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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 5th, Professor W. H. Roberts, Vice-President, being in the chair.

Certificates were read in favour of:—Henry Dryerre, Ph.D., M.R.C.S., L.R.C.P., Ronald William Hoff, A.R.C.S., A.I.C., Laurance John Sidney Lane, B.Sc., Alfred Edward Wright.

The following were elected Members of the Society:—Arthur James Amos, Ph.D., B.Sc., A.I.C., Harry Ronald Fleck, A.I.C., Walter Lee, A.I.C., Edward Burdon Parkes, M.Sc., A.I.C., Francis Cecil Storrs, B.Sc., A.I.C., James Thompson, F.I.C., Ph.D., Robert Sinclair Watson, A.I.C.

The following papers were read and discussed:—"The Question of Tannin in Maté," by W. A. Woodard and A. N. Cowland (*Work done under the Society's Analytical Investigation Scheme*); "A Specification for Enamelled Hollow-ware," by J. H. Coste, F.I.C., and D. C. Garratt, B.Sc., Ph.D., F.I.C.; "Antimony Compounds extracted from Enamel-ware by Citric Acid Solutions," by R. H. Burns, B.Sc., A.I.C.; and "Chemical Examination of the Seeds of *Santalum album* of Mysore," by Y. V. S. Iyer.

NORTH OF ENGLAND SECTION

A MEETING of the above Section was held in Manchester on December 8th, 1934. The Chairman (Prof. W. H. Roberts) presided over an attendance of thirty-one.

The following papers were read and discussed:—"The Effect of Grinding in the Power Mill on the Albuminoid-content of Feeding Stuffs," by F. Robertson Dodd, F.I.C., and C. Robertson Louden, B.Sc., F.I.C.; "The Examination of Ginger," by G. D. Elsdon, B.Sc., F.I.C., and Catherine Mayne, B.Sc., A.M.C.T.; and "The Hortvet Freezing-point Process for the Examination of Milk: Correction Factors and the Influence of Stirring," by J. R. Stubbs, M.Sc., F.I.C.

Deaths

WITH deep regret we record the deaths of the following members of the Society:

Robert Rattray Tatlock, Past-President (an Obituary Notice will be published later).
Daniel John O'Mahoney (Public Analyst for Cork).
George Egerton Scott-Smith (Public Analyst for Chesterfield).

THE PRESIDENT'S ANNUAL ADDRESS

IN the past it has been customary for the President to deliver an annual address at the end of each year of his office. The Council has considered the matter and has decided that in future the President shall be relieved of having to deliver the first of these addresses, and that in its place some distinguished member of the profession shall be invited to address the Society.

The Council has pleasure in announcing that Dr. Dyer will give the first of these addresses at the Annual General Meeting on March 6th, when he will give some reminiscences of the Society and its members.

The meeting will be at 8 p.m., and Dr. Dyer's address will follow the business proceedings.

DEFINITIONS OF VINEGAR AND MALT VINEGAR

THE following definitions are suggested standards for vinegar and malt vinegar agreed as the result of deliberations between the Society of Public Analysts and Other Analytical Chemists and the Malt Vinegar Brewers' Federation:

(i) Vinegar is a product of the alcoholic and acetous fermentation of a saccharine solution without any intermediate distillation, except in the case of Spirit Vinegar as defined in (iv).

(ii) Malt vinegar should be derived, without intermediate distillation, wholly from malted barley, with or without the addition of entire cereal grain malted or otherwise, the starch of which has been saccharified by the diastase of malt.

(iii) When vinegar is demanded, a purchaser should be supplied with malt vinegar, unless due notification is given to the purchaser of the article supplied.

(iv) The name "Vinegar" may be applied to other products which comply with the definition of vinegar (No. (i) above), provided a prefix is used to denote the origin of the product; thus, "Distilled Vinegar," "Spirit Vinegar."

Distilled vinegar is the product of the distillation of vinegar as defined in No. (i) above, and its source should be denoted; such as, distilled malt vinegar.

Spirit Vinegar is the product of the acetous fermentation of a distilled alcoholic fluid.

(v) "Imitation" or "Artificial" Vinegar should in every case be sold specifically marked "Imitation" or "Artificial" Vinegar. It is any substitute for vinegar containing acetic acid which is not wholly the product of alcoholic and subsequent acetous fermentation, and shall not contain any acid other than acetic acid.

(vi) All Vinegars and Imitation or Artificial Vinegars shall contain not less than 4 per cent. w/v of acetic acid. They shall not contain any acid other than acetic acid or those acids produced by normal fermentative processes.

(vii) Caramel may be used as a colouring matter in all Vinegar and in "Imitation" or "Artificial" Vinegars.

Discussion on Quantitative Spectroscopy and its Analytical Applications

(*Held at the Meeting on November* 7, 1934)

INTRODUCTION

By J. J. Fox, O.B.E., D.Sc., F.I.C.

The object of the present discussion is to bring before chemists of this Society certain spectroscopic methods now available for everyday use in the laboratory. Modern instruments are convenient to use and capable of giving readily reproducible results. Ever since Bunsen's time the spectroscope has served for the detection of certain elements, and investigation of the ultra-violet spectrum has increased the utility of the method to chemists. Recent work has placed quantitative emission and absorption spectroscopy on a firm basis, so that it is now possible to detect and determine elements and compounds with speed and accuracy. It can be affirmed that among the great advantages of the spectrographic method of analysis are permanency of record, and the fact that in most cases the material examined is available for other tests. It must be borne in mind that the present-day utility of spectrographic methods is due largely to the pioneer work of Mr. Twyman and the firm with which he has been associated in producing instruments of high precision. The papers which follow amply illustrate the scope and accuracy of the method.

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INSTRUMENTS USED FOR SPECTRUM ANALYSIS AND ABSORPTION SPECTROPHOTOMETRY

BY F. TWYMAN, F.INST.PHYS., F.R.S.

It would be interesting to survey the historical steps in the development of spectrum analysis and to enquire why, since the principles of spectrum analysis and the spectroscope were available in 1861, even now, after the lapse of three-quarters of a century, spectroscopic methods are still not in general use by analysts in any part of the world.

Since much ground has to be covered, however, I have confined my remarks strictly to a description of the external features of instruments actually in use to-day for spectrum analysis and absorption spectrophotometry.

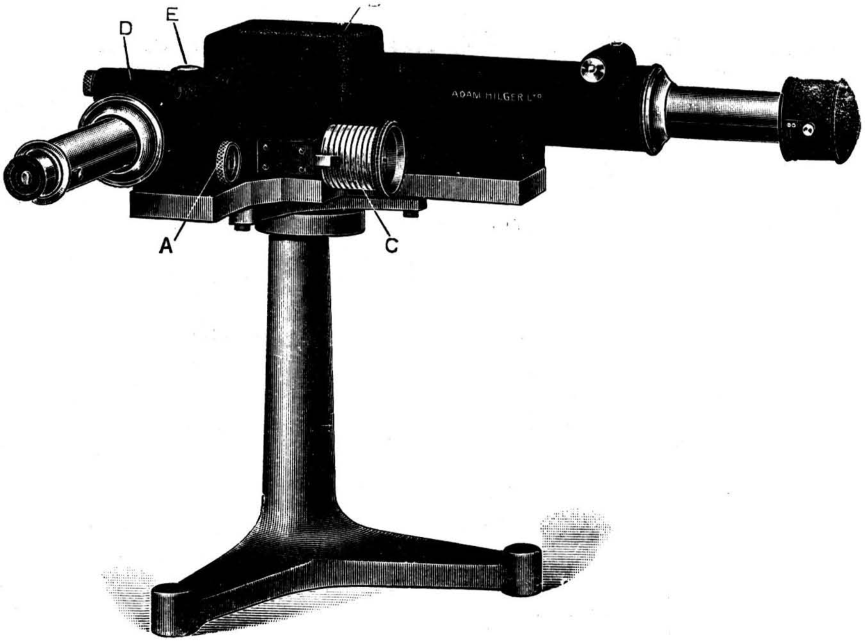

Fig. I
Constant Deviation Wave-length Spectrometer

SPECTRUM ANALYSIS BY EMISSION SPECTRA.—For visual work the instrument in general use is the Constant Deviation Wave-length Spectrometer, shown in Fig. I. In this instrument the collimator and telescope are fixed, and the spectrum is traversed past an index in the eyepiece by a screw. To this screw is fixed a drum, C, on which the wave-length of the line under observation is read off directly, as shown in Fig. II. One thus obtains a wave-length scale over a metre in length. Such an instrument is suitable for rapid reference in the chemical laboratory.

Most of those who practise spectrum analysis use a quartz spectrograph, which photographs not only the part of the spectrum from wave-length 400 to

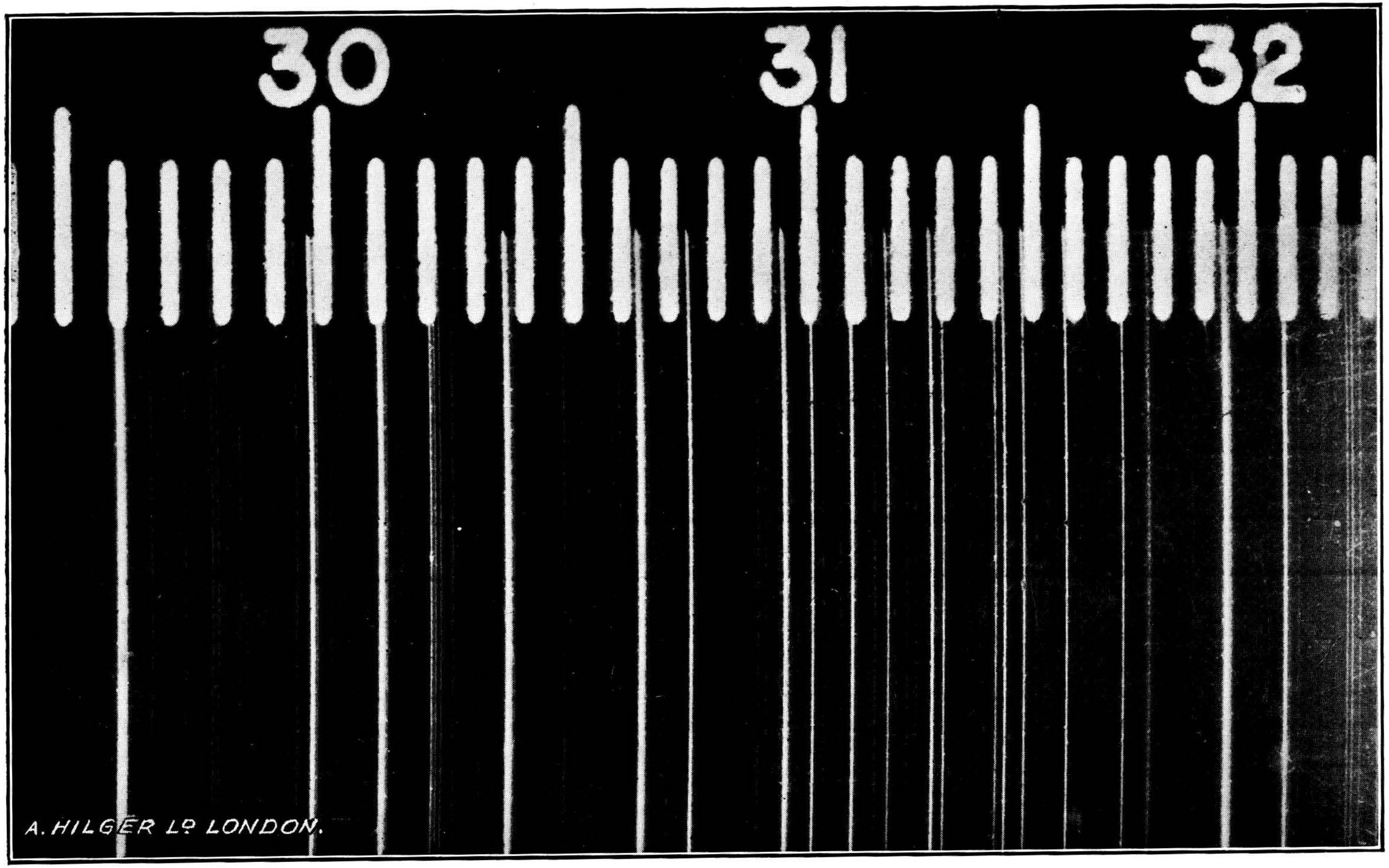

Fig. IV
Spectrum with wave-length scale

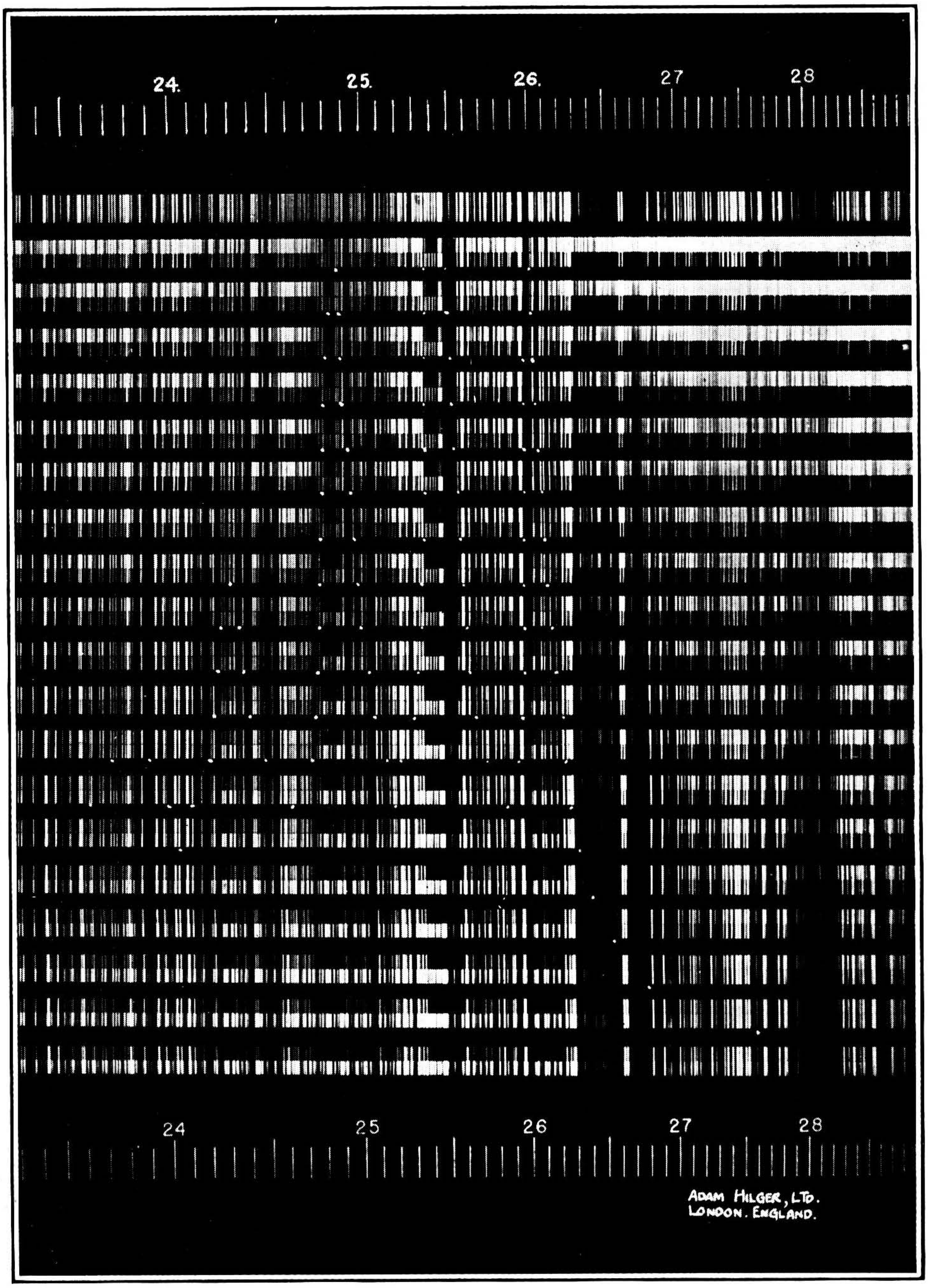

Fig. IX.
Photograph taken with Spekker Photometer

about 819$m\mu$ visible to the eye, but also the range of ultra-violet spectrum from wave-length 200 to 400$m\mu$.

The type of quartz spectrograph used for spectrum analysis is shown in Fig. III. This instrument is adjusted once for all, and to take photographs with it is no more difficult than to do so with a hand-camera. A handle at the side serves to raise and lower the dark slide, and 15 or 20 different spectra can conveniently be taken on one plate. A wave-length scale can be printed on the spectrum and is developed with the spectrum itself. The spectrum is shown in Fig. IV.

Such an instrument, with which the whole spectrum can be taken on a single photographic plate (10″ × 8″), is the most convenient size for general chemical work. It is often referred to as a "medium-size" quartz spectrograph, but it is preferable to distinguish the size by the focal length of the camera lens for a specified wave-length—in the present case 60-cm. focus for wave-length 589$m\mu$.

A larger size, having three times the dispersion, is made, but this requires a number of separate exposures to cover the whole range of the spectrum. Such dispersion is seldom necessary in spectrum analysis, if we except the analysis of steels.

Fig. II
Wave-length Drum

A small instrument, having one-third the dispersion of the medium one, is very useful in metallurgical work for the examination of metals with simple spectra, such as brasses, bronzes, lead alloys and so forth; it was used by Mr. D. M. Smith in the work described in his paper (see p. 17).

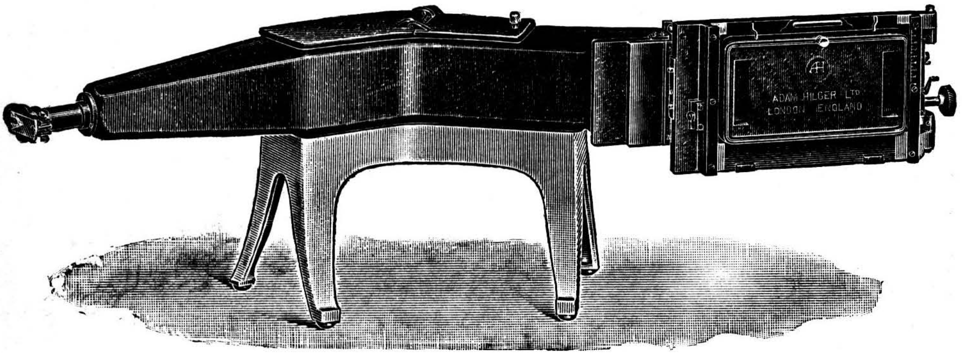

Fig. III
Quartz Spectrograph, 60 cm. focus

Accessories.—Arcs of the metals are very easily produced, provided that direct current is available. Pieces of the metal are used as electrodes; a direct current of 3 amp. or more produces an arc that will reveal all the constituent metals. Small pieces of metal or other samples, such as powders, filtered precipitates, dry residues from solutions, etc., can be examined by putting them in the scooped-out lower carbon electrode of an arc. One advantage of the carbon arc is that, unlike metallic arcs, it can be used with an alternating current.

Numerous other ways of using the arc are available, but, whatever method of producing the arc-discharge is adopted, a suitable form of lamp is that known as the Gramont Arc or Spark Stand (Fig. V), since it is equally suitable for using with the spark. The distinctive feature of the Gramont Stand is that, after the arc or spark has been adjusted to a suitable length, the stand can be raised and lowered by means of a rack and pinion, and thus aligned with the spectrograph without disturbing the discharge.

For some purposes the spark is better than the arc, and the best way of obtaining it is from a ¼-kilowatt transformer giving secondary voltages of from 8000 to 15,000 on an open circuit. With the transformer are associated a condenser and a self-induction coil of simple character.

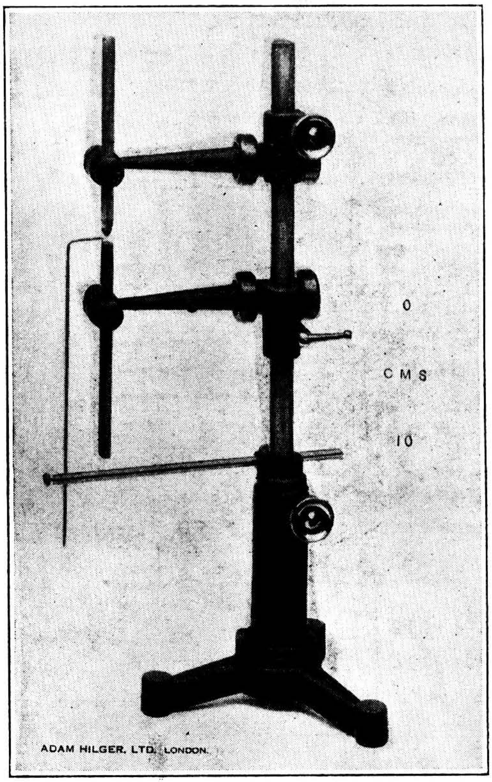

Fig. V
Gramont Arc or Spark Stand

Accessories for Quantitative Spectrum Analysis.—All endeavours to make spectrum analysis quantitative in character depend on the fact that, the greater the percentage of a metal in a sample, the stronger will be the spectrum lines of that metal. Perhaps the most useful method of rendering spectrum analysis quantitative is to synthesise a specimen so that its spectrum exactly matches that of the sample. This method has been very fully worked out by Judd Lewis. It needs no instrumental accessory except a convenient means of comparing the spectra, and this is provided by the Judd Lewis Comparator. The Microphotometer has been used by some observers to measure the intensities of the lines, and with due care it can yield valuable and very accurate results.

In my opinion, the apparatus which, at the present time, best combines convenience and accuracy is the Logarithmic Sector (Fig. VI).[1] This instrument is a disc of metal, the periphery of which is cut into the shape of a logarithmic spiral. This is rotated in front of the slit, and, if the shape of the spiral is properly selected, the effect is to produce on the plate spectrum lines, the differences in the lengths of which are in proportion to the logarithms of the relative intensities of the corresponding radiations. Fig. VII shows the appearance of such photographs.

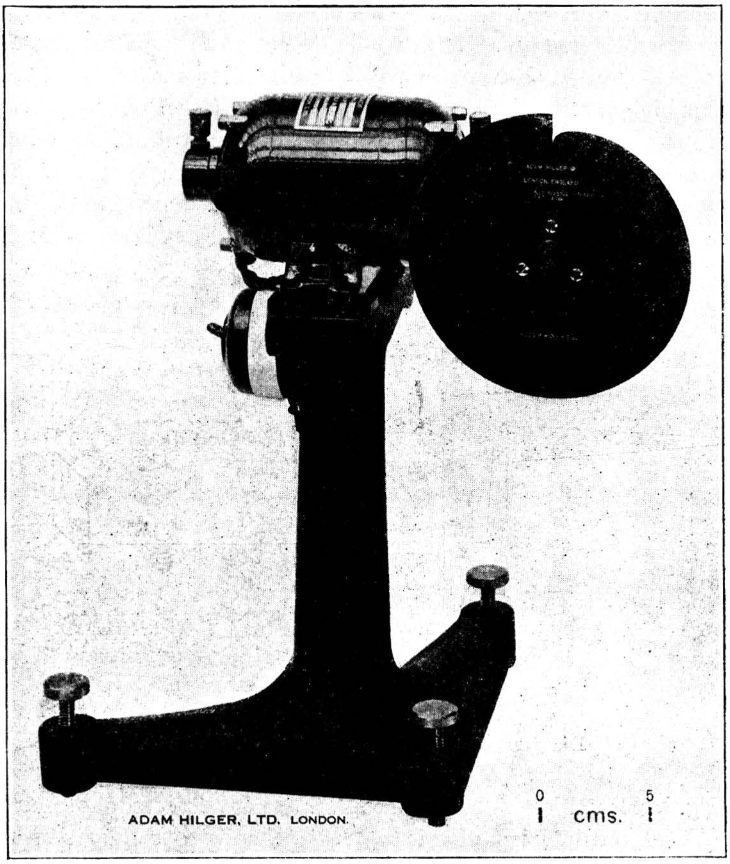

Fig. VI
Logarithmic Sector

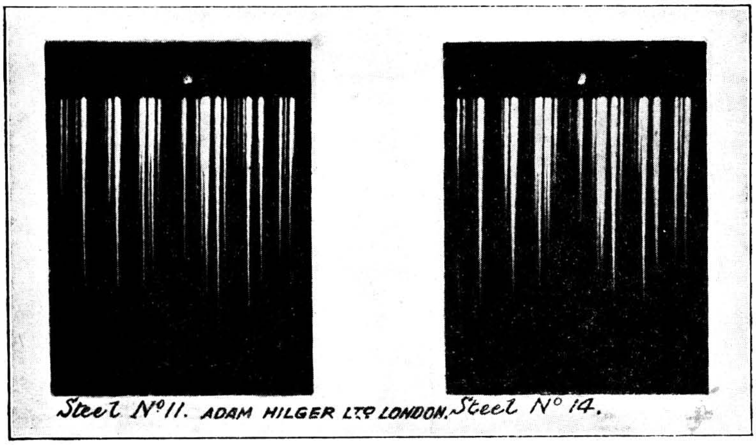

Fig. VII
Spectra taken with Logarithmic Sector

APPARATUS FOR ABSORPTION SPECTROPHOTOMETRY.—Absorption spectrophotometry means the measurement of the absorption of radiation by a substance for various wave-lengths, so that a curve of absorption may be plotted. Such a curve is often highly characteristic of the substance (see Fig. X). The simplest way of doing this is by means of the apparatus, known as the Sector Photometer, which I introduced about 1912. A large proportion of the work on ultra-violet spectrophotometry, in various parts of the world, has been done with this instrument, but this is now superseded by a simplified form of Judd Lewis's spectrophotometer (shown in Fig. VIII), which is known as the "Spekker" Spectrophotometer.[2] It is intended to be placed in front of a spectrograph, such as a quartz spectrograph. Light from a suitable source of ultra-violet rays (A) passes towards the inner edges of two quartz rhombs, C, C, from which beams are diverted upwards and downwards, to be reflected forward through the tubes, F, F, in one of which is placed the absorbing liquid, and in the other the liquid with which comparison is to be made. For instance, in the one tube there may be an organic substance in a solvent, and in the other tube the solvent alone. The beams from the rhombs pass, the one through a fixed rectangular aperture, and the other through an aperture the size of which can be varied by means of a micrometer screw, rotated by a drum, D, with an index which travels along a helix in the drum. This not only simplifies readings, but also acts as a stop to prevent the drum from being turned too far in either direction.

