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dealing with all branches
of analytical chemistry

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THE ANALYST

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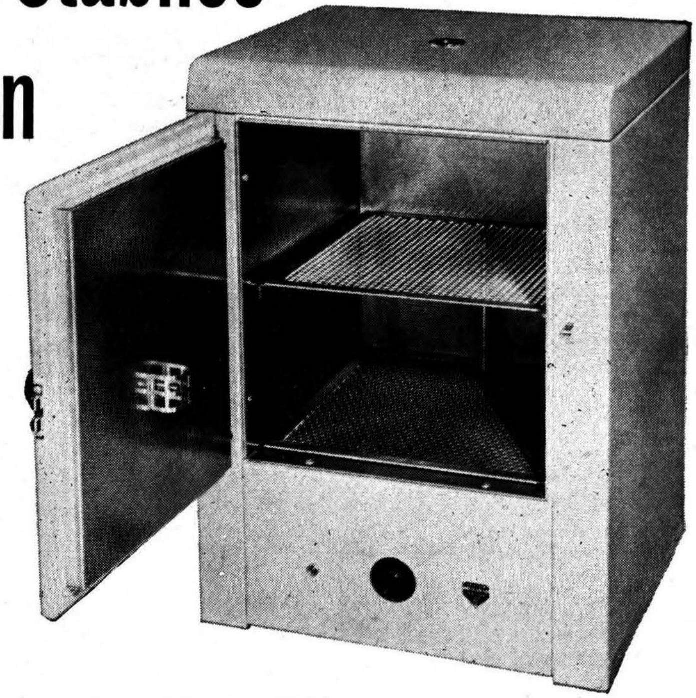

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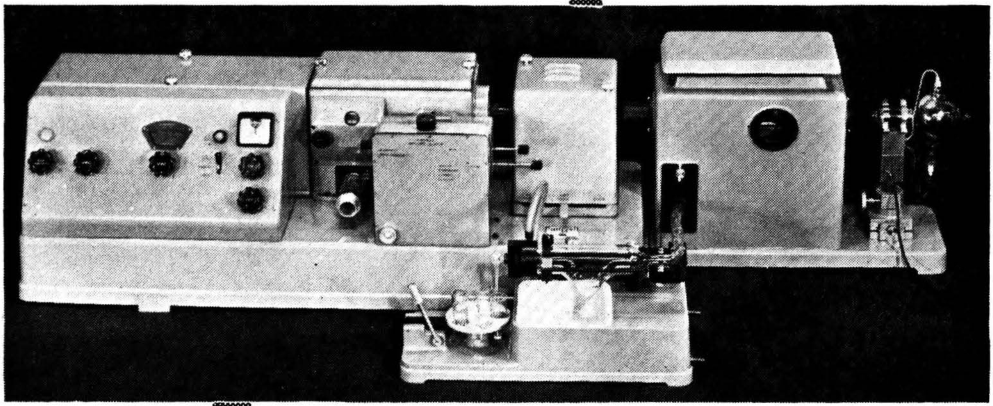

