretted hydrogen has been removed should be nearly neutralized. It is then boiled and a 1% solution of dimethyl-glyoxime in alcohol is added. A brilliant red precipitate (C₄H₇O₂N₂)₂Ni is formed. It is filtered through a tared Gooch capsule, thoroughly washed, dried at 110° C. until constant in weight. The complex contains 20.31% of nickel.

Interpretation of Results.—The interpretation of the results of the analysis is straightforward. The analysis is undertaken either (1) to compare it with that of a bullet of known manufacture, or (2) to compare it with ammunition found in possession of a suspected person. In these circumstances either the analyses will agree or they will not. If they agree there is strong presumptive evidence which may amount to a certainty that the bullets are of the same origin. Conversely, the negative evidence may be equally conclusive. There may be certain

circumstances in which the bullets of differing origin agree fairly closely, but in general if it can be shown that, say, three constituents of two bullets are identical quantitatively, their identity is established.

(c) The Chemical Examination of Explosives and Explosions

This type of examination comes down in practice to being one of exploded or unexploded bombs of a certain type. Until recently such destructive instruments were not commonly met with in this country in connection with criminological enquiries. Recent affairs in England have, however, brought the question into prominence.

For forensic purposes bombs are of two general types, the military and the chemical. If as occasionally happens a military bomb is associated with a crime, it may be brought to the laboratory for examination. Only in exceptional circumstances should the chemist attempt to deal with this kind of bomb. He should refer the matter to an ordnance officer with experience in military bombs if one is available. Special precautions are necessary in opening military bombs. Thus the intervention of an expert is desirable.

Chemical bombs are of an entirely different type. Essentially they consist of an explosive mixture in which is imbedded a glass or other vessel containing strong acid. The explosion results when the acid comes in contact with the mixture. There are different ways of effecting this. The simplest is that in which the acid container is open, and the acid removed from it by some sharp movement. This is the crudest form and can only be used in small bombs which are thrown. There is a second type in which the glass container is very thin but closed. It breaks upon impact and thus explodes the mixture. This type of bomb must also be thrown.

The more elaborate type of "time" chemical bomb includes clockwork mechanism which operates a falling weight. This weight breaks the glass container and so explodes the bomb.

A third type has its timing adjusted in a different way. The

acid-containing vessel consists not of glass but of some material more or less slowly attacked by strong acid. The time required by the acid to disintegrate a material of given quality and thickness is determined empirically. A container is then chosen of such a quality as to release the acid in the required time. Rubber is the material usually employed.

The type of bomb concerned in a criminal enquiry is almost invariably of the home-made chemical type. In the nature of the circumstances it is hardly probable that a military bomb could be secured or manufactured. A chemical examination is therefore generally necessary in criminal cases which involve bomb outrages. Such crimes are generally of the quasi-political type, but this is not necessarily the case. In certain cases the use of bombs may accompany the perpetration, or attempted perpetration of the ordinary criminal offence.

Preliminary Examination of Unexploded Bombs.—The very greatest care should be taken in examining and handling an object suspected to be an unexploded bomb. This warning might appear to be unnecessary, but it is not so in fact. It must be noted in the first place that a chemical infernal machine is not necessarily recognizable as such. Any kind of innocent-looking container may be used. Such articles as petrol cans and paint pots have been used for the purpose. In many cases indeed receptacles of this kind are deliberately chosen by reason of their unsuspecting appearance. Secondly, even trained individuals are sometimes extremely careless, so that the injunction quoted in one textbook that a suspected bomb "should on no account be shaken, inverted, or dropped upon the floor," is not so unnecessary as some might suppose. In one case within the author's own experience, an unexploded bomb contained in a paint pot was left on a laboratory bench for a few moments by the examiner without any warning notice attached to it. It was handled by an assistant unaware of its nature. The bomb exploded, part of the room was severely damaged and the assistant injured.

Before any attempt is made to open the bomb, it is advisable to take a radiograph of it if this is practicable. This will generally give an indication of the disposition of the contents,

and what is most important the position of the glass or other vessel in which the acid is contained. The most dangerous type of unexploded bomb is that which carries an indiarubber acid container. If this is suspected no attempt should be made to open it, and it should not, in fact, be taken to the laboratory at all. The only method to follow is to explode it in any open space and proceed to the examination of the products of explosion.

Bombs containing glass containers can generally be safely opened if proper care is used. It is necessary, however, to work with extreme caution and carefully to consider every step before it is taken. Any moveable parts of the bomb should be detached and in particular any clockwork mechanism if it is visible. The lid or cover should then be removed if possible or if none exists a suitable method of opening should be chosen. It is, of course, impossible to lay down rules. Alike in principle home-made chemical bombs differ greatly in manufacture. The only rule to follow is to make a careful examination and then cautiously to attack the weakest point if it is judged that that point is not connected with any kind of detonating mechanism. If the container is so solid that any great degree of force is necessary, no attempt involving force to open it should be made.

If it becomes evident from the examination that the bomb includes mechanism which operates a hammer or falling weight, steps should first be taken to disconnect this mechanism and make it harmless. Care must be used in this operation or a result contrary to the one desired may occur. It is generally possible, however, to interpose an obstruction between the hammer or weight and the object it is designed to strike before anything else is done.

When a bomb is opened, it will probably be found to contain a glass or other container filled with acid. This may be open or closed. If open the container should be stoppered before removal. Alternatively the acid vessel may contain a lead or iron weight which makes great caution necessary in removing it. The first step to take is to separate the acid container from the surrounding material. It may be possible to do this by merely withdrawing it, but if it is firmly imbedded this may be very unsafe. It is often preferable to remove the explosive

material leaving the container isolated in this way. At this stage the examination of the contents can be safely attempted.

Examination of Exploded Bombs.—The chemist should visit the scene of the explosion and make a careful examination. He should personally search for and collect the debris, and preserve it in labelled bottles with a note as to the position of the fragments collected. This preliminary examination may be of very great value since it will indicate the extent and thus the force of the explosion, the nature of the bomb casing, and of the materials used as projectiles. The explosive mixture usually contains fragments of iron which, of course, fly in every direction when the explosion takes place. All these fragments should be collected and carefully scrutinized since their physical appearance may give some indication as to the nature of the bomb.

Composition of Chemical Bombs.—The substances used to make chemical bombs are not very varied. They consist generally of mixtures of picric acid and potassium chlorate or potassium chlorate and sugar. Sulphur is a more exceptional ingredient. There are, of course, special cases as, for example, when metallic sodium is used as a constituent. In this connection it is important to remember that an unexploded bomb must not be placed in water unless it is certain that it does not contain this metal. Potassium chlorate generally forms one of the main constituents and picric acid is commonly found. A mixture of potassium chlorate and sugar is the simplest to secure so that amateur bombs often consist solely of these constituents.

The acid used is generally sulphuric acid, but nitric acid may be employed in some cases. Hydrochloric acid is very seldom found and where a timed detonation depends upon corrosive effect it is less suitable than the more corrosive agents.

The Products of Explosion.—Chemical bombs when they explode are seldom completely decomposed. Traces and in some cases appreciable quantities of the reacting materials remain unchanged. If these traces can be identified very

valuable evidence may be secured as to the composition of the bomb.

Traces of picric acid, for example, may remain undecomposed. An alcoholic extract of the residue should be made and the alcoholic solution should be evaporated to dryness. The residue is taken up in water. The simplest tests for picric acid are its characteristic yellow colour in aqueous or alcoholic solution, its power to dye wool intense yellow, its acid reaction to litmus paper, and bitter taste. If sufficient of the test material is available a few drops should be warmed with a saturated solution of potassium cyanide. A red coloration indicates picric acid.

In some cases, potassium chlorate may be found unchanged after the explosion, but the normal product of chlorate explosions is chloride. A test must always be made for chlorides and if they are abundant potassium chlorate was probably originally present. This, however, does not necessarily follow since chlorides might have been present in the original mixture.

A test should always be made for sulphates. Their presence usually indicates that sulphuric acid was used in the bomb. This conclusion, however, must be drawn with reserve since sulphate salts may be, although they seldom are, constituents of the explosive mixture. Sulphates also result from the decomposition of elemental sulphur if the original mixture included the element.

Nitrates may be identified by the black ring test or as follows : The aqueous solution is neutralized with sodium carbonate and evaporated to dryness. The residue is then moistened with 0.2 cc. of phenol sulphonie acid and allowed to stand for a few minutes. The mixture is then diluted with a little water and strong ammonia is added in excess. A yellow colour indicates the presence of nitrates.

A test should be made for potassium with hexanitrodiphenylamine (*see p. 31*). Potassium is almost invariably present in chemical bombs, but potassium salts are not absolutely essential. The absence of this metal may be useful evidence of identification since chemical bombs without potassium salts are unusual.

Interpretation of the Results.—It is obvious that the results of the analysis can only be interpreted generally. The presence of nitrates, sulphates, or chlorides does not enable the examiner to draw positive conclusions as to the original combination in which they existed. But the presence of chlorides and potassium probably indicate that potassium chlorate was originally present. If nitrates are present without potassium, nitric acid may have formed part of the original bomb. If potassium and nitrates are present together no definite conclusion can be drawn unless sulphates are also present. If sulphates, nitrates, and potassium co-exist potassium nitrate and sulphuric acid were probably present. These general conclusions should be borne in mind, but they must not be regarded as other than provisional in the absence of confirmatory evidence.

Examination of the Fragments.—The fragment if analysed may provide valuable evidence. It is, of course impossible to suggest a scheme of analysis since every case must be treated individually. The fragments will, of course, be metallic and on complete analysis may give an indication of the source of the container of the bomb. Pieces of drain-pipe have, for example, been used as containers. The piping has ultimately been traced to its source by reason of the evidence of the analysis. In any case, a careful examination should be made of the fragments particularly as to their shape and size even if the analysis is not undertaken.

Examination of Suspects.—In no kind of enquiry is an examination of the suspect's person and clothing so important as in the case of bomb outrages. First, a mere inspection of the skin of the fingers may indicate that picric acid has been handled by reason of the characteristic staining. Secondly, the deposit under the fingernails should be minutely examined. Traces of chemicals in an unchanged state may be identified in this manner, and proof obtained that explosive substances have been handled. Thirdly, the dust on the clothing may contain traces or even sometimes an abundance of these chemicals. This evidence is obviously of first-rate importance

and the more so if the results can be correlated with those secured by the examination of the residues of the explosion. It will be obvious, for example, that if an abundance of chlorides is found in the residue of an explosion, and that potassium chlorate is found in the clothing of a suspect, there is strong presumptive evidence to connect him with the manufacture of the explosive agent.

On the other hand, the examination of the clothing of the victim of an explosion may give information concerning the composition of the bomb. Lucas quotes a case of a policeman injured by an explosion whose white tunic was stained yellow with picric acid at the place where a fragment of the bomb struck him.

CHAPTER V

THE CHEMICAL EXAMINATION OF QUESTIONED DOCUMENTS

(a) Constitution of Inks

General.—Whilst chemical examination of documents is not the only type of examination applicable to them, it forms an increasingly important part of any enquiry relating to a questioned document.

It is essential to remember that from a forensic point of view documents other than those suspected of being forged may have to be examined. There is hardly any kind of criminal enquiry which may not require the examination of a document or documents. Even if they are genuine, it may become necessary to decide their origin, if anonymous, whether they contain writing in recent ink, and the date of writing. Occasionally evidence of identity may be secured by the development of fingerprints upon paper. These are examples of factual demonstration which are not necessarily concerned with the genuineness of the document as such. Forged documents, of course, remain as the principal problem met with, but the term questioned document more completely defines the subject matter of this kind of enquiry.

The Materials.—Essentially the materials of a document examination of any kind are the paper and ink or pencil. There are, of course, documents produced with neither of these materials which may be in question. In practice, however, it is not of great importance to consider them. It is sufficient to assume for all practical purposes that the investigation will be concerned only with paper and ink or pencil.

All paper, which consists essentially of cellulose, and most

inks can properly be described as chemical entities. Thus the materials are amenable to chemical examination which may and often does throw light upon their constitution. From the chemical state of the paper or ink inferences, important from a forensic point of view, can often be drawn. This is particularly true of ink, first, because it varies greatly in composition, and secondly, by reason of chemical changes which take place in it as it matures on paper. Essentially, chemical examination, which is significant from a forensic point of view, consists in a study of the ink and the changes which it undergoes.

Pencil writing has also some forensic importance. Chemically, however, it is of less importance than ink on account of the stable nature of the material used for the manufacture of the pigment. Since in modern pencils this consists mainly of graphite with a suitable filler, it does not undergo the changes associated with ink.

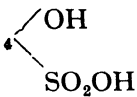
The so-called indelible or copying ink pencil is more readily amenable to chemical examination since it contains aniline dyes of varying types. Chemical tests of a conclusive nature are thus often applicable.

Types of Ink.—There are, of course, many varieties of ink but all modern ink is essentially of five types : carbonaceous inks, iron gall inks, iron gall inks with provisional colouring matter, logwood, and aniline inks.

Carbonaceous inks are very ancient, and the modern type does not differ essentially from the original. It consists of finely divided purified carbon which is mixed with gum and it is now generally supplied in liquid form.

Iron gall inks are in the historical sense much more modern than carbonaceous inks. They were not greatly used in Europe until the sixteenth century. They consist essentially of gallates and tannates of iron. It is, however, important to note that whilst iron is generally necessary many other substances can replace tannin. Condensation products of formaldehyde and phenol and their esters produce inks with iron salts.

It has long been known that the intensity of colour depends upon the hydroxyl structure of the organic agent. Thus

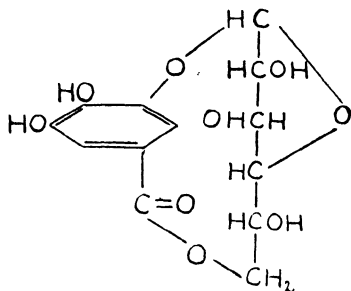
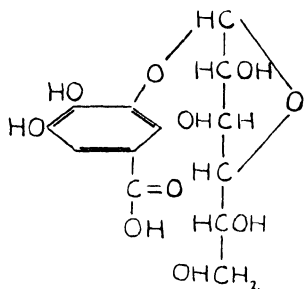
Schiff (*An. Chem. Pharm.* 1871, *clix*, 164) was apparently the first to observe that the coloration was proportional to the hydroxyl groups. Thus phenol sulphonic acid C_6H_4 

gives a violet colour with ferric salts. Gallic acid $C_6H_2(OH)_3COOH$ gives a more intense blue-black coloration.

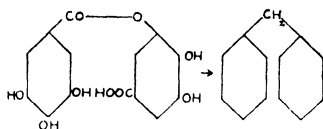
In their classical *Eisengallustinten* Schluttig and Neumann asserted that permanent pigments of this type were produced only by compounds with three juxta-posed hydroxyl groups. Thus haematoxylin, then believed to have the constitution $C_6H_2(OH)_3.C_6H_4.C_6H_2(OH)_3$ and gallic acid $C_6H_2(OH)_3COOH$ produced permanent coloration with iron salts hydroquinine $C_6H_4(OH)_2$ did not yield an ink.

Mitchell (*Analyst*, 1903, *xxviii*, 146) has shown that Schluttig and Neumann's conclusions relating to hydroxyl groupings also hold good for inks prepared with ammonium vanadate in place of iron, vanadium compounds being also "ink forming" substances. In view of more recent studies of the constitution of haematoxylin these conclusions must be modified.

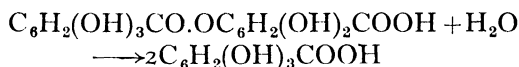
Constitution of Tannic Acid.—In regard to the constitution of tannic acid Feist (*Chem. Zeitg.*, 32, 1898, 918) isolated an acid and a lactone to which he attributed the following formulæ :



Nierenstein (*Ber. d. chem. Ges.*, 1905, 3641) obtained diphenylmethane by reduction of tannic acid and thus attributed the following formula to it :



By hydrolysis of tannic acid, Wittstein obtained gallic acid



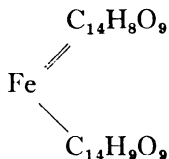
Fischer also regarded tannic acid as galoylgallic acid.

The structure of tannic acid cannot be said to be fully understood, but it seems probable that it contains three juxtaposed hydroxyl groups and that Feist's formula cannot therefore be accepted.

Tannates of Iron.—The manner in which the iron is combined in tannate of iron is not completely understood. The question, however, has considerable forensic importance because the changes which the iron salts undergo when ink is oxidized on paper have a bearing upon the age of the ink and thus upon the period at which the document was written. The table below represents the formulæ of various tannates of iron calculated by Schiff on the bases of Wittstein's findings :

Formula	Fe ₂ O ₃ calculated	Fe ₂ O ₃ found
C ₁₄ H ₉ (FeO)O ₉	20, 3	20, 15
C ₁₄ H ₇ (FeO) ₃ O ₉	44, 8	42, 8
C ₁₄ H ₆ (FeO) ₄ O ₉	52, 8	42, 8-56, 3
C ₁₄ H ₅ (FeO) ₅ O ₉	59, 0	56, 3
Fe(C ₁₄ H ₉ O ₉) ₃	7, 6	8, 4
Fe (C ₁₄ H ₉ O ₉) ₃		

Whilst these formulæ are of great interest as indicating the existence of several different forms of iron tannate they throw very little light upon its actual constitution or upon the changes which take place when the compounds are oxidized. In this connection another author, Hindrichsen (*Die Untersuchung von Eisengallustinten*, 1909) attributes the following formula to ferric tannate formed on the paper by oxidation.



He does not, however, put forward any conclusive evidence in favour of this formula.

The whole question of the oxidation of ferrous tannates in ink is still very obscure. Wittstein's formulæ do not include ferrous salts at all, those which are not ferric salts being of a basic type. At the same time, it has been experimentally shown that fresh iron gall ink does contain ferrous iron. It has already been observed that the oxidation of ink upon paper has considerable importance in judging the age of an ink-written document, but it has to be admitted that the mechanism of the change of the salts from the ferrous to the ferric state is very incompletely understood.

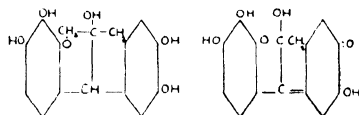
More recently, however, Zetzsche (*Ann.*, 1934, 435, 233; 1925, 445, 283) has studied the oxidation of ink. This author has found that on oxidation carbon dioxide is liberated. The conclusion is drawn that the compounds contain carboxyl groups. Zetzsche considers that the unoxidized ink consists of a soluble ferrous digallate and an insoluble ferrous monogallate and tannate. The preliminary pale colour of the ink is due to these compounds. On oxidation he considers that ferric monogallates and ferric pentatannates are produced. He appears, however, to consider that these salts are "acid" salts, that is to say that they include free carboxyl groups. They are blue-violet in colour. Esterification, however, takes place as the ink increases in age. These are described as secondary com-

pounds. They have a brown tint. The brownish coloration of old ink is thus explained.

Metzger, Rall and Heess (*Zeitschr. für angew. Chem.*, 31, 1931, 645; *Beiträge z. krim. Sympt. u. Techn., Arch. f. Krim.*, 92, 1933, 107) have made elaborate examinations of the pH values of ink on paper. They find that the average pH of paper = 4 and the lowering of hydrogen ion concentration of ink on paper is explained by them as being due to the buffer effect of aluminium sulphate present in paper. They appear to conclude that the natural acidity of inks inhibits the formation of ferric salts. But the reduction of hydrogen ion concentration brought about by contact with the paper increases the rate of oxidation of the iron.

These investigations which are of some practical importance will receive further consideration. Whilst much of the work of these investigators is of a fundamental character, it has been applied in particular by Metzger, Rall and Heess to the study of criminalistic and related questions.

Constitution of Logwood Inks.—Logwood contains two well defined compounds to which its pigmentation is due, haematoxylin and its oxidation product haematein. Rammstedt (*Tinte und Tuche. Chemischer Technologie der Neuzeit 2. Aufl. V. Bd.*) accepts Perkin's constitution of haematoxylin and considers haematein to have the constitution shown below.



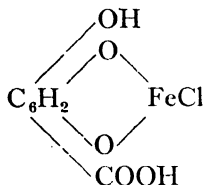
Haematoxylin

Haematein

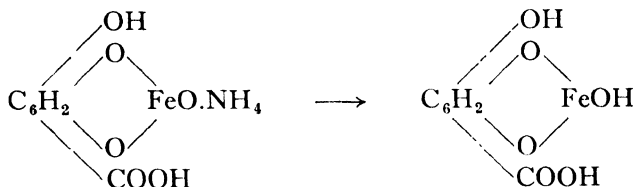
It will be noted that the constitution does not include three adjacent hydroxyl groups so that its behaviour does not agree with Schluttig and Neumann's theory concerning the pigmentation of ink-forming compounds.

The nature of the reaction between haematoxylin and the metallic salts is probably different from that of metallic salts with tannic acid and gallic acid. It has been customary to speak of iron gallotannates as if they were true salts.

Silbermann and Ozorovitz (*Chem. Zentr.*, 1908, II, 1024) have, however, assigned the formula :



to the compound produced by the interaction of ferric chloride and gallic acid. By hydrolysis of a compound which they describe as ammonium hydroxyferrigallate they have produced hydroxyferrigallic acid :



Having regard to the findings of Zetzsche it seems probable that at least some "tannates" may have an analogous constitution. Haematein, however, although it produces highly coloured compounds with iron salts has not an acidic constitution. It is coloured, the aqueous solution in a free state produces dark coloured compounds with alkalis. The structure of the compound it produces with iron is not understood.

The property of pigmentation under these conditions has nevertheless caused it to be used for many years as a constituent of ink. Lewis in 1748 made use of logwood to increase the coloration of iron gall ink. Later Runge (1847) found that logwood, when heated with potassium chromate produced a deep black solution which made satisfactory ink. It had the advantage of being neutral and thus did not corrode the pen.

INKS WITH PROVISIONAL COLOURING MATTER

Eisler in 1770 first introduced indigo into iron gall ink as a provisional colouring matter and to increase the intensity.

Indigo was first used in this country in 1836. Unoxidized iron gall ink is very pale in colour. Indigo and later aniline dyes thus became common constituents of iron gall ink.

The reactions that take place between provisional colouring matters and iron gall ink are not understood but they are in some cases probably of a very complex character. The present author (*infra* p.108) has shown that indigo retards if it does not entirely inhibit the oxidation of the ferrous iron in ink. This ink nevertheless attains great intensity of colour after it has been in contact with the paper for some time. It would thus appear either that the intensity of the coloration of ink does not essentially depend upon the oxidation of the iron or that the indigo reacts with the gallotannate of iron to produce a highly coloured compound more complex than the gallotannate.

Aniline dyes are also now largely used as provisional colouring matter in iron gall ink. They appear to exist in the ink essentially unchanged in the primary stages. Mitchell, however (*Documents and their Scientific Examination*) has made interesting observations concerning the changes in mature ink which contains provisional aniline colouring matter. After some years the aniline dye ceases to diffuse when treated with appropriate reagents. Mitchell suggests that this is due to the formation of a resinous tannate which mechanically fixes the dye. From the forensic point of view this property is very important since it gives an indication of the age of the ink (*infra* p.106). The observed formation of a resinous tannate is also of interest. The resinous gallotannate probably corresponds with the ferric pentatannates of Zetzsche.

A wide range of aniline dyes are appropriate as provisional colouring agents, but in practice methylene blue is most commonly used. The well-known blue-black effect is produced in this way. While the ink is fresh, aniline colour predominates but as the ink oxidizes it becomes darker. The colour appears black under the naked eye but dark purple microscopically. In some circumstances colour is an index of the age of the ink (*infra* p.105).

Aniline Inks.—Coloured inks are commonly aqueous solutions of aniline dyes to which are added some stabilizing agent such

as glycerine or gum. Red, black, green, violet and blue are the most common. Both basic and acid dyes are employed for their preparation. On the Continent a much wider range of colours is used as provisional colouring agents than in this country. In England the most common aniline ink is the black nigrosine fluid. These inks are particularly suitable for fountain pens. Their disadvantages are that the colour is fugitive so that they are unsuitable for documents in which permanency is required. Nigrosine ink does not fade but it can be easily removed from paper by washing.

Carbonaceous Inks.—These inks are less important from a forensic point of view to-day since they are less widely used. Chemically they are of less importance than other inks because they consist essentially only of purified and finely divided carbon suspended in a vehicle of water and gum. At the same time, carbonaceous inks are of great antiquity and were largely employed throughout the Middle Ages. Forensically disputes may arise concerning the authenticity of ancient documents which will require the examination of a carbonaceous ink. The simplicity of their composition and the fact that they remain practically unchanged with time makes their identification a fairly simple matter. Their chemical inertness precludes the more elaborate type of examination which may usefully be applied in the case of other inks.

(b) The Chemical Examination of Ink on Paper

General.—The examination of ink in the form of writing is essentially a problem of micro-chemical technique. This has been recognized for many years. The methods used to-day are, in fact, founded upon research effected by Robertson, Hoffmann and others in the late nineteenth century. The principle of their methods was to apply small quantities of reagents to ink strokes, and note the reaction which took place. The reagents commonly used were acids, alkalis, reducing and oxidizing agents, and reagents for the identification of individual constituents such as iron. Robertson and Hoffmann recommended

the use of a gold nib or glass rod to carry out the tests, minute drops being applied to the ink strokes.