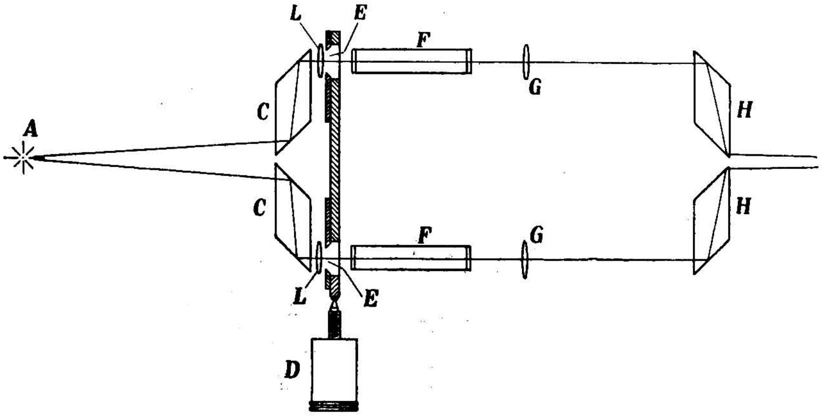

Fig. VIII
Diagram of "Spekker" Spectrophotometer

After passing through the absorbing substance and the non-absorbing substances, the beams pass through lenses, G, G, of quartz, the focal length of which is such that an image of the light source is formed on the face of the slit of the spectrograph. A second pair of quartz rhombs, H, H, is arranged to bring the beams of light together on to the slit in such a way that the image falling from the top rhomb and that from the bottom rhomb on the slit form a complete image of the light source. A number of photographs are taken, one below the other, with various widths of the adjustable aperture (see Fig. IX).

It will be seen that there are a number of pairs of spectra, one spectrum of each pair being cut down in intensity uniformly along its length by a known amount, whilst the other has its intensity locally reduced by reason of the absorption of the liquid under examination. There are certain places, indicated by spots in the figure, where the two spectra match, and at these points, if we know the width of the aperture, we can deduce the absorption of the liquid.

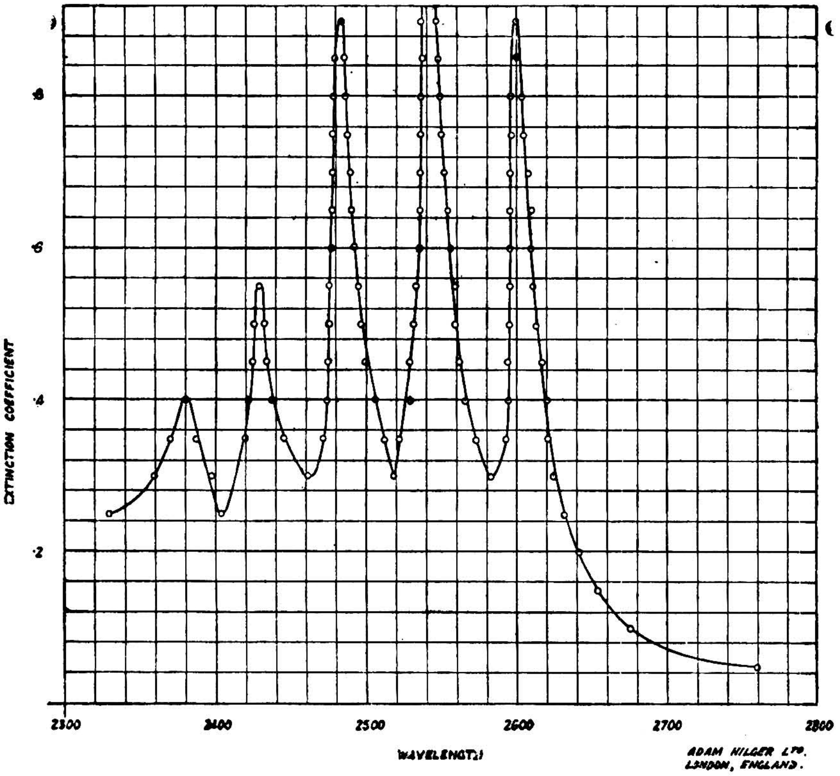

Fig. X.
Absorption Curve of Benzene (in Hexane)

Fig. X shows a curve drawn from the values obtained from the preceding photograph; it is the absorption spectrum of benzene in hexane, 1 in 3300.

REFERENCES

1. F. Twyman and F. Simeon, *Trans. Opt. Soc.*, 1929–30, **31**, No. 4.
2. F. Twyman, *Trans. Opt. Soc.*, 1931–32, **33**, No. 1.

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QUANTITATIVE SPECTROSCOPY AND ITS ANALYTICAL APPLICATIONS

By S. Judd Lewis, D.Sc., Ph.D., F.I.C.

This discussion is concerned with those aspects of the subject which are of direct practical concern to the analytical and consulting chemist in general practice, rather than to those following any particular branch of the subject.

In Mr. Smith's contribution (p. 17) it will be found that it is possible to work with metals in the compact form, and that everything makes for success. On the other hand, non-metallurgical materials, such as the ashes of plants or of textiles or the total solids of a water or a milk, offer none of these advantages. They are usually much less homogeneous than alloys, they are frequently incapable of taking any convenient shape, they are usually inferior conductors of electricity, and they function very irregularly under the influence of any electric discharge. Moreover, it is desirable to work by the arc method rather than by the spark, and here one meets with difficulty of another kind, namely, the wandering and irregular functioning of the arc.

The problem, then, is to formulate some method which will be suitable for such very heterogeneous materials, and this has been done, with a very fair measure of success, in the Ratio Quantitative System, of which I have already given a description.[1] Although the present paper is mainly concerned with the details of this system, one must not lose sight of the excellent *Flame* work of Lundegardh[2] of Stockholm, in dealing with plant ashes and the like. He passes a blast of air through a solution of the ash, contained in the well of a perfume spray of particular form, into an acetylene blow-pipe, where the mixture is burnt in front of the slit of a spectrograph. A spectrogram rich in the lines of a limited range of elements is produced. Every detail is rigorously controlled.

Hartley's method for sparking solutions has been greatly improved of late by Twyman and Hitchen.[3] Mention should also be made of the method of saturating a soft carbon electrode with the solution in question, and arcing on alternating current; also of Ramage's method[4] of burning a weighed quantity of the substance in a rolled filter-paper in an oxy-hydrogen flame.

The reasons for laying stress upon the Ratio Quantitative System by the Arc method are:—(i) It is new; (ii) it is directly applicable to materials of *every* type to an extent not possible with any other method; (iii) it is easily controlled and rendered efficient without resort to special photometric equipment or other special devices; (iv) it records a *complete* quantitative survey of *all* the metallic elements composing the sample, even when the quantity of material is very small; 5 mg. is the normal load, but if one has only 1 mg., or even less, of the sample, the method is still valid, if a like quantity of the standard is used for the comparison; (v) it is applicable both to soluble and insoluble substances.

The conception of " Ratio " is merely mathematical, but in its application to quantitative spectrum analysis the idea is that, if one knows the proportion of a minor element in terms of ratio or percentage to that of a major component, the proportion of which is either known or ascertainable chemically or spectroscopically, one knows the proportion of the minor element in the sample.

For example, if there is in the total solids of a water 0·017 per cent. of manganese relative to calcium, and there are 10 parts of calcium per 100,000 in the water, there is 0·0017 part of manganese per 100,000 in the water.

Moreover, the ratio idea permits of still wider application, for if the ratio of manganese to calcium in the ash of a plant is known, it is known also in the plant or other biological material from which the ash was prepared.

Experimentally, the basic ideas are: (i) To bring the whole sample of ash or other material into some constant homogeneous condition; (ii) to arc (or spark) under well-defined uniform control. The first of these requirements is satisfied by converting the ash into sulphates according to prescription, and the second by well-controlled experimental procedure in order to render the work constant and comparable.

A portion of the vegetable ash, including any phosphate, silicate or other insoluble matter which it may contain, is treated with a small excess of sulphuric acid in a new silica crucible. The mixture is evaporated and gently ignited, just sufficiently to drive off the excess of sulphuric acid. Thus the whole mass is in a condition approximating to normal sulphates, "homogeneously" mixed with the pre-existing phosphates, silica, etc. It is then mixed with an equal weight of spectroscopically pure ammonium sulphate, and is ready for spectrographing.

The use of ammonium sulphate secures three or four advantages: (i) It supplies in effect a constant amount of sulphuric acid to the mass; (ii) it renders the mass more porous; (iii) it generally helps to regularise the action when a portion of the mixture is burnt in the arc.

Ten mg. of the mixture are placed on the lower electrode of a suitable arc-lamp, set in front of the slit of the spectrograph. The next step, *viz.* that of "striking" the arc and exposing the mixture for a suitable time, *e.g.* 60 seconds, is the critical operation; it must be controlled with great care if constant, comparable results are to be obtained. After development of the photograph in the usual way, the first spectrogram is obtained. The same procedure is followed with 10 mg. of a suitable standard ratio powder, and thus a second spectrogram is obtained; in practice, however, this operation is eliminated, since it has already been done once for all. The two spectra are then compared in a "Comparator."[1]

An inspection of the spectrogram of the ash will at once reveal its approximate composition, that is to say, it will be obvious that it is mainly sodium or potassium with much or little calcium and magnesium (or *vice-versa*), together with more or less phosphorus, silicon, etc., and one can then take from the file a standard spectrogram of a suitable ratio powder to serve as standard for comparison.

Assume the major metallic element to be calcium, and consider three standard ratio powders having calcium as a base and containing manganese, lead and tin: (*a*) With 1 per cent. of each element relative to calcium; (*b*) 0·1 per cent.; (*c*) 0·01 per cent.

On comparison of the intensities of the manganese, lead and tin lines in the spectrum of the unknown mixture with those, respectively, in each of these standard spectra in turn, one is able to determine that the manganese is just a little stronger than 0·1 per cent. or about 0·11 per cent.; that the lead is about one-third of 0·1 per cent., and three times 0·01 per cent.; therefore, that the lead is about 0·03 per cent.; and that the tin is a little less than 0·01 per cent., approximately 0·008 per cent. This principle is founded on both theory and laboratory experience. In using a correct mixing a condition of experiment is attained, which justifies usually, although possibly not always, comparison of "homologous pairs" of lines by the "internal standard" method, using for reference the lines of the main component, not those of the electrodes.

Preparation of Special Ratio Powders.—If more precise results are desired, a special ratio powder may be prepared in accordance with these findings, and then the deviation in each case should be so small that any remaining differences may be estimated by inspection.

If still more exact figures are required, they may be obtained by repeating the determination with the quantities as estimated in the second experiment.

As already intimated, this synthesis of a special standard is the systematic and final step, but by comparing the unknown with stock ratio powders, one can, for many purposes, obtain readings sufficiently close without making the synthetic mixture. It must, however, be emphasised that in the final appeal, one should have the major elements in approximately the correct proportion, since the intensity of the lines of the minor element is not precisely the same when the base is mainly calcium, as it is when the base is mainly sodium; and so on.

This sounds, perhaps, a little lengthy, but in practice it is not so, for standard "Specpure" solutions are already available commercially. It must not be assumed, however, that accurate quantitative comparisons can be made until one has acquired some experience.

A most important feature of this method is that it economises time, for *each one* of these determinations applies to the *whole range* of elements concerned, major as well as minor, and *not*, as in most chemical work, to one only. Thus, in making the synthetic mixture one adjusts, by measuring out appropriate quantities of the solutions of the several metals, the proportion of each one of the elements, and so, in the end, one finds that the synthesised spectrum is practically identical in all respects with that of the unknown ash.

ACCURACY OF THE PROCESS.—It remains to show what order of accuracy may be expected from such work, and in order to avoid uncertainty or unconscious bias, determinations controlled by chemical work in other laboratories have been selected.

(i) *Iron in Aluminium.*—The determination of iron in aluminium by chemical processes is frequently a matter of great uncertainty—so much so, that several chemists have resorted to spectrographic methods of one kind or another, and claim greater uniformity of result. With two samples the following percentages were obtained by myself and my assistant, Mr. F. W. J. Garton, respectively, (*a*) by the adopted method, (*b*) by a distinctly modified method, to see whether a marked difference of procedure prejudiced the results seriously.

	No. 1.			No. 2.		
	Adopted method Per Cent.	Modified method Per Cent.	Difference Per Cent.	Adopted method Per Cent.	Modified method Per Cent.	Difference Per Cent.
By S.J.L.	0·083	0·080	0·003	0·101	0·089	0·012
By assistant	0·088	0·087	0·001	0·097	0·092	0·005
Difference	0·005	0·007		0·004	0·003	

These readings are all first-hand laboratory results without subsequent adjustment.

(ii) *Vanadium in Organic Material.*—The next example shows that similar tolerance applies to major components, as exemplified by vanadium in the ash from an industrial organic material, of which only a few mg. were available.

	Spectroscopic Per Cent.	Chemical Per Cent.
Vanadium, as metal	26·6	26·2
	14·5	13·0

With smaller proportions of vanadium the results also agreed well, *e.g.* 0·75, 0·76; 0·80, 0·81, 0·77; 0·71, 0·74 per cent.; these three samples were not controlled chemically.

(iii) *Nickel in Organic Material.*—Similarly, nickel in an organic material was controlled.

	Spectroscopic Per Cent.	Chemical Per Cent.
Nickel, as metal	3·5	3·0
	3·6	3·3

Whilst these figures demonstrate that consistent results are obtainable spectrographically, and that they are closely comparable with those determined chemically, they afford no evidence as to which method is to be preferred. The following investigation with copper tends to favour the spectrographic method, since it is free from complications which beset the chemical method.

(iv) *Copper in a Food.*—The following results, in parts per million, were obtained:

	Spectrographic	Chemical
	0·46	0·56
	0·46	0·56
	0·49	0·56
	0·50	0·56
	0·48	0·53
	0·63	0·68
Duplicates	0·33, 0·33	—
	0·32, 0·36	—
	0·33, 0·29	—

As the chemical findings depended upon the removal of lead in an earlier stage of the process, it is quite possible that the results in the subsequent colorimetric determination of copper may be a little high, owing to incomplete removal of lead.

The following examples illustrate work of a somewhat different class:

(v) *Germanium.*—Germanium, when present in zinc to the extent of only one part in 100 millions, may be estimated quite well by dissolving 5 g. of the zinc in acid and co-precipitating with a suitable heavy metal by means of hydrogen sulphide, filtering, and incorporating homogeneously a little calcium to serve as the standard base, then spectrographing in accordance with the Ratio Quantitative System, and comparing the arc spectrograms with a special standard of Ge/Ca.

(vi) *Biological Fluid.*—Aqueous humour, 0·28 g., yielded 3·5 mg. of sulphated ash, containing about 1 mg. of mixed alkali metals, which was spectrographed with a known weight of spectroscopically pure calcium chloride; upon determining the ratios Na/Ca and K/Ca, it was found that the ratio NaCl/KCl was 15: 1. We have no figures for human aqueous humour, but for the horse the ratio 22 : 1 has been found.[5]

Apart from the ratio method, it has also been shown in detail how 1 part of aluminium can be determined in one million of blood with a very fair approximation to the truth, when using only a single ml. of blood, and, as the result of several experiments on the human subject, it has been found that the blood becomes saturated with aluminium at about that concentration.[6] Reference to the same spectrograms reveals the fact that silicon (in traces only), lead, boron, arsenic, tin, and zinc are among the elements frequently occurring, and that manganese, strontium, barium, and silver are present in only minute quantity, or not at all. By following up these observations quantitatively much light may be thrown on problems depending on the inorganic chemistry of blood.

APPLICATION OF SPECTROSCOPY TO CRIMINOLOGY.—Occasionally spectroscopy has been applied to criminology, as illustrated by the following cases:

(i) The case of the "affaire de la Bonnet Rouge." On the boot-lace of the criminal Almereida, who died mysteriously in the infirmary, two stains were found. M. Bayle was asked to analyse these stains. By comparison of the spectra of: (*a*) the unsoiled part of the boot-lace, (*b*) the two stains, (*c*) the paint on the bedstead in which Almereida had slept, it was shown that one of the stains was due to mud, and the other to paint from the bedstead. The spectrum of the first stain showed aluminium lines, whilst that of the other stain showed the lines of barium, zinc and lead in exactly the same way as did the spectrum of the paint. This gave the police the required information, and confirmed the conclusion that Almereida had hanged himself in prison.[7]

(ii) Wilson,[8] writing in the *Journal of Criminal Law and Criminology*, complains that spectroscopy has not yet found the wide use it deserves in criminal investigation, and then proceeds to describe two or three interesting cases. In one of these the spectrographic analysis of a slight smear on a coat was identified with the putty from a window broken during a burglary, and led to the man's conviction.

(iii) Telephone wire stolen from a Government department in Ceylon was identified spectroscopically as containing traces of certain ingredients which were present in Government stock, but not in any other samples obtained locally.[10]

(iv) In another case, also from Ceylon: "17 lead pellets and slugs were examined spectroscopically, and were found to consist of five different types of lead. The same five types of lead found in these pellets from the scene of the crime were all represented in the pellets, etc., found later with the weapon which was suspected of having been used."[9]

One must anticipate that the question will arise: How far can evidence of the spectroscope be acceptable in a court of law? I have not considered this question exhaustively, but my impression is that the spectroscope will provide very strong evidence when the analyst has become so familiar with the work that he can, with absolute conviction, swear to the results he obtains. I believe that then the evidence will be more readily accepted than is much of the chemical work, since the results may be demonstrated in photographed spectra.

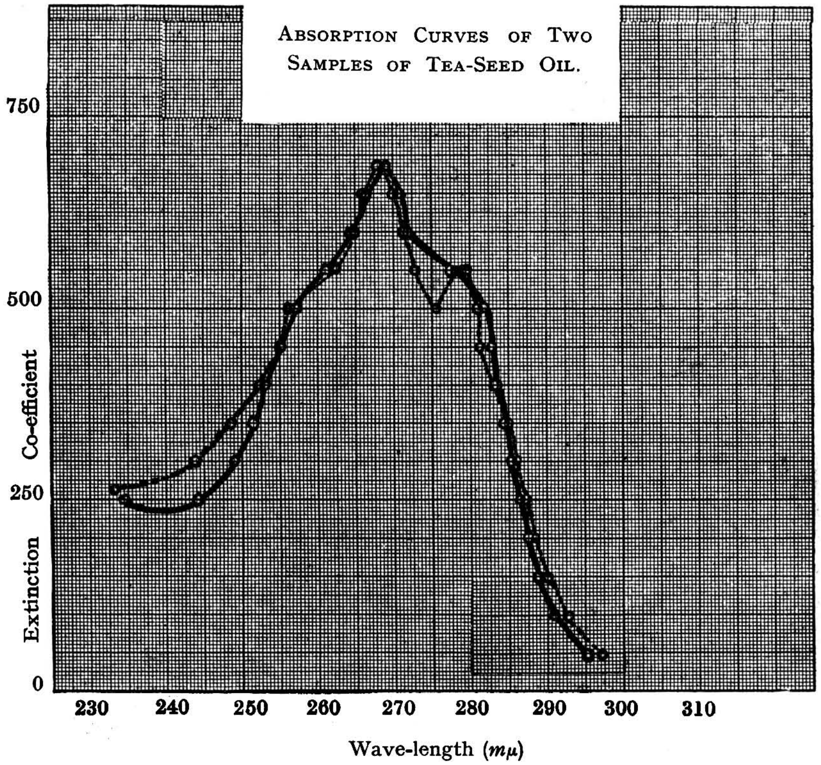

Fig. I

ABSORPTION SPECTROSCOPY.—As time does not permit of a full description, I must ask you to allow half-a-dozen slides to speak for themselves.*

The absorption curve of a special glass exhibited the narrow bands due to neodymium at 332, 425, 436, 502, and 575*mμ*, and to praseodymium at 444, 467, and 480*mμ*, just as would a solution of salts of the two elements. This method of investigating the absorption spectra of the rare earths by spectrophotometry affords the best and most reliable means of analysing quantitatively mixtures of these and certain other elements.

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* Those shown were Figures 29, 30, 31, 32, 38, 39, in *Spectroscopy in Science and Industry*, by S. Judd Lewis (Blackie).

Spectroscopic Detection of Tea-seed Oil in Olive Oil.—The last slide demonstrated the detection of tea-seed oil in olive oil by means of absorption spectroscopy. In Fig. I (p. 15) are seen curves for two samples of tea-seed oil, and in Fig. II the absorption curves for (A) pure olive oil and (B) and (C) the same olive oil to which has been added 1 per cent. and 5 per cent., respectively, of tea-seed oil. It should be observed that the extinction coefficient of olive oil at a wave-length of 268*m*μ is 11, whilst that of tea-seed oil is 690, and that of the 5 per cent. mixture 46, which is in good accord with the calculated figure, $690 \times 0{\cdot}05 + 11 \times 0{\cdot}95 = 45$; similarly, the mixture containing 1 per cent. has an extinction coefficient of 18 on the curve, or by calculation, $690 \times 0{\cdot}01 + 11 \times 0{\cdot}99 = 17{\cdot}8$.