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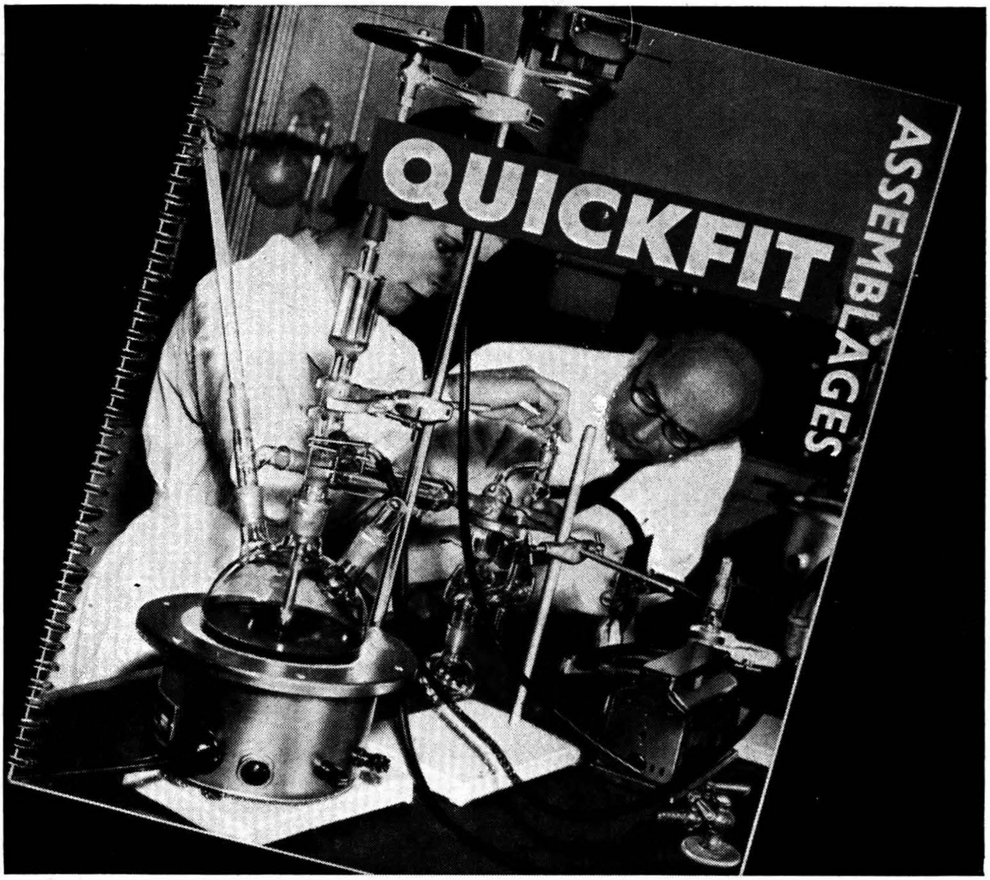

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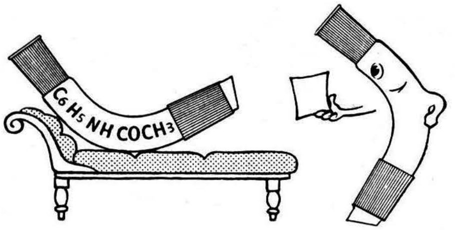

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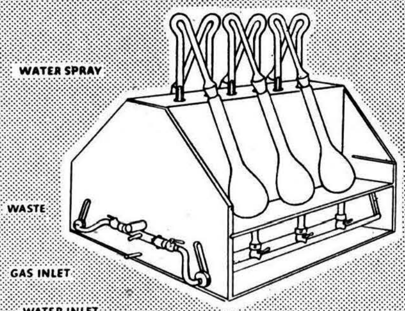

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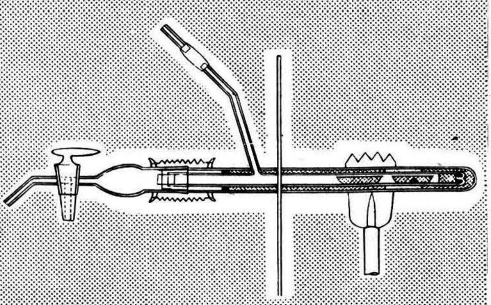

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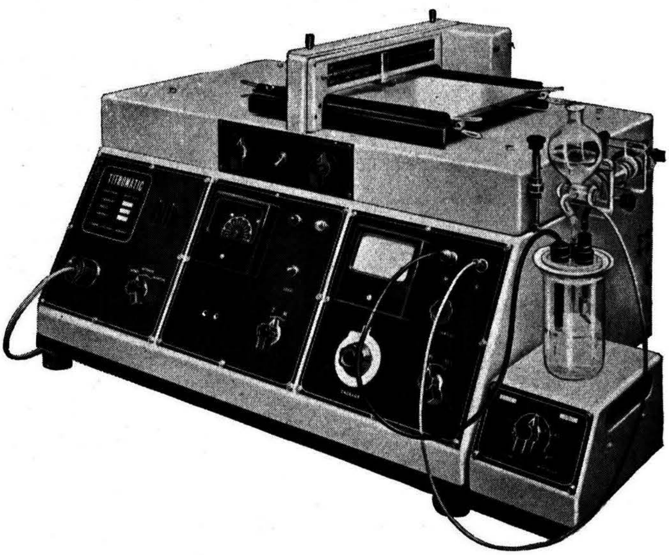