Developments of Chemical Technique.—These classical methods with suitable modifications are still in use to-day. They have been systematized and brought up to date by Mitchell (*Documents and Their Scientific Examination*.) The types of reaction involved are that the acids react upon the iron tannate, the reducing agents, nascent hydrogen or chlorine have a bleaching effect. The oxidizing agents also produce bleaching of a less marked kind.

Bischoff (*Beiträge zur Kriminalistische Symptomatologie und Technik*) uses a similar technique in a somewhat elaborated form. He employs weak acids, strong acids, alkalis, oxidizing agents, reducing agents, reagents to identify iron, and special reagents.

These methods also involve the application of a different technique to the performance of the test itself. In the identification of iron, for example the acid is applied to the ink stroke and the spot is then transferred to filter paper upon which the test is carried out. This may appear to be an unimportant modification, but in fact it represents a radical departure from the earlier method which consists merely in "spotting" the ink stroke and observing the reaction *in situ*.

Technique External to the Document.—The departure consists in the actual removal from the documents of the materials of which it is composed. From a practical point of view this modification is of great importance. It involves greater alteration to the document itself than the spotting method. This must be noted because in a criminal enquiry it is essential to alter the documents examined as little as possible so far as this requirement is compatible with efficiency in examination.

Method of Ward.—One of the least drastic of these methods is that advocated by Ward. (*Analyst*, 59, 1934, 621-2.) A capillary is used from which a small drop of the reagent is delivered inferior in diameter to the breadth of the

ink stroke. The drop is protected by covering with a small watch glass, and the reagent is left in contact with the ink for about two minutes. The same capillary emptied of the reagent is then used to withdraw the reagent. The drop is then transferred to a microscopic slide and allowed to evaporate.

The preparation can then be treated with suitable reagents and the reaction observed under the microscope.

This method is of great practical value in many cases, and is probably capable of considerable development in practice. There is no other form of treatment which makes possible the actual transference of a given quantity of ink to an external medium. This fact has interesting implications from the point of view of quantitative micro-determinations. In the case of fresh inks which are water soluble, it should be possible to transfer a given quantity unchanged to the external medium. The case is different where mature inks are concerned which cannot so readily be removed by solvents which leave them chemically unchanged. This limits the application of the method in a direction which would make it extremely valuable if it could be applied in every case. At the same time this technique is a considerable advance upon classical methods of micro-chemical examination.

Methods of Metzger and Heess.—The methods of examination advocated by these workers, involve the actual removal of small portions of the document. Without this preliminary the tests cannot be carried out. Thus, whilst this technique is more fundamental than the more or less empirical tests of the classical type, it must be used with greater discretion, and in many cases it cannot be used at all. The chemical examiner must bear in mind the essential fact that the minimum damage must be done to the document examined. He will otherwise become involved in great difficulties when the case is tried. It is for this reason that the simpler classical tests are still largely used in practice.

Method of Carrel.—On the other hand, research has been carried with a view to applying the methods of “decoupage” while at the same time doing the minimum of damage to the document. Carrel (*Contribution à l'identification des encres en*

criminalistique Thèse de Lyon, 1934) has devised interesting methods for this purpose. Essentially the method consists (1) in the actual transfer of a portion of the ink from the document to an external medium and (2) the transfer of the ink accompanied by a small portion of the cellulose substratum to an external medium. These are modifications of the methods advocated by Bischoff and Schneeberger who make an incision into the document with a small scalpel to remove the portions to be tested.

Carrel's method is (1) to apply a drop of collodion to the ink stroke to be tested. A microscopic slide is then placed on the spot, and heavy pressure applied. The collodion on drying forms a film which adheres to the slide and absorbs a portion of the ink. This method was finally abandoned in favour of (2) by reason of the fact that not every kind of ink can be transferred in this way and that with some types of paper the collodion adhered too strongly. The present author has, however, found the method quite satisfactory in certain cases, if it is used with discretion.

Method (2). The use of a gelatinized film is more generally adopted. The material used may be either photographic film which has not been sensitized or glass slips covered with a fine film of gelatin.

The transference is effected by slightly moistening the ink stroke with distilled water and then applying the gelatinized surface to the moist area with pressure. The slide or film is then lifted sharply. The ink stroke together with a portion of the cellulous substratum is thus transferred to the gelatin.

If carried out by a practised hand this method of transference does little more damage than the classical spotting methods. From the point of view of analytical technique, the analyst is left with a microscopic preparation which can be much more conveniently and completely examined than if the same area of the document itself were examined.

Comparison of the Methods.—The chemist called upon to make a chemical examination of a document must first decide what technique of examination he proposes to use. He must bear in mind that there are two objects which are not

completely compatible in view. First, it is necessary to make as complete a chemical examination as possible and secondly, as little damage as possible must be done to the documents.

The special circumstances must decide which general method is to be followed. In many cases a certain amount of local damage provided it is not extensive is permissible. On the other hand documents of intrinsic value must obviously be treated with special care. It is, of course, true that no chemical examination can be made which does not involve some damage. Sometimes it is stated that by very skilful manipulation chemical tests can be performed the effects of which are not afterwards visible to the naked eye. It is not, however, the present author's experience that an efficient chemical test can be restricted to so small an area that no visible trace remains.

In general, methods which involve the actual removal of ink from its milieu entail more damage than treatment of the document direct. On the other hand the treatment of detached fragments eliminates the risk of accident which may involve extensive injury to the document. Clumsy manipulation of spot testing is a very dangerous proceeding, and those not experienced in its application should be very cautious in its use.

Certain tests to be described later cannot be performed upon the document direct without serious injury to it. When these tests are to be made no alternative presents itself.

Application of the Methods.—The spot testing of ink is best carried out by delivery of the reagents from fine-drawn capillary pipettes. Ordinary glass tubing can be used. The wide end can be fitted with a piece of rubber tubing closed at the other end with a piece of glass rod. The pipette can be fitted with a stopper which becomes the stopper of the reagent bottle. It is desirable that every reagent bottle be fitted with a pipette of this type.

A small drop of the reagent of any required size can be delivered from a pipette of this kind by gently squeezing the rubber tubing. This method is in our view, preferable to the use either of a glass rod drawn out to a point, or that of a pen, feather or other instrument. In our experience, in fact, both pens and feathers are very unsatisfactory for delivery of reagents.

Table I
IDENTIFICATION OF INKS (Robertson and Hoffmann)

Ink	Oxalic Acid	Citric Acid	HCl 10%	H ₂ SO ₄ 15%	HNO ₃ 20%	SnCl ₂ 1 HCl 1 Water 1	SO ₂ Sat. Sol.	AuCl ₃ 4%	Na ₂ S ₂ O ₂ 1 NH ₄ OH 1 Water 10	K ₄ FeCN ₆ 1 HCl 1 Water 10	NaOH 4%	Chloride of lime
Iron-Gall	Bleached	Bleached	Bleached yellow	Bleached	Bleached	Bleached	Bleached	Bleached slightly	Dark red	Blue	Dark red	Bleached
Logwood with K ₂ CrO ₄	Violet	Violet	Red-purple	Red	Red	Red	Dull violet	Red-brown	Unaltered	Red	Brown	Bleached
Logwood with CuSO ₄	Orange	Orange	Blood-red	Red-purple	Red-purple	Magenta	Red	Brown	Dark blue	Brick-red	Becomes dark red	Bleached
Nigrosin	Unaltered	Runs, becomes blue	Little alteration	Unaltered	Runs	Unaltered	Unaltered	Unaltered	Becomes dark violet	Unaltered	Becomes dark violet	Brown
Vanadium	Bleached	Bleached	Bleached	Bleached	Bleached	Bleached	Bleached	Unaltered	Runs	Unaltered	Becomes dirty brown	Unaltered
Resorcinol	Brill. red	Bleached	Brill. rose	Brill. red	Brill. rose	Bleached	Bleached	Becomes brown	Brown	Rose	Unaltered	Brown

In Table I, Robertson and Hoffmann's micro-chemical results are recorded. These tests are still of value for distinguishing between the inks described.

Table II (Lucas), is of value in distinguishing iron gall ink with provisional colouring matter, and Logwood ink.

Table II

IDENTIFICATION OF INKS

A. LUCAS, *Forensic Chemistry*, p. 102

Edward Arnold and Co., London, 1935

Reagent	Iron Gall Ink without blue Colouring Matter	Iron Gall Ink with blue Colouring Matter	Logwood Ink
Hydrochloric Acid	Slightly yellow	Blue	Red
Oxalic Acid	Bleaches	Blue	Red
Tartaric Acid	Bleaches	Blue	Light brown
Acetic Acid	Bleaches	Blue	Violet
Sodium Hydroxide	Reddish-brown	Reddish-brown	Brown
Potassium Ferrocyanide	Blue	Blue	—
Potassium Thiocyanate	Red	Red	—
Sodium Hypochlorite	Bleaches	Bleaches	Bleaches

Poix, formerly of our Laboratory of Technical Police has devised a more elaborate scheme for the identification of different types of aniline dyes and vegetable colouring matters commonly present in inks. (Tables III and IV).

Bischoff (*supra*) recommends the use of the following reagents. 3% oxalic acid, 10% tartaric acid, hydrochloric acid from 10% to 0.1%, sulphuric acid 15%, nitric acid 20%, sodium hydrate 4%, potassium hydrate 4%, strong ammonium hydrate solution, calcium hypochlorite, stannous chloride in hydrochloric acid, 10%, sodium thiosulphate in ammonia, 10% potassium ferrocyanide, potassium thiocyanate, sulphurous acid and gold chloride.

Table III
IDENTIFICATION OF INKS
Coloured Inks (Poix)

Colouring Matter	Solution in Water	HCl	HNO ₃	NH ₄ OH	Al ₂ (SO ₄) ₃ K ₂ SO ₄	KCN	Chloride of Lime
Prussian Blue	Soluble with blue coloration with oxalic acid	Green coloration, then yellow solution	decolorized when warm	decolorized when warm	—	—	—
Cochineal	Solution in water, reddish-yellow	Orange	—	Violet	With NH ₃ dark red	Dark red-purple	Decolorized white ppt.
Tannin	Feeble yellow	Greenish yellow	—	Dark yellow	—	Reddish	Blue-green decolorized
Indigo Carmine	Blue sol.	Lighter blue	—	Green when heated, light blue	—	Lighter, then light blue	Decolorized

Table IV
ANILINE INKS (Poix)

Ink	Water	Alcohol	H ₂ SO ₄	Dil H ₂ SO ₄	HCl	NaOH or KOH
Malachite Green	Sol.	Sol.	Brownish-yellow	Dark green, dark yellow	Red-brown	In the cold dirty green ppt. Warm red ppt.
Brilliant Green	Sol. Blue green	Sol. Green	Yellow-brown	Yellowish-green	Yellowish-green	Cold green. Warm reddish
Fuchsine	Sol.	Sol.	Reddish-yellow	Red	Reddish-yellow	Cold, reddish ppt.
Methyl Violet	V. sol.	V. sol.	Yellow	Green, then violet	Yellow-brown	Red-brown ppt.
Crystal Violet	Sol.	Sol.	Yellow	Green, then blue	Yellow when dilute	Violet ppt.
Methyl Green	Sol. blue-green	Sol. blue-green	Yellow-brown	Green	Orange. Dilute green	Decolorized
Eosine	Red fluorescent	Red fluorescent	Yellow when warm	Yellow-brown ppt.	Yellow-brown ppt.	Deeper colour
Erythrosine	Cherry-red	Red fluorescent	Yellow	Red-brown ppt.	Red-brown ppt.	—
Methylene Blue	Blue	Blue	Green	Blue	Greenish-blue	Violet warm, then violet ppt.

Mitchell (*loc. cit.*) considers that in ordinary circumstances the following reagents are sufficient, hydrochloric acid 5%, oxalic acid 5%, stannous chloride 10%, nascent hydrogen HCl 50% with zinc. Saturated bromine water, sodium hypochlorite 10%, titanous chloride, potassium ferrocyanide 5% in 1% HCl.

Interpretation of Results.—The method of interpreting the results of these tests is mainly empirical. They are not primarily designed to identify the constituents of the ink as such, but to compare the results of testing one ink with those of another. The inks tested are assumed to be of the same composition if the results agree and of different types if they do not. On the other hand the manner in which certain classes of ink behave to these reagents has been ascertained by experiment, so that the ink can be positively identified on the basis of these tests. Mitchell has stated, for example, that twenty-five types of commercial writing inks have been identified by the use of these reagents. It is essential, however, not to forget the limitations which are necessarily attached to empirical tests of this kind. They must be checked whenever possible against experiments with known types of ink. Two inks of the same composition, for example, may react differently to the same reagents if their physical and chemical condition due to age is different. In short the results of the analysis must not be interpreted rashly as if they were supplied by nature ready made. A fundamental distinction must be preserved between the test which positively identifies a given constituent and the empirical from of comparative test of which the mechanism is not understood.

Micro-Chemical Applications in Carrel's Method.—Where the ink stroke is transferred with its substratum as in Carrel's method a different technique is followed. In the first place the reaction can be observed under high magnification on the stage of the microscope. The preparation is mounted on a microscopic slide and protected with a cover slip. The examination should be made before any reagent is used. By this means the quality of the ink as distinct from its composition may be inferred. For example, ink containing dust can be

identified in this way. Since ink transferred by this method is examined in thin longitudinal section the structure of the stroke is readily observed and the presence of insoluble foreign matter detected.

The micro-chemical tests can be carried out by running a drop of the appropriate reagent under the cover slip. It is then possible to watch the reaction under the microscope.

Comparative tests can be carried out in the same way. Two ink strokes can readily be transferred to the gelatinized medium in such a way that they lie side by side and close enough to each other to be viewed in the same field of the microscope. The appropriate tests can then be applied and a pair of reactions watched simultaneously. Micro-chemical tests carried out under these conditions can be much more efficiently observed than if the tests are made upon the document itself. On the other hand they require more elaborate manipulation and greater practice for their efficient performance.

Micro-Chemical Methods of Metzger, Rall and Heess.—

As we have said the methods of these workers involve a more drastic interference with the document than those previously described. In order to effect this type of examination, they advocate removal of portions of the document with a scalpel. The tests for chlorides and sulphates in ink are also of an elaborate nature which necessitate the use of comparatively large portions of material. After the test is completed the portion removed is replaced *in situ* and secured by means of transparent adhesive paper. From a practical point of view this is a disadvantage since there are frequently legal objections to methods of this kind. From a technical point of view, however, this manner of attack is the most satisfactory. The document is treated as a component in a series of chemical reactions, and its destruction or damage is ignored if the facts are demonstrated to the satisfaction of the analyst.

(c) The Maturing of Ink

General.—One of the properties of ink is that it remains chemically active for long periods of time when exposed to the

air, particularly when it is in thin layers as in the case of writing on paper. This fact has considerable forensic importance because the physical and chemical condition of the ink may provide evidence concerning the length of time it has been upon the paper, and give an indication of the age of the document.

We have already indicated that these changes are very incompletely understood, and until more precise information is available concerning the constitution of the compounds produced by the interaction of iron salts and gallotannic acid very little fundamental progress can be made. On the other hand the behaviour of ink as it matures on the paper has been extensively studied and certain facts of value have become available. Much of the work carried out, whilst it has been of an empirical nature, is of value practically.

Micro-chemical technique is of great assistance in this study since the manner in which certain reagents affect the ink at different periods often throws light upon its age even where the reactions involved are not understood.

In micro-chemical technique colorimetric determinations may be included, and it will be well to consider these in the first place.

The Colour of Ink.—It is an old-established fact that ink darkens with exposure to air. The explanation of this is that the gallotannates of iron deepen in colour with oxidation. Other reactions of a more complex type probably take place, but there is no question that oxidation is accompanied by darkening in colour.

Mitchell (*Documents and their Scientific Examination*) has made a close study of colour changes in inks. He found that if ink were applied to paper in a thin wash, maximum intensity of colour was reached in about a week. Thicker layers, as in writing, attain their maximum colour more slowly. If enclosed in a book, eighteen months may elapse before the process is complete.

For the purpose of recording colour, Osborn's comparison microscope is used and Lovibond's standard tintometer glasses. Mitchell's table (loc. cit., p. 63) indicates the colour changes

against blue, red and yellow taking place in three types of ink from the first to the forty-third day. The results showed that maximum intensity of colour was reached in all cases over this period.

Solubility in Water and Acid.—Ink can be copied by damping its surface and applying to it a second piece of paper with pressure. The solubility of the pigment is, however, a function of the time. Fresh inks can be copied readily, but the property is lost when the ink is old. Still (1891), Habermann, Esternieder and Persifor Frazer studied this question. Still found that if water were used iron gall ink produced faint copies after four weeks, whilst Habermann and Esternieder obtained results after five and in exceptional cases after nineteen months.

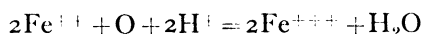
Carré (*C.r. xxviii* 1213) made tests with dilute hydrochloric acid. He found that with this treatment inks produced good copies after eight or ten years and faint reproductions after twenty years.

The results of copying are not concordant. This is probably explained by the varying composition of the inks studied. The presence of aniline dye will increase solubility in water and thus the property of copying, and many subsidiary factors probably influence the result. Mitchell rightly says that it is only in exceptional cases that tests of this kind can give precise evidence of the age of the ink. In cases, however, in which it is required to distinguish between a document very recently written and one more than some months old, the test may be of value. Zetzsche has shown (*loc. cit.*) that the insolubility of the iron tannates increases with time.

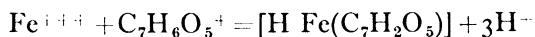
Solubility of Provisional Pigment.—Mitchell (*Analyst*, 1920, *XIV*, 247), has shown that slow oxidation of the preliminary ferrous tannate takes place, and that finally, another tannate is formed which contains a higher percentage of iron. The oxidized compound is of a resinous character and is highly resistant to solution in water or dilute hydrochloric acid. This resinification influences not only the tannate itself but the provisional colouring matter of the ink which is mechanically

protected from the action of solvents. Thus with fresh ink a rapid diffusion of the aniline pigment takes place after treatment with dilute acids. As the insoluble tannate forms this diffusion becomes less marked and finally disappears. It has been shown that the provisional colouring matter becomes completely insoluble after four to five years.

pH of Ink on Paper.—Metzger, Rall and Heess (loc. cit., *p.* 91) have recorded the hydrogen ion concentration value of ink on paper. These workers have made the interesting observation that the chlorides found in the ink exist not as salts but as free hydrochloric acid. They state that the ferrous gallotannates first formed contain 1 molecule of free acid for every molecule of the ferrous salt. The production of the ferric salts is according to the equation :



They consider also that the pigmentation of the ink is due to the conversion of the gallic acid to ferrigallic acid.



It would thus appear that the free acid plays a part in the formation of the ferric salt which finally reacts with the gallic acid to produce ferrigallic acid. In isolation this reaction would result in an increase in hydrogen ion concentration. The presence, however, of buffers in the loading material of the paper modifies this effect. These interesting conclusions should be considered in conjunction with those of Ozorovitz (loc. cit., *p.* 92). See also Zetzsche (loc. cit., *p.* 90).

The Diffusion of Chlorides.—In the sphere of practice these authors have studied the diffusion of the chloride upon paper. They have shown that as the ink matures the chlorides diffuse so that in fresh inks the chloride “stain” is small in area and concentrated; in older inks it diffuses. The test for chloride is carried out upon a portion of the document which has been excised. 10% solution of sodium nitrite is treated with a 1% solution of silver nitrate until a precipitate of silver nitrite is formed. This precipitate is redissolved in 10% nitric

acid. The fragment of paper is moistened in the solution the colour of the ink being destroyed by the nitric acid. Chlorides if present are thus converted to silver chloride. After thorough washing the silver chloride is reduced with an alkaline solution of formalin. The place occupied by the ink stroke then shows a black stain the colour and area of which is referable to the age of the ink. (Türkel.)

Diffusion of Sulphates.—Sulphates also undergo diffusion. In the test for this acid radicle, a fragment of the paper is treated with a 4% solution of lead nitrate containing 4% of perchloric acid and a few drops of a solution of potassium permanganate. This treatment bleaches the ink and converts the sulphates to lead sulphate. The paper is then thoroughly washed with water saturated with lead sulphate to remove the excess of lead nitrate. The residual lead sulphate is then converted to lead sulphide by treatment with an alkaline solution of sodium sulphide. A black stain is, of course, produced.

These tests have a limited application in practice. First, they are not applicable to documents the paper of which contains appreciable quantities of chlorides and sulphates. Secondly, an interpretation of the diffusion of the stains in reference to the maturity of the ink cannot be made with precision. Thirdly, the tests cannot be carried out efficiently unless considerable damage is done to the document. This does not effect the interest and value of the tests themselves from an investigational point of view. Means may be devised in which they can be practically applied to documents the paper of which is free from chlorides and sulphates.

The Oxidation of Ferrous Iron in Ink.—Whilst the nature of the oxidation reactions of ink is not completely known that the ferrous iron is—with some exceptions—completely oxidized is fully established. The rate of this oxidation if it can be determined is clearly an indication of the age of the ink. The present author (*Rhodes l'Identification du Fer ferreux dans les Encres. Thèse de l'Institut de Criminalistique de Lyon*) has investigated this question.

The quantitative performance of tests of this kind has

been greatly facilitated by the use of the organic "spot" reagents already described. For the identification of ferrous iron in ink the reagent *aa'* dipyridyl was used. (*See p. 111.*) The tests can be conveniently carried out by spotting on filter paper. If drops of ink, for example, are weighed on to filter paper and a drop of the reagent applied, a zone of colour sharply differentiated from the colour of the ink spreads on the paper beyond the circumference of the ink spot. It was found that the coloration produced was proportional to the ferrous iron present, so that the iron in small quantities of ink could be estimated against standards prepared in the same way.

A comparison of these results with those obtained by the gravimetric investigation of iron by classical methods showed an error of the order of 12%. The table below shows typical examples of the results.

	<i>Classical Method</i>	<i>Colorimetric Method</i>
	10 gms. of ink	5 mgms. of ink
	Fe %	Fe %
Antoine Bleu-noir	0.40	0.45
Antoine Stylex	0.35	0.35
Waterman Jif	0.32	0.36

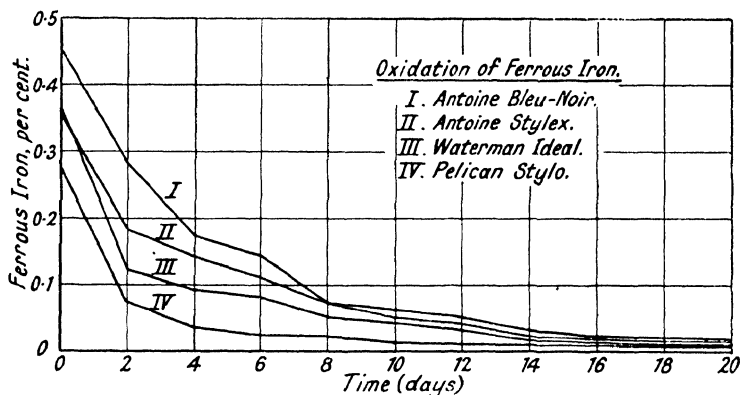
Thus whilst the method does not achieve a high order of accuracy, the colorimetric results being consistent among themselves make comparative studies possible.

Rate of Oxidation of Ferrous Iron.—Spots of ink exposed to air and light for regular periods of time showed progressive reduction in the quantity of ferrous iron present. The graph on page 110 represents the results obtained with four different types of ink. The ordinate represents the quantity of ferrous iron per cent, the abscissæ, the time.

The rate of oxidation is proportional to the quantity of ferrous iron present. At the same time, the period required to oxidize all but the last traces of ferrous iron was approximately the same (26–28 days), for all the inks examined.

Rate of Ferrous Oxidation in Ink Strokes.—It has not as yet been found possible to apply the quantitative method to

portions of ink upon the document itself. Qualitative tests, however, give results which are often of value. In the case of document examination a small drop of the reagent is applied to the ink stroke itself with a glass rod drawn out to a fine point. The reagent is left in contact with the ink for a minute, and is then recovered with a piece of filter paper. In prepared documents with different types of ink it was found that the



iron was completely oxidized except for traces in 26 days to a month. Complete oxidation of the ferrous iron was never observed. Traces can always be detected.

Inks with Provisional Colouring Matter.—The presence of aniline dye as a provisional colouring agent does not appear to affect the oxidation of the ferrous iron. The so-called alizarin inks (those containing indigo) constitute an exception. Experiments with Stephen's ink containing indigo showed that inks which had been thirty years upon the paper still showed a marked ferrous iron reaction. This fact does not appear to have been previously observed. Some authors in fact, have implied that the ferrous iron in inks containing indigo oxidize on paper in the same way as other inks. It has, however, long been known that the presence of indigo in liquid ink retards the oxidation of the iron. An oxidation-reduction state presumably accounts for this condition.

Reagents for the Test.—Hill, (*Proc. Roy. Soc.*, 1930, 107 (b) 205), first suggested the use of *aa'* dipyridyl as a reagent for the detection and estimation of ferrous iron. This author has observed that the sensitivity of the test is not affected between pH limits 3.5 and 8.5. The sensitivity is of the order of 0.2γ. F. Müller (*Mikrochem*, 1933, 12, 207) and others recommend the use of a 1% solution in 0.1 N HCl.

We have found it necessary to increase the concentration of acid in the reagent since the complete solution of the iron is not effected with the concentration recommended. The reagent, therefore, consists of a 1% solution of *aa'* dipyridyl in 0.5 N. HCl. This reduces the sensitivity of the reaction to the order of 7γ. It is sufficient for the efficiency of the test in these conditions.