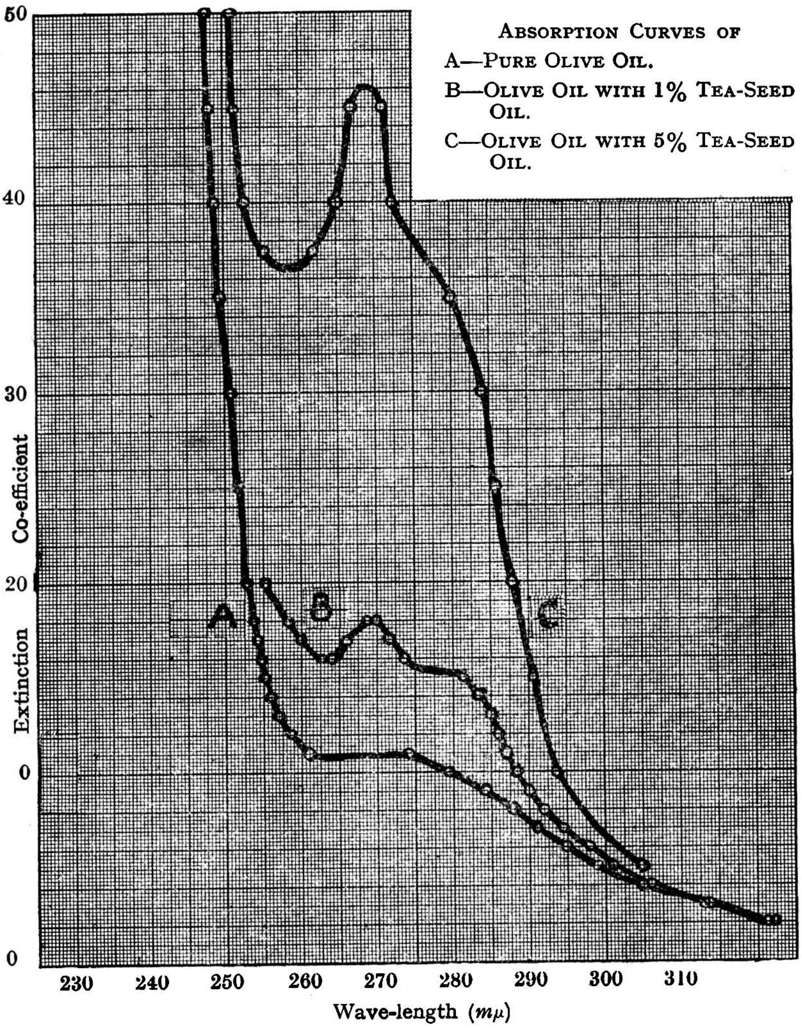

Fig. II

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THE USE OF THE SPECTROGRAPH IN METALLURGICAL ANALYSIS

BY D. M. SMITH, A.R.C.S., B.SC., D.I.C.

INTRODUCTORY.—During the last ten years or so increasing use has been made of spectrographic methods in analytical laboratories, not only as a check on chemical control of material, but also for routine testing. With a view to encouraging the wider adoption of these methods by metallurgists, systematic investigation of the subject has been in progress by the British Non-Ferrous Metals Research Association for some years. This work has been largely concerned with testing the application of these methods to the determination of impurities in metals of commercial importance, by means of a simple and inexpensive technique and equipment. It is the purpose of this contribution to describe briefly what is being done in this direction, and to indicate possible future developments with a view to improving the reliability and accuracy of spectrographic analysis and to extending its scope of application.

TECHNIQUE.—For the analysis of metals and alloys, the quartz spectrograph is generally used, qualitative and quantitative analysis being carried out by observation of the characteristic lines in ordinary photographic records of arc- and spark-spectra. Mr. Twyman has dealt, in ample detail, with the apparatus used in this work, and there is no need, therefore, to enlarge on that part of the subject.

As the amount of an impurity or alloying constituent increases, its characteristic lines show a corresponding increase in intensity, and the general principle of spectrum analysis consists of the correlation of the intensities of these lines with the amounts of the constituents giving rise to them.*

While not wishing to detract from the value of purely visual methods of analysis (*cf.* F. Twyman[1]), I would point out that there are several important advantages of photographed spectra. Apart from the value of having a permanent

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* An illustration was shown of the arc-spectra of the following grades of zinc:—spectroscopically pure; chemically pure; electrolytic; common spelter.

A simple means of rapidly identifying such material is thus obtained.

(The slides shown at the meeting were actual spectra obtained with a small-size spectrograph. In this way the inevitable loss of detail by reproduction was avoided).

record of each analysis, the most sensitive lines used in analytical work are to be found, in the main, in the ultra-violet part of the spectrum, and the most satisfactory method of examining this region is by means of photographic records. Moreover, since quantitative determinations are based on comparisons of the intensities of lines (as represented by the densities of their images on the photographic plate) the absence of colour is much to be preferred.

With regard to the form of the samples, the arc or spark between metallic electrodes, consisting of pieces of the sample under test, has much to commend it from the point of view of convenience in operation. Preliminary treatment, as required in chemical analysis, such as dissolving the metal and subsequently precipitating, is avoided. It is not always possible or convenient to prepare electrodes in a suitable form for an arc to be obtained in this way, and more use is now being made of the arc between pure graphite electrodes. The arc is more sensitive than the spark for the detection of traces of certain impurities, and since it is very difficult to obtain metallic arcs with tin and lead, graphite electrodes have distinct advantages for such metals. In the analysis of small copper samples Milbourn employs a similar technique, but with the small modification of using a pure copper rod in place of the upper graphite electrode.

STANDARD ALLOYS.—Before it is possible to standardise a spectrographic method of analysis of any given metal or alloy, considerable attention must be given to the question of the reliability of the standard alloys, since the method is based on the quantitative interpretation of the spectra of alloys of accurately known composition.*

The most obvious method of controlling the standard alloys is to rely upon the results of careful chemical analyses, checked and confirmed by the independent work of skilled analysts, and in many cases this is the only method available. For metals of low m.p., such as lead, tin, and zinc, however, the melting, mixing and casting of accurately weighed constituents *in vacuo* has proved a very satisfactory method of producing alloys of definite composition. This method of preparation fails in cases where the alloying constituents tend to separate out on cooling. It is often difficult, for example, to obtain in this way homogeneous alloys containing even small quantities of lead.

A method recently found useful for checking the reliability of chemically analysed samples proposed as standards for spectrographic work, involves the use of "synthetic spectra." The spectrum of a standard alloy containing the highest content of the series (which is easier to check by chemical analysis than a sample containing only a trace) is superimposed on that of the pure metal forming the main constituent, the times of exposure being systematically varied.†

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* The arc-spectra of synthetic alloys of zinc with 0·75, 0·25, 0·1, 0·01, and 0·001 per cent. of cadmium were shown as an illustration of quantitative standard spectra.

† Two slides illustrating the principle of this method were shown. The two components of each synthetic spectrum were photographed separately and in juxtaposition in the first slide, the upper spectrum in each case being that of the standard lead alloy (lead containing 0·5 per cent. of tin) and the lower spectrum that of pure lead. The corresponding times of exposure were as follows:

Lead + 0·5 per cent. of tin:	5;	10;	15;	30;	45 seconds.
Pure lead:	55;	50;	45;	30;	15 ,,

By superposing the spectra in each pair, as shown in the second slide, a series of five spectra was obtained, in which the tin lines showed a systematic increase in intensity, the lines due to the primary constituent (lead) remaining of constant intensity.

A curve can then be constructed showing the relation between the percentage of impurity present and the time of exposure of the standard alloy which gives a spectrum identical with that of the sample under examination. Irregularities are then readily detected from the position of individual points with regard to the mean curve. This method has been applied to the determination of small quantities of bismuth in copper,[2] and it shows promise of fairly wide applicability.

METHODS OF ANALYSIS.—*The Necessity for Standardisation of Technique.*—Whether the arc or spark be used as the source of the spectrum, there are a number of variables which require rigid control to secure reproducibility of the spectra. The aim has been so to choose the technique in individual applications as to be able to obtain from the spectrum of the sample itself all the quantitative information required. At the same time it should be pointed out that the method of comparing the spectrum of a sample with those of selected standard alloys (generally referred to as the "comparison sample" method) has been found extremely useful, and is still very largely used, particularly in testing whether a material conforms to specification.

Quantitative Interpretation of the Spectra.—The general applicability of spectrographic methods in different laboratories, under somewhat different conditions, has also received attention, and, wherever possible, the conditions for the production of the spectra have been standardised from this point of view.

The basic principle underlying practically all the methods now in use for quantitative analysis was first described by W. Gerlach[3] in 1925, and is known as the "internal standard" method. Equality of intensity between an impurity line and a line of the main constituent is correlated with the percentage of impurity present. If sufficient pairs of lines of this kind are available, analysis is possible in fairly close steps.

In a large number of cases sufficient lines suitable as internal standards are not available, and, in order to distinguish between more closely-graded percentages, methods using auxiliary spectra "coupled" with those of the samples under examination have been used, as, for example, the tin spectrum, which gives a fairly wide range of lines of different intensity. Owing to the different characters of a number of spectrum lines, the use of an auxiliary *alloy* has been found to give more suitable lines as intensity standards, such as, *e.g.* an alloy of copper with 1 per cent. of tin for the analysis of copper samples. Similarly, an auxiliary alloy of lead with 0·4 per cent. of tin can be used for the analysis of lead samples.[4] Here one is comparing impurity lines with tin lines in the auxiliary spectrum—a procedure which appears more satisfactory, since both types of lines are intrinsically the same.*

In order to increase the accuracy of analysis, methods based on the above principles, but also giving the possibility of assigning numerical values to the intensities of the lines, have been devised. The recording or non-recording

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* Arc-spectra of alloys of copper with various quantities of manganese afforded an illustration of the internal standard method. The superposition of a tin spectrum and the juxtaposition of a spectrum of copper with 1 per cent. of tin was shown in the case of a number of copper-alloy spectra.

microphotometers and the logarithmic sector-wedge methods may be quoted as examples.*

Metallurgical Applications.—Considerable progress has been made in the delicacy of the chemical detection of traces of elements, so that the superiority of spectrographic methods in this respect is not quite so pronounced as formerly. On the other hand, the chemical determination of traces of impurities is usually laborious, involving tedious separations from a large bulk of material, and requiring considerable skill. It is, moreover, in the region of traces of impurities that the spectrograph is shown to its best advantage, and about 1 per cent. may be taken as the upper practical limit of its present sphere of usefulness. In this particular field, standardised methods have been developed by the British Non-Ferrous Metals Research Association for the determination of the usual impurities in zinc, copper, tin, lead and aluminium, and work is now proceeding on the determination of the impurities commonly occurring in nickel.

An excellent example of the value of spectrographic methods is afforded by the analysis of "chemical lead." It is possible to determine the copper, silver, bismuth, antimony, zinc, and cadmium contents of this material with sufficient certainty to determine whether it conforms or not to specification. The determination of traces of bismuth in copper and traces of cadmium in zinc are further examples of metallurgical importance. Such analyses as these can be carried out as a matter of routine with great saving of time.

Many other interesting applications might easily be enumerated, of which the following are typical:—

1. *Testing material for segregation, or non-homogeneous distribution of impurities and alloying constituents.*—The fact that in spectrum analysis only a very small amount of the material takes part in the discharge, becomes an advantage in this case.
2. *The analysis (for metallic constituents) of coatings, dross, inclusions and the like.*—In cases such as these it is generally only possible to give little more than a qualitative analysis, but with experience it is possible to distinguish between the major constituents and those occurring in very small quantities.
3. *The analysis of samples too small for chemical analysis.*—The spectrographic method gives a complete qualitative, if not quantitative, analysis of the material.
4. *Identification of material.*—In addition to the rapid testing of samples of unknown composition, cases are known where it has been possible to identify or indicate the source of supply or the process of refining employed by the presence of traces of residual metallic constituents (of deoxidisers for example).

A large amount of valuable work has been carried out in recent years in other quarters, and the laboratory of Messrs. I.C.I. Metals, Ltd., may be specially mentioned in this connection. Papers giving details of standardised methods for

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* Logarithmic sector-wedge spectrograms were shown of lead-tin alloys, containing up to 3 per cent. of tin, the lengths of the tin lines increasing with increasing percentage and the lead lines remaining of fairly constant length in the different spectra.

the analysis of lead, brass and copper have been published by Brownsdon, and by van Someren[5] and Milbourm.[6] The work for the British Non-Ferrous Metals Association has been considerably assisted by this and other parallel work which has been made available.

In Germany numerous publications have appeared under the authorship of Gerlach and Scheibe[7] and their colleagues, and in Belgium, Breckpot[8] has recently published an account of his extensive study of the analysis of copper. Increasing attention is also being given to spectrographic methods in America, and since the middle of 1933 about fifty publications (from various countries, including our own) of metallurgical interest have appeared.

PRESENT TENDENCIES AND FUTURE DEVELOPMENTS.—Owing to the increasing and widening application of spectrographic methods, several different aspects of the subiect have been investigated, some in considerable detail. Generally speaking, the different lines of attack both in England and abroad have been, and still are, in the following three directions:

(i) Towards greater stability and reproducibility of arc and spark discharges, with a view to obtaining improved regularity in the results. Valves and undamped high-frequency oscillations[9] have been used for spark circuits, for example, and the intermittent arc[10] method has been proposed for rapidly oxidisable metals, such as aluminium.

(ii) Improvements in methods of "sampling" (the word sampling in this connection being taken to mean the selection of samples to be subjected to spectrographic examination), in order to extend the application of the spectrograph in quantitative analysis and to increase the reliability of the results.

Solution and "pastille" methods,[11] oxide and sulphate powder samples have been proposed with this end in view, and the method described and so successfully used by Judd Lewis may be instanced in this connection.

(iii) Increase in sensitivity of detection of traces and in the accuracy of determination. The use of higher currents in the arc, for example, has yielded increased sensitivity in the detection of traces of bismuth, and electrolytic deposition and preliminary chemical separation have given a similar increase in sensitivity.

The use of photometric devices to obtain increased accuracy is also being investigated. It may be observed, however, that there is a danger, when introducing too many refinements, that the simplicity and speed of spectrum analysis, wherein lie its chief attractions, may be lost to a considerable extent. With simplification of photometric methods and the possibility of reducing the personal factor, there is no doubt that such methods will be increasingly used.

An attempt has been made to cover a wide field, although restricted to metallurgical analysis, and more particularly to the investigations on non-ferrous metals and alloys, which have now been proceeding for nearly ten years and are still in progress for the British Non-Ferrous Metals Research Association. It is hoped, however, that this contribution will have been of some general analytical interest.

I wish to thank the Society of Public Analysts for the invitation to take part in the Symposium and the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this contribution.

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DISCUSSION

Mr. J. H. **GARDINER**, referring to the use of the spectroscope in criminology, mentioned that more than sixty years ago Dr. Meymott Tidy, who was then Professor of Medical Jurisprudence at the London Hospital, showed at the Royal Institution the absorption bands of blood that he had extracted from the hat of a suspected criminal; this formed a link in the evidence leading to the conviction of a man named Müller, who "murdered Mr. Briggs on a railway train."

He (Mr. Gardiner) had the honour of working under the late Sir William Crookes from 1881 until his death in 1919, and during all that time the spectroscope was in constant use for the researches carried out in the laboratory. One lengthy work was the spectroscopic examination of some twenty earthy meteorites obtained from the collection in the British Museum, the lines between $m\mu$ 400 and 240 of all the elements present being identified. The method used (for they were all non-conductors of electricity) was to mix the finely powdered aerolite with pure precipitated silver, and by means of a hydraulic press to form the material into blocks from which electrodes could be cut; from the resulting arc-spectra the lines due to the silver could easily be recognised and those due to the aerolite observed. For a particular research it was desired to obtain some absolutely pure iron, but it proved extremely difficult, in fact impossible, to get. Help was given by many metallurgists, and the purest specimen was one from the Bureau of Standards, Washington, but even in this faint traces of the manganese lines were shown. The last work upon which Sir William was engaged was the separation of the element scandium from the rare mineral wiikite; on account of the rarity of the substance the arc-spectrum method could not be followed, and the chemical work of the separation was directed by constant reference to the spark spectrum of a solution of the nitrate. The most difficult step in the work was the removal of traces of holmium that accompanied the scandium in the mineral, and Mr. Gardiner exhibited the first spectrum photograph, which showed that this substance had been successfully removed and "Scandium Purissimum" obtained. Photographs, signed by Sir William, of cathode luminescence spectra of some rare earths of the yttria series, were also exhibited; in these photographs bands were observed that were thought to be due to a novel element which was provisionally named "victorium," but, unfortunately, the work was never completed.

Mr. M. MILBOURN said that he was using spectrographic methods in an industrial laboratory, where they had proved themselves indispensable. Without minimising the value of quantitative work, it would be well to bear in mind that much could be done without making any actual quantitative estimate. For instance, the purity of chemical precipitates could be checked; or one could readily determine whether the metallic constituents of two samples, supposed to be similar, were really identical; or again, when two samples were behaving differently, differences in composition, particularly with regard to the minor constituents, could be rapidly ascertained. In quantitative work, more particularly in routine analyses to specification, some measure of accuracy could be sacrificed to speed, any doubtful results being checked by chemical methods. Close collaboration in the use of chemical and spectrographic analysis ensured that one method acted as a constant check upon the other. Sometimes spectrographic methods were definitely superior to chemical methods, as in the determination of minute quantities of magnesium.

The PRESIDENT, in proposing a hearty vote of thanks to all the speakers for their contribution to the symposium, asked the members to include in their thanks Messrs. Adam Hilger, Ltd., for the special display of spectroscopic instruments.

Occurrence of an Unsaturated Hydrocarbon in Olive Oil

BY T. THORBJARNARSON AND J. C. DRUMMOND, D.Sc., F.I.C.

IN the course of an investigation with the object of distinguishing olive oil from other oils, Bolton and Williams[1] came to the conclusion that the natural oils and fats could be classed in four groups according to the degree of unsaturation of their unsaponifiable matter. Olive oil was peculiar in being characterised by unsaponifiable matter with high iodine value (197 to 204).

So far as we are aware, there is only one subsequent investigation recorded in the literature which throws light on this peculiarity. Sani[2] separated an unsaturated hydrocarbon from the non-saponifiable fraction of olive oil by distillation at reduced pressure. The elementary analyses and determination of molecular weight led him to suggest the formula $C_{21}H_{36}$ for the compound, but he does not appear to have determined its iodine value. His examination of this compound was cursory and suggested the importance of making a more thorough investigation of its nature.

The olive oil employed for the main part of the experiment was an authentic product of Palestinian origin.* It had the following characteristics:

Saponification value, 191; iodine value, 82·6; $n_D^{18°}$, 1·4707; unsaponifiable matter, 1·12 per cent.; iodine value of unsaponifiable matter, 255; mean equivalent of fatty acids, 279; iodine value of fatty acids, 85·3.

PREPARATION OF UNSAPONIFIABLE MATTER.—The olive oil was saponified by 30 minutes' treatment with an excess of hot alcoholic potassium hydroxide solution.

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* We are greatly indebted to Mr. E. R. Bolton, F.I.C., for his help in obtaining this and other representative oils examined during the course of this investigation.

The soap solution was diluted with three volumes of water and repeatedly extracted with redistilled ether. After the ethereal extract had been washed and the solvent distilled off, the residue was re-saponified with sodium ethoxide, and the extraction process was repeated. The final yield of unsaponifiable matter from 1 kg. of oil was 9·6 g.

This material was a soft, yellow wax with iodine value 255, and contained 16·9 per cent. of material (sterol) precipitated by digitonin. An attempt was made to separate the constituents of the unsaponifiable matter by fractional crystallisation from hot methyl alcohol. For this purpose 7 g. were treated with 500 ml. of hot methyl alcohol. A small amount of the substance would not dissolve in spite of continued heating. This insoluble material was filtered off and dried. It was a dark-brown, semi-solid oil (substance A) with iodine value 130. The filtrate was concentrated to half its volume and kept at 0° C. A crystalline substance of a faint yellow colour separated (substance B). It was filtered off, and the filtrate was concentrated to half its volume once more and stored at 0° C. A crystalline substance separated from the concentrated filtrate, along with some oily droplets. This fraction was isolated and again taken up in a small amount of methyl alcohol, the crystalline substance (C) being less soluble than the oil.

The material soluble in the methyl alcohol was obtained by removal of the solvent. It was a heavy colourless oil (D) which, on cooling and standing, deposited a small amount of a soft waxy crystalline material. This treatment with methyl alcohol effected a considérable concentration in the more soluble fractions of the material with high iodine value.

	Iodine value
Original non-saponifiable matter	255
Fraction (A)	130
Fraction (B)	108
Fraction (C)	181
Fraction (D)	342

These fractions were examined chemically, with the result that A and B were found to consist largely of crude "sitosterol." Further examination of these "sterol" fractions and those obtained in the adsorption experiments later to be described showed that they consisted mainly of sitosterol accompanied by the usual small proportions of dihydrositosterol, ergosterol and dihydroergosterol. Fraction D contained a large proportion of a hydrocarbon which, to our surprise, appeared to resemble squalene.

Naturally, our main interest was centred on the last-mentioned fraction, but efforts to free it completely from oxygen-containing substances by the use of solvents were not successful. It was decided, therefore, to try selective adsorption as a means of separating the hydrocarbon more satisfactorily.

A preparation of the unsaponifiable matter was dissolved in a small quantity of a mixture of 90 per cent. of petroleum spirit (b.p. 40–60° C.) and 10 per cent. of benzene and passed slowly through a column of Merck's specially-prepared aluminium oxide. Four coloured zones appeared and gradually moved down the column during washing with the same solvent mixture. The washing was continued until the lowest of the coloured zones had almost reached the bottom of the column. The aluminium oxide column was then divided into portions corresponding with the zones. Each fraction of the aluminium oxide was eluted by washing with a mixture of 75 per cent. of petroleum spirit and 25 per cent. of methyl alcohol. The iodine values of the various fractions were determined, and their spectroscopic properties were examined for us by Dr. R. J. Macwalter, to whom we desire to express our thanks.

TABLE I

2·05 g. OF UNSAPONIFIABLE MATTER ADSORBED

	Weight g.	Iodine value	Absorption bands $m\mu$*
Original unsaponifiable matter	2·05	255	307 W 297 W General absorption
Filtrate material not adsorbed	1·23	345	352 W 333 S+ 324 S+ 301 S+ 286 S+ 275 M
Bottom band of column. Least readily adsorbed.	0·03	209	349 W 326 W 295 W 282 W 270 M 260 M
2nd zone from bottom of column.	0·02	190	303 W 289 W 277 edge
3rd zone from bottom.	0·34	130	Moderate general absorption
Top zone of column. Most strongly adsorbed.	0·43	104	294 M 281 M 261 V.W.

* W signifies weak band; M signifies band of moderate intensity; S signifies well-defined absorption.

The spectroscopic examination of the fractions revealed interesting information. The bands exhibited by the adsorbed material from the top of the column indicated clearly the presence of ergosterol. They were also seen sharply when the material from the next zone (3rd) was recrystallised from methyl alcohol, but were masked in the examination of the crude fraction by general absorption, due in large part to the presence of a pigment of the xanthophyll type. The spectroscopic properties of the hydrocarbon fraction will be referred to again later.

The fraction of the unsaponifiable matter which passed unadsorbed through the column was a colourless and odourless mobile oil. From it there appeared, on standing in a cool place, a small amount of a crystalline waxy substance which was readily separated, and which, after one recrystallisation from methyl alcohol, showed no absorption of iodine and melted indefinitely at 68°. On analysis it gave the following results:—*Carbon, 84·10; hydrogen, 14·77 per cent. (4·714 mg. gave 14·35 mg. of carbon dioxide and 6.22 mg. of water). This analytical result, together with the properties of the material, strongly suggest that it is a mixture of saturated, aliphatic hydrocarbons similar to the preparations isolated by Chibnall and his colleagues from a variety of plant materials (*e.g.* a mixture of $C_{29}H_{60}$ and $C_{31}H_{62}$, m.p. 63–4° C., isolated by Chibnall and Sahai[3] from the wax of brussels sprouts). The amount of the saturated hydrocarbon preparation was insufficient to provide for a more thorough examination.

A sample of the liquid fraction which remained behind after the solid hydrocarbon had been removed was analysed. The results indicated that a great part consisted of an unsaturated hydrocarbon, possibly of the squalene type, but that very small traces of other substances, some of which contained oxygen, were also present. Bromination in anhydrous ether solution or treatment with hydrochloric acid gas in dry acetone gave crystalline derivatives which bore a superficial resemblance to the dodecabromide and hexahydrochloride, respectively, of squalene. It has been found impossible satisfactorily to free the unsaturated hydrocarbon from the saturated hydrocarbons and other substances by distillation under reduced pressure.

After removal of the saturated component as described above, distillation at low pressure effects a satisfactory purification of the unsaturated hydrocarbon. In the fractionation of 4 g. at a pressure of 0·08 mm. most of the liquid passed over in the range 170° C. to 190° C., and a considerable proportion of this was collected between 187° and 190° C.

The distillation effected considerable purification of the hydrocarbon, as judged not only by the analytical results, but also by the spectroscopic examination. The crude hydrocarbon fraction, as reference to Table I will show, exhibited a number of absorption bands. The nature of the substance responsible for these has not been determined, but it is of interest to note that the group of bands recorded here has also been detected in this laboratory in the corresponding fraction from wheat-germ oil. The band at 275*mμ* may possibly be referred to carotene, but the others are more probably related to a cyclic unsaturated hydrocarbon. Further work on this question is in progress. The distilled hydrocarbon showed a much simpler picture, as only three poorly-defined bands, at 324, 292 and 281*mμ*, were detected. So far as we have been able to determine, these bands are due to minute traces of impurity. They are not, we believe, related to the main hydrocarbon constituent. The distilled fraction was a clear, colourless mobile fluid. On analysis it gave the figures: Carbon, 87·53, 87·71; hydrogen, 12·62, 12·44 per cent. (calculated for $C_{30}H_{50}$, C=87·70; H=12·30 per cent.). It is interesting to note that the analytical data recorded by Sani are in agreement with these figures (C=87·45, 87·79; H=12·20, 11·80 per cent.). He undoubtedly isolated almost pure squalene, but was misled by a low figure for his molecular weight determination. He noted absorption of halogens, but did not observe the formation of crystalline derivatives.

Hydrochloride.—In dry acetone saturated with hydrochloric acid gas the distilled hydrocarbon gave a good yield of a crystalline derivative. The crude

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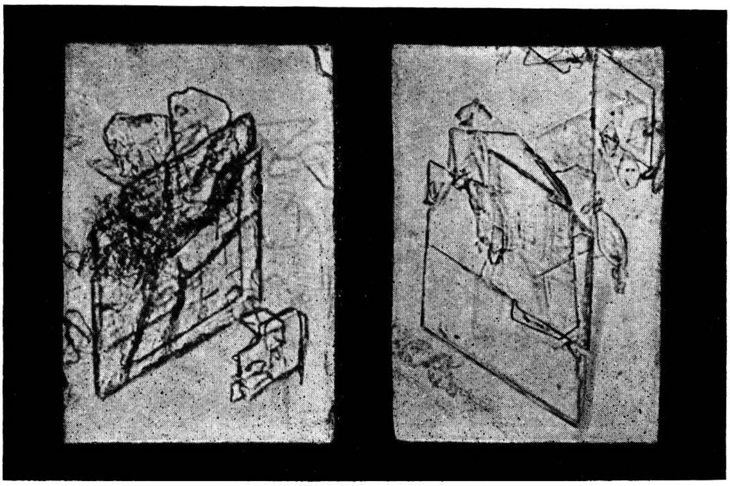
* Elementary analyses recorded in this paper were carried out by Dr. Ing. Schoeller of Berlin and by Dr. G. Weiler of Oxford.

hydrochloride melted rather indefinitely between 112° and 120° C., recalling the similar behaviour of squalene hydrochloride, as described by several authorities. This compound was found to contain 33·61 per cent. of chlorine (calculated for $C_{30}H_{56}Cl_6$ = 33·86 per cent.). It was purified by fractional crystallisation from acetone after the manner described by Heilbron, Kamm and Morton[4] in their studies of the squalene hydrochlorides. The less soluble fractions gave rise to a material of a high m.p. (148–9° C.), which did not change its character on subsequent treatments with the solvent. In a recent experiment one fraction melting as high as 150° C. was obtained.* The main part of the more soluble portion gave a well-defined product melting unsatisfactorily between 118° C. and 124° C., but small amounts of preparations melting as low as 109° to 111° C., and even 100° to 101° C. were obtained from mother liquors. The results of this fractionation resemble those obtained when squalene hydrochloride is similarly treated (André and Canal,[5] Heilbron *et al.*[4]).

The analysis of the two main fractions gave the following figures:

Hydrochloride m.p. 148–9° C. Chlorine 33·14 per cent.
„ „ 100–1° C. „ 33·54 „

Fig. 1 shows the crystalline form of the hydrochloride (m.p. 110–116° C.), and that of squalene isolated from the liver oil of *Scymnorrhinus lichia.*



a. Hydrochloride from hydrocarbon derived from olive oil. *b.* Squalene hydrochloride.

Bromide.—The hydrocarbon dissolved in anhydrous ether and treated with an excess of bromine at —25° C. deposited a white micro-crystalline product superficially resembling the dodecabromide of squalene. The separated bromide darkened at 150° C. and melted, with signs of decomposition, at 187–189° C. The

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* There would appear to be need for a re-investigation of the isomeric hydrochlorides of squalene. Fractionation of the crude hydrochloride may yield a wide range of crystalline products with different melting-points. Other workers have also noted this peculiarity.

percentage of bromine found on analysis was 69·7. (Calculated for $C_{30}H_{50}Br_{12}$; Br = 69·7 per cent.)

PREPARATION OF HYDROCHLORIDE DIRECT FROM OLIVE OIL.—It being apparent, from the iodine value of the unsaponifiable matter and also from the actual yield of the hydrocarbon, that the latter was present in this sample of olive oil to the extent of approximately 0·5 per cent., it seemed of interest to attempt the preparation of the hydrochloride directly from the oil itself. Actually, the attempt was successful, in that characteristic crystals of this derivative separated out when the acetone solution of the oil was subjected to treatment with dry hydrochloric acid gas. The yield was, however, less than one-third of what might have been expected, and the experiment, considered as an analytical test for olive oil, was unsatisfactory, because of the separation of layers and the production of a large amount of dark brown, pigmented material. When heated, the hydrochloride thus produced, and purified by washing with anhydrous ether, showed shrinkage at 110° C., and finally melted rather indefinitely between 120° and 129° C. The chlorine-content was 33·22 per cent.

PROPORTION OF THE HYDROCARBON IN OLIVE OILS OF DIFFERENT ORIGIN.—A number of genuine olive oils of known origin, and one authentic sample of tea-seed oil, were examined for the presence of the hydrocarbon. The oils were saponified as described earlier in the paper, and the iodine values of the unsaponifiable matter were determined. The unsaponifiable fractions were then dissolved in a mixture of 75 per cent. of light petroleum spirit and 25 per cent. of benzene, and passed through a column of adsorbent aluminium oxide. The columns were washed through with a solvent mixture of similar proportions, and the materials which passed through without being adsorbed were recovered. The iodine values of these were determined.

It will be seen from the following table that all the samples of olive oil gave fractions which passed through the adsorption column, and which consisted almost entirely of the hydrocarbon. The presence of the hydrocarbon was in each case confirmed by the preparation of the crystalline hydrochloride. The results of the examination of the sample of tea-seed oil gave no evidence that squalene or any similar compound was present.

TABLE II

Oil	Iodine value of unsaponifiable matter	"Hydrocarbon" in unsaponifiable matter Per Cent.	Iodine value of "hydrocarbon" fraction
Palestine	255	64	345
Tunisian	194	38	360
Spanish (Aragon) ..	203	31	374
Turkish	263	58	364
Italian	235	—	—
Tea-seed	157	7*	130

* In view of the low iodine value of the hydrocarbon fraction from tea-seed oil, it is improbable that any significant amount of squalene is present.

COMPARISON OF PROPERTIES OF OLIVE-OIL HYDROCARBON AND SQUALENE

	Recorded data for squalene $C_{30}H_{50}$	Hydrocarbon from olive oil
Composition	C=87·8 per cent. H=12·2 ,,	C=87·71, 87·53 per cent. H=12·62, 12·44 ,,
B.p.	235–7° C. (0·15 mm.) (*a*)	187–190° C. (0·08 mm.)
Refractive index, $n_D^{20°}$	1·4965–7 (*a, b, c, d*)	1·4964
Iodine value	367·9 (*b*), 377·6 (*d*)	372
Mol.wt. cryoscopic (benzene)	394·391 (*b*), 391 (*d*)	368
Hydrochlorides	m.p. 144–5° C., Cl=33·9 per cent.	m.p. 148–9° C., Cl=33·84 per cent.
	m.p. 107–8° C., Cl=35·3 ,, (*e*)	m.p. 109–11° C., —
	m.p. 144–5° C., Cl=33·2 ,,	m.p. 100–1° C., Cl=33·5 per cent.
	m.p. 107–8° C., Cl=33·9 ,,	
	m.p. 144–5° C., Cl=33·7 ,,	
	m.p. 113–4° C., Cl=33·85 ,, (*d*)	
	m.p. 107–8° C., Cl=33·6 ,,	
Dodecabromide	darkens at 160° C., melts with decomposition at 185° C. Br=69·7 per cent. (*b*)	darkens at 150° C., melts with decomposition at 187° C. Br=69·7 per cent.

(*a*) Majima and Kubota, *Jap. J. Chem.*, 1922, **1**, 9.
(*b*) Chapman, *J. Chem. Soc.*, 1917, 56; 1918, 458.
(*c*) Tsujimoto, *J. Chem. Ind. Tokio*, 1906, **9**, 953; *J. Ind. Eng. Chem.*, 1916, **8**, 889; 1920, **12**, 63.
(*d*) Heilbron, Kamm and Morton, *J. Chem. Soc.*, 1926, 1630.
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The Determination of small Quantities of Chlorine in Commercial Benzaldehyde

BY C. G. DAUBNEY, M.Sc., A.I.C.

THERE are two main types of method available for determining the chlorine-content of commercial benzaldehyde, which is often of the order of 0·01 per cent.:—(i) Wet-oxidation methods, involving the use of mixtures of sulphuric and nitric acids. (ii) Methods in which the benzaldehyde is burnt in a lamp, and the products of combustion are examined for chlorine.

(i) Salamon,[1] and later, Faust and Spangler,[2] advocate treating a known weight of benzaldehyde with a mixture of concentrated sulphuric and nitric acids, distilling the mixture, and collecting the evolved vapours in silver nitrate solution. Methods of this kind have been investigated very fully by the firm of Schimmel,[3] who raise the objection that, by this procedure, chlorine which may be in the benzene nucleus is not necessarily liberated.

Other objections might be urged, such as the inherent disadvantage of using strong acids which produce a violent reaction, the difficulty of scrubbing the rapidly evolved gases, and the necessarily large volume of scrubbing liquid in which to determine a small quantity of chlorine.

(ii) Schimmel & Co.[3] advocate the use of a burning method. This consists in burning a quantity of benzaldehyde in a suitable lamp, scrubbing the products of combustion in towers containing *N*/50 sodium hydroxide solution, and converting the resulting sodium chloride into silver chloride.

To this process, also, objections can be raised: the chlorine may react with the sodium hydroxide to form chlorate or hypochlorite, and a large volume of chlorine-free scrubbing liquid is required.

The modified method adopted in the present investigation is as follows:

Benzaldehyde is burnt in a Richardson lamp[4] in a current of air previously freed from chlorine by passage over heated silver gauze, A, and the products of combustion are passed over a second piece of hot silver gauze, B. The chlorine present is converted into silver chloride, which is subsequently extracted with ammonia (sp.gr. 0·880), re-precipitated, and collected for weighing. The method has the advantage that the final aqueous liquid from which the silver chloride is precipitated is of small bulk.

The determination can proceed as long as is necessary to give a weighable quantity of silver chloride, and the one precaution to observe is the prevention of a sooty flame.

DETAILS OF METHOD.—The two rolls of silver gauze, A and B, are first cleaned by immersion in ammonia solution (sp.gr. 0·880), washed with water, dried and gently heated in a flame. They are then slid into silica tubes (in which they fit tightly), being followed by asbestos plugs and, finally, by rubber stoppers.

The lamp is filled with benzaldehyde, the wick (not glass capillaries) is adjusted to give a small flame, and the whole is weighed. The rest of the Richardson apparatus is connected (without the usual absorption tube) with the silica tubes placed side-by-side in iron-gauze shields. These tubes are heated to dull redness before the apparatus is connected with the suction pump.

The lighted lamp is then slid into position, the air-flow is adjusted to give a small non-smoky flame, and the shield is slipped down on to the mercury seal. The benzaldehyde is thus burning in a chlorine-free stream of air, and the products of combustion are freed from chlorine by the hot silver gauze, B.

When sufficient benzaldehyde has been burnt—this depending upon the expected chlorine-content—the lamp is removed and re-weighed. When cool, the tube with gauze, B, is disconnected, the ends, inside and outside, are cleaned, and, without removal of the gauze, placed in a test-tube. Three successive portions of 1·5 ml. of ammonia (sp.gr. 0·880) are dropped on to the gauze, and after this has been left for 10 minutes some 5 ml. of water are used for washing the gauze and tube. The dilute ammonia solution is then acidified with a minimum quantity of nitric acid, a few drops of silver nitrate solution are added, and the precipitated silver chloride is left to settle. Coagulation is assisted by the addition of a few drops of ether.

The silver chloride is collected in a Gooch crucible, washed first with *N*/100 nitric acid and then with absolute alcohol, dried at 125° C., cooled and weighed. It is then dissolved in ammonia, and the crucible is re-weighed. Usually a few tenths of a milligram of carbon remain undissolved.

The following table shows the results obtained both with commercial samples of benzaldehyde and with genuine natural oil of bitter almonds. Check determinations in which known quantities of chlorine were added to the almost chlorine-free oil of bitter almonds, indicate the reliability of the method.

Description of sample	Weight of substance burnt g.	Silver chloride g.	Chlorine Per Cent.
Oil of bitter almonds, Sample A	5·58	Opalescence	Trace
,, ,, ,, ,, ,, B	10·31	0·0006	0·0014
,, ,, ,, ,, ,, C	9·88	0·0006	0·0015
,, ,, ,, ,, ,, D	12·71	0·0003	0·0006
Oil of bitter almonds			
+0·013 per cent. Cl as *o*-chlorobenzaldehyde	7·39	0·0041	0·014
+0·025 ,, ,, Cl ,, ,,	3·13	0·0033	0·026
+0·074 ,, ,, Cl ,, ,,	1·56	0·0047	0·075
+0·131 ,, ,, Cl as *p*-chlorotoluene + benzyl chloride	1·32	0·0071	0·133
+0·022 ,, ,, Cl as ,, ,,	2·18	0·0019	0·022
Commercial benzaldehyde. Sample E ..	1·92	0·0016	0·021
	4·59	0·0042	0·023
	5·59	0·0045	0·020
Commercial benzaldehyde (chlorine-free). Sample F	2·93	0·0009	0·008
	5·87	0·0018	0·008
	7·44	0·0023	0·007
Commercial benzaldehyde. Sample G ..	4·38	0·0010	0·006
,, H ..	5·32	0·0022	0·010
,, J ..	4·86	0·0057	0·029
	5·05	0·0055	0·027
"Technical" K ..	1·500	0·0239	0·39
	1·201	0·0197	0·40

SUMMARY.—(i) A method is described for the determination of total chlorine in commercial benzaldehyde and oil of bitter almonds.

(ii) Oil of bitter almonds is shown to contain about 0·001 per cent. of chlorine.

(iii) Known amounts of chlorine in the form of organic chlorine compounds added to oil of bitter almonds are recoverable.

(iv) Commercial benzaldehydes contain between 0·005 and 0·03 per cent. of chlorine. One sample of technical benzaldehyde contained 0·40 per cent. of chlorine.

I wish to thank the Government Chemist for permission to publish this paper, and Mr. S. F. Holder, B.Sc., for assistance with the analytical work.

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Erratum.—"Lead in Biological Materials, with Special Reference to Bone," by Roche Lynch, Slater and Osler.

The authors regret an unfortunate error in their paper on pages 801–2 of the December issue. The sentence beginning in the last line of p. 801 should read as follows:—"If we take, for example, a 12-stone man who has 100 p.p.m. of lead in his bones, he will have in his whole skeleton 1·5 grms. (23 grains) of lead (as Pb), or 2·0 grms. (31 grains) of lead phosphate, $Pb_3(PO_4)_2$."

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SOME EXAMPLES OF FLUORESCENCE ACIDIMETRIC AND ADSORPTION INDICATORS

VOLUMETRIC determinations in ultra-violet light have been confined, up to the present, to acidimetric titrations, *e.g.* with quinine sulphate (Mellet and Bischoff, *Compt. rend.*, 1926, **182**, 1616) or umbelliferone (Robl, *Ber.*, 1926, **59B**, 1725) as indicator. Although the *p*H values at which the colour-changes of these indicators take place are different, the end-points observed, in the titrations of *N*/10 hydrochloric acid or sulphuric acid with sodium hydroxide (not carbonate-free) agree with the end-point in visual light with phenolphthalein as indicator. We find the end-point with R-salt (Desha, Sherill and Harrison, *J. Amer. Chem. Soc.*, 1926, **48**, 1493) to be the same as in the above titrations. We find also that magnesium 8-hydroxyquinoline complex can be used as an indicator in a similar way. The indicator is prepared by heating on a steam-bath 0·1 g. of magnesium-oxine complex with 10 ml. of *N*/10 hydrochloric acid and 100 ml. of water for half-an-hour; the solution is then made up to 100 ml. with water and filtered; 3 to 5 drops of this solution are used for a titration. In titrating solutions of acids, a change from colourless to golden-yellow takes place at the end-point, which is reached at the same value as for the above indicators. Neither hydroxyquinoline nor its hydrochloride fluoresces in this way, and the change in fluorescence is doubtless due to the formation of the magnesium-oxine complex at about *p*H 7.

Certain silver nitrate titrations, using adsorption indicators, can be carried out similarly in ultra-violet light. In the titration of chlorides (approx. N/40) with dichlorofluorescein (2 to 4 drops of 0·1 per cent. solution) as indicator, a colour-change takes place at the end-point from a fluorescent yellow-green to a chocolate-coloured suspension in which the fluorescence is extinguished. If the silver nitrate solution is added in a rapid stream, the end-point agrees exactly with that obtained in visual light with this indicator. In the titration of bromides or iodides (*N*/40 approx.) with eosin (2 ml. of 0·1 per cent. solution) as indicator, the change from a fluorescent golden solution to a non-fluorescent chocolate-coloured suspension agrees with the end-point in daylight. Phenosafranine, which shows a change from pink to blue on the precipitate in daylight, does not exhibit any change in ultra-violet light.

In the above titrations the values at which the end-points are reached depend upon the rate of addition of the silver nitrate and the amount of indicator used. The following figures illustrate this:

Sodium chloride (*N*/50, 100 ml.) was titrated with silver nitrate (1·005*N*/10), the silver nitrate being added from the burette in a fine steady stream. Dichlorofluorescein (0·1 per cent. solution) was used as indicator.

Vol. of indicator in ml.	0·1,	0·2,	0·3,	0·5,	0·75,	1·0,	2·0
Titre in ml.	12·5,	16·3,	18·0,	18·6,	19·7,	19·9,	20·2

Slow addition of the silver nitrate, as in this set of experiments, caused only a gradual disappearance of the fluorescence; when 2 ml. of indicator were used, fluorescence persisted in the liquid after the precipitate had settled.

If the silver nitrate solution is added rapidly from the burette, as recorded above, satisfactory and sharp end-points are obtained. The colour-changes are not so striking as in the acidimetric processes, and it is obvious, from the above results, that this type of titration could be of only limited application.

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NOTES ON THE DETERMINATION OF BISMUTH IN COPPER

THE results of experimental work carried out during the last two years on the effects of bismuth on metallic copper and its elimination by heating the solid metal in currents of various gases throw some light on the mechanism of the method of Colbeck, Craven and Murray for the determination of bismuth in copper (ANALYST, 1934, **59**, 395).

It has been found that when copper containing small quantities of bismuth is heated in a current, not only of hydrogen, but also of nitrogen, carbon monoxide or coal gas, at suitable temperatures and for sufficient time, the bismuth is entirely eliminated and carried forward. This negatives the formation of a hydride, and indicates that the mechanism of removal consists in outward passage of the bismuth from the copper and its distillation or sublimation from the surface in a current of inert or reducing gas.

The temperature at which this distillation begins is quite low, the first actual loss in hydrogen or nitrogen taking place at 500° to 550° C. At such a low temperature too long a time would be required for the total elimination of bismuth, but, on the other hand, too high a temperature must be avoided, as immediately even incipient fusion takes place the elimination of bismuth from the fused portions ceases.

The method for coarse particles of copper given by Colbeck and his collaborators (*supra*) (*i.e.* fusion at 1100–1120° C.) has never, in our hands, effected complete elimination of the bismuth; for example, copper containing 0·0056 per cent. of bismuth was heated in hydrogen to 1100° C. and melted, and, after being thus heated for two hours and allowed to cool in the furnace, the residual copper was found to retain 0·0035 per cent. of bismuth. This was confirmed by experiments carried out by Dr. Brislee, who found it impossible to eliminate any bismuth from molten copper by passing a stream of hydrogen or ammonia through the metal. (Private communication from Dr. F. J. Brislee of Messrs. British Insulated Cables, Ltd.)

It has been found that, with copper in a state of suitably fine division, a temperature of 950° to 1000° C. is the most efficient, and that when pure dry nitrogen or hydrogen is used, two hours' treatment, with a flow of about four l. per hour, is necessary for the process.

The size of the copper sample is of considerable importance, total elimination of the bismuth taking place with ordinary fine turnings, ground to pass a 20-mesh sieve and to be retained by a 30-mesh sieve; with copper wires of various diameters, total elimination was effected in two hours in hydrogen at 950° C. with wire of diameter up to, but not above 0·025 in.

We consider that the temperature given in the above-mentioned paper for copper millings, *viz.* 1050° to 1060° C., is too high for most brands of copper, as incipient fusion is liable to take place, causing retention of bismuth in the sample, and so leading to low results when used as a method of analysis; also that 1 hour is not sufficient for total elimination of the bismuth.

Some results on wire-bar copper are given in the following table:

WIRE-BAR COPPER (Original bismuth-content = 0·0056 per cent.)

Two hours' treatment at the following temperatures (heating up and cooling down in the furnace) °C.	Bismuth-content after treatment in hydrogen Per Cent.	Bismuth-content after treatment in nitrogen Per Cent.	Percentage of original bismuth eliminated in hydrogen	Percentage of original bismuth eliminated in nitrogen
450	0·0056	0·0056	Nil	Nil
550	0·0038	0·0042	32·1	25·0
650	0·0035	0·0023	37·5	58·9
750	0·0025	0·0011	55·3	80·3
850	0·0010	0·0006	82·1	89·3
950	Nil	Trace	100·0	100·0
1000	Nil	Nil	100·0	100·0
1050	0·00143	0·00185	74·4	66·9
1100	0·0034	0·0037	39·3	33·9

The optimum temperature to be used depends to some extent on the quality of the copper; *e.g.* with wire-bar copper of good quality there was total elimination in hydrogen and nitrogen after two hours at 950° C., whilst at temperatures above 1000° C. total elimination was not obtained. With blister copper containing cuprous oxide total elimination of bismuth was also effected in hydrogen at 950° C., but when nitrogen was used there was total elimination at as low a temperature as 870° C.

For the colorimetric determination of bismuth in copper the iodide method has been used, modified by the addition of 0·25 g. of ferrous ammonium sulphate per 10 g. of sample, the iron acting as a collector for the bismuth when it is precipitated with sodium carbonate. After this precipitation it is necessary to boil the liquid for ten minutes and to allow it to stand for at least six hours, or preferably overnight, before proceeding with the filtration, etc. Under these conditions perfect agreement is obtained between the direct colorimetric method and the mirror method.

For electrolytic copper and for various brands of commercial copper the chemical separation of the bismuth is preferred to the mirror method. (See also *Bull. Inst. Mining and Metall.*, No. 363, Dec., 1934.)

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THE DETERMINATION OF FREE SILICA IN COAL-MEASURE ROCKS

BEING engaged upon the examination of a ground shale used for stone-dusting in a New Zealand coal-mine when Shaw's paper (ANALYST, 1934, **59**, 446) appeared, I tried the method recommended, and the results may be of interest.

The only variation introduced was the use of a 1500-ml. Pyrex beaker in place of a porcelain dish; all digestions were carried out on a hot plate. After each acid treatment the contents of the beaker were allowed to settle overnight, but in subsequent treatments with Lunge's solution two hours' settling was sufficient. The use of a syphon was found satisfactory.

In a preliminary determination the percentage of free silica obtained was 14·6. Duplicate determinations were then made, and the results were 13·8 and 14·1 per cent., respectively.

This confirmed the author's statements as to the reliability of the method.

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Official Appointments

THE Minister of Agriculture and Fisheries has approved the following appointments:

RHYS PENDRILL CHARLES as Agricultural Analyst for the County Borough of Bournemouth, in place of R. A. Cripps (retired).

THOMAS REGINALD HODGSON as Agricultural Analyst for the County Borough of Stockport, in place of W. Marshall (deceased).