(d) The Chemical Examination of Pencil Writing

General.—Pencil writing is of two general types. (1) That produced with graphite pencil and (2) that of the so-called indelible pencil. Of these the indelible pencil is usually more amenable to chemical examination since the materials composing it are chemically more active. But it is not the case, as has sometimes been suggested, that a chemical examination of graphite pencil writing is of no use. Graphite pencils even of the best quality contain constituents which can be identified and which serve to distinguish one from another with some degree of precision.

At the same time pencil writing is not subject to the same type of chemical change as iron gall inks undergo on the paper. The writing remains more or less unchanged, and it is, of course, not possible to infer the age of pencil writing from a chemical examination of it. The scope of the examination of graphite pencil writing is necessarily much more restricted than that of ink whilst the examination of copying ink pencils more or less resembles that undertaken in the case of aniline inks. In spite of these restrictions definite conclusions can often be arrived at, if a suitable technique is followed in the chemical examination of pencil strokes.

PIGMENTS IN MODERN PENCILS

C. A. MITCHELL, *Documents and their Scientific Examination.*

Charles Griffin and Co., London, 1922.

Pencil	Carbon	Loss at 210° C. Wax, Lampblack	Ash	Silicates	Iron oxide and Alumina
	%	%	%	%	%
1. Acheson Graphite, No. 515, between BB and BBB	64.00	13.23	22.77	21.84	0.66
2. Conte, No. 5, about HH	57.19	8.41	55.53	36.29	5.35
3. Faber, hard pencil	50.60	5.26	37.55	32.42	1.99
4. Hardmuth's Koh- i-Noor, 2B	16.56	15.14	30.00	20.30	1.52
5. Hardmuth's Koh- i-Noor, 6B	43.29	43.00	40.44	32.16	3.30
6. Japanese Pencil, HB	20.06	1.85	54.86	52.15	2.57
7. Rowney's Indelible	29.06	19.94	51.00	43.40	1.45
8. Spear. Carpenter's pencil	49.12	0.4	50.48	33.97	6.10
9. Wolff's Indelible	29.19	28.00	42.81	40.40	2.40

Composition of Graphite Pencils.—Graphite pencils are still commonly but incorrectly described as lead pencils. In fact, pencils containing lead practically disappeared at the end of the eighteenth century, although they are still in occasional use to-day for special purposes. Graphite has been used in pencils since the sixteenth century, but the use of anything approaching a pure composition is comparatively modern. High grade graphite was not unknown in the middle of the nineteenth century, but the composition varied between wide limits. Modern pencils are more standardized and those of

good quality extremely constant in composition. The organic constituents are essentially carbon, lampblack and wax; the inorganic ingredient is clay which is used as a binder. The table opposite shows the composition of well-known types of pencil.

It will thus be evident that the constituents are not such as to make an extensive chemical examination possible. There must be added, however, to the constituents chlorides, which are frequently present in graphite pencils, and sulphates are, according to Mitchell, occasionally found. Their presence, however, like that of titanium, is rare and they have therefore great value in identification of an individual pigment.

Qualitative Testing of Pencil Strokes.—The methods described for the examination of ink strokes (*supra pp.* 91-102) are also applicable to the examination of pencils. In testing the stroke for iron Mitchell recommends treatment of the writing respectively with a drop of acetic acid and a drop of strong nitric acid. Potassium ferrocyanide is then applied for the detection of iron.

Titanium is identified with hydrochloric acid and hydrogen peroxide. Chlorides when present are identified as silver chloride with silver nitrate, and sulphates with nitric acid and barium chloride.

A number of other empirical tests have been recommended which include the resistance of the pigment to strong acids, and it has also been suggested that the use of osmium tetroxide which is reduced by organic matter is a method by which the presence of wax can be detected in pencil writing.

Quantitative Analysis of Pencil Strokes.—The mere identification of constituents of this type is not generally of great value in the differentiation of pencil pigments. With the exception of titanium they are present in most pencils. For this reason Dennstedt, Voigtländer, Türkkel and others attach very little importance to a qualitative examination. Jacques Locard (*Thèse de Lyon. Analyse des traits de crayon*), has, however, elaborated a form of examination of great interest. In a comparative sense it can be said to be quantitative.

IDENTIFICATION OF PENCIL PIGMENTS (J. LOCARD.)

Pencils	No.	Potassium Ferrocyanide		Ammonium Thiocyanate		Hydrogen Peroxide		Silver Nitrate	
		10%	.05%	10%	.05%	12 vol.	0.12 vol.	10%	.05%
Graphite Conte 1010	0	+	+	+	+	+	—	+	—
Graphite Conte 1010	1	+	+	+	+	—	—	+	+
Graphite Conte 1010	2	+	+	+	+	+	—	+	+
Graphite Conte 1010	3	+	+	+	+	+	—	+	+
Graphite Conte 1010	4	+	+	+	+	—	—	+	+
Graphite Conte 1010	5	+	+	+	—	+	+	+	+
Conte a Paris 1038	1	+	—	+	—	+	—	+	—
Conte a Paris 1038	2	+	—	+	—	+	—	—	—
Conte a Paris 1038	3	+	—	+	—	+	—	+	—
Bagnol et Farjon 104	2	+	—	+	—	—	—	—	—
Papeteries Generales Lyon	2	+	+	+	—	—	—	+	—
Graphite Français 1068	1	+	+	+	+	+	—	+	—
Graphite Français 1068	2	+	+	+	+	+	+	+	+
Franbel Paris 1290	2	+	+	+	—	+	+	—	—
Aw. Faber, Cedre	2	+	+	+	+	+	+	+	—
Aw. Faber, Castell, H.B.	2	+	+	+	+	+	—	+	—
L. & C. Hardmuth 110	2	+	+	+	—	+	—	+	—
L. & C. Hardmuth, Koh-i-Noor, H.B.		+	+	+	—	+	—	+	—
Caran d'Ache 778 stenodactyl		+	—	+	—	+	+	+	—
Venus, special drawing, B.B.		+	—	+	—	+	+	+	—
E. Wolff, Royal Sovereign, H.	0	+	—	+	—	+	—	+	—

The principle of Locard's method is to employ reagents of decreasing concentration so adjusted that the stronger will produce a reaction with a given pigment and the weaker will not. Thus a certain group of pencil pigment may produce a reaction for ferric iron with a 5% solution of ammonium thiocyanate whilst the same group produces a negative result with the same reagent at 0.5% concentration. On the other hand other pigments react positively and negatively with different concentrations. In practice the tests are carried out with a pair of reagents with concentrations corresponding to 10% and 0.05%. The table (*p.* 114) indicates the scheme of the reactions.

Locard has pointed out that this method does not make individual identification of a pencil pigment possible. It does, however, ensure a higher degree of differentiation than the qualitative method. In the case of iron, for example, two types of pigment can be distinguished with certainty, those which react with neither reagent and those which react with the weaker. In regard to titanium, three reactions have been observed. The metal reacts with 0.12 vol. hydrogen peroxide. It reacts only with 12 vol. hydrogen peroxide or titanium is absent. In regard to chlorides there are three possibilities. The chlorides react with 0.02 N silver nitrate. They react only with 0.1 N silver nitrate or chlorides are absent. Using these pairs of reagents there is thus a 1/18 chance of error. A much higher probability of differentiation than in the case of a simple qualitative examination is therefore attainable.

Composition of Indelible Pencils.—The examination of pencil marks of this type is more closely related to the examination of ink strokes than to those of graphite pencils. Copying ink pencil pigment consists essentially of kaolin graphite and aniline dye compressed into rods. The dye used is generally methyl violet. The composition can often be partly inferred from the colour of the writing. Where a kaolin or alumina filler is used, the colour is brighter than if graphite is present. The kaolin filled pigments are also softer and mark the paper more readily.

Tests of Copying Ink Pencil Writing.—Differential results can often be obtained by treatment of the pencil

stroke with a small drop of distilled water. The speed of diffusion of the pigment varies with different pencils. In some cases the diffusion may be extremely rapid whilst in others a period of five minutes or longer may elapse before spreading takes place. These differences are due to the nature of the filler, its particle size and degree of compression. The quality of the dye also influences the result.

Similar tests may also be applied using alcohol and ether as solvents. In the case of these reagents the diffusion is always more rapid and the zones of coloration as the solvent spreads may also be distinctive.

Ash of the Pigment.—Mitchell (*Documents and their Scientific Examination*, p. 123), in an interesting survey describes among other features of the analysis of copying ink pigments, the colours of the ash. These are varied, being red, white, buff, putty coloured and yellowish-grey. In those rare cases where it is permissible to excise a portion of the document the pigment may be burnt in a micro crucible. The colour of the ash of the pigment can then be observed. A putty coloured or red ash indicates the presence of iron in varying proportions. A yellowish-grey ash indicates traces of iron. Alumina produces a white ash.

Analysis of the Aniline Dye.—Spot reactions of the same type as are applied in the examination of aniline inks can be used in the identification of pencil writing. It is essential to note, however, that the quality of the paper on which the writing is made has an influence upon the reaction. Thus, sized papers and absorbent papers give somewhat different colour reactions for the same dyes.

Mitchell recommends the use of nitric and sulphuric and hydrochloric acids, stannous chloride, sodium nitrite with acetic acid and titanous chloride. At Lyon we have been accustomed to use besides the strong acids, oxalic acid, sodium hypochlorite and potassium hydrate.

Whilst they are of an empirical type these tests, particularly when used comparatively, give precise results. Mitchell reports an interesting case (*Rex v. Wood*), in which it was sought

to identify an indelible ink pencil found on the accused with the writing upon a note which was found half charred on the scene of the crime. The reactions of the pigment of the pencil were compared with those of six others from which it was readily distinguished. The comparative tests applied to the writing of the pencil found and that of the note showed close correspondence. Identity of the writings was assumed, and was, in fact, later independently established.

(e) The Chemical Examination of Paper

The best quality paper consists of almost pure cellulose. Inferior qualities contain pecto-cellulose, ligno-cellulose and other impurities. Very inferior types contain fragments of undigested wood.

Besides the grosser forms of impurity paper may contain traces of substances used in its manufacture. In the sulphite digestion process the wood is treated with calcium bi-sulphite which removes the non-cellulose portions of the wood. Traces and in some cases appreciable quantities of sulphates are therefore not infrequently found.

Chlorides are also a common impurity. Their presence is due to the chlorination process to which the raw material may be subjected.

Other constituents are found in paper which are not impurities but loading materials to fill the pores of the paper. These materials include china clay, talc, chalk, and calcium sulphate.

Other additions are sometimes made for the purpose of colouring paper. These colouring matters are of two kinds, mineral and aniline dyes. Mineral pigments include ultramarine, prussian blue, lead chromate, oxide of iron and manganese. Among the aniline dyes methylene blue, auramine and metanil yellow are used.

The surface of paper may be sized with gelatin, glue, rosin, casein or starch. This treatment is adopted to give the paper a smooth or glossy surface.

Thus it is obvious that paper is a complex mixture which is highly characteristic chemically. A chemical examination will often give valuable evidence of identification.

The Identification of Cellulose Fibres.—Herzberg (*Papierprüfung*, 1915, p. 94) recommends the use of two reagents, namely 1.15 gm. of iodine dissolved in 2 gm. of potassium iodide 2 cc. of glycerine and 20 cc. of water, and (A) 20 gms. of anhydrous zinc chloride in 10 cc. of water and (B) 0.1 gm. of iodine dissolved in 2.1 gms. of potassium iodide in 5 cc. of water. Solutions A and B are mixed and the supernatant liquor decanted off.

THE IDENTIFICATION OF CELLULOSE FIBRES

HERZBERG (*Papierprüfung*, 1915, p. 94.)

		Iodine and Pot. Iodide	Zinc Chloride and Iodine
I. Lignified Fibres	Mechanical Wood Pulp Jute Fibres containing undissociated cellulose	Fibres yellow to yellowish-brown according to lignification	Pale to dark yellow
II. Cellulose	Straw Cellulose Jute Cellulose Wood Cellulose Andansonina Esparto Manila hemp	Grey Grey to brown Some grey, some brown Grey-brown and yellowish-brown	Blue to bluish- violet Blue to reddish- violet Blue to bluish- red Blue, bluish-violet red-violet, dirty yellow
III.	Linen Hemp Cotton	Pale to dark brown	Pale to dark bluish-red

Jenke utilizes a saturated solution of magnesium chloride with 23 gms. of potassium iodide and 1.5 gm. of iodine in 20 cc.

of water. With this reagent, cotton, linen and jute cellulose give a blue coloration. Straw gives blue-violet, mechanical wood gives a yellow colour, chemical wood fibres are uncoloured or give a faint red.

Identification of Sizing.—Gelatin.—The paper is extracted with boiling water and the extract evaporated to a small bulk. The solution is treated with gallotannic acid. A flocculent yellow precipitate forms if gelatin is present.

Rosin.—For the detection of rosin the paper must be extracted with hot alcohol. The alcoholic solution is then treated with sulphuric acid and acetic anhydride (Storch-Morawski reaction). A red-violet coloration indicates rosin.

Casein.—If gelatin is absent, Millon's reagent for the detection of proteins is applied. Casein gives a pink coloration with this reagent.

In cases where it is necessary to isolate the casein, the paper is boiled with sodium carbonate solution. Acetic acid is added to the filtrate. The casein is precipitated and can be examined after washing free from the acid.

Starch.—Starch can be identified by the usual test with iodine.

Identification of Loading Materials.—The principal bases to be sought are aluminium (hydrated aluminium silicate), calcium (calcium sulphate), barium (barium sulphate), magnesium (magnesium silicate). If one of these bases is identified, it is an indication of the type of loading used in the paper. The "spot" reactions already described should be used. A small portion of the paper should be burnt in a micro crucible and the ash taken up with hydrochloric acid and evaporated to dryness. The alizarin test should be used (*p.* 25) for aluminium. Calcium may be detected with picronic acid (*p.* 32). Diphenyl carbazide (*p.* 28) is used for magnesium.

Barium sulphate which is to a large extent insoluble in strong acids will remain as a white precipitate.

If one of these bases is present it will most probably correspond to one of the substances specified in brackets above. If aluminium and calcium are associated and sulphates are also present the loading material is probably a mixture of alumina and precipitated calcium sulphate, the so-called satin-white.

Identification of Pigments.—Pigments as we have indicated are of two kinds, inorganic and organic.

Blue.—(Inorganic.) Blue papers of good quality are generally coloured with ultramarine, a double silicate of aluminium and sodium containing sulphur. Prussian blue, ferric ferrocyanide or ferric potassium ferrocyanide of which several varieties exist is also used as a pigment.

Two simple tests can be applied for identification. Ultramarine is bleached by strong acids whilst Prussian blue is decolorized by alkalis.

A third blue pigment occasionally used in expensive paper is smalt (cobalt silicate). This has considerable interest since it has been little used in paper manufacture since the middle of the nineteenth century. Thus its presence may in some circumstances indicate the date of the paper. Smalt is readily detected because the ash of the paper containing it is blue. A confirmatory test for cobalt can be made.

Yellow.—Yellow papers may contain lead chromate. Chrome yellow and ferric oxide may be mixed to produce buff shades.

Brown and Green.—These papers may contain iron or manganese or a mixture of chrome yellow and Prussian blue. Appropriate tests for lead, iron and manganese require no special description.

Organic Pigments.—Organic pigments are readily extracted from paper by treatment with hot alcohol. It is generally sufficient to note the colour of the alcoholic extract and to apply the tests with acids and alkalis already described (*p.* 102).

Interpretation of Results.—Since in a given paper it may be possible to identify (1) The nature of the cellular fibre. (2) The impurities. (3) The nature of the loading materials. (4) The sizing. (5) The colouring matter, very precise conclusions concerning the paper may be made available by a chemical examination. All these substances do not, of course, exist together in all writing papers, but the nature of the fibre can always be examined and the impurities sought. Loading materials are also generally present. The object of the examination is either to match the paper with that of some other document, to determine the approximate date at which the paper was produced or to determine its origin.

Fraudulent Characteristics.—The watermark upon paper may have an important bearing upon its genuineness. The watermark is normally produced by means of a wire design fixed to the dandy roll so that the increased pressure at that point upon the pulp compresses it, making the surface more transparent.

Fraudulent watermarks are sometimes produced by the use of carnauba wax, spermaceti and a drying oil. If the paper is treated with ether the wax is dissolved and the watermark disappears.

Paper is occasionally stained artificially to give it the appearance of age. Various colouring matters of which an infusion of tea is one are used for this purpose. This type of fraud can usually be detected by inspection. Chemical tests can occasionally be applied, but no general rule can be laid down.

(f) The Examination of the Forged Document

General.—There are two types of forgery of documents, the imitative and the manipulative. Chemical examination is usually applicable only to the second type. Imitative forgery is confined to the imitation of a piece of handwriting. The detection of the fraud can generally only be achieved by physical examination with the microscope and by methods of micro-measurement. Manipulative forgery, however, involves the physical or chemical examination of the document. Alter-

ation of this kind can often be detected by chemical methods.

Manipulative forgery is of two kinds (1) by addition to the document and (2) by subtraction from it. An example of the first form of technique is the alteration of figures or the interpolation of a word or words which alters the document's meaning. The second form of manipulation involves the removal of words or figures by chemical or physical means with the same intention.

The two forms of manipulation can, of course, be associated with the same document as when writing or figures are removed and others substituted. Again addition may involve the process of subtraction as when writing is scored out with a view to falsification.

An examination which aims at the detection of forgery of this kind may involve the examination of both the ink and the paper. In regard to the ink it may be required to decide (1) if the ink is of the same type throughout the document, (2) if the age of the ink is the same at all points, (3) if traces of the constituents of the ink remain the pigment having been removed by bleaching, (4) if the type of ink used is consistent with the reputed date of the document, (5) if the writing has been bleached out whether the text can be reconstituted, (6) if the ink is mixed with foreign material as when pencil writing has been inked over.

In regard to the paper, it may be necessary to determine (1) the type of paper used, (2) any manipulation of the paper, such as the fabrication of a watermark, the treatment of the paper with chemicals or mechanical interference.

Forgery by Addition.—Forgery by addition may be so clumsy as hardly to call for expert examination, or so skilful as to make it extremely difficult to detect even by the most refined methods. A common form of addition is the "raising" of cheques to a higher figure than that for which they were originally drawn, and the alteration of dates upon documents. In examples of this kind the alteration may only involve the change of a single figure and the addition of one letter to a word. Great care may be taken in matching the ink, and using a suitable pen to make the interpolation appear natural.

Forgery by Subtraction.—This method of falsification is more varied and elaborate. There are two general methods of subtraction, the physical and the chemical. The physical method which is the cruder of the two involves the removal of ink or pencil writing by erasure. It may be very skilfully performed so that there is little trace showing the point of attack. The surface of the paper may be restored by appropriate treatment.

The chemical method of deletion is usually known as "washing." Washing involves treatment of the document with a bleaching agent which decolorizes the pigment of the ink. If skill and knowledge are brought to this technique little evidence of the treatment remains. Acids such as nitric and oxalic acid are used for this purpose and bleaching agents such as sodium hypochlorite.

Chemical Examination.—It is first essential to bear in mind that the chemical examination of a document should not be undertaken if other methods which do not involve it can achieve the desired result. Photography both with ordinary light and with ultra-violet rays and infra-red sensitive plates has been greatly developed of recent years. A discussion of these methods would be out of place here. The fact is mentioned so as to emphasize the desirability of using these methods if they are applicable. In any case, before any chemical examination is made of a document, it must be photographed in natural size. In no circumstances must this precaution be neglected. It is also advisable to repeat that when a chemical examination is undertaken, the minimum damage must be done to the document. Every step should be carefully considered before it is undertaken. As far as possible the tests should be carried out in the least conspicuous parts of the document. When the experiments are not being done, documents must be protected between sheets of glass or cellophane.

The Chemical Examination of Erasure.—The simplest test should be made first. The most obvious is to hold the

document up to the light to ascertain if more light is transmitted at the suspected point of attack. This simple test may be conclusive. In many cases, however, sufficient skill has been used to make the test uncertain. This is true in particular if the surface of the paper has been reconditioned.

Where the surface has not been reconditioned the paper may be exposed to iodine vapour. The result of this treatment is that the iodine is absorbed in the locality of the attack, and the manipulated area is thus clearly defined.

It is, however, preferable to use a volatile solvent such as benzene. If a drop is applied to the normal surface, it retains a circular shape. If, however, the paper has been manipulated by erasure, the benzene drop follows the contour of the point of attack.

If the surface has been reconditioned the suspected part should be treated with (1) water and (2) with alcohol. A piece of filter paper is moistened and applied to the paper, the process being repeated several times. If the reconditioning agent is water soluble, the erasure will be disclosed either by inspection or by one of the methods described. Treatment with alcohol will remove such substances as rosin.

Chemical Washing.—Various reagents are used for “washing” documents.

- (1) Chlorine water.
- (2) Sodium hypochlorite.
- (3) Oxalic acid.
- (4) Citric acid.
- (5) Sodium bisulphate.
- (6) A mixture of ammonium carbonate and sulphur.
- (7) Potassium permanganate.
- (8) Chromic acid in sulphuric acid.
- (9) Solution of (1) potassium permanganate.
,, ,, (2) sodium bisulphite.

In regard to (6) the mixture is used dry in a small muslin bag which is rubbed gently over the ink to be removed. The result is not generally satisfactory. For certain kinds of ink, citric acid is a powerful decolorizing agent. (9) however, which in

France is called a "corrector" and is used for non-criminal purposes, is very efficient.

Mitchell has experimented with the bleaching effect of hydrochloric and oxalic acids and bromine water. All these reagents have a marked bleaching effect upon iron gall ink and those of the logwood type. Vanadium inks are most resistant to the action of bleaching agents.

Examination of the Washed Document.—Chevallier whose classical methods still have much to recommend them makes use of litmus paper to test the reaction of the suspected portion of the document. The application of moist litmus paper must, however, be used with caution if other tests are to be made.

It is preferable to make use of a more sensitive reagent such as the universal indicator. A minute drop of the indicator is applied to the suspected area. This is then removed with a piece of filter paper. A similar test is made upon a portion of the document which is known to be in its original condition. Any difference in the hydrogen ion concentration is noted.

Nature of the Bleaching Agent.—It is not generally possible to decide positively the nature of the bleaching agent used. It is advisable, however, to make a test for chlorides and for sulphates. A small drop of dilute potassium permanganate can also be applied. Decolorization will indicate that sulphites have been used for bleaching. These tests, however, must be used with discretion. They are not sufficiently conclusive to warrant the risk of defacing the document. It is in all cases advisable before applying any chemical test to examine the surface carefully with a lens and to note any local discoloration or other sign that the surface has been treated chemically.

The Reconstitution of the Text.—Chemical methods for the restitution of "washed" writing are often effective if the manipulation is skilful. The greatest care, however, must be taken or the document may be damaged and the desired result not achieved.

When ink writing is bleached the pigment only is removed.

The iron salts although a portion of them may be removed remain upon the fibres of the paper. Classical methods for reconstituting a faded text included the use of gallic acid. A "true" ink is thus produced by reaction between the gallic acid and the residual iron. The method is not satisfactory and is now never used.

Potassium ferrocyanide is a more efficient reagent. The method of application is to soak a piece of filter or blotting paper with the reagent, place it in contact with the document and apply pressure on a copy press. In the case of newly washed documents, the method rarely fails to restore the writing. Much longer application is necessary in the case of older documents.

Before resort is had to the treatment with potassium ferrocyanide, it is necessary to ensure that the residual iron is in a soluble condition. It is thus advisable preliminarily to treat the surface with dilute nitric acid which is removed with water before the reagent is applied.

The most satisfactory method of development is, however, to treat the document with ammonium sulphide. The reagent must not be applied to the document direct, but in vaporized form. A satisfactory method of effecting this is to connect the Kipp apparatus with a wash-bottle containing ammonia. The outlet tube of the wash-bottle should be fitted with a funnel of convenient size. The document is rested upon the mouth of the funnel and arranged so that the suspected print is in contact with the vapours.

The time required for redevelopment of the text will depend upon the particular conditions. If the ink has been recently bleached the coloration may be restored fairly rapidly. Older documents react more slowly. The nature of the bleaching agent also affects the result. In general, acids act more drastically and remove a greater proportion of the iron, so that a text which has been acid washed is more difficult to reconstitute. The original iron content of the ink also, of course, influences the reaction. At the same time where an iron gall ink has been used, it is nearly always possible to reconstitute the bleached pigment by this method.

The reaction, however, is slower than that obtained with

potassium ferrocyanide. If after four hours' treatment no result is obtained, the experiment can be regarded as negative, but it should never be abandoned at too early a stage.

Deletion by Scoring Out.—Examples of this are rare in criminal cases, but they may occur in documents where it has been sought to alter the meaning by striking out a word or passage with ink. Such an act, equally with that of bleaching or erasure, may be forgery.

The greatest discretion must be used in employing chemical methods for the removal of the superimposed layer of ink. Resort should not be had to them until photographic methods with infra red plates or fluorescent photography have been tried and have failed.

First, micro-chemical tests should be carried out to decide if the two inks are of different composition and react differently to bleaching agents. If this is found to be the case the reagent chosen should be one which produces the maximum bleaching effect in respect of the superimposed layer of ink but where the effect is less marked upon the original ink of the text. Filter paper moistened with the chosen reagent is then applied to the deleted passage. The paper must be lifted from time to time to watch the progress of the bleaching and to ensure that it is not overdone. A piece of filter paper moistened with distilled water is then applied to remove the excess of the reagent. The present author (*Rhodes, The Scientific Examination of an Historic Document, Chem. and Industry, April 10th, 1931, 303*) has described in detail the method to be applied in a case where the ink of the text proved to be more resistant to bleaching agents than the superimposed layer.