HENRY TURNER LEA as Agricultural Analyst for the County Borough of Huddersfield, in place of L. G. Paul (resigned).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1934

OF the 1186 samples submitted under the Sale of Food and Drugs Acts, 1143 were bought informally. The 43 formal samples were samples of milk.

FAT IN SHREDDED SUET. SOYA-BEAN FLOUR IN SUET.—The label of a sample contained the words "1½ lbs. equals 2 lbs. of raw suet." The amount of fat present was 94 per cent., which approximates to the amount found in ordinary butcher's suet. Some years ago samples of suet obtained from butchers were analysed, the suet being stripped from the membrane as it would be in an ordinary household. It was found that the amount of fat in the portion separated varied from 93·4 to 97·2 per cent., with an average of 95 per cent. of the whole bulk of the material. The separated membrane contained only small amounts of fat, varying from 1·0 to 4·7 per cent. of the total bulk of the sample.

For 1½ lbs. of the shredded suet in question to be equal to 2 lbs. of raw suet, the latter would have to contain only about 70 per cent. of available fat, and this would be the case only if there had been extraordinary carelessness in separating the membrane from the suet. Representations were made to the firm packing the suet, and they have agreed to cease using the label in its present form.

A further claim was made for this article. It was stated to be free from starch and to contain "a pure food product introducing valuable proteins, carbohydrates and vitamins." This material, which was used in place of the usual rice flour for separating the shreds of suet, was found to consist of soya-bean flour which, of course, does not contain starch and has a definite food value as a source of protein and vitamin *A*.

GREY POWDER TABLETS.—A sample of half-grain grey powder tablets was deficient in mercury and in chalk to the extent of 15 per cent. Although there is a tendency for mercury to volatilise from tablets such as these, yet, as the deficiency for both mercury and chalk was the same, it seemed more probable that the initial amounts of both ingredients were too small. The suppliers were cautioned.

H. H. BAGNALL

CITY OF LONDON

ANNUAL REPORT OF THE PUBLIC ANALYST FOR 1933

THE Report of the Public Analyst (Mr. A. J. C. Lickorish, F.I.C.) is included as a section of the Report of the Medical Officer of Health of the City of London.

Of the 1012 samples of food and drugs examined, 807 were informal samples, and 17 of these were condemned.

ICE CREAM.—The consumption of ice cream has greatly increased during the past few years, and it is to be regretted that there is no legal definition or standard of quality for it. Analyses of the 28 samples taken in the City showed a very wide range in the percentage fat-content, which bore little relationship to the prices charged. Thirteen of the samples, purchased at restaurants, had a fat-content of 8 per cent. or more, ranging from 8·5 per cent. to 24·4 per cent., with an average of 13·5 per cent. Fifteen samples, taken principally from itinerant vendors, had a fat-content ranging from 0·6 to 4·6 per cent., with an average of 2·6 per cent.

It may reasonably be submitted that ice cream should have a milk-fat content of at least 8 per cent., and should consist only of butter fat, milk solids-not-fat, sugar, gelatin and water. Mixtures consisting mainly of milk, sugar, cornflour, eggs, etc., should be permitted to be sold, not as ice cream, but under an appropriate designation, such as Ice or Ice Custard.

GLYCERIN OF ALUM.—An informal sample was found to be deficient, to the extent of 13·3 per cent. in alum, and the deficiency in the subsequent formal sample was 15 per cent. The vendor was cautioned.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

DESCRIPTION OF BRANDED ARTICLES

AMMONIATED QUININE TABLETS

ON November 30th a pharmacist was summoned at the West London Police Court for supplying ammoniated quinine tablets containing no ammonia. Mr. H. Glyn-Jones, for the defence, pleaded that his client had committed an unintentional offence, in that he had bought the goods on a warranty, nine months before the retail purchase took place. He gave an undertaking that the defendant would not sell any tablets of this nature in future without taking care, as far as possible, that the goods corresponded with their description, and the magistrate (Mr. Marshall) thereupon dismissed the case on payment of £3 3s. 0d. costs.

Department of Scientific and Industrial Research

REPORT OF THE WATER POLLUTION BOARD

FOR THE YEAR ENDED 30TH JUNE, 1934*

IN the Seventh Annual Report of the Water Pollution Research Board reference is made to the exceptional conditions of weather during 1933 and 1934. The long spell of dry weather not only caused difficulties in the provision of ample quantities of water for various purposes, but also had a serious detrimental effect on the quality of the water in rivers and streams into which sewage and trade effluents are discharged, as less water than usual was available for dilution of the discharges. At the present time there are many undertakings utilising polluted river water, after treatment, for domestic and industrial supplies, and there is no doubt that other polluted rivers will have to be similarly utilised in the future to meet the increasing demands of the community. It is important, therefore, that further efforts should be made to prevent, as far as possible without unnecessary expense, the pollution of rivers and streams and other sources of water supply if expensive methods of water treatment and danger to public health are to be avoided. This necessitates intensive, systematic research, as in many cases entirely satisfactory methods of treatment and disposal of trade effluents at a reasonable cost are not known. Further, as industry develops, new processes of manufacture are devised and new methods of dealing with the waste waters will be required.

The investigations initiated by the Board may be divided into four main groups dealing, respectively, with purification of water for public supply, methods of treatment and disposal of sewage, methods of treatment and disposal of trade effluents, and various problems of river pollution.

BASE-EXCHANGE PROCESS OF WATER SOFTENING.—In experiments on the use of commercial base-exchange materials for softening waters containing calcium bicarbonate, calcium sulphate and magnesium sulphate, it was found that the base-

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* H.M. Stationery Office, Kingsway, London, W.C.2. 1934. Pp. 44. Price 9d. net.

exchange values of the treated minerals, kenzelite and natrolith, were respectively equivalent to about 0·4 and 0·6 lb. of calcium oxide per cu.ft. of material; they were approximately the same for hard waters containing magnesium salts as for those containing calcium salts. The base-exchange value of doucil (a synthetic material) was equivalent to about 1·0 lb. of calcium oxide per cu.ft. with hard water containing calcium salts, but only to about 0·7 lb. with solutions of magnesium sulphate.

In attempts to determine the conditions of equilibrium between zeolites of alkali and alkaline earth metals, true conditions of equilibrium were not attained even after circulation of the solutions over the prepared zeolites for several weeks.

Many samples of British clays have been treated by various methods, and in a few instances substances with base-exchange values greater than those of some imported commercial materials have been obtained.

CONTAMINATION OF WATER BY LEAD.—A summary of existing knowledge on the action of water on lead has been published as Water Pollution Research Technical Paper No. 4 (*cf.* ANALYST, 1934, **59**, 346). Experiments have been made to determine how far tests under apparently similar conditions may be expected to give results in close agreement. In some cases the quantity of lead removed from standard lengths of commercial lead piping by distilled water in 24 hours agreed well; in others there were wide differences in the results. In experiments in which flat rectangular plates of lead were immersed in flasks of distilled water for definite periods of time there was fair agreement in the quantities of lead removed by the water.

MILK FACTORY EFFLUENTS.—Further progress has been made in experiments at Rothamsted (*cf.* ANALYST, 1934, **59**, 282) on the conditions affecting the purification of effluents containing milk by a process involving anaerobic fermentation followed by biological filtration. Anaerobic fermentation of mixtures containing 1 per cent. of milk in water causes separation of the fat and of some of the protein. The separated liquid can then be readily oxidised in percolating filters, with an efficiency of oxidation of about 99 per cent. Experiments have also been carried out on the treatment of milk by the activated sludge process. Several creameries and factories have been visited, and an outline is given of the methods in use for the treatment and disposal of the liquid effluents.

BIOLOGICAL OXIDATION OF FATS AND SOAPS.—Experiments at the Rothamsted Experimental Station on the biological filtration of solutions of sodium stearate, alone and in admixture with domestic sewage, have shown that soap in concentrations as high as 25 parts per 100,000 in sewage is readily oxidised in percolating filters.

SEWAGE DISPOSAL.—In the investigation being carried out for the Department at the London School of Hygiene, Barcroft respirometers have been employed in experiments on the effects of various factors on the rates of oxidation of sewage, sewage effluents, and activated sludge in contact with air at 24° C. Under the conditions employed the rates of oxidation of sewage and sewage effluents were greater than under the conditions ordinarily adopted in the test for biochemical oxygen demand. It was also found that the rate of oxidation of mixtures of sewage and activated sludge is greater than the sum of the rates for the separate constituents, especially during the early stages of oxidation. Maximum rates of oxidation for sewage and effluents were obtained at *p*H values between 6·6 and 9·0 and for activated sludge at *p*H values between 6 and 10. It has been shown that sewage and sludge previously sterilised by heating, by filtration through a Seitz filter, or by treatment with certain disinfectants do not absorb oxygen from air. Inoculation of the sterilised sewage or sludge by the addition of small quantities of untreated sewage or sludge or of washed suspensions of certain bacteria at once initiates absorption of oxygen.

The addition to sewage of potassium cyanide in concentrations ranging from *M*/200 to *M*/10,000 considerably reduced the rates of oxidation of the sewage by air at 24° C. during the first five hours. After this period the effect of the cyanide gradually decreased until the rate of oxidation became the same as for the sewage alone.

In view of the presence of protozoa in percolating filters at sewage works and in sewage undergoing treatment by activated sludge, experiments have been made to ascertain the effect of *Polytoma uvella* on the oxidation of sewage and sewage sludge by air. It has been found that this protozoan flagellate initiates the oxidation of previously sterilised sewage, but not so actively as certain bacteria.

The oxidation of solutions of an ammonium salt, sugars, amino acids, formate, lactate, glycerol, olive oil and phenol in the presence of activated sewage sludge has also been studied. The rate of oxidation of ammonia in the presence of activated sludge reached a maximum when the *p*H value was between 8·0 and 9·2. In the concentrations employed and in the presence of activated sludge, all the organic substances used, with the exception of phenol, were oxidised.

The investigation of the nature and amount of the colloidal and other dispersed matter in sewage has been continued for the Department at University College, London, under the immediate direction of Professor F. G. Donnan. During the past year the work has included experiments on the flocculation or coagulation of dispersed matter by passing finely-divided streams of air, oxygen, hydrogen, and nitrogen through samples of domestic sewage at 25° C. It has been shown that all four gases have a similar effect in causing, in a few hours, coagulation of a considerable amount of the dispersed material. Even particles originally so small as to pass an ultra-filter were coagulated by the action of the bubbles of gas.

RIVER MERSEY INVESTIGATION.—Considerable progress has been made in the work of the River Mersey investigation which was begun in April, 1933, with the object of determining the effect of discharges of crude sewage into the estuary on the amount and nature of silt and other solid matter deposited. The banks exposed at low tide have been surveyed and classified into two groups according to whether they are covered by sand or by mud. An attempt has also been made to determine the relative stabilities of the different banks from the changes in size and position as shown by the surveys since 1861, and from a biological survey of the banks; areas subject to frequent change as a result of tidal action are not likely to support certain types of organisms. The chemical section of the work has included the examination of samples of water from all parts of the estuary at different depths and at various states of the tide and the examination of numerous samples of solid matter from exposed banks. The material of the mud bank near Mount Manisty appears to be a mixture of sand and clay; the proportion of clay in this bank is greater near the shore, where the tidal currents are probably weakest. In general, the concentration of organic matter increases with the proportion of clay and with a decrease in the average size of the particles. The carbon-content rarely exceeds 3·5 per cent. of the dry weight of the mud.

Information has also been collected with regard to the quantity and nature of the discharges of sewage and trade effluents into the estuary.

GAS WORKS EFFLUENTS.—The Liquor Effluents and Ammonia Sub-Committee of the Institution of Gas Engineers has continued its investigations on the disposal of effluents from gas works, and has issued a third report on the results obtained. It cannot be assumed that the acid permanganate test measures the relative effects of constituents of gas liquor effluents on biological methods of sewage purification. For this reason the Committee has begun a comprehensive investigation on the biological oxidation, by percolating filters and the activated sludge process, of sewage to which known quantities of gas liquor effluents and their various constituents have been added. These experiments have indicated that sewage to which phenol, thiocyanate or catechol (representing higher tar acids) has been added, even in amounts sufficient to increase the oxygen absorption value of the sewage by 32 parts per 100,000, is readily oxidised by biological filtration. Under the conditions of the experiments, the quality of the effluents from the filters was not appreciably affected by the addition of any one of these three constituents. Thiosulphate and sulphide added in amounts sufficient to increase the oxygen absorption values of the sewage by 16 to 32 and 8 to 16 parts per 100,000, respectively, caused deterioration in the quality of the effluents, but had little effect in smaller concentrations. It was found necessary to increase the concentration of added thiocyanate and thiosulphate gradually, otherwise the quality of the treated effluent deteriorated for a time, presumably until suitable organisms had developed in sufficient numbers on the filtering medium.

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE 30TH, 1934

IN his Annual Report the Government Analyst (Mr. J. B. Henderson) states that 12,217 samples were examined, this being a record number. Of these, 6314 were for the Health Department, 2079 for the Customs, and 1511 for the Geological Survey. The 2447 samples of foods submitted by inspectors under the provisions of the Health Acts included 2259 of milk, 127 of fresh fruit, 30 of spirituous liquor, and 20 of meat (sausage and minced). Of these, 491 (351 milks) were condemned. Twelve of the 50 disinfectants, 19 of the 59 drugs and medicines, and 16 of 23 toilet preparations were condemned, mostly for mislabelling, the contents of the packages not justifying the claims on the label.

STANDARDS FOR BREAD.—Sixty-one samples from that number of bakeries in the Brisbane area were examined. Only 2 samples (with 45·7 and 45·4 per cent.) contained water in excess of the maximum allowance of 45 per cent. of water laid down in the standard. In the other samples the amounts of water ranged from 41·8 to 45 per cent., the average being 43·8 per cent. All the samples were normal with regard to crust, colour, pile, texture and flavour.

AMMONIACAL CANNED FISH.—Twenty-six of 38 samples of imported canned fish, mostly sardines and sild, were condemned because of decomposition or excessive tin-content. All the samples high in tin were markedly alkaline in reaction, some containing free ammonia. Even fresh stock was found to be ammoniacal shortly after arrival, this suggesting that the fish was in a state of incipient decomposition when packed.

LEAD ARSENATE IN VEGETABLES AND FRUIT.—Eleven consignments of cabbage contained lead arsenate in material quantity, the highest proportion found being 4·8 grains per pound. There has fortunately been a marked reduction recently in the use of lead arsenate on vegetables, as compared with previous years.

Of 246 samples of apples and pears taken from consignments from Southern States, 57 contained less than 1-100th part of a grain of arsenic to the pound, and 189 contained over this proportion, the highest figure being a quarter of a grain per pound. These samples were taken because they showed the presence of spray residues on the skins, and so do not afford much evidence of the actual proportion of fruit coming forward that is contaminated with arsenic. The British authorities placed a limit of 1-100th part of a grain of arsenic to the pound on imported fruit, and this limit has tentatively been adopted in Queensland. It is unfortunate for both public and growers that this dangerous practice of using poisonous insecticides cannot be stopped. It affects the public because it renders the foods poisonous, and affects the growers because the public buy less, being afraid of the poison.

ARSENIC IN TOBACCO.—The use of lead arsenate on tobacco plants, both in Australia and overseas, has led to the examination of all tobacco sold either in leaf or in the manufactured form. Of the 2664 samples examined, the great majority were free from, or showed only traces of, lead arsenate. Experiments have shown that, although most of the arsenic in contaminated tobacco is left in the ash, if there is more than a trace of lead arsenate in the tobacco, some passes over in the smoke. All consignments showing more than a trace are therefore condemned. As buyers do not buy leaf until it has been certified as conforming to the Health Department's requirements, all batches have to be tested; hence the recent large increase in the number of tobacco samples.

ARTIFICIAL COLORATION OF FRUIT BY MEANS OF GASES.—The practice of leaving green, unripe fruit for a short time, generally overnight, in an atmosphere containing certain gases has recently been widely adopted. Several gases have been used for the purpose, even the exhaust gases from motor engines, and several kinds of fruit are treated. The great bulk of citrus fruits are now being changed from a green to a yellow colour in this way, while a proportion of the bananas and pineapples are also being treated. The appearance of ripeness, however, is entirely fictitious, except when the gas is used as part of a complete ripening process. When used by itself, the treatment leaves green, sour, unripe oranges, still sour and unripe, and hard unripe bananas still hard and unripe, despite their deceitful, attractive yellow skin. There is no question that in such cases the practice is fraudulent, as the sole object is to give unripe fruit the appearance of being ripe, and so to deceive the buyers. Unfortunately, the problem of determining when a fruit is really ripe, by definite chemical tests, has not yet been solved. There is, however, already evidence that some consumers are noticing the unripe quality of certain fruits of ripe appearance, and are buying less fruit, owing to the difficulty of obtaining it in an edible condition. This loss of market may help to stop the practice, but in the best interests of the consumers, and therefore also of the growers, the problem created by the new fraud might be met by a new regulation definitely prohibiting such misleading artificial colouring.

LEAD IN PAINTS FOR GATES AND RAILINGS.—Under the Health Acts the use, for verandah rails, gates or fences, of paints containing more than 5 per cent. of soluble lead is not permitted. The proportion of soluble lead is determined by treating the paint pigment with a 0·25 per cent. solution of hydrogen chloride, this strength being equivalent to the hydrochloric acid content of normal gastric juice. Of 91 samples of paint examined from verandah rails or fences, 67 exceeded the limit of 5 per cent. of soluble lead.

CORROSION OF RABBIT-PROOF FENCES.—Analyses of 26 samples of both old and new nettings, some only slightly corroded and others badly corroded, and of 26 samples of the soils in which they had been buried, gave no conclusive evidence as to the reasons for the short life of some of the nettings. The evidence obtained was not sufficient to support final recommendations for preventing the trouble. One striking result was obtained with regard to the effect of laying new wire netting in contact with the old rusted netting left in the ground. In the presence of ordinary soil water the new and rusted metals in contact give rise to quite marked electrical currents, and the corrosion of the new metal in such cases is very rapid—much more rapid than was expected. At a conference of representatives of the Lands Department, the Leichhardt Rabbit Board, and the Government Analyst it was decided to erect test panels in various localities in order to determine the relative importance in improving the life of the netting of—(i) Elimination of the possibility of electrolytic action between new and old netting; (ii) the use of a bituminous coating on the netting; and (iii) the use of heavier gauges of netting; and also (iv) to compare Australian and imported nettings. Eight sites with varying conditions of soil types and soil moisture and salinity have been selected, and a comprehensive series of test panels will shortly be erected.

Scientific Glassware Standards

B.S.I. SPECIFICATIONS FOR DISTILLATION FLASKS AND FOR GROUND-GLASS JOINTS

THE British Standards Institution has issued specifications for distillation flasks and for interchangeable conical ground-glass joints. These are the first glassware specifications to be issued by the Scientific Glassware Committee, which was taken over from the Institute of Chemistry when the Chemical Division of the Institution was formed.

DISTILLATION FLASKS SPECIFICATION (No. 571)

This specification provides for a complete series of fourteen flasks ranging from a distillation capacity of 30 ml. to 3000 ml. Prior to the publication of the specification, four manufacturers were making, between them, over this range of capacity, flasks having twenty different nominal capacities, and having forty different bulb capacities. The general adoption of the standard series will, therefore, not only diminish the different sizes of flasks now being made, but will also ensure identity of actual capacity between flasks having the same nominal capacity.

Nominal Capacity and Distillation Capacity.—The following three conditions are fulfilled by each flask in the series: (1) the centre of the side-tube is 75 mm. from the top of the neck; (ii) the centre of the side tube is 90 mm. from the liquid surface when the flask is vertical and contains a quantity of liquid equal in volume to the distillation-capacity of the flask; (iii) the bulb-capacity is 30 per cent. greater than the distillation capacity.

The first condition ensures the same immersion of the stem of the thermometer in each size of flask, the thermometer being placed so that the top of the bulb is level with the bottom of the side-tube at its junction with the neck. Thermometers calibrated for 100 mm. immersion are convenient for use with the flasks. When the thermometer is fixed as directed above, the immersion line of the thermometer will be in the neighbourhood of the top of the cork holding the thermometer in position in the neck.

The second condition helps to secure reproducibility of results in distillation by ensuring that the thermometer-bulb is at a constant distance from the level of the liquid surface at the beginning of a distillation. The third condition ensures a definite bulb-capacity for each nominal capacity, the bulb-capacity being taken as 30 per cent. greater than the distillation-capacity. Considerable variation was found in the bulb-capacity of flasks from different sources having the same nominal capacity.

SPECIFICATION FOR GROUND-GLASS JOINTS (No. 572)

This specification has been prepared to secure the interchangeability of conical ground-glass joints in laboratory and industrial glassware. In order to ensure interchangeability, the following elements have been specified for each joint: (i) Taper; (ii) diameter of larger end of socket; (iii) diameter of smaller end of cone; (iv) length of ground portions of cone and socket. A taper of 1 in 10 on diameter, equivalent to a cone semi-angle 2° 51′ 45″ has been adopted for all joints.

To meet the requirements of different types of apparatus, four series of standard joints, designated Series A, Series B, Series C and Series D, have been provided. The dimensions for the standard Series A have been chosen to fit in with foreign standards already in existence. Joints in the additional series have the same diameter at the larger end as the corresponding joints in Series A, but have different lengths of engagement; thus, Series B, three-quarters; Series C, a half; and Series D, a quarter the length of Series A.

The four series of joints together afford a very wide choice, so that provision is made for the replacement of existing joints and for special requirements. It is considered, however, that the following sizes would meet almost all normal requirements: A 14, A 16, A 19, A 24, A 29; B 24, B 29, B 34, B 40, B 45, B 50. It is, therefore, recommended that these sizes be adopted for general use, and that the remaining sizes be employed only when it is impossible to use one of the recommended sizes.

The dimensions and tolerances specified were adopted only after very careful measurement and examination, at the National Physical Laboratory, of conical ground-glass joints in present-day use.

Copies of these specifications (Nos. 571 and 572—1934) can be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d. each, post free.

Standardisation of the Methods of Testing the Fastness of Dyed Materials*

THE Report of the Fastness Committee of the Society of Dyers and Colourists deals with three fastness requirements, *viz.* (i) fastness to light; (ii) fastness to perspiration; (iii) fastness to washing.

FASTNESS TO LIGHT.—The Committee adheres to the international practice of employing 8 grades of fastness to light (*cf.* ANALYST, 1934, **59**, 784). The standard dyes selected are as follows:

Red Standards.—(2) 0·5 per cent. Acid Magenta IIS (I.C.I.) (C.I.692); (3) 0·5 per cent. Polar Red 3B Conc. (Gy.); (4) 1 per cent. Cloth Fast Red R (S.C.I.); (5) 1 per cent. Alizarine Rubinole GW (I.G.) (C.I.1091); (6) 1 per cent. Kiton Fast Red 4BL (S.C.I.); (7) 1·2 per cent. Alizarine Orange A425 Powder (I.C.I.) on zinc (C.I.1033); (8) Durindone Red B400 Powder (I.C.I.) (C.I.1207).

Blue Standards.—(2) 0·5 per cent. Lissamine Violet 6BNS (I.C.I.) (C.I.717); (3) 0·6 per cent. Brilliant Indocyanine 6B (I.G.); (4) 1·1 per cent. Polar Blue G. Conc. (Gy.); (5) 0·5 per cent. Solway Blue R.S. (I.C.I.) (C.I.1076); (6) 2 per cent. Alizarine Light Blue 4GL (S.); (7) 4 per cent. Caledon Blue GCP300 Powder (I.C.I.) (C.I.1113); (8) 3 per cent. Indigosol Blue AGG (D. & H.).

FASTNESS TO PERSPIRATION.—It has been found possible to make up artificial test solutions representing acid and alkaline perspiration, based on the results obtained by Voss and McSwiney in their investigations on the composition of human sweat (*cf.* ANALYST, 1934, **59**, 496). These solutions are:

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* Obtainable from the Secretary, The Society of Dyers and Colourists, 32, Piccadilly, Bradford, Yorkshire. Price 7/6 net.

Acid Perspiration Liquor.—2·65 g. of sodium chloride and 0·75 g. of urea per l., brought to *p*H 5·6 with $N/10$ acetic acid.

Alkaline Perspiration Liquor.—0·839 g. of ammonium chloride, 1·732 g. of sodium chloride and 0·424 ml. of ammonia solution (sp.gr. 0·88) per l., brought to *p*H 7·8 with $N/10$ acetic acid.

A schedule of tests is given indicating the manner in which these solutions should be used.

FASTNESS TO WASHING.—"Four tests of increasing severity are prescribed and cover all degrees of severity from a mild home wash to a test representing the cumulative action of several severe power washes." Two sets of standards are then given, one in the red series and the other in the blue.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Cold Storage of Poultry. Chemical Changes in the Fat of Gas-stored Chickens. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 347–349.)—Young birds (12 weeks old) were stored in carbon dioxide and in air at 0° to −1° C. The fat was extracted from the minced skin with petroleum spirit, and from the minced breast muscle with peroxide-free ether; the solvent was distilled and the last traces removed *in vacuo* below 50° C. The figures for free acidity of the fat show a rapid rise coincident with appearance of mould on the air-stored samples, but a much slower development of acidity in the fat of gas-stored birds. For the determination of peroxide oxygen 1 g. of the skin fat, or the whole of the muscle fat (about 0·5 g.), was heated with powdered potassium iodide in a mixture of glacial acetic acid and chloroform (20 ml.), and the liberated iodine was titrated with 0·002 N thiosulphate solution, all operations being carried out in the dark or in weak artificial light to prevent oxidation of the fat. The amount of fat recovered from the skin samples was 9 to 21 per cent., and from breast muscle 0·16 to 0·35 per cent. Determinations of peroxide oxygen in the breast fat gave zero values throughout the carbon dioxide experiment; in the air experiment at 17, 24, and 46 days values of 3, 3 and 5 ml. per g. of fat, respectively, were obtained. It must be remembered that a considerable proportion of linolic acid is present in chicken fat, and also that in young chickens the proportions of fat are small. It is concluded that, whilst carbon dioxide practically eliminates mould and bacterial spoilage in chickens at 0° C., autolysis of the tissues by enzymes prevents prolongation of storage-life for undrawn birds. After long gas-storage periods oxidation of the fat may cause spoilage unless the carbon dioxide concentration closely approaches 100 per cent. D. G. H.

Scheme for the Approximate Determination of the Proteins of Muscle. E. C. Smith. (*J. Soc. Chem. Ind.*, 1934, **53**, 351–354T.)—A method has been worked out for the determination of the more important fractions of muscle protein, viz.: (i) Intracellular proteins, these being myogen, which is soluble in both water and salt solutions, and myosin, which is soluble only in salt solutions. (ii) Extracellular proteins (insoluble in water or salt solutions): collagen, which is converted into water-soluble gelatine when heated, and elastin, which is resistant to the action of trypsin. The efficiency of a solution for extracting the soluble proteins depends not only on the ease with which a protein dissolves in the solvent, but also on the effect of the solvent on the cell-walls and connective tissue, which hinder penetration of solvent and escape of solution. Tests made with a number of salt solutions show that 10 per cent. ammonium chloride solution is the most effective solvent. Six extractions, with continuous gentle agitation, assisted by occasional grinding with sand, remove about 95 per cent. of the total extractable protein, and much time is saved and little error involved by limiting the number of extractions to six.

The extraction is carried out by placing four 5-g. lots of the minced and mixed muscle in four 50-ml. centrifuge cups, together with 35 ml. of cold 5 per cent. magnesium sulphate (or 10 per cent. ammonium chloride) solution and 10 g. of washed sand. The muscle is ground for 3 minutes with a flattened glass rod, and the tubes are then closed with rubber stoppers and shaken in a horizontal position for 30 minutes at 0° C. at such a rate that little froth is formed. The suspension is centrifuged and, after the clear supernatant layer has been transferred to a flask, the extraction and grinding are repeated, six such operations being performed.

To determine myosin, 10 g. of the protein sol are poured into 100 ml. of ice-cold water in a centrifuge cup and well stirred, the protein separating as an opalescent gelatinous precipitate. After being kept at 0° C. for not less than 4 or more than 18 hours, the liquid is centrifuged. Any floating particles are removed to a filter, and the residue is washed three times on the centrifuge with water and then with 10 per cent. trichloroacetic acid solution to ensure complete removal of ammonium salts. The precipitate in the centrifuge cup and the filter-paper (washed similarly) are transferred to a Kjeldahl flask and the nitrogen is determined as usual; triplicate determinations should be made. The myosin determined in this way in solutions containing between 0·15 and 0·13 per cent. of myosin-nitrogen is 88 ± 2 per cent. of that present; myogen interferes appreciably only when present at a concentration six times that of the extracts made as described. The non-myosin extractable protein is regarded as consisting almost entirely of myogen. There is said to be a third protein, globulin X, present, but this is probably only a small fraction of the total. The pigments, haemoglobin and myoglobin, may be determined by the usual physiological methods.

The insoluble residues remaining after extraction with ammonium chloride or magnesium sulphate are washed with 80 ml. of water into a 200-ml. beaker and autoclaved for 2 hours at 2 atmospheres' pressure (121° C.). The hot liquid is filtered and the residue on the filter is washed with boiling water until the wash water shows practically no biuret reaction. The nitrogen in the filtrate is collagen-nitrogen. The undissolved residue is washed back into the beaker with 25 ml. of water, and 25 ml. of a solution of trypsin (0·2 g. of B.D.H. trypsin and 0·6 g. of sodium carbonate in 100 ml. of water) are added. The suspension is digested for 16 hours at 37–40° C. and then boiled, and the precipitate is filtered off and washed. The nitrogen in the filtrate is residual intracellular protein-nitrogen (plus that introduced with the trypsin solution), whilst that in the precipitate is elastin-nitrogen.

This method has given concordant results on triplicate samples. When the residual intracellular fraction is large, there is evidence of a small loss of nitrogen from this fraction, possibly by evolution of ammonia during the digestion. Results of partial and complete analyses of rabbit and ox muscle are given. During storage of the muscle, the residual intracellular fraction increases, owing to part of the protein becoming insoluble, but the rate and extent of this change are much less than have been recorded by others. T. H. P.

Cassava Products from British Honduras. (*Bull. Imp. Inst.*, 1934, **32**, 370–374.)—Samples of cassava starch and of dried cassava root (chips) from British Honduras were analysed. Sample (*a*) consisted of slices of scraped roots assumed to be sweet cassava chips, creamy-white in colour with an occasional brown tinge; (*b*) assumed to be dried bitter cassava chips consisting of slices of scraped roots rather browner than (*a*); (*c*) Stann Creek sweet cassava starch—a white powder and small creamy-tinted lumps; and (*d*) similar to (*c*), but of a better colour. The composition of the samples was as follows:

	(*a*) Per Cent.	(*b*) Per Cent.	(*c*) Per Cent.	(*d*) Per Cent.
Moisture	12·3	12·1	14·2	13·9
Crude proteins	1·0	1·0	0·1	0·2
Starch (by acid hydrolysis)	71·6	70·3	78·2	78·4
Crude fibre..	1·9	2·2	0·2	0·3
Ash	1·7	1·9	0·5	0·4
Hydrocyanic acid.. ..	0·0006	0·0012	Nil	0·0008

The roots were thus of normal composition; also the starches, except that the percentages of actual starch were low. Gelatinisation tests showed sample (*d*) to be better than (*c*). A sample of a fine buff-coloured meal, described as "specially prepared starch from the refuse of starch previously made," would probably prove suitable only for such uses as the manufacture of cattle foods, and gelatinisation tests showed it to be much inferior to samples (*c*) and (*d*). D. G. H.

***Zamia Furfuracea* Starch from British Honduras.** (*Bull. Imp. Inst.*, 1934, **32**, 374–375.)—The starch examined was stated to have been prepared from the underground stems of *Zamia furfuracea*, a plant indigenous to British Honduras; it consisted of slightly granular starch of fair colour but gritty in the mouth. It contained:—Moisture, 14·6; crude proteins, 0·4; fat, 0·2; starch (by acid hydrolysis), 80·6; other carbohydrates (by diff.), 2·6; crude fibre, 0·2; and ash, 1·4 per cent. The ash contained a high proportion of silica, possibly owing to contamination during preparation. A gelatinisation test with 10 g. of Zamia starch and 100 ml. of water produced a jelly somewhat firmer than was yielded by St. Vincent arrowroot under similar conditions, but of rather inferior colour. D. G. H.

Fluosilicates and Wines. H. Fabre and E. Brémond. (*Ann. Falsif.*, 1934, **27**, 453–466.)—The proportion of fluorine regarded as normal in a wine is 5 mg. per litre. Any amount appreciably exceeding this may be due to either

(i) fraudulent addition of soluble fluoride with the object of masking or combating bacterial disease, or (ii) treatment of the vines, too late in the season, with insecticidal powders with a basis of barium or sodium fluosilicate. The second of these practices may result in delay or premature stoppage of the fermentation.

T. H. P.

Tests of the Suitability of Acetic Acid for Clinical Work. J. Hillen. (*Pharm. Weekblad*, 1934, 71, 1210–1214.)—The benzidine test (*cf.* K. Serke, *Apoth. Zeit.*, 1929, 1018) is unreliable, as samples of acetic acid may give a yellow colour when this reagent is dissolved in them, and still be suitable for clinical work. It is suggested that (i) a solution of 10 mg. of benzidine in 5 ml. of the sample should be mixed with 2 ml. of 3 per cent. hydrogen peroxide; there should be no green colour after 5 minutes; (ii) a mixture of 1 ml. each of Schiff's reagent and of the sample is allowed to stand for 5 minutes, and 10 ml. of dilute sulphuric acid are added. A red or purple colour should not appear, although a blue colour is permissible.

J. G.

Stability of Mixtures of Hydrogen Peroxide and Ethyl Alcohol. W. A. Woodard and J. Pickles. (*Quart. J. Pharm.*, 1934, 7, 418–421.)—Mixtures of ethyl alcohol and hydrogen peroxide (10 vol.) prescribed as ear-drops are frequently supplied ready-mixed, and have then been known to occasion stinging and irritation if used after a relatively long period. It is shown that about 1 per cent. of acetic acid and 0·44 per cent. of acetaldehyde may be produced after storage for 3 months at 60° to 65° F. in greenish-white bottles in a bright light, and that the *p*H value falls from 4·8 to 2·6. The residual peroxide-content is less than that of the corresponding solution of hydrogen peroxide stored separately. The constituents should therefore be dispensed separately in amber bottles and stored in a cool, dark place.

J. G.

Preparation and Properties of *Mentholum Valerianicum*. B. Bobranski. (*J. Pharm. Chim.*, 1934, 20, 437–442.)—*Mentholum valerianicum* ("Validol"), which is a solution of menthol in menthyl isovalerate, should contain 66 to 73 per cent. of ester, corresponding with the saponification value 155 to 170. It may be prepared either by the action of isovaleryl chloride on menthol, or by the esterification of menthol with valeric acid, menthol being then dissolved in the product. The method with isovaleryl chloride gives good yields but a poor product, owing to impurities in the acid chloride, which is prepared by means of thionyl chloride or one of the phosphorus chlorides. The esterification process requires either sulphuric or gaseous hydrochloric acid as a catalyst. The former causes the formation of menthene and not menthyl isovalerate. The use of gaseous hydrochloric acid results in a product having an agreeable odour, and closely resembling "Validol." The isovaleric acid is mixed with about 18 per cent. of menthol in excess of the theoretical amount, and gaseous hydrochloric acid is passed through the mixture for an hour in the cold. The flask is then heated on the water-bath, beneath a reflux condenser, for seven hours, the acid gas still being bubbled through the mixture. After cooling, the product is washed twice with water, once with 5 per cent. sodium hydroxide solution, and once again with water, the same volume of wash liquid as of ester being used. The product is then dried with anhydrous potassium carbonate (2 g. for each 20 g. of menthol) and distilled at a pressure of 1·5 mm. of mercury. Natural menthol, B.P., gave a product having a boiling range, at 1·5 mm., of 80°–125° C.; synthetic menthol (Schimmel), 70°–115° C.; and another synthetic menthol (Schering), 65°–118° C. The optical rotations were:—Natural $[\alpha]_D^{21^\circ}$ $-51{\cdot}8^\circ$; synthetic (Schimmel), $-20{\cdot}40^\circ$; and synthetic (Schering), $+1{\cdot}3^\circ$. *l*-Menthyl isovalerate should have $[\alpha]_D^{21^\circ}-64{\cdot}02^\circ$ and saponification value 233. S. G. S.

Determination of Nicotine by the Silicotungstic Acid Method. N. H. Pizer. (*J. Soc. Chem. Ind.*, 1934, **53**, 356–357T.)—The application of this method to the determination of nicotine in concentrations of 0·01 per cent. or less has been investigated. Particular attention has been given to the temperature of ignition of the nicotine silicotungstate which must be such that all the carbon is burnt off and the silicic acid dehydrated, and no loss of tungsten trioxide occurs by volatilisation. The temperature 1000° C. fulfils these requirements. With the A.O.A.C. official method (*Methods of Analysis*, 1930, 55), and taking quantities of "pure" nicotine varying from 0·1 to 0·01 g., the percentages found lie between 99·63 and 100·20; with 0·005 g. of nicotine, 99·15 per cent. was obtained. T. H. P.

Colorimetric Determination of the Preservative Value of Hops. A. A. D. Comrie. (*J. Inst. Brewing*, 1934, **40**, 420–424.)—Earlier methods (*cf.* Guthrie and Philip, ANALYST, 1933, **58**, 411) have been improved as follows:—About 50 g. of the freshly-minced and mixed sample are shaken with 100 ml. of methylated spirit, and 1 ml. of the supernatant liquor is diluted to 50 ml. with methylated spirit in a graduated flask; this is stable for 24 hours. A mixture of *A* (usually 5) ml. of this extract and 1 ml. of a 1 per cent. solution of uranium nitrate in methylated spirit is matched in a colorimeter against a 10 per cent. solution of (A.R.) ferric chloride, every 100 ml. of which contains 1 ml. of *N* hydrochloric acid. The liquids are brought to the same level with methylated spirit, and the final match is obtained by adding to or removing from the ferric chloride standard and so varying the depth, the solutions being viewed vertically; the depth is measured (*B* mm.) and should fall within the range 40 to 70 mm. In order to calibrate the standard iron solution 0·0316 g. of the α-resin lead salt is prepared (*loc. cit.*) and ground with 5 ml. of methylated spirit and 0·4 ml. of 20 per cent. sulphuric acid until the lead salt has decomposed completely. It is then washed with methylated spirit into a separating-funnel containing 20 ml. of a 1 per cent. solution of common salt, and is extracted 4 times with 10 ml. portions of petroleum spirit (b.p. 38° to 40° C.), the extracts being filtered and evaporated first at 140° F., and finally, when 5 ml. remain, at 110° F. To a solution of the residue in methylated spirit are added 5 ml. of a 0·1 per cent. solution of bromothymol blue and sufficient of a 0·1 per cent. solution of xylene cyanol-*FF* to give a shade of green which matches that of a normal 10 per cent. hop extract, methylated spirit being the solvent in all cases. The mixture is diluted to 100 ml., and the depth of the ferric chloride solution (*C* mm.) required to give a colour which matches that of 4 ml. of the standard (≡ 0·8 mg. of α-resin) is determined. Then the preservative value is $16\,AB/C$. The methylated spirit for use is prepared by distillation of the industrial quality, the first 50 ml. being rejected and the last three-quarters of the total volume collected. The same supply should be used both for the standardisation and for the actual determination, and 10 ml. should show no turbidity for 1 hour after the addition of 1 ml. of a 1 per cent. solution of uranium nitrate; this test may be used to determine the end-point of the distillation. The graph given in the paper demonstrates the linear relationship between the α-resin present and *B*. The results obtained for 6 samples of English (1933) hops from different localities agree reasonably well with the gravimetric method of Hastings and Walker (*id.*, 1933, **58**, 702) for hops of good quality if the formula 10 $(\alpha + \beta/3{\cdot}0)$ is used to calculate the preservative value in the latter case. The poorer hops show wider divergencies, although not so great as that observed by Guthrie and Philip (*loc. cit.*) for a sample of old hops; these discrepancies may be due to differences in the source of light used, since Van Laer has shown that the light absorbed by the uranium compounds of the α- and β-resins varies throughout the spectrum. The method is not intended to replace the gravimetric procedure, but has the advantages of speed and simplicity. J. G.

Biochemical

Further Studies on the Availability of Iron in Biological Materials. W. C. Sherman, C. A. Elvehjem and E. B. Hart. (*J. Biol. Chem.*, 1934, **107**, 383–394.)—In previous papers (*J. Biol. Chem.*, 1933, **103**, 61; *J. Pediat.*, 1934, **4**, 65), the authors have shown that with sufficient copper, the iron of simple inorganic salts is used for haemoglobin regeneration in anaemic rats much more efficiently than the iron in the form in which it is found in a number of foods. The previous papers deal also with a method of determining the "available" iron present by the use of the α, α′-bipyridine reagent. The present paper deals with the availability of iron in liver, cardiac muscle, skeletal muscle, oysters, blood, soya beans, spinach and alfalfa. Beef and pork liver and cardiac muscle and soya beans have an availability of over 60 per cent., and beef skeletal muscle of 50 per cent., whilst that of oysters, spinach, alfalfa and blood is 25 per cent. or less. Results closely resembling those given by the bipyridine method were obtained by boiling the finely-ground, fresh material with 15 ml. of 5 *N* hydrochloric acid for 10 minutes in a 100-ml. beaker. The solution was then cooled and the protein was precipitated with 20 per cent. trichloroacetic acid; the precipitate was filtered off and washed with dilute trichloroacetic acid. The combined filtrates were then boiled with 0·25 ml. of 30 per cent. hydrogen peroxide and diluted to 50 ml. The iron in aliquot portions of this was determined by the thiocyanate and amyl alcohol extraction method. S. G. S.

Note on Bombicysterol. W. Bergmann. (*J. Biol. Chem.*, 1934, **107**, 527–532.)—The unsaponifiable fraction of the chrysalis oil of the silk moth, *Bombyx mori*, amounting to about 1·6 per cent. of the oil, contains, in addition to large amounts of hydrocarbons, 33 per cent. of cholesterol and 15 per cent. of sitosterols. The presence of bombicysterol was not detected. S. G. S.

Further Studies on the Concentration and Chemical Nature of Vitamin B_2 (*G*). L. E. Booher. (*J. Biol. Chem.*, 1934, **107**, 591–597.)—By the use of a specially prepared fuller's earth, vitamin B_2 has been concentrated from whey powder to between 200 and 300 times the original strength, the resulting product being an orange-red powder with an activity of between 3000 and 3500 Sherman units of B_2 per g. The author is of opinion that the water-soluble, yellow-green fluorescent pigment of whey is either the vitamin itself, or an integral part of it. Analyses of two separate batches gave: (i) C, 44·77; H, 6·87; N, 16·02; and (ii) C, 46·27; H, 7·46; N, 16·21; sulphur and phosphorus were absent.

S. G. S.

Investigation of the Growth-promoting Properties of Vitamin B_2 (*G*) Concentrates. L. E. Booher, H. M. Blodgett and J. W. Page. (*J. Biol. Chem.*, 1934, **107**, 599–605.)—A close correlation between the requirements for vitamin B_2 and the body-weights of growing animals has been established. This is responsible for certain ambiguities of interpretation of flattened growth-curves. When liberal quantities of highly active concentrates of vitamin B_1 and B_2 were fed to rats, growth was inappreciable, but an 80 per cent. alcoholic extract of whole wheat contained a factor (or factors) which supplemented these vitamins and promoted continuous growth. This new material in the wheat extract was relatively heat-stable, as compared with vitamin B_1, and was not dissolved by ether from the dried alcohol-extractives. S. G. S.

Toxicological

Extraction of Barbituric Acid Derivatives from Viscera by means of Acetone. P. Chéramy and R. Lobo. (*J. Pharm. Chim.*, 1934, **20**, 400–403.)—The use of acetone for extraction in the Stas–Otto–Ogier method has been found to simplify and accelerate the procedure. It causes the coagulation of protein and is a good solvent for barbiturates, but does not dissolve substances, such as lecithin, which form emulsions with other volatile solvents. The finely-divided viscera are placed in a flask, and a solution of tartaric acid (20 per cent.) is added until the reaction is definitely acid, when 2½ volumes of rectified acetone are added in small portions and with shaking. The flask, to which is affixed a reflux condenser, is heated for two hours on the water-bath. After cooling, the contents of the flask are collected on a filter which has been moistened with acetone. The flask is rinsed out twice with small portions of acetone, and finally the residue on the filter is pressed. The acetone solution is then distilled under reduced pressure, by the method described by Ogier and Kohn-Abrest (*Traité de Toxicologie*, Vol. II, p. 88), which prevents the formation of froth. The concentration is taken to the point at which the residue has the consistence of a soft extract, after which, it is re-dissolved, in the same flask, in 200 ml. of pure acetone. Solution is assisted by warming and by shaking with glass beads; a turbid liquid is always obtained. The contents of the flask are then cooled as rapidly as possible (preferably on ice) and collected on a small filter moistened with acetone, the flask being rinsed out with the same solvent. The filtrate is distilled at normal pressure, as there is no fear of frothing and the temperature is sufficiently low for no alteration of barbiturates to take place. The syrupy residue is then dissolved in 200 ml. of water, 20 to 30 g. of ammonium sulphate are added, and the solution is warmed to drive off the last traces of acetone. It is then rapidly cooled and collected on a moistened filter, the filter and flask being washed with a small amount of 10 per cent. ammonium sulphate solution. The filtrate, which must be definitely acid, is shaken three times with half its volume of ether. The combined ethereal extracts are washed with a small amount of water and, after being dried with anhydrous sodium sulphate, are distilled on the water-bath. The residue, which corresponds with the "acid ether extract" of the Stas–Otto method, contains the barbiturates. With organs containing large amounts of lipins, the residue from the first acetone extraction is dissolved in 200 ml. of warm water and 20 g. of ammonium sulphate are added. This solution is then cooled and filtered. The filtrate and wash-liquids are distilled under reduced pressure, and the residue is dissolved in 200 ml. of anhydrous acetone and treated as before (second acetone extraction). If the final product of the extraction is coloured, it is re-dissolved in water, the solution is treated with a little decolorising charcoal (Norit), then warmed and filtered, and the residue is washed with warm water. The aqueous solution is then acidified with hydrochloric acid and extracted with ether. S. G. S.

Identification of Barbiturates in Urine. M. Fauchet. (*J. Pharm. Chim.*, **1934**, **20**, 403–406.)—The urine is treated with one-tenth of its volume of neutral lead acetate solution and filtered, the filtrate is acidified and extracted with half its volume of ether or, preferably, ethyl acetate, and the ethereal extracts are mixed and washed twice with half their volume of water. The barbiturates, now in the ethereal solution, can be quantitatively extracted by means of 4 per cent. ammonia solution; by this method they can be obtained in an alkaline solution, which can then be concentrated to a small volume on the water-bath. Several ml. of the liquid under examination are treated in a centrifuge tube with 2 ml. of a copper-pyridine reagent. (This is prepared by adding pyridine in slight excess to a 3 per cent. solution of copper sulphate until the precipitated hydroxide re-dissolves and then centrifuging the liquid to obtain a clear product.) A characteristic violet precipitate is formed and can be separated from the mixed solutions by centrifuging (the supernatant liquid should still be blue). The precipitate is washed (not more than twice) with a little water, collected, and dried on a small filter-paper. This is sufficient to establish the fact that a barbiturate has been ingested, but confirmation may be obtained by submitting the violet precipitate (previously dried on the water-bath) to micro-sublimation in a tube, 3 to 4 cm. long and 0·005 cm. diameter, which is heated in a Bunsen flame. The copper-pyridine-barbiturate decomposes, and the barbiturate sublimes. The sublimate can then be compared with known substances. Alternatively, the violet precipitate may be treated with a drop of 10 per cent. sulphuric acid on a microscope slide, and the crystals so formed compared with those obtained under similar conditions from known substances. Allyl derivatives of barbituric acid (*e.g.* dial) are not usually found in the urine, as they are decomposed in the body;

the newer preparations, having a substituted methyl group attached to one of the nitrogen atoms (*e.g.* prominal and evipan), which are used in the form of a sodium salt, do not give the violet precipitate with the copper-pyridine reagent.