In cases where the inks are of the same type, it may be impossible to bleach the superimposed layer without decolorization of the underlying ink. This, however, is not necessarily the case. If the ink used to make the deletion is of more recent date than that of the original writing, a suitable bleaching agent may remove the superimposed pigment, leaving the underlying text relatively unattacked.

Reconstitution of Erased Text.—It is not generally possible to reconstitute an erased text by chemical methods.

But in exceptional cases this can be done. It has been shown that a proportion of the iron salts sink deeply into the fibres of the paper and thus cannot be entirely removed by erasure. In some cases the quantity is sufficient to make chemical reconstruction possible. Fuming with ammonium sulphide is, in our experience, the only method by which an erased text can be restored. The method described (*vide supra*, p. 126) should be used and the treatment should be continued for four hours. If the surface remains unchanged after this lapse of time, the experiment must be considered negative, but even if traces of iron sulphide are observed, the treatment should be continued for a further hour. In our experience the results even if positive seldom make the text legible, but the experiment should always be tried since reconstitution of the text can be effected by this means in exceptional cases.

Forgery by Interpolation.—Chemical examination of suspected interpolations involves the micro-chemical examination of the ink. Where words or figures have been altered chemical tests of the kind already described are applied, both to the genuine and suspected parts of the writing. A colorimetric examination should first be made with a comparison microscope. It must be noted, however, that differences in colour, even if pronounced, are not necessarily evidence of manipulation. The quantity of ink with which the pen was charged, and the local condition of the paper will influence the colour of the same ink.

Well-chosen micro-chemical tests will, however, generally distinguish between different types of ink. Whilst evidence that a document has been written with more than one type of ink is not proof of forgery, it is always a highly suspicious circumstance.

The increasing use of the fountain pen, and the consequent standardization of ink has tended to reduce the scope of tests of this kind. An insignificant interpolation such as the addition of a cipher after another figure made with the same ink as that with which the document was originally written presents great difficulties to the examiner. If it can be shown in cases of this kind that the suspected interpolation was made at a later date

than the rest of the document there is then strong presumptive evidence of fraudulent manipulation.

An examination of the degree of oxidation of the ferrous iron in the ink may be of value in these circumstances (*see p. 108*). The present author has dealt with a case of a receipt in connection with which it was alleged that the actual author of the receipt had secured possession of it a fortnight after it was drawn for the purpose of altering the date. It was shown that the degree of oxidation of the ferrous iron in the ink of the suspected interpolation was less than in the ink of the undisputed parts of the document. The ink was, however, of the same type. This fact was consistent with the view that interpolation had, in fact, taken place at a later date.

THE DATE OF THE DOCUMENT

The question of the date at which a document was or was not written is one which is continually arising in connection with disputed documents. It may provide conclusive evidence of forgery or on the other hand establish the genuineness of a document, the authenticity of which is disputed. A chemical examination of the ink may in some cases supply the evidence required concerning the period at which the document was written.

There are certain historical facts which are relevant in this connection. Patents for the use of aniline dyes in ink were first taken out in England in 1861. The first aniline ink appears to have been made from Hoffmann's violet which was discovered in 1863. Eosine was discovered in 1874, and malachite green in 1878. It is thus obvious that if the presence of these pigments can be demonstrated in documents purporting to belong to a date prior to the discovery or use of these pigments, they are not genuine. Cavalho (*Crime in Ink*, N.Y., 1929) describes a case in which he showed that certain marginal references in red ink in a document stated to have been written prior to 1874 had been made with a red ink containing eosine.

Method of Examination.—Fully matured ink retains its provisional colouring matter tenaciously (*see p. 106*). In order

to bring it into solution it is necessary to treat it with concentrated acid. The ink stroke should be attacked with a drop of hydrochloric acid of a concentration of about 50%. After two or three minutes it is removed with a piece of filter paper. The spot is then neutralized with ammonium hydrate. Aniline dye if present will then regain its colour. Appropriate tests can then be applied (*p.* 102) to identify it.

The combination of the provisional pigment with the iron tannate in mature ink has been studied by Mitchell (*loc. cit.*, *p.* 106). The results in relation to the date of the document have wide application in practice. Mitchell recommends the use of a 5% solution of oxalic acid. The effect of this reagent upon fresh ink is to bleach the black pigment and liberate the aniline dye which spreads on the paper. With increasing age the dye diffuses less and less rapidly and after five to six years diffusion ceases altogether.

Whilst this test gives no indication of the precise date of the writing, it can distinguish fresh ink from that which is some years old with certainty. Thus in the case of *Rex v. Pilcher*, a disputed will was alleged to have been written in 1898. It was shown that the ink used to write a number of contemporary documents contained provisional colouring matter which showed no diffusion on treatment with 5% oxalic acid. Similar treatment of the ink on the will produced rapid diffusion of the aniline dye. It was thus concluded that the ink was less than six years old.

Locard (*Traité de Criminalistique*, VI, 793) uses a 20% solution of oxalic acid or a dilute solution of hydrochloric acid.

Copying Power.—Theoretically the solubility of the pigment in water and other solvents is an indication of the age of the ink. In practice, however, this method should not be applied except in special circumstances since it involves too large an area of the document. At the same time, if a copy can be made of an iron gall ink with water it is evidence that the ink is fresh. The method cannot be used to distinguish between inks which are close together in date, and it is not reliable except to distinguish fully matured ink from that quite recently used.

Chloride Diffusion.—Türkel developing the method of Metzger, Rall, and Heess for the detection of chloride (*p.* 107) has claimed that the area and depth of the stain produced on the paper by the reduced silver chloride makes possible an accurate estimation of the age of the ink on the document. In the present author's experience the technique is too complicated to recommend the method for general use. On the other hand, if it is properly performed the test is extremely delicate, and will give comparative results upon the same document of considerable value. A portion of the suspected ink is removed and a portion of that known to form a genuine part of the document. The two chloride tests should be run side by side. If any marked difference is noted in the diffusion of the chloride stain, the writing is of different periods. The migration of the chloride is, in our view, of no value except as a comparative test between portions of writing upon the same document.

Diffusion of Sulphates.—This is also true of the test for sulphates (*p.* 108). The test is less delicate than that for chlorides and its manipulation more complicated. But in inks which contain appreciable quantities of sulphates results of some precision can be obtained. In this case, as in the case of chlorides, comparative results are the only ones upon which reliance can be placed. The rate of diffusion is profoundly affected by the moisture of the paper, the temperature and probably by other factors which have not been determined, but where the tests are made upon the same document, and where other factors are constant, comparative results can safely be interpreted.

Colorimetric Method.—Mitchell has shown (*Analyst*, 1908 *xxxiii*, 80; *ibid xlv*, 247) that thin washes of iron gall ink with provisional colouring matter attain their maximum intensity of colour in about a week. Thicker layers corresponding to those made with a pen require much longer periods and if light is excluded may require eight to ten months to attain maximum coloration.

The colour of suspected ink should thus be determined with a comparison microscope against Lovibond's standard colour

scale. If it is found that the coloration increases rapidly the ink is comparatively fresh, and if it increases in colour at all within a fortnight the conclusion would be that it was less than eighteen months old. If on the same document certain portions of the ink darken whilst others do not, the ink is not contemporaneous. In cases where the date of the document is in question a colorimetric determination should never be omitted since it in no way alters the document and it may supply evidence of great value.

(g) The Chemical Examination of Sympathetic Inks

General.—Sympathetic inks are those compounds which when used as ink are invisible until treated by physical or chemical means which develop them and make the writing visible. They are often encountered in criminal cases although less frequently than formerly, but they are still extensively used as an aid to espionage. They thus have considerable forensic importance particularly in time of war, when vital issues may hang upon the ability to develop a message in secret writing.

Sympathetic inks are of four general types. (1) Those that become visible by reason of a dehydration effect which affects either the ink itself or the paper with which it is in contact. (2) Inks which are developed by photo-chemical effect or by reduction. (3) Inks that are developed by the agency of a chemical compound with which they produce a coloured compound. (4) Substances such as organic secretions or physiological liquids which act in some cases as oxidizing agents or as mordants.

Examples of (1) are the strong acids such as sulphuric acid and nitric acid. These compounds dehydrate the cellulose of the paper where it is heated and thus slightly char it. The salts of cobalt are also in this class. In this case, however, the change of colour on the application of heat is due to the dehydration of the salt itself. Sympathetic inks have been made with cobalt chloride and with cobaltous oxide, these substances being mixed with some hygroscopic compounds such as potassium carbonate or potassium nitrate to prevent dehydration on the paper. As with the acids these inks are developed by the simple application of heat.

(2) Soluble silver salts may obviously be used as secret inks since they are reduced in daylight. A silver sympathetic ink can be made by bleaching a bromide print of the writing with mercuric chloride. It is developed by treatment with sodium thiosulphate.

There is another photo-chemical effect which relies upon the use of solutions of quinine salts as sympathetic inks. These fluoresce strongly when exposed to ultra-violet light.

(3) The largest class of sympathetic inks are those which are developed by treatment with a reagent with which they produce a coloured compound. A very large number of compounds of this type can be made provided that they are initially colourless. Ferrous sulphate is developed with gallic acid, lead salts with a sulphide, cobalt nitrate with oxalic acid, starch with iodine.

(4) Physiological fluids which form sympathetic inks include saliva, urine, milk and blood serum. The value of saliva as a sympathetic ink depends upon its properties as an oxidizing agent. If dilute ink is applied to writing made with saliva it becomes visible. This is assumed to be due to the presence of an oxidizing enzyme in the saliva which induces a rapid oxidation and therefore darkening of the ink. Saliva and the other substances mentioned also act as mordants and thus produce differential staining of an ink which contains provisional colouring matter due to aniline dye.

The Development of Sympathetic Ink.—A table is reproduced below which includes sympathetic inks most commonly used and the treatment or reagent which develops them.

In practice since the composition of the sympathetic ink is not known except in unusual circumstances the nature of the developing agent to be applied cannot be directly ascertained. The preliminary test of heating the paper should, however, always be made. If this fails, a developing agent must be found.

During the late war chemists employed in ink laboratories of the Cypher Department used the empirical method applying stripes of different reagents to the paper in parallel lines side by side. Later it appears to have been discovered that iodine

DEVELOPMENT OF SYMPATHETIC INKS (LOCARD)

Sympathetic Ink	Developer	Colour
Very Dilute Sulphuric Acid	Heat	Brown
Very Dilute Nitric Acid	Heat	Black
Ferrous Sulphate	Galls	Black
Gold Chloride	Stannous Chloride	Purple
Copper Nitrate	Pot. Ferrocyanide	Brown
Basic Lead Acetate	Sodium Sulphide	Black
Potassium Arsenate	Copper Nitrate	Green
Oxalic Acid	Cobalt Nitrate	Blue
Ferrous Sulphate	Pot. Ferrocyanide	Blue(Oxid.)
Mercuric Chloride	Lime Water	Yellow
Mercuric Chloride	Stannous Chloride	Black
Basic Lead Acetate	Oxalic Acid	Yellow
Basic Lead Acetate	Hydriodic Acid	Yellow
Cobalt Chloride	Gentle heat	Blue-green

vapour acted as a universal developer. The stripe method is in any case very unsatisfactory and resort should on no account be had to it.

Development with Iodine.—The classical method of development with iodine is to expose the document to iodine vapour. This usually results in the development of the writing. The method has now largely been superseded by the use of a special developing reagent prepared as follows :—

Pot. Iodide	.	.	4 gm.
Iodine	.	.	0.1 gm.
Sodium Chloride	.	.	5 gm.
Aluminium Chloride	.	.	2 gm.
Glycerin	.	.	3.5 gm.
Water	.	.	30 cc.

This reagent must be prepared with caution since the aluminium chloride if added too rapidly to the solution of the other ingredients will produce a violent reaction. It must be added little by little and the solution kept cool.

The developer is applied to the document by means of a pad of cotton wool. Only in exceptional cases does this reagent fail to develop secret writing. It has the disadvantage that accidental abrasions and other local damage to the surface even if slight is also revealed in great detail by this treatment, but in practice this is seldom a serious inconvenience.

Of recent years a number of complex organic derivatives of silver have been synthesized. The object of using these compounds is to produce a type of sympathetic ink which cannot be developed by other means than with a specific reagent. These compounds are highly reactive and can be used at very great dilutions. The use of the iodine reagent described will, however, generally develop writing made with these types of ink.

(h) The Examination of Burnt Documents

There are circumstances in which it may be necessary to determine what has been written upon documents which have been burnt. The motive of the burning may be precisely to conceal what has been written, or may have been accidental so far as the document itself is concerned. In either case, however, the ability to discover what, in fact, has been written may advance the enquiry.

The examination of such documents calls for manipulative skill of the character possessed by the chemist although the treatment is not chemical in the narrow sense.

Effect of Ignition upon Ink.—Different types of ink are affected in different ways by ignition. Aniline inks are entirely

decomposed and do not usually leave traces upon the paper which retain their identity as writing. Carbonaceous inks and iron gall inks, however, leave sufficient residue to make the writing legible if the charred paper is suitably treated.

The traces left by iron gall ink are the most marked. Ink of this kind on ignition leaves a residue of iron oxide which stands out in contrast to the ash of the paper.

When the document is merely charred, however, the writing is not clearly visible. The paper itself is carbonized and therefore remains black in colour. The ink being incompletely ignited is not completely oxidized and does not develop a colour in definite contrast to the paper.

Mitchell (*Science and the Criminal*) was the first to suggest the method of incineration. If the document is charred and black the incineration is continued until the paper is reduced to a white ash. The inorganic constituents of the ink are then completely oxidized and contrast clearly with the white ash of the paper.

The method requires careful manipulation and failure is not uncommon. It is desirable to carry out the ignition in a large flat-bottomed vessel of pyrex glass which should be covered except for a small opening. This is essential to prevent the destruction of the ash by air currents. The incineration should be gentle and should be continued until the ash is completely white.

Photo-chemical Methods.—It should be noted that the incineration method should not be used until every other has failed. Here, as elsewhere, the principle applies that a document, whatever its condition, should be damaged as little as possible.

Davis (Police Department, Washington) has devised a method which seems to involve photo-chemical principles. He has reported that charred paper when placed in contact with a rapid photographic plate in darkness reproduces an image of any writing upon it if the exposure is continued for a fortnight. It appears that the reaction upon the emulsion is produced by the paper and not by the ink. It would appear, however, that if a film is used in place of a plate the effect is reversed, the reaction taking place as between the emulsion and the ink.

These incompatible results cannot readily be explained. The present author has not attempted them experimentally, or in actual practice. In general, however, photographic methods, if applicable, are more satisfactory in practice since they involve no change of state in the document. This is particularly desirable when dealing with so fragile a material as charred paper. The method of incineration described is theoretically sound but there are grave manipulative difficulties which are inseparable from it. For this reason every possible precaution should be taken, and recourse should not be had to the method if less drastic treatment is likely to prove successful.

(i) The Examination of Subsidiary Materials

Besides ink or pencil and paper, documents are sometimes associated with subsidiary material such as wax or gum. In the case of anonymous letters and fraudulently manipulated envelopes an examination of these subsidiary materials may become important.

Sealing Wax.—Sealing wax consists essentially of a mixture of resins and mineral colouring matter. Since it is used in fairly large quantities for sealing letters or parcels it is generally possible to secure sufficient to make an analysis. The melting point should be taken, the ash determined, the resins and the colouring matter noted.

Melting Point.—Lucas recommends floating a small portion of the wax upon a little mercury in which a thermometer is immersed. The mercury is heated by means of an oil bath, the temperature of which must be raised slowly with a small flame.

Resins.—The wax must be reduced to a fine powder in mortar with a pestle. It is then extracted with hot alcohol. It is usual to estimate the resins by difference by weighing the exhausted residue.

The resins can further be identified by their behaviour to different solvents thus :

Shellac.—Soluble in alcohol. Almost insoluble in benzene and ether.

Turpentine.—Soluble in alcohol, carbon bisulphides, and benzene.

Sandarac.—Soluble in alcohol and ether. Almost insoluble in benzene.

Rosin.—Soluble in alcohol, ether, and carbon bisulphide.

Dammar.—Partially soluble in alcohol, methyl, alcohol and ether. Soluble in benzene.

Copal.—Partially soluble in benzene.

Shellac and sandarac being insoluble in benzene are thus separable from the benzene soluble dammar and copal. The insolubility of shellac in ether also serves to distinguish it from the other resins.

Resins can be identified by adding a small quantity of acetic anhydride to a little of the wax in a test tube. The mixture is boiled, cooled, and a few cc. are transferred to a small porcelain dish. If a drop of sulphuric acid is added a red-violet colour develops if resin is present.

Examination of the Pigment.—The red pigment of sealing wax generally consists of vermilion (mercuric sulphide). There is a so-called vermilion substitute which consists of red lead (Pb_3O_4) coloured with tetrabromo-fluorescein (eosin). Red sealing wax may thus contain either mercury or lead.

Estimation of Mercury.—The sealing wax is treated with *aqua regia* which destroys the organic matter and dissolves the mercuric sulphide. The method of electrolysis is the most satisfactory for the estimation of mercury. The cathode, however, must be of gold or of platinum, heavily gilded. The solution must be slightly acid.

Bamberger, Feigl, Stock and others have utilized the reaction of diphenyl carbazone with mercuric salts. The coloration produced is blue-violet and the reaction is said to be quantitative. The present author has found the estimation very difficult in practice. A careful pH control is necessary, and it

should be between 6.5 and 8. The results, however, are not in our experience, consistent. If, however, only small quantities of the wax are available, no other method of estimation will give more satisfactory results.

Estimation of Lead.—The wax is treated with strong nitric acid to oxidize the organic matter. The solution is evaporated to dryness and the lead estimated as sulphate after precipitation with sulphuric acid in the usual way.

Comparative Analysis.—For the purposes of comparison, Mitchell (*Documents and their Scientific Examination*, p. 187) estimates the ash, the ash insoluble in hydrochloric acid, the sulphates, the resins, and the pigment. This scheme of analysis is sufficient to identify a given sample.

In the case of *Rex v. Fink* (Mitchell, loc. cit.), this scheme of analysis was used to distinguish various samples of sealing wax and to show the correspondence between sealing wax found in the possession of the defendant and that of certain seals found upon documents in question. It was clearly established that the defendant's wax was identical with that found upon these documents.

THE EXAMINATION OF GUM

The adhesive materials used upon envelopes are of a very varied character both in regard to their basic constitution and in the nature of the subsidiary material composing them. The adhesive material itself is of two general types, animal and vegetable. The animal adhesives, so-called glues, are hydrolytic derivatives of nitrogenous tissue. These adhesives normally harden on cooling but they can be retained in a liquid state by the addition of acids, calcium chloride, and zinc salts. The vegetable adhesives are produced from proteins or alkali-proteins associated with the oils from certain seeds. These are treated with the hydroxides of the alkaline earths or magnesia and with such salts as sodium fluoride or arsenate which, by hydrolysis and interaction with the bases liberate sodium hydroxide. Proteins of the casein type are also used mainly for the preparation of "cements" but also in certain

viscous types of adhesive. The third type of vegetable adhesive is that which is prepared from starch or dextrin. These are often in the form of pastes.

Reaction of Gum.—It is an important fact that with the exception of some adhesives made from starch, gums are never neutral. The animal adhesives are acid with the exception of those with a casein base, which are alkaline. The vegetable bases commonly used in adhesives for correspondence are also acid. A determination of the pH value with suitable indicators should thus always be made. Even a small difference in the pH value of the adhesive on a questioned envelope from that upon a control of the same type may in itself be conclusive evidence that the envelope has been regummed. If there are gross differences in the reaction, it may be positively assumed that there has been manipulation in the absence of special conditions which might influence the result.

Södermann applies the following tests to identify various adhesives :

ANIMAL ADHESIVES

Common Glue.—has an acid reaction. If heated on platinum foil it burns with a characteristic and unmistakable smell.

Albumin.—also produces an acid reaction. If a small quantity is dissolved in acetic acid and potassium ferrocyanide is added, a heavy precipitate is formed.

Liquid Animal Adhesives.—These are also acid in reaction since they are prepared with acids or with calcium and zinc salts. The appropriate acid radicles are sought.

Nitric Acid.—The test recommended is that with diphenylamine which produces a blue colour in the presence of nitric acid or nitrates.

Acetic Acid.—Ferric chloride produces a maroon precipitate of ferric acetate which is insoluble in the viscous medium.

Oxalic Acid.—With calcium chloride a white precipitate of calcium oxalate is produced.

Boric Acid.—The presence of this acid can be detected by its reaction with turmeric paper.

Zinc Salts.—The presence of zinc is shown by its reaction with potassium ferrocyanide with which it produces a voluminous white precipitate.

Casein Adhesives.—Casein adhesives are alkaline in reaction and usually strongly so. Casein gives a pink coloration with Millon's reagent (*p.* 119).

VEGETABLE ADHESIVES

Gum Arabic.—The reaction of this adhesive is usually acid by reason of the presence of formic acid present in it as a preservative. In spite of this yeasts and moulds are generally found in it and can be identified microscopically. The ash of gum arabic is alkaline. The alkalinity is due to carbonates which can be identified by the usual test.

Starch Pastes.—These commonly consist of wheat, rice, or maize starch. The type of starch is identified microscopically. The classical test with iodine should be applied in the first place.

Starch adhesives are of two types. The pastes are neutral, but liquid starch paste is acid in reaction. If the adhesive is found to be acid, the acid radicle should be sought by the usual tests.

Dextrinous Adhesives.—Those of good quality are white and acid in reaction. Most dextrinous adhesives give the starch reaction with iodine. They reduce Fehlings Solution. Dextrinous adhesives of poorer quality are brown. They are acid in reaction, reduce Fehlings Solution.

Interpretation of Results.—If sufficient of the material is available, it is generally possible to identify the adhesive by means of these tests if they are systematically applied. The object of the analysis is usually to compare the gum upon a suspected envelope or stamp with that of a standard known to be genuine. The results can readily be interpreted since marked differences in the result always point to falsification. It is not

uncommon to find, for example, a starch reaction in an adhesive whilst the genuine standard shows no such reaction. This indicates that the envelope or stamp has been regummed with a starch paste.

(j) The Development of Skin Prints on Documents

First, the development of skin prints on documents must be attempted only in certain circumstances. A good deal of damage can be done to a document in an attempt to develop prints. If it is to be examined for forgery the establishing of the fact of falsification or the reverse is the first consideration. Nothing must be done which is likely to interfere with this process. Since the development of skin print usually involves an extensive area of attack, it is obvious that the treatment may interfere with the more important examination. Inexperienced examiners can also reduce the document to such a condition that its production in court will result in disputes prejudicial to the enquiry.

Secondly, the results even if technically successful may be impossible to interpret because the document in question has been extensively handled and in consequence carries a number of skin impressions which have no bearing upon the enquiry and may actually conceal the evidence sought.

Thirdly, on the other hand, documents such as some anonymous letters which have not been forged can often be usefully dealt with in this way provided that proper precautions are taken with the examination.

Types of Impression.—Finger-prints, palm-prints, and exceptionally impressions of the lips and other parts of the body may be found upon documents. Lerich, *juge d'instruction* of Lattaquié, has reported the case of the correspondence of a Syrian prostitute who was accustomed to impress her letters with the lips, leaving a visible pattern due to the lip salve. Claps (*Rev. Inter. de Crim.*, 1931, 9, 704), after a detailed and elaborate study of lip prints concluded that :—

L'empreinte labiale ne pourrait guère être utilisée, en criminalistique, que pour la reconnaissance des individus, dans

le cas ou l'on n'aurait à sa disposition ni des empreintes digitales, ni des marques particulières permettant une identification.

In regard to other impressions in a case where it was known that a French prostitute was in the habit of applying certain of her correspondence to the vulva, attempts were made in our laboratory to develop the impressions without much success. In regard to the identification of such impressions, see also Locard (*Traité de Criminalistique*, I, 445). Whilst these questions are of considerable theoretical interest, in practice the development of finger and palm impressions and occasionally those of the feet are the only ones of importance.

Development of Skin Prints.—Lerich (*Rev. Inter. de Crim.*, April, 1932) has successfully developed both finger-and palm-prints upon Syrian documents. In the same paper he also reports an interesting example of the development of the prints of a fingernail upon a document which was identified as that of the auricular finger. In any case the author has conclusively shown that both finger-and palm-prints can be developed upon documents and identified with sufficient frequency to make the method of value in criminalistic practice.

Method of Development.—Methods of development of finger-prints on paper have already been described (*p. 5 et seq.*). The reagents commonly used in practice are iodine, iodine and aqueous vapour, osmium tetroxide (Mitchell), and ruthenium tetroxide.

Locard (*Traité de Criminalistique*, VI, 773) has recommended a special preparation of iodine which he describes as nascent iodine. Iodine is liberated from potassium iodide by mixing the iodide with manganese dioxide in hydrochloric acid. Liberated iodine in this form is a very sensitive developer. It has the further advantage of disappearing rapidly, leaving the document essentially unchanged.

Photo-chemical Development.—Development with silver nitrate is the most sensitive method, but it has certain features which make it unsuitable for use on documents. The prints are permanent and if many exist on the surface the paper may

be severely stained in a number of places. Further, it must be noted that a silver developer may fail where others would succeed. The reason is that this developer utilizes the chloride only. Owing to the migration of the chloride the print when developed may be too faint for identification. Fresh prints are thus the only ones which can be developed by this method. Once recourse has been had to this method it is not possible to redevelop by other means.