S. G. S.

Rapid Method for the Identification of Barbiturates in Blood. P. Chéramy and R. Lobo. (*J. Pharm. Chim.*, 1934, **20**, 461–462.)—Persons suffering from barbiturate poisoning bleed easily, and the blood samples may be examined rapidly by a modification of the acetone method previously described (*supra*). Fifty ml. of blood are taken, and as this has usually coagulated, the serum is poured into a flask, and the clot is triturated in a mortar with its own volume of washed sand. This is then stirred with small portions of pure acetone, which is decanted into the flask containing the serum. The flask must be shaken so that a flocculent precipitate of the proteins may be formed. Finally, the contents of the mortar are transferred to the flask by means of acetone with the aid of a spatula, the total volume of acetone being at least four times that of the blood taken. A solution of tartaric acid (20 per cent.) is then added until the reaction is definitely acid, when the flask is attached to a reflux condenser and boiled for 20 to 30 minutes on the water-bath. The flask is then cooled rapidly in ice-water, and the contents are collected on a filter which has been wetted with acetone, and the filter is washed with a little acetone and carefully pressed. The acetone solution is distilled in a fairly large flask (to avoid frothing) on a water-bath at normal pressure. The contents of the flask are then transferred to a dish, and the rest of the acetone is evaporated in the open air. The aqueous residue is treated in the dish with a solution of ammonium sulphate such that the final volume is 100 ml. and contains 15 g. of ammonium sulphate. Heating on the water-bath is continued for several minutes, after which the dish is cooled in ice-water and its contents are collected on a filter which has been moistened with ammonium sulphate solution, and washed with a little ammonium sulphate solution. The filtrate and washings, which must be acid, are extracted three times with half their volume of ether. The mixed ethereal solution is washed with a little water, dried with anhydrous sodium sulphate, and evaporated to dryness in a tared crystallising dish. The presence of a crystalline residue indicates a barbiturate, which may be identified by the usual reactions. S. G. S.

Agricultural

Determination of Magnesium in Extracts of Soil in Hydrochloric Acid by the Oxine Method. H. J. Hardon and W. Wirjodihardjo. (*Chem. Weekblad*, 1934, **31**, 662.)—Ten ml. of an extract of 55 g. of soil in 125 ml. of cold 25 per cent. hydrochloric acid are heated with 1 ml. of concentrated nitric acid, and when red fumes are no longer evolved, the solution is cooled and 100 ml. of 20 per cent. sodium tartrate solution, 100 ml. of *N* sodium hydroxide solution, and then 20 ml. (a drop at a time) of a 2 per cent. solution of oxine in alcohol are added; the *p*H value should be about 11·5 (*cf.* Fleck and Ward, ANALYST, 1933, **58**, 388). The solution is heated at 70° C. and stirred well to cause flocculation of the precipitate, which is removed by filtration and washed with a 2 per cent. alkaline solution of sodium tartrate until the filtrate is colourless. It is then dissolved in 10 per cent. hydrochloric acid, 10 drops of concentrated sulphuric acid are added, and the solution is evaporated, the residue being re-dissolved in 25 per cent. hydrochloric acid. Manganese is precipitated by adding 10 ml. of 10 per cent. ammonium chloride solution, bromine water and ammonia and warming; if the manganese-content is high, re-precipitation is desirable. Calcium is next precipitated with ammonium oxalate and ammonia, and, after 1 hour on the water-bath, the liquid is boiled with 10 ml. of 25 per cent. ammonia, and excess of a 2 per cent. solution of oxine in alcohol is added. After 30 minutes on the water-bath the precipitate is filtered off, washed with 2·5 per cent. ammonia, and dissolved in 10 ml. of warm 10 per cent. hydrochloric acid, and the solution is titrated with *N*/10 potassium bromate solution in the presence of 5 ml. of 10 per cent. potassium bromide solution, with methyl red as indicator. The extreme errors for extracts of soils containing 5·55 to 24·01 mg. of magnesium per 10 ml. and varying quantities of iron, aluminium, manganese and calcium, were — 0·18 to + 0·24 mg. J. G.

Organic

Determination of Copper in Organic Compounds. N. N. Melnikow. (*Z. anal. Chem.*, 1934, **99**, 182–184.)—The compound (0·1 to 0·5 g.) is treated exactly as described for the determination of thallium (ANALYST, 1934, **59**, 843) to the point where the excess of permanganate has been removed. The solution is cooled, diluted to 200 ml., treated with 0·5 g. of potassium iodide and 20 to 25 ml. of 10 per cent. potassium thiocyanate solution, and titrated with 0·02 *N* thiosulphate solution, with or without starch indicator. W. R. S.

Identification of Metanilic and Sulphanilic Acids. R. B. Forster. (*J. Soc. Chem. Ind.*, 1934, **53**, 358T.)—These acids may be identified by converting them, by the Gattermann reaction, into the corresponding chlorobenzenesulphonic acids, acting on these with phosphorus pentachloride to form the chlorobenzenesulphonyl chlorides, and then preparing the chlorobenzenesulphonamides, which are characterised by their melting-points. The properties of various arylamine salts of the two chlorobenzenesulphonic acids are given. It has been shown that naphthylaminemonosulphonic acids may be identified by means of suitable arylamine salts of their acetyl derivatives (Förster and Watson, *ibid.*, 1927, **46**, 224T), but attempts to form similar salts of metanilic and sulphanilic acids failed, owing to the ease with which their acetyl derivatives are hydrolysed. If, however, the amino-group of the acids is replaced by chlorine, the resulting chloro-compounds readily yield arylamine salts, some of which are easily purified and melt sharply. T. H. P.

Inorganic

New Test for Mercury. E. Stathis. (*Z. anal. Chem.*, 1934, **99**, 106–108.)—One ml. of the solution to be tested is treated with 0·5 ml. of 1 per cent. potassium iodide solution, 1 ml. of 20 per cent. potassium hydroxide solution and 5 ml. of 0·01 per cent. gold chloride solution. If mercury is present, a violet colour is immediately produced, owing to the formation of colloidal gold. In the detection of minute amounts of mercury, a blank test is made; this shows a faint reddish tinge after about 5 minutes. W. R. S.

Study of Dotreppe's Method for the Determination of Tungsten. M. L. Holt. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 476.)—The author has studied Dotreppe's method (*Chim. et Ind.*, Special No. 173–8, March, 1931), which involves reduction of tungstate by zinc and hydrochloric acid in an atmosphere of carbon dioxide and subsequent titration with the aid of ferric alum and permanganate, the calculation being based on an apparent reduction of WO_3 to W_4O_7. He has found that the reduction was incomplete and variable, and that consistent results could not be obtained, and therefore concludes that the method is unsatisfactory.

S. G. C.

Volumetric Determination of Nickel and Cobalt. J. T. Dobbins and J. P. Sanders. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 459–460.)—The solution (150 ml.), containing 0·05 to 0·1 g. of cobalt or nickel, is rendered just acid to litmus with nitric acid, and 3 ml. of pyridine and an excess of standard ammonium thiocyanate solution ($N/10$) are added, with the result that the metals are precipitated in a filterable form as the complex pyridine thiocyanates. The liquid is diluted to 250 ml. and filtered. A 50-ml. portion of the filtrate is diluted to 100 ml., 1 ml. of concentrated nitric acid is added, and an excess of standard silver nitrate solution ($N/10$) is added to precipitate the ammonium thiocyanate in solution. The excess of silver nitrate is titrated with standard ammonium thiocyanate, ferric alum being used as indicator. The calculation of the result is based on the reaction of 1 atom of the metal with 2 molecules of thiocyanate to form an insoluble compound of the general formula $MPy_4(SCN)_2$. The results of test-titrations carried out with solutions of cobalt and nickel salts were in close agreement with those obtained by the electrolytic method for cobalt and the dimethylglyoxime method for nickel. When cobalt and nickel are present together, the total quantity may be determined as outlined above, and, if the nickel is determined separately by the dimethylglyoxime method, the cobalt may be obtained by difference. S. G. C.

Use of *Cyclo*hexanol in the Colorimetric Determination of Molybdenum. L. C. Hurd and F. Reynolds. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 477–478.)—*Cyclo*hexanol is claimed to be superior to ether or ether mixtures as solvent for extracting the red molybdenum thiocyanate from aqueous solution, since in *cyclo*hexanol the coloured compound is more stable and more soluble; the lower volatility of *cyclo*hexanol is also regarded as an advantage. In tests carried out on a range of steels and molybdenum alloys, the ether extraction method (*cf.* James, *id.*, 1932, **4**, 89; King, *Ind. Eng. Chem.*, 1923, **15**, 350) gave errors of 0 to 10 per cent., whilst, with the use of *cyclo*hexanol, the maximum error was 5·5 per cent.

S. G. C.

Determination of Tellurium in Tellurium-Lead Alloys. W. J. Brown. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 428–429.)—I. *Tellurium Lead.*—A 12·5-g. sample of the alloy sawings is dissolved in 100 ml. of dilute nitric acid (1 : 4) by heating on a water-bath; 25 ml. of sulphuric acid (1 : 1) are added, the liquid is cooled, diluted to 500 ml. and filtered, and 400 ml. of the filtrate are taken. This is evaporated until fumes of sulphuric acid are given off, and, after cooling, the residue is diluted to 50 ml., 5 g. of tartaric acid are added, and the solution is boiled, cooled, kept for 2 hours and filtered; the residue is washed and discarded. The tellurium, copper, bismuth, etc., in the liquid are precipitated by saturating it with hydrogen sulphide, and the precipitate is ultimately filtered off and washed with hydrogen sulphide water. The precipitate is returned to the precipitating vessel with the minimum quantity of water; a few g. of sodium bicarbonate and 5 ml. of sodium sulphide solution (10 per cent.) are added, and the liquid is warmed for some time. This procedure causes most of the tellurium disulphide in the precipitate to dissolve, but leaves a little entrapped in it. The solution is filtered and the residue is reserved (see below). The filtrate is acidified with sulphuric acid, the tellurium is precipitated with hydrogen sulphide, and the precipitate is filtered off, washed, and returned to the beaker with the minimum quantity of water. The tellurium sulphide is dissolved by adding an equal volume of concentrated hydrochloric acid and 1 g. of potassium chlorate, and heating to boiling; any residue is filtered off and rejected. The solution is evaporated to dryness on a water-bath after the addition of a few ml. of nitric acid. The residue is dissolved in 100 ml. of hydrochloric acid (9 : 1), and a few g. of tartaric acid are added; the solution is heated to boiling, and sulphur dioxide is passed into it for 5 minutes; then 100 ml. of boiling water are added, and the passage of sulphur dioxide is continued for 30 minutes. The liquid is kept for 1 hour in a warm place, sulphur dioxide is again passed for 20 minutes, and the precipitate of elemental tellurium is filtered off on a Gooch crucible, washed with hot water and finally with alcohol, dried at 100° C. for 1 hour, and weighed. "Treat the residue held in reserve (above) with hot hydrochloric acid to which potassium chlorate has been added, and proceed as described above. The final precipitate of tellurium may be filtered separately or combined with the main portion." II. *Antimonial Tellurium Lead* (containing up to 10 per cent. of antimony).—A 10-g. sample of the alloy sawings is dissolved, so far as possible, by heating with 175 ml. of "bearing metal solution" (a mixture of 400 ml. of concentrated hydrochloric acid, 200 ml. of concentrated nitric acid, 40 g. of potassium chloride and 1000 ml. of water). The solution is decanted from the residue and the crystalline mass of lead chloride. A further 175-ml. quantity of the "bearing metal solution" is added to the residue, and the whole is heated until complete solution is secured. Both solutions are cooled and kept overnight; the lead chloride is filtered off, washed with cold dilute hydrochloric acid (1 : 1), and rejected. The combined filtrates are evaporated to dryness on a water-bath. The residue is dissolved in 100 ml. of hydrochloric acid (9 : 1) and heated to boiling; sulphur dioxide is passed into the liquid for 1 hour, 100 ml. of boiling water being added after the first 30 minutes. The liquid is kept in a warm place for 1 hour, and sulphur dioxide is again passed for 20 minutes. The precipitate of tellurium is filtered off on an asbestos filter and washed a few times with dilute hydrochloric acid (1 : 2), and finally with water. The filter and precipitate are heated with a mixture of 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulphuric acid until the precipitate is dissolved, and the liquid is diluted and filtered. The filtrate is evaporated until fumes of sulphuric acid are given off; the residue is diluted to 50 ml., 5 g. of tartaric acid are added, and the solution is heated to boiling. The liquid is cooled and kept for 1 to 2 hours, when any precipitate which has formed is filtered off and discarded. The solution is treated further as in I. In test experiments, 0·01 g. quantities of tellurium were recovered from admixture with 12·5 g. of lead or 10 g. of antimonial lead, 0·005 g. of copper and 0·005 g. of bismuth, the maximum errors being +0·0003 g. and −0·0004 g. S. G. C.

Microchemical

Spot Tests for Organic Compounds. I. F. Feigl. (*Mikrochem.*, 1934, **15**, 1–8.)—*Identification of atomic groupings* $>C{=}S$ and $\geqslant C{-}SH$.—The reaction $2NaN_3+I_2=2NaI+3N_2$ proceeds very slowly, but is catalysed by traces of divalent sulphur compounds such as sulphides and thiocyanates. Organic sulphur compounds containing the groups $>C{=}S$ and $\geqslant C{-}SH$ also catalyse the reaction, but other sulphur compounds, *e.g.* $R{-}S{-}R$, $R{-}S{-}S{-}R$, $R{-}SO_2{-}R$, $R{-}SO_2H$ and $R{-}SO_3H$ and their salts, are without effect. The test is carried out on a watch-glass, a drop of the organic sulphur compound in solution in water or an organic solvent (not carbon disulphide) being mixed with a drop of the iodine and azide reagent, and any evolution of minute bubbles of nitrogen noted. The substance can also be tested in the solid or liquid form after evaporation of the solvent, when even smaller amounts can be detected. The reagent is prepared by dissolving 3 g. of sodium azide in 100 ml. of $N/10$ iodine solution, and will keep for some months. A table of the 25 compounds tested is given, together with the limit of identification and the limit concentration, and the solvent used in each case. The limit of identification ranges from $2{\cdot}5\gamma$ to $0{\cdot}0003\gamma$, and the concentration limit from 1:10,000 to 1:10,000,000. The test is most sensitive for thioacetic acid.

Sulphur dyestuffs.—The behaviour of the sulphur dyestuffs in the iodine and azide test indicates differences in constitution. The following were examined:—(i) Primuline yellow: no reaction; (ii) Katigen brown extra: vigorous development of nitrogen; (iii) Katigen brilliant green: development of nitrogen; (iv) Katigen yellow 66, extra: very vigorous development of nitrogen; (v) Katigen black: S.W., extra: very vigorous development of nitrogen; (vi) Katigen indigo C.L. extra: very vigorous development; (vii) Katigen violet 3K: very vigorous development. As primuline yellow contains only the thio-ether group, a positive reaction was not to be expected. A thread of material dyed with the dyestuff under examination may be used for the test.

III. *Differentiation between animal and vegetable fibres by means of the azide and iodine reaction.*—Animal fibres contain protein, in which the cysteine sulphur gives the reaction with azide and iodine, whilst vegetable fibres do not react. The thread to be tested is placed on a watch-glass and moistened with a drop of water or acetone, and one or two drops of the reagent are added. After a short time the thread (if animal) is covered with minute bubbles. Cotton fibres are coloured violet by the iodine, but the colour of wool fibres remains unchanged. Both bleached and unbleached cotton give the violet colour, but bubbles are not formed in either case. J. W. M.

Spot Tests for Organic Compounds. II. F. Feigl, V. Anger and O. Frehden. (*Mikrochem.*, 1934, **15**, 8–22.)—*Detection of Carboxylic acids and their derivatives* (anhydrides, esters, halogenides).—The so-called hydroxamic acids, *R*–CO(NHOH), react in acid solution with ferric chloride to give a red or violet colour, through the interaction of the acid CO(CNOH)- group and the ferric ion to form an inner complex salt. Hydroxamic acids are easily prepared from the carboxylic acid anhydrides, esters, amides and halogenides by treatment with hydroxylamine and addition of alkali; the reaction is rapid and can be carried out on the micro-scale. Free carboxylic acids must first be converted into the acid chlorides by treatment with thionyl chloride. *Methods.*—(i) *Carboxylic acid anhydrides.*—The anhydride is dissolved in ether, and a drop of the solution is placed in a micro-crucible, together with a drop of the reagent solution (an approximately 0·5 per cent. solution of ferric chloride, acidified with a little concentrated hydrochloric acid, and then saturated with hydroxylamine hydrochloride). The mixture is evaporated to dryness, and a few drops of water are added. In the presence of an anhydride, a violet, lilac or rose colour develops, according to the amount present; the blank test remains colourless. (Alternatively, this reaction may be used as a test for hydroxylamine.) A table is given of eight different acid anhydrides, together with the limit of identification and colour produced in each case. The limit of identification varies between 5γ and 10γ. (ii) *Carboxylic acid esters.*—A drop of the ethereal ester solution is treated in a micro-crucible with a drop of a saturated alcoholic solution of hydroxylamine hydrochloride and a drop of saturated alcoholic alkali, and warmed gently until the reaction begins. A drop of alcoholic hydrochloric acid is added and, finally, a drop of a very dilute aqueous solution of ferric chloride; a brown-red to blue-violet colour indicates the presence of the ester. The blank test shows only the pale yellow colour of the ferric chloride. All esters react, including lactones, and orthocarboxylic esters and thiocarboxylic acid esters give orange or red colours, and in one instance a dark green colour. Formic acid, which gives a red colour under the same conditions, must not be present. A table is given of 50 esters, together with the description of the colour and the limit of identification in each case; this ranges from 1 to 13γ. (iii) *Carboxylic acid chlorides.*—A drop of the ethereal solution of the acid chloride is treated on a spot plate or in a micro-crucible with a sodium hydroxide hydroxylamine solution, acidified with hydrochloric acid, and, finally, a drop of a dilute aqueous solution of ferric chloride is added. A brown-red to violet colour indicates the presence of the acid chloride. (iv) *Carboxylic acids.*—A drop of the solution of the acid is evaporated to dryness, or the test is carried out on a granule of the solid substance, both in a crucible; 10 drops of thionyl chloride are added, and the mixture is evaporated almost to dryness, whereby the acid is converted into chloride. Two drops of a saturated alcoholic solution of hydroxylamine hydrochloride and a few drops of alcoholic alkali to render the mixture alkaline are added, and, after being heated, the mixture is acidified with a few drops of hydrochloric acid, followed by the dilute ferric chloride solution. A table is given showing the colour formed and the limit of identification for the test with 20 different acids. The range of identification limit is from 11γ to 100γ, the test being least sensitive for sodium acetate. (v) *Use of the ester test for* *technical samples.*—The method is used for various tests of purity of oils and fats, such as the detection of fat present as an impurity in medicinal vaseline, or in any mineral oils (which give a negative reaction). The 38 different oils, fats and waxes tested gave a positive reaction, the colours ranging from violet to violet-red and violet-brown or greenish-brown (yellow beeswax, refined lard). J. W. M.

Detection of Coumarin. A. Kofler and J. Geyr. (*Mikrochem.*, 1934, **15**, 67–73.)—For the identification of coumarin in plant material, micro-sublimation alone does not afford sufficiently characteristic crystals to be conclusive, and even the van Zijp (*Pharm. Weekbl.*, 1927, **64**, 841) reaction with mercuric iodide carried out on the sublimate is not always satisfactory, as many other substances give coloured addition compounds with iodine. If, however, the m.p. of the crystalline sublimate is determined on the cover-slip by means of the Kofler and Hilbck micro-melting-point apparatus (*Mikrochem.*, 1931, **9**, 38; Abst., ANALYST, 1932, **57**, 130) with either a thermometer or a thermo-electric couple, identification is certain. There are two modifications of coumarin, the stable form of which is in rhombic hemimorphous crystals, with positive optical character, and with angle $2V=80°$; it melts under the microscope at 67° C. The meta-stable form is monoclinic, has negative optical properties with a small crystal angle, and melts at 64° C. The micro-sublimate of *Herba herniariae*, contrary to recorded statements, was found to be not coumarin, but methyl-umbelliferone. J. W. M.

Microchemistry of Diethyl Bromoacetyl Urea (Adaline). M. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 1261–1264.)—Adaline, $(CH_3CH_2)_2.CBr.CO.NH.CONH_2$, is a colourless and odourless micro-crystalline powder, m.p. 116 to 118° C., with a slightly bitter taste. It sublimes in droplets or in micro-crystals which, when moistened with acetone, form identifiable crystals, and provide a test sensitive to 1 mg. If a suspension of a crystal in a drop of water is mixed with a drop of acetone or of chloral hydrate, and the solvents are removed by evaporation (*cf.* C. Génot, *Chim. et Ind.*, 1925, II, 679), feathery tufts of needles are obtained (sensitiveness 0·5 mg.). When a solution of a crystal in concentrated sulphuric or nitric acid is diluted considerably, needle- and star-shaped complex crystalline forms result, which resemble those obtained from acetone-water (*supra*); rectangles also occur, and the crystals show interference colours with crossed Nicol prisms (sensitiveness 0·1 mg.). The bromine atom in adaline reacts with silver nitrate, and a solution of the resulting silver bromide in ammonia yields characteristic rectangles on evaporation. Similarly, the action of warm platinum sulphate acidified with sulphuric acid produces octahedra of ammonium platinum bromide, and, on addition of a crystal of potassium bisulphate, well-defined octahedra of potassium platinum bromide result (sensitiveness 0·5 mg.). J. G.

Detection of Zinc by Induced Precipitation. P. Krumholz and J. Vazquez Sanchez. (*Mikrochem.*, 1934, **15**, 114–118.)—Cobalt salts give with alkali mercuri-thiocyanates a crystalline precipitate of the blue cobalt salt: $Co[Hg(CNS)_4]$. The precipitation takes place very slowly and incompletely in dilute solutions; if, however, even a trace of the white zinc salt $Zn[Hg(CNS)_4]$ is also precipitated in the solution, the whole of the cobalt is brought down, and the blue colour of the precipitate enables the zinc to be identified. *Detail.*—The neutral or slightly acid (with mineral acid) test solution is mixed with an equal volume (about 1 ml.) of the cobalt solution (containing 0·02 per cent. of cobalt, in $N/2$ hydrochloric acid) and of the reagent solution (made by dissolving 8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 ml. of water and allowing the solution to stand for 3 or 4 days). After 3 minutes the mixture is shaken with 1 or 2 ml. of ether. In the presence of zinc a blue precipitate appears at once on the layer between the two liquids, the depth of colour depending upon the amount of zinc. In the absence of zinc the precipitate is apparent only after 4 or 5 minutes. The sensitivity of the test varies with the acidity; in neutral solution the *detection limit is* 2γ and *concentration limit,* 1 : 500,000; in $N/10$ hydrochloric acid the *detection limit* is 5γ, and *concentration limit,* 1 : 200,000. The test can also be carried out as a "spot" test, when 1 drop of the test solution and 1 drop of the cobalt solution are mixed on a "spot" plate or in a micro-crucible with a drop of the reagent and "scratched" for about 15 seconds with a glass rod. With a rapidity depending on the amount of zinc present, and at all events within 2 minutes, a blue precipitate appears. In the absence of zinc the precipitation is first apparent after 2 to 3 minutes. A blank test should be made. In neutral solution:—*Detection limit,* $0{\cdot}2\gamma$; *concentration limit,* 1 : 250,000; in $N/2$ hydrochloric acid:—*Detection limit,* $0{\cdot}5\gamma$; *concentration limit,* 1 : 100,000. The following table shows the sensitivity of the test in the presence of the limiting proportions of various other substances, 1 ml. of the various solutions being used:

Substance	Detection limit in γ zinc		Proportion limit	
	Neutral	$N/2$ HCl	Neutral	$N/2$ HCl
Ammonium chloride	5	10	1:1000	1:500
Potassium sulphate	5	10	1:2000	1:1000
Aluminium chloride	5	10	1:700	1:700
Chromium nitrate	5	5	1:200	1:100
Manganese sulphate	10	10	1:50	1:50
Ferric chloride	10	10	1:60	1:60
Cadmium chloride	10	10	1:200	1:100
Lead nitrate	10	10	1:500	1:300

When carried out as a "spot" test the following values were obtained:

Substance	Detection limit in γ zinc		Proportion limit	
	Neutral	$N/2$ HCl	Neutral	$N/2$ HCl
Ammonium chloride	2	2	1:250	1:250
Potassium sulphate	0·5	1	1:1000	1:500
Aluminium chloride	0·5	1	1:700	1:350
Chromium nitrate	0·5	0·5	1:100	1:100
Manganese sulphate	2	2	1:100	1:100
Ferric chloride	2	2	1:120	1:120
Cadmium chloride	2	2	1:200	1:200
Lead nitrate	1	2	1:500	1:250

J. W. M.

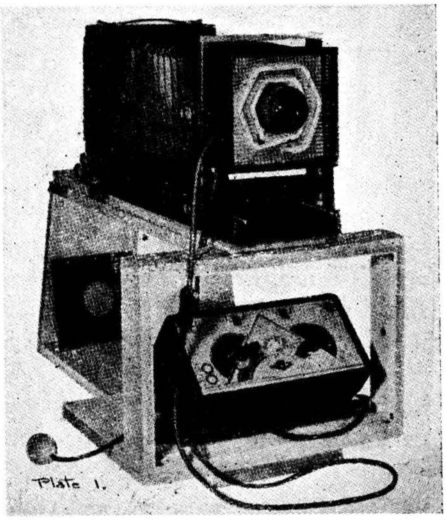
Spot Test for Hydrogen Peroxide. E. Plank. (*Z. anal. Chem.*, 1934, **99**, 105–106.)—Cerous sulphate solution is treated with strong potassium carbonate solution until the white precipitate redissolves. One to two drops of this solution are mixed on a spot-plate with the solution to be tested. Hydrogen peroxide produces a yellow to reddish-brown colour, due to potassium perceric carbonate. The reagent should always be freshly prepared. The test detects 0·001 mg. of hydrogen peroxide. W. R. S.