In our experience, development with iodine freshly liberated from potassium iodide is the best method of development in all but exceptional cases. The use of iodine in aqueous solution of potassium iodide from which the iodine is liberated by heating gives satisfactory results, but it has the disadvantage of acting upon the ink of the written document.

CHAPTER VI

THE CHEMICAL EXAMINATION OF COUNTERFEIT MONEY

(a) Counterfeit Banknotes

THE forging of banknotes has become of recent years an occupation which requires considerable skill and knowledge of printing and engraving. Chemical examination is generally of little use in examining documents of this kind except so far as a chemical examination of the paper may be necessary.

There is, however, another type of counterfeiting which is still very popular, namely, forgery of notes by free hand drawing or tracing. When the work is undertaken by skilled draughtsmen, as it frequently is, the results are often the production of a counterfeit note which is superficially indistinguishable from the genuine note. In England and in most civilized countries, vigilance in connection with forgery is so great that clumsy counterfeiting would be immediately detected. The result is that inefficient work is rare, and a high percentage of forged notes shows a great degree of technical skill.

Whilst the examination of printed or even drawn banknotes ought in general to be undertaken by an expert with an intimate knowledge of the manufacture of genuine notes, chemical examination may in certain circumstances be of assistance. The chemist should in any case acquaint himself with the methods used in printing banknotes for the same reason that he should acquaint himself with the composition of writing materials and paper. He should do this if only to avoid the undertaking of an examination he is not qualified to perform. In the Portuguese Banknote Case, for example, (*Rhodes, The Craft of Forgery*, 1934, p. 182), the examination of the disputed notes was entrusted to experts in engraving, employed in

England and Portugal. The experts employed were alone qualified to make an authoritative judgment.

Colorimetric Examination.—The colorimetric examination with a comparison microscope may in some circumstances give information of value. Differences in colour must not, however, be interpreted rashly. Genuine notes may and sometimes do vary in colour from printing to printing. This was shown to be the case in the Portuguese Banknote Case (*Rhodes*, loc. cit.). On the other hand, differences in colour should be carefully recorded since if they are marked, the circumstance is always suspicious.

Hand-drawn Forgeries.—A micro-chemical examination of the ink may provide valuable evidence in the case of hand-drawn forgeries. Five and ten pound notes which are extremely accurate copies of the originals can be produced with a mapping pen and chinese ink. If carbonaceous ink of this type is identified by micro-chemical tests, the forgery is established.

In the case of hand-drawn forgeries generally, the same technique of micro-chemical examination should be applied as in the examination of written documents. The coloured inks used are usually of the ordinary aniline type and present no special difficulties of identification not associated with ordinary ink-written documents. Chemical tests with dilute acids and bleaching agents distinguish sharply between printing inks used on genuine notes and the writing inks used by the free-hand forger, so that positive conclusions can nearly always be drawn.

Forged Water Marks.—Forged water marks are produced by the preparation of a rubber stamp of the design of the mark it is desired to imitate. The stamp is then moistened with a wax or a drying oil, and it is pressed upon the paper using a firm and even pressure. The imitation if examined in detail is generally found to be defective.

A conclusive test is treatment of the suspected watermark with a solvent such as ether. Since ether-soluble substances are invariably used for this type of counterfeiting the material

forming the watermark will dissolve. If this occurs, the watermark is not genuine.

Examination of the Paper.—The paper of genuine banknotes is always of high quality. In no case in our experience has a counterfeit note matched even approximately the paper of the genuine note. The chemical tests already described (p. 117) can be applied. Lucas (*Forensic Chemistry*, p. 83) employs, besides iodine and zinc-chlor-iodine, phloroglucine and aniline sulphate. These reagents give red and yellow colorations respectively with mechanical wood paper. The reactions are negative with linen, straw, cotton, esparto, and chemical wood.

Tests of this kind may not be conclusive since the paper of the forged and genuine notes may be of the same cellulose type, and yet of different quality. At the same time, the chemical tests should not be neglected since they may prove important evidence of identification if the paper of the forged note is found to be of the same composition as that of paper found in the possession of a suspected person.

Seizure of Suspected Materials.—In cases of note forgery it is of vital importance, first, to get the counterfeit notes out of circulation as soon as possible, and, secondly, to trace without delay the origin of the forgeries themselves. Where hand-drawn forgeries are concerned in particular a chemist should co-operate with the police in the conduct of the search of suspected persons and premises. Bottles of ink, draughtmen's materials and paper should all be carefully scrutinized, packed, and taken to the laboratory for examination. The source of the forgeries may be conclusively established in this way.

Forgery by Tracing.—As with other forged documents the banknote design may be reproduced by tracing and the inking over of the traced model. The tracing may be effected by the use of carbon paper, or as is more common, by a direct pencil tracing carried out on a "forgery table" (a glass-topped desk with a strong light beneath).

The chemical examination in this case aims at exposing the underlying pigment with which the tracing was effected. For this test the ink is treated with acid, 10 to 20% in strength, which removes the ink but leaves the pencil pigment unaffected. The demonstration that the design was traced in pencil is, of course, conclusive evidence of forgery.

(b) The Examination of Counterfeit Coin

General.—The chemical examination of counterfeit coin forms a very important part of any enquiry into coining. Unlike an enquiry into many other crimes, the object of the investigation is not only the detection of the criminal but the discovery of the real nature and extent of his work. Forgery and counterfeiting are peculiar in this—that a considerable period of time may elapse before it becomes evident that a crime is being committed at all. Even when this is known, the extent of it may be largely a matter of surmise. Primarily, at any rate, these considerations are more urgent even than the detection of the coiners. It is necessary to discover first if the counterfeiting is being carried out on a large or small scale; secondly, in what areas the money is circulating; and thirdly, if all the counterfeit money is emanating from one source.

Chemical analysis of the coins themselves is usually the most convenient method of deciding the third point, although there are various methods of physical examination by which counterfeit coins may be identified. The same group of coiners may, however, produce coins which show physical variations. A change in chemical composition generally indicates conclusively that different groups are at work.

Conclusive proof of the discovery of the source of the coins may depend upon chemical examination. If the material found at the suspected source proves to be of the same chemical composition as the coins it is obvious that the source has been located.

Occupational Dust.—The question of occupational dust is also of importance. It is not uncommon to find metallic fragments associated with the clothing of coiners, which may even

agree substantially with the composition of the coins themselves. The establishing of a fact of this kind may be vital in certain circumstances. It is a common defence of the coiner that he had unintentionally passed counterfeit coin but had not manufactured it. If it can be shown that the clothing carries even traces of the raw material from which the coins are made, this is conclusive evidence that the suspect has been associated with the manufacture.

Plaster of paris (*infra*) may also be associated with the clothing of coiners. The source of this is the moulds from which certain types of counterfeit coins are made.

Methods of Manufacture.—There are essentially two methods of manufacture of counterfeit coins, namely, production by moulding and striking from dies. It is, of course, possible to produce coins by the electrotypes process, but this method is seldom if ever used. In practice the coins are moulded or struck, moulded coins being by far the most common in England and Europe generally.

Dies require considerable skill for their manufacture and have to be prepared by an engraver. They may be cast and then finished by engraving or engraved direct. Coiners who produce stamped money are well organized and even command the services of skilled engravers and mechanics. Cases are on record where dies and stamping machinery were almost equal to that employed by legal mints. An example is the plant produced by Bonnot (*Locard, Traité de Crim.*), whose dies and stamping machines were of the best quality. Where the work is of a high standard the coiner works not on the original die but upon secondary dies prepared from the master engraving. Owing to the high standard of workmanship and the consistent result produced, the difficulty of detection is increased. On the other hand, the plant is cumbersome and cannot readily be disposed of. It is, in this way, a considerable danger to its possessor.

For this reason moulded coins are much more common. The process of manufacture is simple. The mould is small and it can be destroyed at a moment's notice. It consists of a superior and inferior part made of plaster of paris which is moulded,

using a genuine coin to produce the impression in reverse and obverse of the coin. The two parts of the mould fit closely but a groove is made in one section to allow the expulsion of the excess of metal. The coin is made from an easily fusible alloy which is melted and poured into the mould. The second section is placed in position and pressed down, the excess of metal escaping through the vent made by the groove. The milling is, of course, reproduced in the mould, but it has to be finished with a file. With skilful manipulation, very good reproductions can be produced by this method. All such coins, however, show minute faults by which they can often be identified as coming from the same mould.

THE COMPOSITION OF COUNTERFEIT COINS

Counterfeit coins vary greatly in composition. In the first place the stamped coin is naturally of greater hardness and tensile strength than the moulded coin. It is, in fact, by no means unknown for counterfeit coins to be of the same composition as genuine currency since it is sometimes possible for counterfeiters to take advantage of favourable movements in the price of metal and so manufacture coin more cheaply than the official mint. This is exceptional, but in the case of Bonnot (*Locard*, loc. cit.), the technical police seized a large number of unstruck discs which upon analysis proved to be of the same composition as the contemporary French coin.

The quantity of silver in English coin is now the same as it was in the fifteenth century. It contains 7.5% of copper (fineness of 925). French silver coinage used to contain 10% of copper (fineness 900). The German coinage also contained the same quantity of silver as the French.

In countries which still employ silver coinage these facts are of some importance. The highest quality of counterfeit coin contains a reduced quantity of silver with copper and the addition of nickel and tin to replace the loss of the silver. Suitable alloys of this type if well struck are very difficult to detect by inspection.

Moulded coins always contain a high percentage of lead since they must be made readily fusible. The usual constituents

of moulded coins are antimony, tin, and lead. In those of better quality the percentage of lead is reduced as much as possible since the coin rich in lead rapidly becomes discoloured and takes on a greyish tint which cannot be easily mistaken once it has been observed.

Coins of this type have silver deposited upon them electrolytically. For the time being this gives them a superficially genuine appearance. By reason, however, of galvanic action, the silver coating quickly wears off, exposing the greyish surface underneath.

Indirect Evidence supplied by Analysis.—In no kind of forensic enquiry is the co-operation of the investigating officers and the laboratory more important than in the case of counterfeit money. The chemist should request that every sample submitted to him for analysis should include particulars of the area in which the counterfeit coin was found. If this information is available, it may be possible to map the areas where different types of coin are being made or trace the movements of the distributors or of the coiners themselves. Without data concerning the composition of the coins, it is much more difficult for the investigating officers to trace their movements. If this cannot be done, it is not possible to trace the movements of the coiners themselves. The significance of this must be emphasized. Forgers of notes and coiners often continue their work for two or three years before they are detected; a few have enjoyed immunity from arrest for as long as ten years. A systematic correlation of the identity of the counterfeit material (supplied by analysis) and the area in which it is found may shorten the enquiry considerably.

ANALYSIS OF COUNTERFEIT COIN

Colour.—The colour of the surface should always be carefully noted since this in itself may be a means of identifying similar coins. Counterfeit coin is often yellow or grey. A yellow tinge may be due to an excess of copper or to the sulphiding of the alloy. On the other hand, coins with an excess of lead have a leaden appearance which reflects very little light. Abnormal

coloration does not always indicate a lack of genuineness. Silver which has been mixed with copper coins may develop an abnormal coloration which appears suspicious at first sight.

Weight and Specific Gravity.—These physical characteristics must always be recorded. If the coin is found to be heavier than the legal mint of the genuine coin, it is certainly counterfeit. The weight of genuine coins is so carefully controlled that they never exceed a certain limit. On the other hand, a defect in weight is much less conclusive since it may be due to wear. If, however, the coin shows little sign of wear and is defective in weight, it is a very suspicious circumstance.

The figures of density of the coin must be interpreted with caution. Differences in density between two coins do not necessarily indicate that they are composed of different alloys. Coins of the same size should be of the same density, but the density is inversely as the size of the coin. The reason for this is that a constant crushing strength has a greater effect upon a more limited area.

The density of counterfeit coins may bear an even less definite relation to their composition. The stamps may vary greatly in efficiency so that alloys of the same composition show wide variations in density. The density of the moulded coin is more consistent since the treatment does not bring about a variable change of state.

DETECTION OF METALS

The metals which may be found in counterfeit coins are the following in order of their frequency. Lead, tin, antimony, zinc, nickel, copper, aluminium, iron, silver, gold, chromium, tungsten, and bismuth. Iron, gold, tungsten, and bismuth are rarely present except as impurities, but their presence even in minute amounts may be important for the purposes of identification.

It is advisable to make a qualitative analysis before proceeding to the estimation of the metals. Only in exceptional cases are more than three metals present in any quantity. In the case of moulded coins the alloy will almost certainly consist of

antimony, lead, and tin. Traces, at least, of silver will also be found due to silver plating. Copper and tin will probably be present in struck coins with or without silver. Nickel may also be present.

It is advisable, however, to proceed systematically with the classical group separation since this is generally the most certain and rapid method of ascertaining the nature of the alloy.

Detection of Impurities.—Where traces of impurities are sought, however, the spot reactions may be applied.

Where traces of bismuth, silver, or gold are suspected, for example, the hexamethylene tetramine micro-chemical test may be applied.

Antimony, if present in large quantities should be removed. The solution to be tested should be only slightly acid. A fragment of the solid reagent should be added to a drop of the test solution on a microscopic slide, and the drop stirred with a fine-pointed glass rod.

Bismuth.—forms colourless and highly refractive octahedra and dodecahedra of the isometric system. If potassium iodide is added yellow octahedra are formed.

Gold.—forms pale yellow needles or plates showing strong polarization with parallel extinction.

Silver.—produces colourless needles or plates of the monoclinic system.

Tungsten.—The reaction with benzidine may be used for the detection of this metal. The solution should be neutralized and then made acid with 0.1 N sulphuric acid. The reagent consists of a 2% solution of benzidine in 1% hydrochloric acid.

Slight excess of the reagent is added to the test solution. In the cold and on standing a precipitate of benzidine tungstate and benzidine sulphate is formed. The reaction is quantitative. It is essential that distinct excess of sulphuric acid is

present since this facilitates the precipitation of benzidine sulphate. The object of the formation of the mixed precipitate is that the benzidine tungstate alone clogs the filter paper and may render the solution practically unfilterable.

QUANTITATIVE ANALYSIS

Iron, copper, lead, antimony tin, zinc, and silver are the metals which most commonly require to be estimated.

The samples for analysis should be taken by making drillings of the coins at various points and mixing the drillings made from which the sample to be analysed is taken. Fair sampling cannot be assured unless this is done. If more than one coin is available drillings should be taken from each coin and the drillings mixed. If sufficient material is available about five grams should be taken for analysis.

Iron.—The iron can be estimated in the usual way by precipitation as ferric hydrate and incineration to ferric oxide. The precipitation should, however, be made with potassium hydrate if traces of aluminium are suspected. The precipitate is redissolved in hydrochloric acid and precipitated with ammonia.

Copper.—The copper can be precipitated with hydrogen sulphide and weighed as cuprous sulphide. Alternatively it can be determined by iodometry which is in our experience the most satisfactory method for its determination in counterfeit coin.

Lead, Antimony and Tin.—These metals are usually found in conjunction in coins which have been made by moulding. Other metals are not usually present except in traces as impurities. They are estimated by the methods already described (*p.* 76).

Zinc.—This metal is most conveniently estimated in counterfeit coin volumetrically with potassium ferrocyanide. Excess of potassium ferrocyanide is added to the dissolved metal

in slightly acid solution. The excess of potassium ferrocyanide is then titrated back with a standard solution of zinc in hydrochloric acid using uranium acetate as indicator. Alternatively, the zinc may be titrated direct with potassium ferrocyanide. Back titration gives a sharper end point.

Silver.—This metal should be estimated by precipitation as chloride with hydrochloric acid, the usual precautions being taken to avoid excess of acid and reduction of the silver chloride by exposure to strong light.

It must be noted that these methods give a general indication only of the procedure to be followed. The composition of the alloy from which the coins are made may make the separation of interfering metals necessary. Bismuth, nickel, and copper, for example, interfere with the volumetric estimation of zinc. One of these metals may form part of a coin alloy containing zinc. It is for this reason always advisable first to make a complete qualitative analysis of the alloy so that the necessary separations can be effected before the quantitative analysis of a given metal is undertaken. It is rare, however, to find more than three metals as the main constituents of a coin alloy. Others may be present as impurities although often in such small quantities as not to interfere.

Dusts.—Since in cases of coining occupational dusts and those of location are very characteristic a careful examination should be made of the clothing of all suspected persons and of the dust and debris found at the suspected place of manufacture. The evidence is, of course, conclusive if specimens of the alloy itself are found, the analysis of which agrees with that of the coins. The presence of lead and tin alone is suspicious, but might be explicable on other grounds in the absence of confirmatory evidence. Metallic occupational dusts are associated with other workers such as mechanics and fitters. In one case within the author's experience, the coiner was a foreman mechanic who actually produced his counterfeit coin on the premises where he worked. On these premises metals were to be found which served both a legitimate and illegitimate purpose. The coiner in question was, in fact, arrested *in*

flagrante delicto. In this case, the circumstantial evidence supplied by an examination of occupational dust would clearly have been inconclusive. This will serve as an indication of the caution which is necessary in the interpretation of this kind of evidence if all the surrounding circumstances are not known.

The presence of calcium sulphate may sometimes be detected in association with metals from which counterfeit coins might have been made. If this substance is found it is always highly suspicious.

If traces of potassium and silver cyanides are found either in clothing or elsewhere this will indicate that silver plating has been undertaken. If these substances are found associated with other materials belonging to the act of coining it is strong presumptive evidence that counterfeiting is being carried on.

CHAPTER VII

THE EXAMINATION OF TOXIC AGENTS

General.—The term toxicology includes more than the chemical examination of poisonous substances. Toxicology has been defined as including not only the chemical composition but the physiological action of poisons and their antidotes. Definition of the term is important because it is essential to recognize that there are many aspects of toxicology which do not fall within the scope of the chemist. There still exist a number of poisons which cannot be identified positively by chemical methods. The chemist is not concerned with the physiological action of poisons, nor with therapeutic properties possessed by many of them, nor with any clinical problem which their administration may present. This consideration is not merely academic. It is essential that the chemist should confine himself to the technique concerned with the chemical properties, the detection and determination of toxic substances.

Section II of the Offences Against the Person Act says that : Whosoever shall administer or cause to be administered to or taken by, any person, any poison or other destructive thing with intent to murder, shall be guilty of felony.

Section 23 says that : Whosoever shall unlawfully and maliciously administer to, or cause to be administered to, or taken by, any other person, any poison or other destructive or noxious thing, so as thereby to endanger the life of such person, or so as thereby to inflict upon such person any grievous bodily harm, shall be guilty of felony.

And Section 22 says that : Whosoever shall unlawfully apply or administer to, or cause to be taken by, or attempt to apply or administer to, or attempt to cause to be administered

to or taken by any person, any chloroform, laudanum, or other stupefying or overpowering drug, matter, or thing . . . shall be guilty of felony.

The law makes a distinction between poison and a destructive or noxious thing. It has been held that a destructive thing means an agent which may cause death or injury by mechanical action. The term noxious has given rise to controversy. In the case of *Rex v. Cramp* (1880) the defence sought to show that an agent must be proved to be noxious in itself. Coleridge, L. C. J., ruled, however, that "if a person administers . . . something which, as administered, is 'noxious' he administers 'a noxious thing.'"

These considerations have some importance from the chemical point of view. The chemist is not primarily concerned with the toxic properties of the substance but with its identification. The chemical aspect of toxicology is thus a problem of identification of material amenable to chemical analysis and not its effects upon the human organism.

The problem of identification is of two kinds. (1) The identification of the material sought independently and (2) its identification within the body. The first method calls for no special consideration but the second involves problems which do not arise in the course of ordinary laboratory practice. It is for this reason that toxicology must be considered as a special branch of chemical practice requiring considerable experience.

Classification of Poisons.—From the chemical point of view the classification of poisons is best considered in relation to their physical and chemical properties rather than on the basis of their physiological action. A poison may be either an inorganic or an organic compound, and it may be either solid, liquid, or gaseous. The ordinary physical condition of the substance may have a profound bearing upon the general technique to be applied for its identification. Solids, for example, may be found unchanged in the body and liquids may also occasionally so be found whilst gaseous poisons will require special technique for their identification. It is also true in general that inorganic substances are more readily identified than organic compounds which are more difficult to isolate,

and are more readily confused with naturally occurring substances of metabolism or decomposition.

The chemist is entitled to acquire any information which is likely to assist him in his preliminary examination. He should ascertain, if possible, the symptoms from which the victim of the alleged poisoning suffered, and any other circumstances which may give him a clue to the nature of the toxic agent employed. As a matter of routine the chemist should be informed concerning :

(1) The time elapsing between the taking of the last meal and the appearance of the symptoms of poisoning or death.

(2) The nature of the symptoms.

(3) Whether there was (a) Vomiting and purging, (b) Deep sleep or coma, (c) Tingling of the skin, (d) Convulsions, (e) Delusions.

(4) The nature of other symptoms if any.

(5) Whether more than one person was affected and if so how many and to what extent.

(6) Any other information.

If information on these points can be supplied it will indicate what type of poison has been used and will facilitate the identification of the toxic agent.

Toxic Agents External to the Body.—As we have said, the examination of toxic substances in these circumstances does not generally involve any special problem, but in some cases it may do so. The examination of the person and clothing of a suspect may be necessary. Traces may be found in utensils or elsewhere which may throw light upon the enquiry.

In these circumstances micro-analysis may be necessary in order to identify the substances found. Poisons found under these conditions can be considered as occupational dusts and the same general methods of examination apply to them.

It is necessary in all cases to make a minute examination of the room or other place where the poisoning has occurred with a view to the discovery of traces which have a bearing upon the investigation.

A number of cases are on record in which traces of poison have been discovered and identified in the pockets of those

suspected of the administration of poison. In cases of abortion, also, it is not uncommon to find traces of abortifacient drugs in the clothing of suspects.

Toxic Agents within the Body.—Samples of the organs suspected to contain poison are taken by the physician who carries out the post-mortem if the poisoning has proved fatal. The organs should reach the laboratory separately packed. The stomach and its contents should be placed in one receptacle, the intestines in a second; the liver should be placed in a separate receptacle, and the bladder with any urine should also be packed independently. Finally, any vomited material should be packed separately.

In cases where gaseous poisoning is suspected the lungs must also be included in the sampling. (*Glaister.*)

The chemist should ascertain if any preservative has been added to the samples submitted to him. The addition of preservatives of any kind should never be made unless it is absolutely necessary and it is the business of the chemist to discourage a practice to which resort is sometimes had without sufficient reason. (*Locard.*) Those without chemical training often do not realize the importance of avoiding the use of preservatives which may interfere with the reactions for certain poisons, and they should be warned not to employ preservatives other than perhaps alcohol without a chemical consultation. Formalin has sometimes been used with the most disastrous consequences since this substance decomposes many alkaloids and produces a physical condition in animal tissue which interferes with the extraction of foreign substances from it. (*Lacassagne.*)

It is very desirable that the chemist should be responsible for the preparation of the receptacles in which the viscera are contained. The receptacles should be wide-mouthed glass bottles fitted with glass stoppers. They should be thoroughly cleaned with potassium bichromate and sulphuric acid and thoroughly rinsed with water, the last washings being made with distilled water. The stoppers should be lubricated with non-reactive jelly.

As far as he can the chemist should himself supervise all

these details. Those untrained in chemistry have no clear understanding of such phrases as "chemically clean" or a full comprehension of the manner in which minute traces of foreign materials may vitiate the results of a chemical analysis. Matters which are common-places of procedure in a chemical laboratory are often ignored or misunderstood outside it. Since, however, everything may depend upon these preliminary details, it is essential that proper attention is given to them.

(a) The Technique of Examination

The special technique of toxicological examination consists in the separation of the substance sought from the materials with which it is associated. When this has been accomplished the examination follows the ordinary course of examination appropriate to the compound to be identified. Details cannot be given to cover all cases, but there are general principles, which if followed are applicable in all but exceptional circumstances. Upon the adequacy of the preliminary steps taken the success of the examination may depend.

Two prerequisites are the use of chemically clean apparatus and absolutely pure reagents. Even with these precautions blank experiments should be run to check the purity of all reagents used. There is no kind of analytical technique in which the blank experiment is more necessary.

Preliminary Tests.—The first test is to note carefully the odour of the sample. A number of volatile poisons such as phenol, chloroform, and hydrocyanic acid can often be detected in this way. A practised nose is, however, an essential. The sample itself may have an odour which masks that of the poison, and alters its character. The experienced nose will, however, often detect the substance by its smell even when masked in this way.

The sample should then be tested with litmus paper and the reaction noted. A careful examination should then be made for the presence of particles of foreign material. Insoluble mineral substances, portions of leaves, seeds, or other vegetable debris may be detected. If foreign particles are detected they should be mechanically separated, washed, and

more closely examined. Some of the material thus isolated may not be amenable to chemical examination. In this case it should be preserved for examination by the pharmacologist or botanist.

General Methods of Separation.—Lucas (*Forensic Chemistry*, p. 286) has classified toxic agents according to their behaviour when submitted to certain specific laboratory procedure. Thus, he divides poisons into four groups (1) Volatile substances which can be separated from the menstruum by distillation. (2) Non-volatile substances which can be extracted with solvents. (3) Substances which resist the action of oxidising agents sufficiently to allow their use to destroy organic matter. (4) Special cases.

This classification is very valuable because it is founded upon the chemical behaviour of the substance in question ; and it is, in fact, true that the majority of toxic agents found in the body can be dealt with by one of these methods. Further, the methods in practice may actually reveal the identity of the substance or at least classify it and thus narrow the field of investigation. Lucas recommends the division of the sample into at least three parts. The first is used for distillation for the separation of the volatile substances, the second is used for extraction with solvents, and the third is retained as a control.

(1) **Separation by Distillation.**—This is carried out by distillation with steam. The sample is placed in a distillation flask of the standard type with a capacity of about 1000 cc. The flask is fitted with two tubes, one which connects with the steam can and the other with a condenser of the Liebig type. It is preferable that the distilling flask be fitted with a glass stopper ground in with the inlet and outlet tube fused into it. A rubber bung should not in any case be used. If a glass connection is not available a stopper of ordinary cork should be used.

Water of as low a temperature as possible should be run through the condenser in a rapid stream. The distillate may be collected in test-tubes which should preferably be immersed in ice.

Before distillation the mixture should be acidified. A non-volatile acid should be used, Tartaric acid is commonly found convenient. The distillation should not be allowed to proceed too violently. The distillate should be collected in quantities of from 8 to 10 cc. and the tubes numbered in sequence from the first to the last runnings.

The substances separated by this method are alcohols, certain phenols (including carbolic acid), volatile oils, hydrocyanic acid, chloroform.

(2) **Separation by Extraction.**—The substances separated by extraction are alkaloids and a number of synthetic drugs. The principle of the method is to use a solvent such as alcohol which effects a general extraction since a large number of the substances sought are soluble in alcohol, and to follow it with a differential extraction of the alcoholic extract with other solvents.

The Stas-Otto process, for example, uses a preliminary extraction with warm alcohol. This will dissolve the alkaloids and synthetic drugs as well as colouring matter and albumin.

The second stage consists in the removal of the alcohol by evaporation under reduced pressure, leaving a residue of mixed extract.

This residue is then extracted with acidulated water. The object of acidification is to convert the alkaloids into acid salts which are soluble in water. This extraction effects a partial separation of the alkaloids and synthetic drugs since the latter are often sparingly soluble in water.

The aqueous extract is then treated with a solvent such as ether, petroleum ether, or chloroform. This extraction removes the impurities and certain synthetic drugs soluble in these solvents. The alkaloids being in the form of acid salts remain in the aqueous solution.

The acidified aqueous extract is then made alkaline which liberates the alkaloids. They can then be extracted with chloroform or ether-ethyl acetate. The alkaloids and synthetic drugs soluble in water can then be identified.

Inorganic Residues.—Inorganic substances are left behind in the residue from distillation and only those soluble in

alcohol will be found in that extract. It is usual to make the examination for inorganic substances in the distilled residue.

This is the general method to be followed for the extraction of toxic substances from human remains. There exist, of course, cases which require special treatment. Thus if oxalates or oxalic acid are present, the extraction should be carried out with hydrochloric acid (*Elsdon and Stubbs, Analyst*, 55, 321). The scheme described, however, should always be carried out even if the presence of some substance known to require special methods is suspected.

(b) The Detection of Abortifacients

The detection of so-called abortifacient drugs is an important part of the chemico-legal practice. We are not here concerned with the fact that the majority of the substances reported to be abortifacients are not so in fact and that their sale is not only a danger to the public but constitutes a sort of fraud upon the victims who purchase them. But they are, in fact, poisons or at least "noxious things," their administration may result in death, and their use is criminal.

The following substances are very commonly used as abortifacients: Ergot, Savin, Pennyroyal, Tansy, Apiol, Cantharides Absinthe, Artemisia (Mugwort), Rue, Aloes, *Taxus baccata* (Yew), Gamboge. Not all these substances are amenable to chemical identification but at our laboratories at Lyon a number of empirical tests have been devised which in many cases serve to identify them.

(1) **Ergot**.—Since it acts selectively upon the uterus this substance can be classified as a true abortifacient. The active principle of this fungus is ergotinine $C_{34}H_{40}N_4O_6$ (*Fauret*) $C_{35}H_{41}N_5O_6$ (*Fr. Codex Supp.*), and ergotamine $C_{35}H_{39}O_5N_5$ (*Barger and Carr*).

Being an alkaloid it can be extracted by the methods described. If a portion of the extract is made alkaline with potassium hydrate and heated, trimethylamine is produced and detected by its characteristic smell. Sulphuric acid 1 : 7 produces a red-violet colour, changing to blue. In ethereal

solution the addition of crystals of oxalic acid produce a red colour.

(2) **Savin.**—This oil contains a terpene $C_{10}H_{16}$ known as sabinene. It is dangerously toxic producing gastro-enteritis and tetanic spasms.

The following tests are characteristic. Mixed with an equal volume of chloroform and after the addition of sulphuric acid, the acid and chloroform layers separate. The acid layer becomes blood red in the presence of sabinene. Hydrochloric acid in alcohol gives pale red and then violet, sulphuric acid, orange-brown. Fröhde's reagent, red-brown. Iron perchlorate in sulphuric acid a slow reaction, cherry-red.

(3) **Gamboge.**—Gamboge is a yellow resin, which can be separated from such oils as apiol and savin by steam distillation. It remains as a residue in the form of a yellow emulsion. If this emulsion cannot be filtered clear and retains its yellow colour the resin is present. This test distinguishes it from aloes, which leaves a residue after distillation which is also yellow in colour. The solution can, however, be filtered clear. A yellow precipitate forms in the filtrate on the addition of potassium hydrate and lead acetate.

(4) **Aloes.**—Besides the tests described the active principle, aloetine, can be identified by the following reactions. In benzene solution aloetine produces a red colour when shaken with potassium hydroxide solution or ammonia. In aqueous solution aloines give a blue-black coloration with ferric chloride in the cold (*Guillemard*). Heated with a drop of copper sulphate solution and 1 or 2 cc. of hydrogen peroxide aloine gives a strawberry-red coloration.

(5) **Absinthe.**—The active principle of absinthe is santonin, a crystalline substance composed of four-sided flat prisms which are white or faintly yellow. If santonin is dissolved in strong sulphuric acid, and the mixture is warmed and ferric chloride added a red colour changing to purple is produced.

(6) **Mugwort (*Artemisia*)**.—Although quite ineffective as an abortifacient the decoction is frequently taken to induce abortion, Jacques Locard (*Laboratoire de Police Technique, Lyon*), states that the following tests serve to identify mugwort. Ferrous sulphate produces a dark green precipitate. Potassium bichromate produces a coloration resembling tincture of iodine. An abundant precipitate slow in formation is produced with silver nitrate. Strong acids produce a dark coloured precipitate.

(7) **Rue**.—Sulphuric acid gives a very dark red-brown coloration which assumes a chocolate colour on the addition of alcohol. Nitric acid gives a dark cherry-red.

(8) **Apiol**.—This substance is the active principle of parsley.

A method for the identification of apiol was devised by Guillemard working in our laboratories at Lyon. A few drops of Millon's reagent are added to the material to be tested. On shaking, a very intense red colour is produced. Alternatively, a few drops of the material are extracted with carbon disulphide. Bromine sulphocarbonate is then added until the coloration persists. On evaporation, crystals of tri-brom-apiol are deposited which can be recrystallized from absolute alcohol in the form of white needles melting at 80° to 90° C.

Tansy, cantharides, and yew are not readily identified by chemical methods.

The Stas-Otto process already described is, in general, applicable for the isolation of these substances from the stomach or viscera. It will have been noted that the majority of these substances are either alkaloidal or they are volatile oils, or resins. The volatile oils pass over when the material is steam distilled while the resins remain behind. Substances of an alkaloidal nature can be extracted with alcohol and subsequently with acidulated water in the manner described.

Dusts.—In cases where it is suspected that an abortion has been procured, besides an examination of the victim's stomach a search of the premises of suspected persons may be necessary. It is quite common to find both in the houses and clothing of

professional abortionists, traces of drugs of a highly suspicious character. The examination and identification of these traces calls, however, for considerable experience. The chemical tests described although of value are not generally applicable to the identification of traces of abortifacient drugs.

It is, in fact, generally necessary to seek the co-operation of a pharmacologist or botanist who has specialized in the microscopic detection of materials of this type. He may be able to identify by microscopical inspection minute fragments of leaves and other vegetable debris which chemical tests would be unable to recognize.

(c) The Detection of Inorganic Poisons ACIDS

Corrosive acids are used for suicidal purposes to a very large extent. They are less frequently found in cases of murder.

Sulphuric Acid.—The identification and estimation of this acid presents no special difficulty. It may have to be examined as concentrated acid, as dilute acid, mixed with the contents of the stomach, or as a stain upon fabric.

The concentrated acid should be tested by its charring effect upon sugar or other organic matter, and its reduction by copper foil or other reducing agent.

The dilute acid can be identified by precipitation with barium chloride in the usual way.

In connection with stains upon clothing it should be noted that the strong acid produces a brown stain while dilute acid stains the cloth red. The colour of the stain is thus a guide to the strength of the acid used. This may be of importance in the enquiry.

Hydrochloric Acid.—This acid may also have to be examined either in a strong or dilute acid in the stomach or as stains upon clothing. No special modifications of the classical tests are necessary. In the quantitative estimation of the acid in the stomach, however, a complete extraction until the washings are completely neutral must be made.

Nitric Acid.—The concentrated and dilute acids can be recognized by the usual tests such as the evolution of the oxides of nitrogen by treatment with copper foil. The black ring test may also be applied.

STRONG ALKALIS

Sodium Hydrate.—Where this alkali is found mixed with the contents of the stomach, the material has a soapy consistency and a strong alkaline reaction. The alkali must be estimated volumetrically. The contents of the stomach must be thoroughly extracted with distilled water until the washings are neutral. The mixture is then filtered and the filtrate concentrated. The titration should be made with N or 0.1 N sulphuric acid, using methyl orange as indicator.

Potassium Hydrate.—The same methods are applicable. The potassium, however, may be estimated by means of the sodium salt of the 6-chloro-5-nitrotoluene-3-sulphonic acid. Rosenthaler (*Mikrochem*, 1934, 14, 368), or identified by means of hexanitro-diphenylamine.

Ammonium Hydrate.—Ammonium hydrate is recovered by distillation of stomachic contents, absorption in standard acid and subsequent titration back.

METALLIC POISONS

Arsenic.—Arsenic as is well known is one of the most common toxic agents occurring in criminal cases. It is probable that more work has been done upon its identification and estimation than upon any other poison.

Arsenious acid (white arsenic) is the most common of the poisons found in connection with homicide, but by solution in alkali it may be in the form of sodium arsenite which exists in weedkiller and fly-papers, both of which have been used by poisoners. The sulphides of arsenic being insoluble are not poisonous and organic preparations of the cacodyl type are less toxic than white arsenic (*Glaister*). There now exist a number of therapeutic preparations such as the arsphenamines, of

which salvarsan is an example, which are seldom administered except by the intravenous route.

Poisoning may be produced accidentally by the action of certain moulds and fungi upon arsenical pigment in wallpaper in a room where dampness favours the growth of certain moulds. It has been shown that the cause of the poisoning is the formation of the gaseous diethylarsine.

In whatever form the arsenic exists, however, it is amenable to the same tests both qualitative and quantitative.

Preparation of Material to be Tested.—In criminal cases the arsenic is generally found associated with organic matter such as the viscera stomachic contents, hair, or nails. It is necessary to destroy the organic matter before the tests are carried out. There are three methods commonly used for this purpose. (1) That of Fresenius-Babo. (2) Method advocated by the Royal Commission on arsenical poisoning. (3) The method of Stryzowski.

(1) **Fresenius-Babo.**—The material is reduced to a fine state of division. 70 cc. of hydrochloric acid are added to every 150 gms. and three times the volume of water. Pure potassium chlorate is added to the mixture to oxidize any trivalent arsenic which may be present. This must be done in the cold or the volatile arsenic trichloride may be lost. The mixture is then heated on a water bath with stirring, potassium chlorate being added from time to time. The solid matter is finally completely dissolved and the liquid becomes yellow. The addition of potassium chlorate is continued as long as any brown colour develops, and the liquid is then heated until the excess of potassium chlorate is decomposed. This is indicated by a darkening in colour of the liquid.

The solution is then cooled which causes the separation of a quantity of solid matter. The supernatant liquor is decanted and filtered and the residue washed two or three times with warm dilute hydrochloric acid. These washings must be cooled before being filtered and added to the main bulk or a further filtration will be necessary.

The filtrate and washings are then evaporated on a water-

bath to a volume of about 200 cc. If the liquid darkens a few fragments of potassium chlorate are added.

In order to reduce the arsenic to the arsenious condition 10 to 15 cc. of a saturated aqueous solution of sulphurous acid are added. After the mixture has stood for some time the sulphurous acid is removed by evaporation. The concentration of hydrochloric acid must be kept down or arsenic trichloride will be lost.

The solution is then cooled, filtered if necessary, and a slow current of hydrogen sulphide passed through it for an hour. This operation should be carried out in a flask, which can be cooled. It is then allowed to stand for twelve hours, and hydrogen sulphide is again passed through it. If after being allowed to stand for two days the liquid still smells of hydrogen sulphide it should be filtered through a Gooch capsule with asbestos. The precipitate is then washed with sulphuretted hydrogen water. The washing must be small or colloidal arsenic sulphide will be formed and will pass through the filter.

This method is lengthy and elaborate and requires careful manipulation. There is danger of loss of arsenic as arsenic trichloride and later as colloidal arsenic sulphide. There is further the necessity of using hydrogen sulphide which is free from arsenic. The gas must thus be made from specially prepared calcium or barium sulphide. Alternatively, Crookes recommends the preparation of magnesium hydrosulphide by passing hydrogen sulphide into a suspension of magnesium oxide in water.

(2) Method of the Royal Commission.—This method is simpler. Ten grams of the substance are treated with pure redistilled nitric acid (10 cc.) in a porcelain crucible. The mixture is then heated on a water-bath until no more brown fumes are evolved. 3 cc. of pure arsenic free sulphuric acid are then added and the mixture is again heated. When the mass begins to char, 5 cc. of nitric acid are added. The acid is then removed by heat and the charred mass is treated with water containing hydrochloric or sulphuric acid. The mixture is digested for half an hour. It is then filtered and washed with hot water.

(3) **Method of Stryzowski.**—We have been accustomed to use this method which is the simplest of the three. 100 grams of the material are mixed with 35 cc. of a saturated solution of magnesium nitrate made alkaline with magnesium oxide. The mixture is gently heated at first until the mass softens and chars. The charred mass can then be heated more strongly and is thus converted to a grey ash. The ash now consists of magnesium oxide mixed with any arsenic or antimony present in the form of magnesium pyro-arsenate or pyro-antimonate. Neither of these compounds is volatilized by heat.

The ash is now dissolved in hydrochloric acid and filtered.

This method being simpler than those previously described eliminates the danger of loss due to long manipulation. It is rapid and only small quantities of the reagents are involved.

THE IDENTIFICATION AND ESTIMATION OF ARSENIC

The Reinsch Test.—This test if properly performed is the most satisfactory for the detection of arsenic. It is, however, so simple that it is often carelessly and even recklessly done. The principle is that copper heated in a solution containing arsenic is coated with the metal in the form of a grey film.

The copper used in the test must be free from arsenic. A solution of pure arsenic free hydrochloric acid (one part in five parts of water) is prepared and a few drops of a weak solution of ferric chloride or ferric sulphate are added. The liquid is boiled and after the boiling has been continued for a few moments the copper foil is added and the boiling continued for a few moments. If the copper is free from arsenic its bright colour should be unchanged.

For the test itself, the solution should be made slightly acid with hydrochloric acid. Two or three small pieces of the copper foil are placed in the boiling solution and allowed to remain in contact with it for fifteen minutes. The test should not be considered negative until the boiling has been continued for half an hour. Hot water should be added to the solution from time to time to prevent undue increase in the concentration of acid.

Inhibiting Conditions.—If too much acid is present it will interfere with the deposition of the arsenic. If the arsenic has been converted to sulphide by putrefactive decomposition of the original material the arsenic will not respond. If conditions exist which prevent the reduction of arsenates to arsenites the test is inapplicable. These conditions should not obtain if the original material has been treated by one of the methods described. It is not safe to employ the test, as is sometimes recommended, upon the material in which the organic matter has not been destroyed.

Interference by other Metals.—Antimony, bismuth, gold, mercury, platinum, silver, and tin are also deposited upon copper by this method. The presence of arsenic must thus be confirmed.

The film is dried between filter paper and heated in a warm oven. The foil is then cut into small pieces and introduced into a small dry tube. The foil is gently heated. If arsenic is present it forms a sublimate on the walls of the tube of arsenious oxide. On microscopical examination the crystals, if of arsenic, are well-marked octahedra.

By reason of its simplicity this test is of great value, but it is not infallible, particularly where small quantities of arsenic are concerned. The Royal Commission on Arsenical Poisoning, says (*Part I, Final Report, p. 20*), "But we are now satisfied that the use of the Reinsch test entails considerable risk of missing quantities of arsenic which, though small, are not to be regarded as negligible."

THE ESTIMATION OF ARSENIC

There are two general methods by which arsenic is estimated for forensic purposes, namely, by the classical gravimetric methods and by the micro methods which determine larger or smaller traces of arsenic. In practice, the classical methods are seldom employed since large quantities of arsenic are not generally found in criminal cases.

Classical Method.—The method of separation of the arsenic depends upon the volatility of arsenic trichloride. The

material to be examined is first dried and then placed in a distillation flask with sufficient pure hydrochloric acid. The flask is attached to a condenser and adapter which dips into a receiver containing sodium or potassium hydrate solution. The receiver as well as the condenser should be cooled. Three-quarters of the contents of the flask should be distilled over and after cooling, the operation should be repeated, using more hydrochloric acid. The distillates are then mixed.

Arsenic-free hydrogen sulphide is then passed into the warm liquid for several hours, and the flask let stand in a warm place until the smell of hydrogen sulphide has disappeared. The arsenic trisulphide is collected upon a tared filter, and washed with alcohol, ether, and finally, carbon bisulphide to dissolve any sulphur.

MICRO-CHEMICAL METHODS

The Gutzeit Test.—The Gutzeit test relies essentially upon the same principle as the classical Marsh-Berzelius test. It has the advantage of being rapid and simple, and as recently modified it is quantitatively accurate. The classical form of the test was to produce arsine by the generation of hydrogen in the presence of the arseniferous material and to bring it into contact with bibulous paper, moistened with silver nitrate. A black stain was produced. Silver nitrate is, however, unsuitable by reason of its sensitiveness to other agents such as light and traces of hydrogen sulphide. Mercuric chloride has now replaced silver nitrate as a detector. This salt is, of course, also affected by hydrogen sulphide, but it is much less sensitive than silver salts. On the other hand, it is extremely sensitive to the presence of traces of arsenic, producing with it a yellow stain, which passes through lemon-yellow, bright yellow, orange to orange-brown, according to the amount of arsenic present. The test is more sensitive than the Marsh test and when sulphides are removed it is extremely satisfactory either for the detection or estimation of traces of arsenic.

Dowzard (*J. Chem. Soc.*, lxxix, lxxx, 463, 715) has devised a method of efficiently washing the gas. It consists of a superimposed series of glass cells, the lowest of which fits the neck

of an Erlenmeyer flask. These cells are filled with lead acetate and cuprous chloride in hydrochloric acid and are so constructed that the generated gas bubbles through the solution before it escapes. By this double washing, phosphoretted hydrogen and hydrogen sulphide both of which react with mercuric chloride are removed.

The test does not require elaborate manipulation. A weighed portion of the sample is mixed with 5 cc. of pure arsenic-free hydrochloric acid, four drops of a 15% solution of cuprous chloride are added, and the volume made up to 30 cc. with water. The volume may be increased but the concentration of acid must be constant. A rod of arsenic-free zinc is placed in the flask and the mixture added. The cells containing the lead acetate and cuprous chloride are placed in position and the bibulous paper moistened with mercuric chloride adjusted over the mouth of the exit tube. If after forty minutes no stain is observed, no arsenic is present. Light yellow stains indicate minute traces, orange-brown, heavy traces.

Standards can be prepared in the same manner, using a solution containing known quantities of arsenic.

The Marsh-Berzelius Test.—Despite refinement in the technique of the Gutzeit test which makes it available for quantitative determination, it is still generally used only as a sorting test. Officially, the Marsh-Berzelius test is still employed for all quantitative determinations of traces. The principle of the test is well known as depending upon the reduction of compounds of arsenic and antimony to produce arsine and stibine respectively by nascent hydrogen in an apparatus which consists of a hydrogen generator, a calcium chloride tube to dry the evolved gas and a capillary in which the arsenic is sublimed. This is cooled by a drip-flow of water.

Evolution of Hydrogen.—Three different methods are used for the evolution of hydrogen. The Joint Committee of the Societies of Chemical Industry and of Public Analysts (*Analyst*, 27, 1902), (*J.C.S.I.*, 21, 1902), recommend an apparatus in which the hydrogen is generated from pure zinc and sulphuric acid. The second method is the electrolytic in which a dilute solution of sulphuric acid is electrolysed between platinum

electrodes. The third method which is not commonly used is one in which the hydrogen is generated independently.

The first of these methods is the simplest but it depends upon the absolute purity of the zinc whereas the electrolysis between platinum electrodes eliminates this requirement. There is, however, an electrolytic method which we have used at Lyon in which the anode is of platinum and the kathode of pure zinc. The advantage of this method is that the arsine is liberated with great readiness and completeness even from zinc which is defective in "sensitiveness" (*vide infra*). The disadvantage is that zinc must be used which is one of the objects of the electrolytic method to avoid.

THE REAGENTS

Zinc.—Lack of "sensitiveness" in the zinc means that despite its ready reaction with acid which is common to all zinc the gas evolved by the metal will not always release the arsenic from the test solution. The cause of this interesting phenomenon is not understood. It was found by Chapman (*Analyst*, 32, 1907, 247-9) that if the zinc is coated with cadmium it becomes sensitive. It is, however, essential that the cadmium coating should be uniform. Cadmium being below zinc in the electro-chemical series is deposited upon it if the metal is placed in a solution of a cadmium salt. In practice, 25 grams of pure granulated zinc are treated with dilute nitric acid and then quickly washed. The zinc is then placed in a flask with 50 cc. of a 4% solution of cadmium sulphate or chloride. The mixture then stands with occasional shaking on a water bath until the spongy deposit of cadmium covers the zinc. The couple is finally washed.

A control test is made with a solution containing 0.01 mgm. of arsenious oxide. A distinct mirror should be formed. If the zinc is still found to be insensitive the cadmium coating is increased. If the zinc still remains insensitive it should be rejected and a fresh sample chosen.

If the zinc is used in connection with the electrolytic process we have not found it so liable to insensitiveness. Some workers have questioned the utility of cadmium treatment of the zinc

rod. They consider that if the zinc is insensitive in the electrolytic process it must be rejected. No final conclusion upon this point can be offered.

Sulphuric Acid.—Arsenic is a common impurity of this acid, but it is now always possible to secure an arsenic-free supply. The acid can, however, be purified by distillation over pure sodium chloride (*Royal Comm. on Arsenical Poisoning*, 2.206). Since most bottle-glass contains traces of arsenic it must not be stored for long in bottles.

Calcium Chloride.—This salt often contains heavy traces of arsenic, but it is now commonly supplied arsenic free. It can be purified by moistening with pure hydrochloric acid fusing and regranulating. It has been stated that under certain conditions which have not been defined, calcium chloride absorbs arsine (*Dyer*).

Glass Wool.—Cotton wool should on no account be used to plug the calcium chloride tubes. Ward has shown (*Analyst* 51 (1926), 457) that cellulose will in certain conditions absorb arsenic. Glass wool should always be used to plug the tubes.

Interfering Substances.—The following metals in the form of salts interfere with the evolution of arsine: iron, platinum, copper, nickel, and cobalt.

Oxidizing agents are, of course, destructive of the gas. Thus potassium chlorate, chlorine, bromine, nitrates, and nitric acid must not be present. Reducing agents such as stannous chloride (which is the most satisfactory), sodium sulphite, or potassium metabisulphite may be used for reduction. Excess of stannous chloride must be avoided, since tin, although unobjectionable in small quantities, is said to interfere if in excess.

Blank Experiments.—It is essential that blank experiments be carried out on all reagents and a final test using the reagents together as in the test itself should be made. After every precaution has been taken there is a tendency for the reagent

to absorb arsenic from surrounding materials or from the atmosphere. Blank experiments must therefore be carried out periodically. It is also essential to guard against the apparatus itself absorbing arsenic in the region of the calcium chloride tube. If, for example, the apparatus consistently produces absolutely clean blanks, it should be thoroughly overhauled, since it may be an indication that absorption is taking place within the apparatus.

Standard Mirrors.—Mirrors should be prepared from a standard solution of pure arsenious oxide in hydrochloric or sulphuric acid equivalent to 0.001 mgm. of As_2O_3 per cc. In our experience sulphuric acid is the more suitable. A series of mirrors are prepared, equivalent to 0.002 mgm. to 0.2 mgm., each increasing by 0.002 mgm. Comparison is not possible with quantities in excess of 0.2 mgm.