Physical Methods, Apparatus, Etc.

Spectroscopic Detection of Argon in Argon-Nitrogen Mixtures. J. A. M. Van Liempt and S. H. R. Visser. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 1084–1086.)—In the usual Ruhmkorff method, or with a high-voltage, high-frequency alternating-current discharge (*e.g.* 300 kilocycles per second), the intensity of the nitrogen spectrum renders the argon lines visible only with difficulty; this applies even if the lengthy process of removal of most of the nitrogen by means of lithium or magnesium is first applied. The apparatus described is applicable to gas-filled lamps, which are connected by means of a special joint with a diffusion-pump, so that the gases can be transferred to a discharge-tube fitted with platinum electrodes at a pressure of 2 cm., the effect of the mercury lines being eliminated by interposition of a U-tube cooled in liquid oxygen or nitrogen. In this way it is possible to isolate the rings of the glow-discharge close to the upper electrode, and by observing, in particular, the line 415·9 $m\mu$, the effect of the argon spectrum is enhanced, as compared with that of the nitrogen. The method may be made quantitative. J. G.

Use of Ultra-Violet Light as a Sensitive Method for the Measurement of the Degree of Water-Resistance of Paper. J. Grant. (*J. Soc. Chem. Ind.*, 1934, **53**, 349–350T.)—The author's method for the identification of imitation watermarks (ANALYST, 1934, **59**, 749) is used. The mixture of rhodamine-6G and sugar is sprinkled on a piece of the specimen (about 2 inches square), which is then floated on the surface of distilled water at 21° ±0·5° C., the time being noted with a stop-watch. The float described in the tentative standard method of the Technical Association of the Pulp and Paper Industry of America (*Tech. Assoc. Papers*, 1925, **8**, 91; P. W. Codwise, *id.*, 1932, **15**, 234) is convenient and prevents curling. The dry upper surface of the paper is observed in a dark room in filtered ultra-violet light, and the first sign of penetration is indicated by the almost instantaneous appearance on a dark background of the bright golden fluorescence resulting from the solution of the dye. The time is then again noted. The method overcomes the defects of the numerous other methods suggested (*cf.* F. T. Carson, *Tech. Papers Bur. Standards*, 1926, **20**, 703). The error, judged by the variation in consecutive readings, is less than 5 per cent., as compared with 15 per cent. for the ferric tannate test and 10 per cent. for the American dry-indicator test (*loc. cit.*). This increased accuracy is due to the smaller penetration times (about 60 per cent. of those obtained by the ferric tannate test), and to the extremely sharp end-points. It is advisable to test 10 specimens, *i.e.* 5 places on each side of the paper. J. G.

Ultra-Violet Light Source for Documentary Photography. L. Bendikson (*Library J.*, 15th Sept., 1934.)—A discharge coil or spiral of quartz-tubing (diameter 0·25 in.), sealed at both ends, and containing a mixture of helium, argon and mercury vapour at a very low pressure encircles the lens of the camera two or three times. Behind it is a metal reflector with a chequered surface encased in a square, black-lacquered housing (7 × 7 × 2¼ in.), through which projects a cylinder (diameter 2¼ in.), the front edge of the housing being provided with rims to take filters. Since the lens of the camera protrudes through the cylinder, the object is illuminated uniformly, so that shadows due to wrinkles or folds are minimised. Other advantages claimed are that the apparatus is cheap, and that very little heat is radiated, with the result that there is no danger of injuring the object to be photographed; 70 per cent. of the ultra-radiation has a wave-length between 254 and 257 $m\mu$ (18 per cent. at about 290$m\mu$); only short exposures are required. The illustration shows the camera on its base, with a portable adjustable transformer of the type used in therapeutic work, and in the background, a Corning filter cut to fit the front of the housing. Illustrations are provided of a palimpsest, of ink-eradication, a spurious bank-note and of a message in invisible ink, which was developed 150 years ago, but which has since faded (cf. *ibid.*, 1932, **57**, 784.)



J. G.

Reviews

HANDBUCH DER BIOLOGISCHEN ARBEITSMETHODEN. Edited by Professor EMIL ABDERHALDEN. Abteilung IV, "Angewandte chemische und physikalische Methoden"; Teil 13, "Quantitative Stoffwechseluntersuchungen"; Heft 5; Lieferung 412. Pp. 182, 48 illustrations. Berlin and Vienna: Urban and Schwarzenberg. Price RM. 8.60.

This number of Professor Abderhalden's enormous encyclopaedia comprises four expert contributions on the technique of experiments dealing with the chemical processes of respiration. From the point of view of the analytical chemist, the main items of interest are the determination of gaseous carbon dioxide and oxygen.

The first article, by Dr. F. Dickens (London) and Dr. F. Šimer (Bratislava), describes clearly and systematically the determination, by the phosphate and the bicarbonate methods, of the respiratory quotients in severed portions of living tissue. Both these processes involve interesting small-scale technique with the Warburg manometer—a technique which should have some application to general gas-volumetric methods. The second article, by Professor F. G. Benedict (Boston), is a detailed description of the design and use of the various types of helmet respiration apparatus; considerable space is given to the interesting "Rotameter" type of flow-meter. Dr. E. Simonsen (Frankfurt) and Dr. H. Hebestreit (Dresden) contribute an article of 67 pages on the use of the Simonsen respiration apparatus. The latter part of this article describes some interesting modifications of the Haldane gas-analysis apparatus; a feature of these is that the levelling-marks above the absorption pipettes are made movable, so that by adjustment of these the volume of gas sample taken originally in the measuring burette can be made exactly the same each time, calculation being thus facilitated. The reviewer agrees with the authors' preference for the use of small samples (10 ml.) as being much more convenient to work with than larger samples, and involving little or no loss in accuracy. A feature which might find other applications, *mutatis mutandis,* in routine analysis is the simultaneous manipulation of two instruments, one of which determines carbon dioxide only, and the other, carbon dioxide *plus* oxygen. The abolition of the Haldane compensator, even taking into account the greatly enlarged water jacket (17 litres) and the short time of working, seems rather a retrograde step. Professor T. M. Carpenter (Boston) contributes a very full description of his latest modification of the Haldane apparatus; the chief characteristic of this is a special absorption-vessel for oxygen, in which the pyrogallol solution is mechanically circulated. By this means, the oxygen determination, which is always the limiting time-factor in air analysis, is greatly accelerated. A modification for the determination of methane by combustion in a platinum-filled capillary is also described; a table of results of analyses by two different observers shows a definite personal factor which is, however, so small as to be of negligible importance. Figures of this kind are a valuable guide to analysts and assure confidence in a method. The only criticism to make of this article is that it fails to discuss the much-debated question of the extent of the evolution of carbon monoxide from pyrogallol. It is obvious from the figures given for the analysis of air that, with the apparatus and procedure described, the effect is negligible. In view, however, of the abundant evidence that in some circumstances it can cause serious error in air analyses, the subject ought to have been dealt with in an article of such length, which describes analyses of such high accuracy.

What faults there are in the publication as a whole seem to be due to insufficient editorial planning, rather than to any shortcomings in the contributions, the writers of which have, presumably, given only what they have been asked to give. Space which might have been more usefully filled is wasted by overlapping, as, for example, in the descriptions of (different) modifications of the Haldane apparatus in two of the articles. Some cross-references from one contribution to another would have been useful, and would have given a greater appearance of unity to the book. One cannot but feel that Professor Carpenter might well have been asked to contribute a more directly biological article, instead of a description of an instrument for general analysis which is applicable to certain biological investigations. Moreover, an article given over to a very detailed account of one elaborate instrument, however excellent, is of doubtful value to anyone who is not going to the length of buying an apparatus of exactly that pattern.

In a work of this scale, which in no way aims at brevity, it is allowable, if anywhere, to give space to any tables of factors which may assist calculations. When, however, one sees fifteen and a half pages of tables of corrections of gas volumes to N.T.P. (pp. 567–582), one is inclined to wonder how many people will find this worth while, and would not feel adequately served by a slide rule or by some calculator such as Farmer's nomograph (see ANALYST, **1910**, **35**, 396).

The print and paper are excellent, and the diagrams clear.

H. R. AMBLER

PHYSIKALISCHE METHODEN DER ANALYTISCHEN CHEMIE. Vol. I. SPEKTROSKOPISCHE UND RADIOMETRISCHE ANALYSE. By G. SCHEIBE, H. MARK and R. EHRENBERG. Pp. x+388. Leipzig: Akademische Verlag. **1933.**

This volume is the first of two volumes on physico-chemical methods of analysis which are being compiled under the editorship of Dr. Böttger of Leipzig University. The present volume consists of three sections by eminent contributors. The first on Spectrum Analysis is by Dr. Scheibe, 175 pages; the second, on X-ray Spectrum Analysis, is by Dr. Mark, 148 pages; and the last, by Dr. Ehrenberg, deals with Radiometric Analysis. The treatment of the three subjects is essentially that of a laboratory manual, for especial attention is directed to the various types of apparatus and the technique of the different methods. Moreover, the first two sections contain excellent tables giving the intensities and wave-lengths of emission and X-ray spectral lines, respectively. In the last section, which is based on the work of Hevesy and Paneth and of Ehrenberg, ingenious methods are described of carrying out analytical determinations of widely differing types by the use of various radio-active indicators. Although such an indicator, "Radiothor," is now procurable *in gut emanierenden Zustand* at about 100 RM. per 1 Radium-Milligram-Equivalent, the method is very expensive, and is likely to find only limited application. The book, which is replete with references to the original memoirs, is well-written and produced, and, being authoritative, should appeal to all who are interested in these subjects.

H. T. S. BRITTON

"ANALAR" STANDARDS FOR LABORATORY CHEMICALS. The British Drug Houses, Ltd., and Hopkin and Williams, Ltd. Pp. xvi+296. Price 3s. 6d.

The preparation of fine chemicals in this country has, since 1914, progressed to such an extent that English laboratory chemicals are of as high a standard as those produced in any other country. This progress is reflected in the book recently published conjointly by the two firms who have done much important work in the production of fine chemicals for laboratory use. Each firm has, in the past, published its own book of specifications for analytical reagents, and both have been very useful; the new publication, in which the knowledge and resources of both companies have been pooled, should make an even stronger appeal to chemists than the previous ones. There are in it over 200 specifications, for practically all the reagents that a chemical laboratory is likely to need, and these are not merely statements of the amounts of the various impurities likely to be found in each, but contain short descriptions of the tests used in determining such impurities. The explanatory notes and appendices contain valuable information that should prove very useful to all laboratory workers. No analyst can afford to be without this volume, which will also be of great assistance to industrial laboratories.

S. G. STEVENSON

ANCIENT EGYPTIAN MATERIALS AND INDUSTRIES. Second Edition, Revised. By A. LUCAS, O.B.E., F.I.C. Pp. 447. London: Edward Arnold & Co. 1934. Price 16s.

It is a matter for congratulation that since the publication of the first edition in 1926 (ANALYST, 1927, **52**, 59) the author should have so progressed in his researches as to be able to present, in this new edition, a work altogether more complete and mature. Much of the subject-matter has been re-arranged and amplified; several fresh chapters have been added (necessitating an amplification of the title to include "Industries"), these dealing, *inter alia,* with brewing, faience-making, glass-making, metal-working, mining, pottery-making, quarrying, stone-working and wine-making. The knowledge of materials has been greatly increased by tracking down cross-references in scientific, classical and archaeological literature, and not least by practical studies carried out in the laboratory.

Mr. Lucas, with his long experience in the chemical world and his well-known sympathetic leaning towards Egyptian archaeology, is eminently qualified to produce a text-book of this kind, for a text-book it is, of almost encyclopedic proportions, and one which is destined to become a classic.

The task of compiling such a work has been complicated by the difficulties attending the translation of the names of chemical substances in the ancient records, and, further, by the unscientific descriptions of their finds by many of the early excavators. There is in future little excuse for errors of the second class, for the book abounds with definitions and a healthy scientific dogmatism regarding nomenclature. It forms a striking contribution to Egyptian archaeology.

If it is so received by the archaeologist, the appeal to the scientist cannot fail to be almost equally strong, because for him it is that rare phenomenon, a book which is extraordinarily easy to read and digest, while being at the same time an authoritative reference work dealing with a subject which is not devoid of a certain glamour and of intrinsic scientific interest. The whole is knit together by a short Chronological Introduction and a concluding chapter devoted to a Historical Summary. The technician will appreciate accounts of the early efforts of a primitive people to make pottery, glaze and alloys and to work in wood and metal; the analyst cannot fail to be entertained by some of the more out-of-the-way problems of identification and by the light which is thrown upon the changes undergone by common substances in process of time. A lengthy appendix is devoted entirely to a collection of analytical data.

Of the new matter presented, the first chaper on "Alcoholic Beverages and Sugar" is of outstanding merit. When one considers the slender material available for analysis, and how even this has become transformed with time, it is surely a feat of scholarship to have presented a picture of the industries concerned which is so complete and convincing. Unfortunately, the same cannot be said of the section on "Faience and Glass." Here we find statements which, in being too emphatic, are almost bound to mislead. For example, from statements on p. 106, the implication seems to be that pottery was not glazed in Egypt prior to the Arab conquest (A.D. 640), when lead and salt glazes appear. This is surely not so certain. Glazed pottery, be it remembered, is known in Mesopotamia from as early as the second millennium B.C. Glazed pottery of Persian origin has also been found in Egypt dating from the sixth and fifth centuries, B.C., and from later periods. Examination of some of these specimens suggests that the ancients must have had a way of using their glaze direct on baked clay, so that its contraction on cooling did not tear the surface of the ware. The statement that "vitreous glazes . . . are only satisfactory on highly siliceous material" is essentially correct (with the exception of the glazed steatite group later referred to), but it would seem to leave no room for the vagaries of technique and the variations in the materials which have resulted in the many good examples of ancient glazed pottery that have come down to us.

The book is well printed and, considering the number of footnotes, remarkably free from error. A group of references has been omitted from p. 91, and other minor flaws in the text occur on pp. 135 and 305. One regrets that a work of such obvious merit is not accompanied by maps and by a selection of line blocks from the tomb paintings, illustrating the ancient craftsman at work (good examples of which are on the paper wrapper), but perhaps the author is reserving this for a later re-incarnation.

H. J. PLENDERLEITH

THE BUCHEUM. By Sir ROBERT MOND AND OTHERS. Large 4to. 3 Vols. Egypt Exploration Society, Manchester Square, London. 1934. Price 50s.

These three volumes deal with the excavations carried out from 1927 to 1932 in the burial places of the sacred bulls and cows of Ancient Egypt—the Bucheum and the Baqaria—sites in use from the fourth century B.C. until the end of the third century A.D. The supposed miraculous birth, the ceremonies of installation (attended by the king in person), the processional splendour of the triumphal progresses through the country, the elaborate ritual associated with the mummification and funeral rites after death, and the transport of the sacred bull to the huge sarcophagus in the Bucheum, together form one of the most amazing chapters in the history of animal worship.

The detailed summaries of the discoveries and the discussions of their significance show the extent to which the modern archaeologist relies on the expert to assist him in the study and interpretation of the data collected. The list of contributors includes the names of experts in metallurgy, mineralogy, petrology, textiles, wood, osteology, and ancient musical instruments. In this work the analytical and the metallurgical chemists have played an important part. A few of the more interesting methods and results may be mentioned here.

For cleaning copper and bronze objects, cold 25 per cent. sulphuric acid has proved most useful. Great care must be taken to remove all traces of acid after treatment, and washings are repeated until no reaction is given with B.D.H. Universal Detector, which will show the presence of as little as 1 part in 8 millions. A solution of Rochelle salt and sodium hydroxide proved effective in removing obdurate corrosion. After this treatment, the scratches due to ancient sand-cleaning were clearly visible.

Details are given of analyses which throw much light on the use and composition of alloys and on methods of manufacture. It seems clear that the ancient craftsmen knew that the addition of lead to the copper-tin alloys facilitated casting and subsequent engraving. On wire, the ancient draw-marks are visible, pointing to the method of manufacture by drawing through a rather rough die. Microscopic examination has shown that the metal had been cold worked and annealed many times from the original cast ingot. The lead-content is low (less than 1 per cent.), showing that the Egyptian was aware of the harmful effect of lead in alloys subjected to considerable cold working. The harder-wearing properties associated with a higher tin-content also appear to have been recognised, for the tin-content is kept low in cases where a large amount of hammering was necessary to reduce the thickness during manufacture. Clamps (88 per cent. Cu) used for the attachments of bandages to secure the limbs of the mummified bull, appear to have been drawn in square section or hammered from round wire.

An enema (used in the purification of the intestines—the bull was not eviscerated) consists of a vessel of very leady bronze, furnished with a spout, which was affixed by running molten bronze over the two portions held in a mould. The excess of metal was smoothed off, after cooling. Minute blow-holes in castings were troublesome, as they are occasionally now. They were often made good by casting on metal of similar composition and smoothing off. A more ancient method was to insert a solid plug of bronze and hammer over the ends.

A flute, with four finger holes, had been made by thinning down from a slab casting. The material was then cut to size and bent to shape, and the joint soldered. The analysis of the solder agrees with that of best-quality solder in present-day use.

A mixture of resin and whiting was used as an adhesive for fastening stone and glass inlay in jewellery and other objects. White of egg was employed for cementing gold leaf on plaster.

It is suggested that analyses on a large scale of coins from various mints, and of ores from different mines, might enable the metallurgist to determine at what point the percentages of tin, zinc, iron, etc., may be regarded as intentional, and also, if they prove to be impurities, to decide whence the ore was obtained.

These volumes, like all the publications of the Egyptian Exploration Society, are a model of what the records of excavation should be. The plates, of which Volume III is entirely composed, are excellent.

R. W. SLOLEY

DUST. By S. C. BLACKTIN, M.Sc., Ph.D., A.I.C. Pp. xii+296, with four illustrations. London: Chapman & Hall, Ltd. 1934. Price 18s. net.

This volume comprises a co-ordinated summary of the widely-scattered European and American literature on dusts, and appears to be the first of its kind to deal with this very extensive subject. That such a compilation was needed is indicated by reference to two well-known and comprehensive scientific dictionaries, in neither of which is a general article on dust to be found. The contents of this work include the production of dusts and smokes in nature, everyday life and industry, their distribution and characteristics, physical, physiological and pathological effects, enumeration, elimination, and methods employed in their scientific investigation. It is evident that the author has shown extreme assiduity in the production of his book, for the list of references contains considerably over 500 items, ranging from Homer's "Iliad" to articles in *Nature,* dated June, 1933. The text, however, is far more than a collection of extracts from the works mentioned, for it is a more or less continuous narrative including erudite criticisms and interpositions by the author, with in some degree the overlapping inevitable in a work of this description.

Dr. Blacktin has coined the name "Staubosphere" for the dust-content of the atmosphere, although the term would have been more appropriate to an atmosphere charged with dust. From the text it is evident that he is an enthusiast on his subject, even tending to convey to the reader's mind an idea that the one thing of importance in human life in its many phases is dust. This is by no means unnatural, and allowance will readily be made for it, but at times the author's concentration has resulted in a disrespect for correct grammar, spelling, and the lucid and simple style so essential in a scientific text-book, while the continuity of the narrative is occasionally broken by excessive punctuation and by the introduction of abrupt (and in one case) verbless sentences.

From the text we learn that it is only within recent years that attention has been directed to the investigation and amelioration of the effects of dust, although Georg Agricola in the sixteenth century recognised the poisonous nature of metal dusts, and in 1721 pathological effects were attributed to the inhalation of stone dust. Incidentally, the contributions to our knowledge of bacteriology made by a pure physicist, John Tyndall, about the year 1870, are recalled.

Perhaps the weakest section of the whole book is that consisting of 16 lines only, and dealing with "Dust and Crime." The names of two popular writers are given, but no mention is made of Gross, Locard, Lucas, and others, or of the paragraphs on dust published occasionally in THE ANALYST. It is, perhaps, invidious to mention that in a volume of this nature one naturally expects to find some reference to the physical, chemical and microscopical identification of dust particles—a subject of increasing importance in scientific investigations—but this has been omitted.

But few errors of fact occur in the text, although on page 232 a redundant acute accent is placed over the final letter in E. H. Kettle; the term "Brewing" is substituted for "Malting" on p. 235, and on p. 202 the fumes of burning sulphur used for fumigating glass-houses are stated to combine, forming *zinc sulphate.* This may possibly refer to the action of the gaseous products upon zinc vessels in the houses, but, if so, this should be stated.

The last 40 pages of the book contain a glossary giving the metric and English linear and cubic equivalents, an extensive table of references mentioned above, and both author- and subject-indexes. These all show a high degree of accuracy, but the subject-index requires extension.

Notwithstanding its faults, this work forms an exhaustive and valuable compilation which will not only serve to show what has been accomplished in the past, but will also indicate to future workers the immense field still open for further investigation. Though future editions should be subjected to more drastic proof-reading before publication, the author is to be congratulated upon the zeal with which he has collected material from a vast number of sources—a task which must have proved onerous indeed.

T. J. WARD

LUMINESZENZ-ANALYSE IM FILTRIERTEN ULTRAVIOLETTEN LICHT. By P. W. DANCKWORTT. Third Edition. Pp. 190. Leipzig: Akademische Verlagsges. m.b.H. Price RM. 8.50.

The name of Professor Danckwortt will be familiar to all readers of THE ANALYST, for his descriptive summary of the analytical applications of ultra-violet rays, which was one of the earliest collective contributions on the subject, appeared in this journal (1927, **52**, 707). Since then the first edition of this book was published (1928), and the author is to be congratulated upon it being so successful that two more editions have been required within the short space of six years. The present volume, which contains 47 pages more than the last edition, follows the arrangement of its predecessors: it begins with a description of the different types of lamps and accessory apparatus, including an outline of the practical technique, and then systematically summarises recorded results under their appropriate headings (pharmacy, botany, technology, etc.). All these sections have been brought up to date, and the references cover a very wide range of journals. In this connection it is of interest to note that Kitching's pioneering work published in this journal (ANALYST, 1922, **47**, 206) has not been overlooked in the bibliography, which contains 890 entries, as compared with 315 in the second edition.

The new matter in Chapter XIII, which deals with photographic methods of recording ultra-violet phenomena, will be found particularly useful, for it gives full practical details of the technique, including that of photomicrography, and is well illustrated by typical examples.

The last chapter (XVI) occupies 33 pages, and is essentially a complete treatise, written by Dr. J. Eisenbrand, on quantitative measurements relating to fluorescence. It deals, *inter alia*, with the distribution of fluorescence intensities over the spectrum, physiological aspects of fluorescence colours, "fluorometry" and fluorescence indicators, the measurement of light absorption with the aid of fluorescence indicators, and the theory of fluorescence phenomena. The whole chapter is a welcome contribution towards the systematisation and elucidation of the physical laws that underly the plethora of isolated empirical results recorded in the literature. This section, alone, makes the book worth acquiring, even by those who possess the previous editions.

EDITOR