It is very important that the tubes should be uniform at the point where the mirror is deposited. This uniformity can be assured by the use of a copper rod which is pushed into the capillary until it engages with the walls. A mark is then made at this point with a grease pencil. When the test is made the filter paper which is placed on the tube to distribute the water for cooling is so arranged as to correspond with the pencil mark. This ensures that the sublimed arsenic will be deposited in the tubes at points where the bore is uniform. The importance of this cannot be exaggerated. If mirrors, which are quantitatively equal, are distributed upon a different area, it is obvious that their density will vary. Since the comparative test is, in fact, a comparison of density, serious errors will arise if the area of the tubes at the point where the deposition occurs is a variable.

Micro-Gravimetric and Volumetric Methods.—The method of comparison has been shown to be such as to distinguish between mirrors differing by quantities of the order of 0.002 mgm. It is, however, possible to utilize the micro-balance for the purpose of weighing the deposit. This is, of course, strictly a sounder method providing a micro-balance of sufficient accuracy is available.

In practice, however, the micro-volumetric method is more satisfactory. The mirror is dissolved in 0.005 N iodine containing a little sodium bicarbonate. The solution is then made faintly acid with HCl and titrated back with sodium thiosulphate using starch as indicator. A micro-burette graduated in 0.002 cc. must be used. In all cases these methods should be used as a check against the method of comparison with standard mirrors.

Antimony.—This metal is also detected both by the Reinsch and the Marsh tests. In criminal cases it is common to find larger quantities of antimony than of arsenic in similar circumstances because of the more toxic nature of arsenic. Further, the most common form is potassium antimonyl tartrate which is the only soluble salt which is readily obtainable.

Gravimetric Estimation.—It is usual to estimate the antimony as the sulphide. The material is extracted with hot hydrochloric acid 1 : 5. Small quantities of potassium chlorate are added from time to time during the extraction to decompose the organic matter. The mixture is then cooled and filtered. Hydrogen sulphide is then passed through the filtrate for four or five hours. The precipitate after settling is filtered and washed with water containing hydrogen sulphide. The precipitate is then dried, transferred to a porcelain boat and ignited in combustion tube in an atmosphere of pure dry carbon dioxide. The boat is then cooled and weighed Sb_2S_3 to $\text{Sb} = 0.7177$.

Micro-method.—Bamford (*Analyst*, 59, 1934, 101-2) has devised a colorimetric method for the determination of small quantities of antimony. The material is first treated in the manner described (*Method of Stryzowski*, p.171). The ash when cold is taken up with sufficient hydrochloric acid to make the mixture acid.

If iron is present in the mixture it must be removed. The solution is then saturated with hydrogen sulphide, and the precipitate filtered off and washed. The antimony sulphide is then redissolved in a small quantity of hydrochloric acid. Gum

arabic (1 cc. of a 5% solution for every 100 cc. of liquid) is then added and the solution is then made up to a definite volume. Hydrogen sulphide is again passed through the liquid. The solution is colorimetrically compared with standards.

Mercury.—This metal can be detected by the Reinsch Test. Quantitatively it can be estimated electrolytically or gravimetrically in the form of sulphide. The material is digested with about one-fourth of its weight by hydrochloric acid. The mixture is then heated and potassium chlorate is added until the liquid is homogenous. It is then heated further to remove all traces of chlorine. The liquid is then filtered and the residue washed. Hydrogen sulphide is then passed through the liquid. The precipitate is filtered through a tared Gooch capsule, dried, and weighed.

Lead.—Lead salts are seldom used in cases of murder but frequently as abortifacients. The lead may be estimated by the usual classical methods. If traces are present the method of Roche Lynch, which relies upon wet oxidation, extraction of the lead with diphenyl-thiocarbazon, and colorimetric determination of the sulphide. The method is very accurate for the determination of traces.

(d) The Volatile Poisons

By volatile poison, is meant that type of compound which passes over by distillation with steam. Besides the volatile oils used as abortifacients to which allusion has already been made, there exists a number of other substances which are commonly used as poisons and which are in this respect volatile.

Carbolic Acid (Phenol).—Phenol is commonly used by suicides. It is generally recognizable by its characteristic smell. Phenol is also strongly acid.

The formation of tribromphenol is one of the characteristic tests. The phenol should be extracted with ether. A few drops

of bromine water are added and the mixture shaken. A heavy precipitate, white or white-yellow, is formed in the presence of phenol. (*Glaister*.)

Phenol can be estimated by this method. The material is distilled with hydrochloric acid twice. In certain cases it may be necessary to distil a third time. The distillation must in any case be continued until the distillate gives no reaction with bromine water for phenol. The whole distillate is then precipitated with bromine-water and the tribromphenol collected upon a tared Gooch filter. The precipitate is dried until constant and weighed.

Millon's reagent gives a red coloration when warmed in the presence of phenol.

Trichloraldehyde (Chloral).—A few drops of aniline and a few cc's of alcoholic potash are added to the material to be tested and the mixture is warmed slightly. The characteristic smell of phenylisocyanide is noticed.

1 cc. of a 5% solution of resorsinol is added to the solution to be tested and 3 drops of a 4% solution of sodium hydrate. On boiling and diluting a pink coloration is produced.

Chloroform.—Chloroform reacts in the same way to the reagents described. Lucas, however (*Forensic Chemistry*, p. 289) describes a specific test.

A small quantity of the distillate is placed in a small flask fitted with a tube to admit air which is immersed in the liquid and an outlet tube of hard glass bent at a right-angle. Air is injected by pressure and the outlet tube heated strongly. If chloroform is present it is cracked, producing free chlorine and and hydrochloric acid. Chlorine can be recognized by its reaction with iodized starch paper, and hydrochloric acid by passing the vapour into silver nitrate acidified with nitric acid.

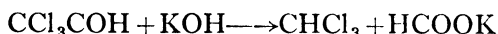
Estimation of Chloral and Chloroform.—By treatment with alcoholic potash chloroform is decomposed according to the equation



A determination of the chloride ion is thus a measure of the chloroform present.

10 cc. of an 8% solution of alcoholic potash is used for every 0.2 gm. of chloroform. The flask is heated under a reflux for three hours on a boiling water bath. After cooling a slight excess of nitric acid is added and the chloride estimated by precipitation with silver nitrate.

Chloral can be determined by alkalimetry according to the equation



The aqueous coloration of chloral is treated with a normal solution of potassium hydrate. Excess of normal sulphuric acid is then added and the mixture is titrated back with normal potassium hydrate.

Before the determinations are carried out the chloral or chloroform must, of course, be identified by means of the tests described. Neither method is of a high order of accuracy but both give an indication of the amount of the constituents present. (*Barral.*)

Hydrocyanic Acid.—Both hydrocyanic acid and most cyanides pass over when distilled in acid solution. Mercuric cyanide does not decompose unless considerable quantities of protein are present. (*Fabre and Jossett.*)

Ferrocyanides, thiocyanates, and ferricyanides also yield hydrocyanic acid on distillation in acid solution.

If a little ferrous sulphate and ferric chloride are added to the distillate, prussian blue will be formed if hydrocyanic acid is present. The intensity of the coloration is an indication of the quantity present. If the concentration is faint, the coloration is bluish-green, if large the blue colour is pronounced and a blue precipitate settles on standing. (*Glaister.*)

(e) Extraction with Solvents (Alkaloids)

Alkaloids and synthetic drugs are removed by the extraction process, the principles of which have already been described (*p.* 163).

In practice the material to be examined is finely minced or otherwise reduced to a fine state of division. Vomited material

which is acid should be partially neutralized with sodium bicarbonate, but it must be left faintly acid. The mixture is then evaporated to a syrupy consistency. Evaporation must be carried out at a low temperature and in a current of hot air.

Extraction with alcohol.—(1) The material is extracted with alcohol, faintly acidified with tartaric acid. The extraction flask should be refluxed and the extraction continued for a quarter of an hour. The mixture is then filtered through muslin which is finally squeezed. The filtration is generally difficult if viscera are being extracted and it is advisable to allow the extract to settle over night, decant the supernatant liquor, and wash by decantation.

(2) The alcoholic extract is then again treated with sodium bicarbonate, left faintly acid and evaporated at a temperature of 45°C . in a current of hot air. In the process of the evaporation oil and fat will separate and are removed.

(3) After the fat-free extract has been evaporated to a syrupy consistency, it is again treated with alcohol in successive quantities which are left in contact with the residue for about three minutes and then poured off. This operation is repeated until the residue granulates. The residue is finally mixed thoroughly with alcohol until all the colouring matter is extracted.

(4) The mixed alcoholic extracts are then nearly neutralized with sodium bicarbonate and filtered. The residue is washed with alcohol. The filtrate is then evaporated to a syrupy consistency at a low temperature as before.

(5) The residue is then extracted with faintly acidulated water. After a thorough extraction the mixture is filtered and washed with acidulated water. The residue consists of fat not removed in the previous extraction and certain things sparingly soluble in acidified water. The residue is reserved for further examination.

EXAMINATION OF THE AQUEOUS EXTRACT

The taste of the extract should be noted and the physiological effect upon the tongue. Aconitine and cocaine produce numbness, a very bitter taste may indicate strychnine.

If ferric chloride is added to a portion of the extract upon a white tile a red coloration indicates meconic acid and therefore opium.

Meconic Acid and Morphine.—Lead acetate is added to the extract. This precipitates the meconic acid as lead meconate and leaves morphine in solution. The solution is filtered and the residue washed with distilled water. The filter is then transferred to another receiver and a hole is made in the filter paper, the residue being washed through. After the precipitate has settled as much of the supernatant liquor as possible is poured off and hydrogen sulphide is passed through the liquid. The meconic acid is liberated and lead sulphide precipitated. The precipitate is filtered off and the excess of hydrogen sulphide removed by heating the filtrate. It is then tested with ferric chloride to confirm the presence of meconic acid.

The Filtrate.—Sulphuretted hydrogen is passed through the solution to remove excess of lead acetate. The liquid is then filtered and the filtrate evaporated to dryness. The residue is redissolved in water and again filtered. The filtrate is made alkaline with potassium carbonate. Ether is then added and the mixture well shaken. The treatment effects the separation of the morphine from other opium derivatives and colouring matter since the morphine remains in solution in the alkaline liquid.

(1) The liquid is extracted with a mixture of ether and alcohol. This extract is evaporated to dryness. Crystals of morphine are deposited.

(2) The liquid may be extracted with hot amyl alcohol.

(3) The extraction may be made with ethyl acetate or with a mixture of ethyl acetate and ether.

Tests for Morphine.—Nitric acid produces a red colour. Neutral ferric chloride produces a fugitive blue colour. Sulphuric acid containing formaldehyde produces a red-purple (*Marquis*).

Extraction of Alkaloids and Other Drugs.—A portion of the aqueous extract which has not been treated with

hydrogen sulphide or from which the gas has been removed is slightly acidified with sulphuric acid. This solution is then successively extracted with petroleum ether, ether and chloroform.

The petroleum ether extract contains mainly fat and may be rejected. The ether and chloroform extracts are mixed and washed with acidified water.

This effects the separation of synthetic drugs and alkaloids. The synthetic drugs are extracted by the solvents. The alkaloids remain in solution in the acidified water.

The Separation of Alkaloids.—The acidulated solution is treated with a mixture of ether and ethyl acetate. It is then heated to about 40°C. to remove the ether and if necessary filtered. Chloroform is then added and dilute sodium hydrate until the mixture is slightly alkaline. The alkali liberates the alkaloids present and dissolves morphine if present. After separation of the chloroform layer, more chloroform is added, and the extraction repeated twice. This chloroform extract removes all the alkaloids except morphine.

The Synthetic Drugs.—These are found in the ether-chloroform extract originally made. The original residue from cold acidulated water after the first alcoholic extraction also contains synthetic drugs. This residue is extracted with hot water and, after cooling, with chloroform. It is added to the ether-chloroform extract.

The mixed extracts are allowed to evaporate spontaneously. The residue is allowed to stand for twelve hours with free access to the air. It is then treated with petroleum ether to remove the fat. The fat-free residue is treated with alcohol and this extract is allowed to evaporate spontaneously. It is again extracted with alcohol and evaporated. The residue contains the purified synthetic drugs.

THE DETECTION OF ALKALOIDS

There exist several general tests which must be applied to the alkaloidal extract to determine if alkaloids are present. These tests are not specific. Their value is greater in the negative

than in the positive sense. If the general tests are negative, alkaloids are absent, if they are positive they may be present.

It is essential that all tests for alkaloids should be carefully confirmed and whenever possible supplemented by physiological tests made by a physician specialized in the identification of alkaloids by these tests. On no account, however, should reliance be placed upon physiological tests alone since they are often difficult to interpret. The chemist should not in any case attempt either to carry out physiological tests or to interpret them. The injection of mice and other small animals may result in their death from causes which have nothing to do with the material of the injection if the operation is performed by an inexperienced person.

Unfortunately there still exist some alkaloids which cannot be detected positively by chemical tests alone. When this is the case the work of the forensic chemist ends with the extraction and separation of the alkaloid. The matter becomes one for the pathologist.

Three general reagents are used for the detection of alkaloids. A 10% solution of sodium phosphomolybdate in 10% nitric acid, dilute sulphuric acid and iodine solution in potassium iodide, and Mayer's reagent which consists of precipitated mercuric iodide dissolved in excess of potassium iodide.

With the first of these reagents alkaloids give a yellow precipitate. In the second test the solution of the suspected alkaloid is made acid with the smallest possible quantity of dilute sulphuric acid. The addition of the iodine solution produces a chocolate precipitate.

Mayer's reagent produces a pale yellow precipitate with alkaloids. In exceptional circumstances it may be white.

(f) The Identification of Alkaloids

The classical colour tests which have been employed for more than forty years still remain in use. If the isolation of the alkaloids in the manner described has been satisfactorily carried out the tests are quite satisfactory.

Aconitine.—There is no specific test for aconitine. Sulphuric acid gives a yellow-brown colour, passing to violet.

Nitric acid gives yellow. Physiological tests must be used to identify aconitine.

Atropine

Sulphuric Acid	Brown
Fröhde's Reagent	Green, brown-red to yellow, finally decolorized

If sufficient of the material is available to prepare the picrate of the alkaloid its melting point is 175 to 176°C.

Brucine

Nitric Acid	Red
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Cocaine

Fröhde's Reagent	Dirty Green
Mandelin's Reagent	Blue-green

A drop of potassium permanganate is evaporated upon a microscopic slide. Near the residue of the permanganate place a drop of alum and a drop of the solution to be tested. Mix the alum mixture with the permanganate residue and cover with a cover slip. Characteristic crystals of cocaine permanganate are formed.

If treated with chromic acid, cocaine produces a precipitate which disappears on shaking and if hydrochloric acid is added to the mixture an orange precipitate forms.

Codeine

Sulphuric Acid	Dark green-brown
Fröhde's Reagent	Green then yellow
Mandelin's Reagent	Blue-green

Curarine.—This dangerous alkaloid gives no specific chemical tests. Sulphuric acid, however, gives a red colour passing to reddish-purple. Nitric acid gives purple.

Morphine

Sulphuric Acid	Red then violet
Fröhde's Reagent	Violet then green
Mandelin's Reagent	Reddish
Nitric Acid	Orange

Nicotine.—This alkaloid does not give specific chemical tests. Fröhde's reagent gives green, then yellow and red. Nitric acid gives yellow.

Strychnine

Mandelin's Reagent	Violet then rose
Nitric Acid	Light Yellow
Potassium ferrocyanide	Bluish

Potassium ferrocyanide in hydrochloric acid produces long slender needles of a characteristic type. The most delicate test for strychnine is that with strong sulphuric acid in the presence of an oxidizing agent such as potassium bichromate. If the material is mixed with the acid and a fragment of potassium bichromate is stirred in a blue-purple colour changing to purple, crimson, and orange-red is produced if strychnine is present.

Hyocyamine and Hyocine.—These mydriatic alkaloids require special treatment. In the first place hyocyamine is very liable to pass into the racemic modification atropine or be hydrolysed to tropine or tropic acid. In the Crippen case, Willcox extracted the viscera with pure ethyl alcohol several times and united the extracts. More elaborate methods of extraction may lead to its decomposition. Strong alkalinity to phenolphthalein indicates a vegetable mydriatic alkaloid. Vitali's test which was reported in the Crippen case is a confirmation. A few drops of strong nitric acid are added to the material and it is then evaporated to dryness on a water bath. Alcoholic potash is then added when a reddish-violet colour forms.

Wormley's test was also applied by Willcox in the Crippen case. A drop of hydrochloric acid saturated with bromine is added to the material to be tested, which is dissolved in sulphuric acid (1 to 50). A yellow precipitate forms which crystallizes on standing. The crystals can be identified under the microscope.

Micro-chemical Tests for Alkaloids.—The colorimetric tests for alkaloids are classical. The test for brucine with nitric acid was first used over seventy years ago. (*Kertsing*,

Annalen, 1863, 125, 254.) A number of the other colour reactions have also been in use for many years.

More recently the micro-chemical reactions of alkaloids have been studied. It has long been known that alkaloids form insoluble crystalline compounds with a number of reagents, gold chloride, mercuric chloride and picric acid being typical examples.

These methods require highly standardized manipulation since changes in the physical conditions of a very insignificant character may profoundly affect the results.

The crystallizing agent which may now be regarded almost as classical is that of Marmé. It consists of cadmium iodide 3 grams, potassium iodide 6 grams, water 18 cc. If a drop of this reagent is added to a trace of the alkaloid in aqueous solution a crystalline precipitate is formed, the form of the crystals being recognizable microscopically. These crystalline compounds have sharp melting points, but there is seldom sufficient of the material available to make a melting point determination.

Identification of Picrates.—Burt E. Nelson and Helen A. Leonard (*J. Amer. Chem. Soc.*, 1922, 369) describe a method for the micro-identification of picrates. These authors consider that the picrate derivatives give the most satisfactory results particularly where small quantities of the material are available. They stress the fact that a rigid control of the physical conditions is necessary. Among the most influential of these factors are temperature, concentration and purity of the material crystallized. They point out that minute traces of foreign substances such as grease upon the microscopic slide may seriously interfere with the reaction and lead to an incorrect interpretation of the results.

Method.—The aqueous solution of the separated alkaloid is made faintly acid with hydrochloric acid in a micro test tube. A saturated aqueous solution of picric acid is added. The precipitate formed is deposited centrifugally and washed by decantation several times. The residue is dissolved in a minimum quantity of 95% alcohol and the mixture is warmed on a water

bath. This warm solution is allowed to cool slowly, the crystals separating on cooling. After this preliminary treatment more rapid cooling increases the yield. The mixture is then centrifuged, until the deposit is firmly packed. The supernatant liquor is poured off into a second micro test tube and preserved. A small portion of the crystalline deposit is now transferred to a paraffin ringed slide for microscopic examination.

The second tube containing the supernatant alcoholic liquor is now diluted with an equal volume of water. This alcohol water mixture is now added to the remaining crystals of the first precipitation. The mixture is warmed until the deposit dissolves. On repeating the cooling, the crystals are redeposited.

By this means two microscopic preparations are obtained (1) crystallized from 95% alcohol and (2) from 50% alcohol.

These preparations are examined microscopically. The authors state that highly characteristic crystalline forms are produced in all cases, and that two preparations of the same alkaloid obtained under these different physical conditions serve in effect as confirmatory tests for a given alkaloid. They supply no crystallographic data, but the crystalline formations are illustrated by means of drawings.

The importance of this technique is that it serves to show the need for the standardization of the conditions under which the test is carried out. Both heating and cooling must be controlled and the volumes of the solvents must be equal in all cases. Aerial contamination must be avoided since the deposition of minute quantities of dust will seriously interfere with crystallographic methods in general. It is also necessary to ensure absolute cleanliness of the microscopic slides. They should be treated first with hot alkali, washed, dried, and finally immersed in ether to remove every trace of grease. These precautions apply to all crystallographic determinations carried out on a micro scale. Serious errors of identification may result if the precautions are neglected.

(g) The Identification of Synthetic Drugs

Acetanilide.— $\text{C}_6\text{H}_5\text{NH.CO.CH}_3$. This drug is a white crystalline compound readily soluble in hot water, alcohol,

ether, and chloroform. It is prepared by the action of glacial acetic acid upon aniline. Aniline is regenerated from it by heating with potassium hydroxide. Lucas recommends this test. Phenyl isocyanide is produced if acetanilide is treated with potassium hydroxide and chloroform.

Winton and Bailey (*J. Am. Chem. Soc.*, 1905, 721) recommend the following tests. A portion of the material to be tested is treated with hydrochloric acid for one minute and then diluted with water. The solution is divided into four parts.

A few drops of chlorated lime are added to the first portion. This should be run carefully down the side of the tube so that the solutions do not mix. A light blue colour forms at the junction of the two liquids if acetanilide is present.

Chromic acid is added to the second portion (3% solution). A yellow-green solution is formed changing to dark green. Potassium hydroxide produces a dark bluish-green precipitate.

Potassium permanganate forms a clear green solution with acetanilide.

To the fourth portion a few drops of a 5% solution of sodium nitrite are added. Make alkaline with sodium hydroxide and add a drop of beta naphol in alcohol. A red colour due to the formation of a basic azo dye is produced.

Antipyrine (Phenazone).—($C_6H_5(CH_3)_2C_3HN_2O$). This is a white crystalline compound melting at $113^{\circ}C$. It is soluble in water, alcohol, and ether.

Ferric chloride gives a blood-red coloration which is dispersed by mineral acids. Potassium or sodium nitrite with sulphuric acid give a green colour.

Steensma's reaction is the most sensitive. One gram of paradimethyl-amino-benzaldehyde is dissolved in 100 cc. of 1% hydrochloric acid in absolute alcohol. 5 cc. of this reagent are added to a small quantity of the material to be tested. A rose-red coloration is produced if antipyrine is present.

Phenacetin.—Aceto-*p*-phenetidine ($C_{10}H_{13}O_2N$.) Phenacetin is a colourless crystalline compound soluble in water, alcohol, and ether. Melting point $135^{\circ}C$.

A 10% solution of nitric acid when boiled with a solution containing phenacetin produces a yellow or orange coloration. Neither acetanilide nor antipyrine responds to this test. If the solution is concentrated yellow needles of nitro-phenacetine are formed. The melting point is 103°C.

Phenacetin produces a similar reaction with chlorinated lime as does acetanilide.

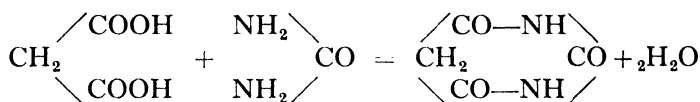
A few drops of hydrochloric acid are boiled with the material to be tested and the mixture is diluted with water, cooled, and a few drops of chromic acid solution are added. A deep red colour is formed in the presence of phenacetin.

Sulphonal (Sulphone Methane).— $(\text{CH}_3)_2\text{C}(\text{SO}_2\cdot\text{C}_2\text{H}_5)_2$.

A colourless crystalline substance melting at 125°C. It is soluble in alcohol. The drug is prepared by the action of hydrochloric acid upon acetone and mercaptan.

Mercaptan is, in fact, formed when sulphonal is heated with potassium cyanide. It can be recognized by its characteristic and disagreeable smell. The residue acidified with hydrochloric acid gives a reddish colour with ferric chloride.

Barbituric Acid and Barbiturates.—These compounds are the most modern form of hypnotic drugs. Barbituric acid is, in fact, a ureide produced by the action of malonic acid upon urea.



The diethyl derivative barbitone or veronal, diethyl barbituric acid $(\text{C}_2\text{H}_5)_2\text{C}(\text{CONH})_2\text{CO}$ is one of the best known derivatives. There exist a very large number of derivatives, many of the aromatic series which are sold under trade names. Evipan, luminal, medinal, noctal, monal, and proponal are among the best known. All are powerful hypnotics and are commonly found in cases of suicide.

Veronal.—This drug is a white crystalline substance, soluble in water. The melting point is 191°C.

If veronal is fused with potassium hydrate, ammonia is evolved. If the residue is dissolved in dilute hydrochloric acid, and a solution of a ferrous salt is added, Prussian blue is formed.

Millon's reagent in the presence of a trace of nitric acid produces a white gelatinous precipitate with veronal which is soluble in excess of the reagent.

If a solution containing veronal is dissolved in water with a trace of hydrochloric acid and then made alkaline with sodium hydroxide, Nessler's solution produces a red precipitate.

THE MICRO-CHEMICAL IDENTIFICATION OF SYNTHETIC DRUGS

G. Denigès (*Mikrochem.*, 1931, 9, 316-323) has described a method for the micro-chemical identification of synthetic drugs. The following are compounds whose micro-chemical reactions have been studied:—veronal, soneryl, rutonal, luminal, dial, allyl-iso-propyl malonylurate, and allonal.

A small quantity of the material (less than a milligram) is dissolved in ammonium hydroxide. This operation should be carried out on a microscopic slide which has been scrupulously cleaned, first by treatment with sodium hydroxide and, finally, after drying, with ether to remove the last traces of grease from the surface.

The ammoniacal mixture is now made slightly acid with sulphuric acid, 1 : 10. A cover slip then placed over the acidified drop and the preparation is examined microscopically with a magnification of about 60 diameters. Under these conditions most of the synthetic drugs form highly characteristic crystalline structures which are readily identified. Veronal forms rectangular plates either isolated or in groups. Soneryl forms long needles radiating from the centre. Rutonal produces regular hexagonal plates or groups of crystals which produce the appearance of foliage. Luminal forms rosettes. Dial is characterized by the formation of hexagonal plates and groups of rhomboids. Allyl-iso-propyl malonylurate forms elongated hexagonal plates.

Allonal is a compound of allyl-iso-propyl malonylurate with

pyramidon. Under this treatment allonal forms the elongated hexagonal plates characteristic of allyl-iso-propyl malonylurate whilst with picric acid, yellow elongated prisms are formed which are characteristic of the pyramidon part of the molecule.

It will be noted that the crystalline forms observed after treatment by this method are highly characteristic and serve sharply to distinguish these synthetic drugs from each other. At the same time, dial and rutonal, both of which form hexagonal plates, may in some circumstances be confused.

Rutonal is, however, a phenyl derivative whilst dial is not. If a drop of 2% sulphuric acid is added to the material to be tested on a microscopic slide and the mixture is gently warmed, phenyl substituted compounds such as rutonal and luminal give an intense brown coloration and yield a precipitate on dilution. Non-phenyl derivatives such as dial give a red-brown colour.

If proper precautions are taken in carrying out this test the results are reliable. The same care must, however, be taken to control the conditions of temperature and concentration, as in the case of the micro-chemical identification of alkaloids. Aerial contamination must be avoided as in all other cases where micro-chemical tests of a crystallographic type are being carried out.

(h) Organic Acids

Oxalic Acid.—This is the only organic acid besides hydrocyanic acid which is commonly found in criminal cases. It requires special methods of extraction. In spite of the fact that it is readily soluble in water, oxalic acid and oxalates are sometimes retained, particularly if the acid is mixed with vomited material. This makes an acid extraction necessary as a precautionary measure. The material is first extracted with water and the mixture is centrifuged. The clear supernatant liquor is decanted off and the process is repeated twice. The aqueous extract does not always contain all the oxalic acid or oxalates, and the residue must be treated with 15% hydrochloric acid, the acid mixture being digested upon a water bath for two hours with periodic shaking. It is then filtered and added to the united aqueous extracts.

Estimation of Oxalic Acid.—The solution is first made alkaline with ammonium hydrate, and then acid with acetic acid. Calcium chloride is then added in slight excess. The precipitate is allowed to settle for several hours in a warm place at 75 to 80°C. The precipitated calcium oxalate is then filtered, washed with boiling water, ignited strongly, and weighed as calcium oxide.

Blyth (*Poisons : Their Effects and Detection*, 1920) recommends precipitation with calcium acetate. The present author has found this modification produces a precipitate which does not occlude the coloured substances which are generally associated with the classical method of precipitation. The precipitate also granulates and settles more readily. If calcium chloride is used reprecipitation may be necessary to remove the impurities carried down with the first precipitate.

If the volumetric method of estimation is used reprecipitation is not necessary. The precipitated calcium oxalate is washed with hot water and dissolved in dilute sulphuric acid. It is then titrated in the usual way with 0.1 N potassium permanganate. The direct estimation of the oxalic acid upon the acid extract must not be attempted since the extract contains other substances which reduce potassium permanganate.

Pyrogallic Acid.—This acid is occasionally found in criminal cases, mainly those of suicide. The acid is dangerously toxic. It may cause death by absorption through the skin (*Neisser*).

Pyrogallic acid if present in the stomach will be found in the alcoholic extract of the material. Since it is also soluble in ether the alcoholic extract is evaporated to dryness and again extracted with ether. This extract is evaporated to dryness.

The most characteristic test for pyrogallic acid is the formation of "ink" with a ferrous salt. On addition of ferrous sulphate a blue-black colour is formed.

Lime-water produces a purple colour with pyrogallic acid.

(i) Gaseous Poisons

Carbon Monoxide.—This is the only gas which has much forensic importance. It is the cause of death in cases of suicide,

where death has been brought about by inhalation of the exhaust-gases from a motor-car in a confined space.

The presence of carbon monoxide must be sought in the blood. The appearance of the blood itself is characteristic since it develops a bright red colour. If a drop of normal blood is diluted with water in a test tube the solution will be light yellow. If carbon monoxide is present the solution will show a definite pink coloration.

The following chemical tests should also be applied.

Hoppe-Seyler's test consists in adding sodium hydroxide solution to the blood. A bright red colour develops if carbon monoxide is present. Normal blood on the other hand develops a dirty green coloration.

Kunkel's Test.—The blood is diluted with nine times its volume of water. A few drops of an aqueous solution of tannin are added. If carbon monoxide is present a pink precipitate is slowly formed. If the blood is normal the precipitate is brownish.

The Estimation of Carbon Monoxide.—The classical method of Haldane is still in use. It relies simply upon the evaluation of the colour of blood by inspection. A 1% solution of the blood to be examined is made, and a similar aqueous solution of a normal sample of blood. A third sample is prepared from normal blood, saturated with carbon monoxide.

A standard solution of carmine is prepared as follows :—1 gram of pure carmine is mixed in a mortar with a few drops of ammonia. The paste is then dissolved in 100 cc. of pure glycerin. The standard solution is made by diluting 5 cc. of this solution with 500 cc. of water. A standard corresponding to blood saturated with carbon monoxide is made by the addition of about 6 cc. of the standard solution to 5 cc. of ox blood of 1% strength in water.

The blood under examination will be brighter in colour if carbon monoxide is present. It is next compared with the sample tube containing the blood saturated with carbon monoxide. If the colour of the sample under examination is less marked than in the saturated solution, carmine solution is

added until the colours are matched. The evaluation of the carbon monoxide, can be arrived at in two ways. (1) Add the carmine solution to the normal blood until the tint matches that of the sample to be tested. (2) Add the carmine solution to the blood-sample in a quantity matching it with carbon monoxide saturated sample.

(1) Since 6 cc. of the carmine solution is equivalent to the colour of carbon monoxide-saturated blood, if the normal blood required 1.5 cc. to match it with the sample to be tested then $\frac{100 \times 1.5}{6}$ = percentage of carbon monoxide taken up by the

haemoglobin.

(2) If 4.5 cc. of carmine solution is required to match the suspected blood with the carbon monoxide saturated-sample then

$$\frac{100 \times 4.5}{6} = 75\% \text{ and } 100 \div 75 = 25$$

which equals the quantity of carbon monoxide taken up.

Haldane has pointed out and it is extremely important to note that in cases of nitrite poisoning the blood assumes a colour similar to that of carboxyhaemoglobin due to the formation of nitric oxide-haemoglobin. This compound can be distinguished from carboxyhaemoglobin by boiling the solution. The nitric oxide compound retains a pink colour in the precipitate. The carboxyhaemoglobin turns grey.

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NAME INDEX

A

Alten, 197
Ames, 197
Aubert, 9

B

Bailey, 190
Bamburger, 138
Bamford, 178
Barger, 164
Beam and Freak, 58
Behrens, 197
Berouch, 197
Beroud, 65
Bischoff, 95, 100
Blackburn, 197
Blyth, 194
Brewster, 197
Brieger and Diesselhorst, 13
Brouardel, 197
Brunck, 197
Buchwald, 197
Burrard, 197

C

Cadell, 197
Carr, 164
Carrell, 96, 103, 197
Carvalho, 129, 197
Cazaneuve, 197
Chapman, 175
Charpy, 8
Chiarottino, 197

Claps, 3, 142, 197
Cornish, 13, 198
Crookes, 170
Cross and Bevan, 197

D

Dangl, 62
Davis, 136
De Rechter, 198
Deniges, 192
Dennstedt, 113
Dervieux, 49
Diesselhorst, 13
Dowzard, 173

E

Elsdon, 164
Eruich, 198
Esternieder, 106
Evans, 198

F

Fauret, 164
Feigl, 138, 197
Feist, 87
Finn and Cornish, 13, 198
Finn, 13, 198
Fischer, 88
Forgeot, 8, 9, 12
Foutell, 202
Foyatier, 198
Frazer, 198

G

Gand, 198
Giblin, 198
Glaister, 160, 168, 180, 181
Gouillon, 198
Grey, 18, 20, 21
Griffin, 198
Grop, 198
Gross, 67
Guillemard, 165

H

Habermann, 106
Harvey, 49
Heess, 91, 96, 104, 107, 131
Henry, 199
Hepworth, 200
Hill, 111
Hindrichson, 90
Hoffman, 94, 99, 100
Hopler, 198
Hudson, 14

I

Icard, 17, 22

J

Jenke, 118

K

Kersting, 35, 187
Knippenberg, 197

L

Lacassagne, 100
Lampitt, 199
Landsteiner, 47

Lattes, 199
Lecha-Marzo, 199
Lehner, 199
Leonard, 188
Lerich, 143
Leung, 4
Lewin, 199
Lewis, 19, 92
Little, 198
Locard, 3, 8, 12, 16, 17, 22,
37, 42, 49, 63, 130
Locard, 134, 143, 149, 150,
160
Locard, J., 113, 114, 115, 166
Loock, 200
Lovibond, 131
Lucas, 57, 68, 71, 100, 147,
162, 180
Lynch, 200

M

Majer, 200
Marshall, 200
Martin, 199
Martley, 48
Medinger, 44, 56
Metzger, 91, 96, 104, 107, 131
Minovici, 200
Mitchell, 5, 8, 87, 93, 95, 103,
105, 106, 112, 116, 125
Mitchell, 131, 136, 139
Muller, 111

N

Naudin, 201
Neisser, 194
Nelson, 188
Neuber, 198

Neumann, 87, 91
Nierenstein, 87

O

Osborn, 201
Ozorovitz, 92

P

Pass, 201
Pavetka, 201
Pittius van, 201
Poix, 100, 101
Pollard, 201
Poluektoff, 201
Poore, 201
Popp, 8, 22, 201
Pregl, 201
Prideaux, 200

Q

Quirke, 201

R

Rall, 91, 104, 107, 131
Rammstedt, 91
Reiss, 201
Rhodes, 6, 44, 62, 108, 127,
145, 146
Robertson, 94, 99, 100
Rosenthaler, 168
Runge, 92

S

Schiff, 87, 88
Schluttig, 87, 91
Schneeberger, 97
Schneickert, 201
Scott, 77

Shore, 202
Silbermann, 92
Silvera, 68
Smith, 202
Södermann, 17, 73
Solaro, 202
Sommer, 202
Stephenson, 202
Stern, 198
Still, 106
Stirling, 3
Stock, 138
Stockis, 7
Stover, 202
Stryzowski, 57, 60, 171
Stubbs, 164
Sylvester, 199
Symons, 202

T

Tihon, 198
Türkel, 108, 113

V

Voigtländer, 113
Vuillemin, 202

W

Ward, 95
Webster, 202
Wilkins, 202
Wilthaus, 202
Winton, 190
Wittstein, 88

Y

Yoe, 71

Z

Zetzsche, 90, 93, 107

S U B J E C T I N D E X

A

Abortifacients, 164
 Absinthe, 165
 Acetanilide, 189
 Acid Radicles
 Dust, 33
 Spot Reactions, 35
 Aconitine, 185
 Acridine Hydrochloride, 25
 Adhesives
 Animal, 140
 Casein, 141
 Dextrinous, 141
 Liquid, 140
 Agglutinogens, 47
 Agglutinins, 47
 Albumin, 140
 Alcoholic Extract
 Dust, 40
 Alizarin, 25
 Alkaloids, 55, 183, 185
 Detection, 183
 Extraction, 183
 Picrates, 188
 Separation, 184
 Allonal, 192
 Aloes, 165
 Aloines, 165
 Aloetine, 165
 Aluminium
 Detection, 22, 25
 Ammonium Hydrate
 Poison, 168

Antimony, 178
 Detection, 178
 Estimation, 178
 Micro Method, 178
 Antipyrine, 190
 Apiol, 164, 166
 Aqueous Extract
 Dust, 19, 39
 Arsenic
 Blank, 176
 Calcium Chloride, 176
 Control Test, 176
 Detection, 171
 Estimation, 172
 Glass Wool, 176
 Hydrogen, 174
 Identification, 171
 Interfering Substances, 176
 Micro Method, 173, 178
 Mirrors, 177
 Reagents, 175
 Royal Commission, 170
 Sulphuric Acid, 176
 Zinc, 175
 Arsenious Acid, 168
 Arsenite Sodium, 168
 Artemisia, 184
 Atropine, 186

B

Banknotes
 Drawn, 145, 146, 147
 Barbituric Acid, 191

- Barium
 - Detection, 21, 22
- Benzidine Reaction, 55
- Benzoin-Oxime, 26
- Bleaching Agents, 124, 125
- Blood
 - Dust, 44
 - Finger Nails, 39
- Blood Groups
 - Classification, 46
 - Determination, 47
 - Examination, 46
- Blood Stains
 - Appearance, 55
 - Chemical Examination, 55
- Blood Tests
 - Interfering Agents, 59
- Bombs
 - Chemical, 78
 - Exploded, 81
 - Fragments, 81
 - Glass Containers, 78, 80
 - Products of Explosion, 81
 - Time, 78
 - Unexploded, 79
- Bromine, 36
- Brucine, 35
- Bullets
 - Analysis, 75 *et seq.*
 - Chemical Examination, 75
 - Coatings, 75
 - Determination of Ni, 77
 - Determination of Pb, 76
 - Determination of Sb, 76
 - Determination of Sb and Sn, 76
 - Preliminary Examination, 75
- Burnt Documents
 - Examination, 135
- Photo-Chemical Methods, 136
- C
 - Cacotheline, 26
 - Cadmium
 - Detection, 23, 28
 - Calcium
 - Detection, 23, 32
 - Cantharides, 164
 - Carbolic Acid, 163, 179
 - Carbon Monoxide, 194
 - Estimation, 195
 - Carnauba Wax, 63
 - Cellulose
 - Identification, 118
 - China Wax, 63
 - Chloral, 180
 - Estimation, 181
 - Chloride Diffusion, 107, 131
 - Chloride Ions (Migration), 13
 - Chloroform, 180
 - Chloroform Estimation, 180
 - Chromium Detection, 25, 28, 29
 - Cinchonine, 27, 42
 - Cobalt
 - Detection, 25
 - Cocaine, 186
 - Codeine, 186
 - Coins
 - Evidence of Analysis, 155
 - Moulded, 149, 151
 - Coleridge, L. C. J., 158
 - Colorimetric Estimation, 131
 - Comparison Microscope, 146
 - Copper Estimation, 154
 - Copying of Ink, 130

Corpus Delicti, 53
 Counterfeit Banknotes, 145
 Counterfeit Coin, 148
 Analysis, 151
 Antimony, 154
 Bismuth, 153
 Colour, 151
 Composition, 150
 Detection of Metals, 152
 Gold, 153
 Impurities, 153
 Manufacture, 149
 Quantitative Analysis, 154
 Silver, 153
 Specific Gravity, 152
 Stamped, 149
 Tungsten, 153
 Weight, 152
 Counterfeiters'
 Occupational Dust, 148
 Counterfeit Money, 145
 Crippen Case, 187
 Crystallographic Identification, 22, 25, 152
 Curarine, 186

D

Deletion
 Scoring Out, 127
 Development
 Absorption, 7
 Photochemical, 4, 10
 Reagents, 6
 Reduction, 8
 Skin Prints, 3
 Dial, 192
 Dies for Coins, 149
 Diffusion of Sulphates, 131
 Dimethyl-Glyoxime, 28

Dimethylamino - Benzal
 Rhodanine, 27
 Diphenyl-Carbazide, 28
 Diphenyl-Carbazone, 29
 Dipyridyl, 29, 71, 109
 Direct Identification, 3
 Documents
 Date, 129
 Examination, 85
 Materials, 85
 Subsidiary Materials, 137
 Tests External to, 95
 Drugs
 Micro-chemical Identification, 192
 Synthetic, 163
 Dust
 Abortifacient, 166
 Chemical Examination, 20
 Classification, 17
 Coiners, 37, 45
 Collections, 17
 Explosions, 83
 Extracted, 18
 Occupational, 16, 18
 Organic, 37
 Preliminary Treatment, 18
 Spectroscopic Examination, 19
 Treatment, 18
 Dyes
 Dust, 39

E

Ears
 Wax, 18
 Eosine, 129
 Erasures
 Examination, 123, 124, 127

- Ergot, 164
Ergotamine, 164
Ergotinine, 164
Ether Extract
 Dust, 41
Explosion
 Products, 81
Explosives
 Chemical Examination, 78
- F
- Fæces, 61
Ferric Pentagallate, 90
Ferric Tannate, 90
Ferrigallic Acid, 92
Ferrous Digallate, 90
Ferrous Iron
 Oxidation, 108, 109
Fingerprints
 Documents, 142
Fingerprints on Documents
 Development, 143
Fingerprints
 Photochemical Develop-
 ment, 10 *et seq.*
Firearms
 Chemical Examination, 67
Flagellate Protozoa, 60
Florence Reaction, 60
Forged Documents
 Examination, 121
Forgeries
 Hand Drawn, 145
Forgery by Addition, 122
Forgery by Subtraction, 123
Forgery
 Interpolation, 128
 Manipulative, 121
 Tracing, 145
Forgery Table, 147
Formaloxime, 30
Fresenius-Babo Method, 169
Fröhde's Reagent, 42, 186
- G
- Gallocyanine, 31
Gamboge, 165
Gaseous Poisons, 194
Glue, 140
Gome, 44
Graphite, 111, 112
Group Separation, 22
Group Test
 Development, 49
Guaiac Reaction, 55
Gum Arabic, 141
Gum
 Examination, 139
 Reaction, 140
Gun Barrel
 Examination, 70
Gun Barrel Residues
 Alkalinity, 73
 Deposit, 73
 Ferrous and Ferric Iron, 71
 Hydrogen Sulphide, 71, 73
 Nitrates, 71
 Nitrites, 72
 Potassium, 72
 Potassium and Sodium, 74
 Smell, 73
 Sulphates, 73
 Sulphides, 71, 73
 Thiosulphates, 74
Gunpowder Black
 Composition, 68
Gunpowder
 Decomposition Products, 68

Gunpowder
 Smokeless, 69
 Types, 67
 Variation in Composition,
 68
 Gutzeit Test, 173

H

Hæmatin, 91
 Hæmatoxylin, 91
 Hexanitro-diphenylamine, 31
 Hoppe-Seyler Test, 195
 Hydrochloric Acid
 Poison, 167
 Hydroquinone, 35
 Hydrocyanic Acid, 181
 Hyocine, 187
 Hyocyanine, 187

I

Identification
 Indirect, 16
 Identity
 Definition, 16
 Ink on Paper, 94
 Chemical Technique, 95
 Ink Strokes
 Oxidation, 109
 Ink
 Alizarin, 110
 Chlorides, 107
 Colour, 105
 Colorimetric Test, 105
 Comparison of Methods,
 103
 Copying Power, 106, 130
 Diffusion of Chloride, 107
 Diffusion of Sulphate, 108
 Effect of Ignition, 135

Estimation of Ferrous
 Iron, 109
 Free Acid in, 107
 Maturing, 104 *et seq.*
 Methods of Examination,
 94 *et seq.*
 Micro-chemical Tests, 100,
 103
 Oxidation of Ferrous Iron,
 109
 pH, 107
 Rate of Oxidation, 109, 110
 Reagents, 100, 103
 Solubility, 106
 Spot Testing, 95, 109
 Stephen's, 110
 Sulphates, 108

Inks

Aniline, 93, 102
 Carbonaceous, 94
 Iron Gall, 86
 Provisional Colouring
 Matter, 92
 Types, 86

Iodine

Development, 7, 134, 135
 Nascent, 143
 Fixation, 7
 7-Iodo-8-Hydroxyquinoline-
 5-Sulphonic Acid, 32

Iron

Estimation, 65, 71 and 154
 Ferrous, 88, 90, 107
 Tannate, 88
 Iron Ferric
 Detection, 32, 71

J

Japan Wax, 63

K

Kunkel's Test, 195

L

Lead, 31

Detection, 76

Estimation, 76

Leuco Malachite Reaction, 56

Logwood Ink, 91

Lovibond Colour Scale, 131

Luminal, 192

M

Magnesium

Detection, 28, 29

Mandelin's Reagent, 42, 186

Manganese, 30

Detection, 30

Marmé's Reagent, 188

Marsh-Berzelius Test, 174

Mayer's Reagent, 40, 185

Meconic Acid, 183

Mercury, 29, 179

Detection, 29

Metals

In Dust, 17

In Gome, 45

Micro-chemical examination,
20 *et seq.*

Millon's Reagent, 119, 141

Morphine, 42, 186

Tests, 42

Mud

Examination, 64

Composition, 65, 66

Stains, 64

Mugwort, 166

Mydriatic Alkaloids, 187

N

Nickel

Detection, 28

Nicotine, 42, 187

Nitrates, 35, 71

Nitric Acid

Poison, 168

"Noxious Thing," 157, 158

O

Obstetrical Stains, 61

Offences Against the Person,
157

Oil Stains, 63

Organic Acids

Dust, 38

Organic Compounds

Dust, 38

Osmium Tetroxide, 8, 143

Oxalic Acid, 193

Oxalic Acid Estimation, 194

P

Paint Stains, 63

Paper, 120

Aniline Pigments, 117

Chlorides, 117

Examination, 117

Loading, 119

Mechanical Wood, 118

Mineral Pigments, 120

Organic Pigments, 120

Pigment, 120

Sizing, 119

Straw In, 117

Sulphites, 117

Watermarks, 121

- Pencil Pigment
 - Ash, 116
 - Pencil Strokes
 - Tests, 113, 115
 - Pencil
 - Tracing, 147
 - Writing, 111
 - Pencil Writing
 - Examination, 111
 - Pencils
 - Aniline Dye, 115
 - Copying, 115, 116
 - Graphite, 112
 - Iron In, 112, 114
 - Titancium In, 113
 - Pencils, Indelible
 - Composition, 115
 - Tests, 116
 - Penny Royal, 164
 - Perfume
 - Dust, 39
 - Phenacetin, 190
 - Phenol, 179
 - Phosphates
 - Detection, 35
 - Picrolouic Acid, 32
 - Poison
 - Identification, 57
 - Metallic, 168
 - Poisoning
 - Symptoms, 159
 - Poisons
 - Alkalis, 168
 - Classification, 158, 162
 - Distillation, 162
 - Extraction, 163
 - Inorganic, 158, 167
 - Inorganic Residue, 163
 - Microanalysis, 173, 177, 178, 187, 192
 - Nonvolatile, 164
 - Preliminary Tests, 161
 - Separation, 162
 - Volatile, 179
 - Portugese Note Case, 145, 146
 - Potassium
 - Bombs, 82
 - Detection, 31, 82
 - Potassium Chlorate, 81
 - Potassium Hydrate
 - Poison, 168
 - Pyrogallic Acid, 194
- R
- Reagents for Developments, 6
 - Reinsch Test, 171
 - Results
 - Interpretation, 36, 83
 - Rex v. Cramp, 158
 - Rex v. Finck, 139
 - Rex v. Pilcher, 130
 - Rex v. Wood, 116
 - Rue, 166
 - Ruthenium Hematrioxide, 9
 - Ruthenium Textroxide, 9
 - Rutonal, 192
 - Identification, 192
 - Royal Commission, 170
- S
- Sabinene, 165
 - Saliva as Secret Ink, 133
 - Santonin, 165
 - Savin, 165
 - Sealing Wax, 137
 - Lead, 138
 - Mercury, 138
 - Pigment, 138

- Seminal Stains, 49
 - Shellac
 - Dust, 39, 137
 - Silver Chloride
 - Reduction, 12, 107, 131
 - Silver Estimation, 155
 - Silver in Coin, 152, 153
 - Silver Nitrate, 4
 - Development, 11
 - Skin Prints, 3
 - Location, 5
 - On Documents, 142
 - On Paper, 5, 142
 - On Wood, 5, 11
 - Types, 3
 - Sodium Hydrate
 - Poison, 168
 - Sodium
 - Metallic, 81
 - Soneryl, 192
 - Sperm
 - Examination, 49, 60
 - Spermatozoa
 - Staining, 60
 - Spot Reaction
 - Utility, 35
 - Spot Reagents, 24
 - Stains
 - General Tests, 55
 - Search for, 53
 - Starch
 - Dust, 39
 - Paste, 141
 - Stas-Otto Process, 163, 166
 - Stearic Acid, 62
 - Strontium
 - Detection, 24
 - Strychnine, 42, 187
 - Stryzowski Method, 171
 - Stryzowski Reaction, 57
 - Sugar
 - Dust, 39
 - In Explosives, 81
 - Sulphonal, 191
 - Sulphuric Acid
 - Poison, 167
 - Suspects
 - Examination, 83
 - Sympathetic Ink
 - Acids, 134
 - Complex Organic, 135
 - Development, 133
 - Examination, 132
 - Physiological, 132, 133
 - Silver Nitrate, 133
 - Types, 132
 - Synthetic Drugs
 - Identification, 189
 - Micro-chemical Tests, 192
 - Sweat
 - Analysis, 4
- T
- Tannic Acid, 39, 87
 - Tannins
 - Dust, 39
 - Tansy, 164
 - Taxus Bæccata, 164
 - Teichmann Reaction, 56
 - Text
 - Erased, 123, 124
 - Textile Fabrics, 44
 - Tin
 - Detection, 152
 - Estimation, 76, 154
 - Tobacco, 43
 - Toxic Agents, 157
 - Toxicological Technique, 161

Trichloraldehyde, 180

Tropic Acid, 187

Tropine, 187

U

Urine Stains, 61

V

Vacuum Cleaner, 17

Veronal, 191

Volatile Poison, 163

W

Washed Documents

Examination, 125

Washed Text

Reconstitution, 125

Washing

Chemical, 124

Watermarks, 121, 146

Wax

Extraction, 61, 62

Identification, 62

Wax Stains, 61

Weapons

Stains upon, 54

Wormley's Test, 187

Y

Yew, 164

Z

Zinc

Estimation, 154

Insensitive, 175