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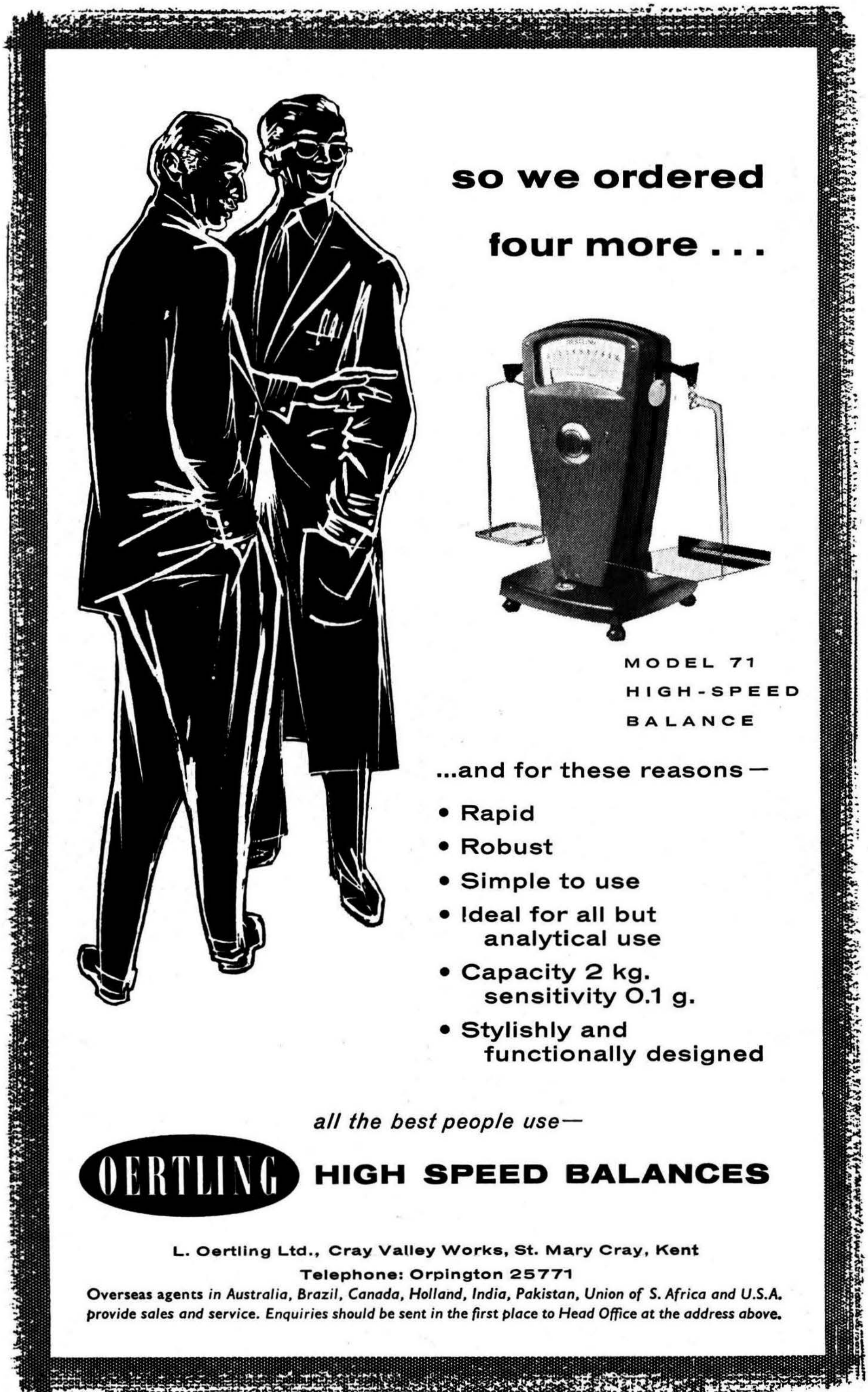

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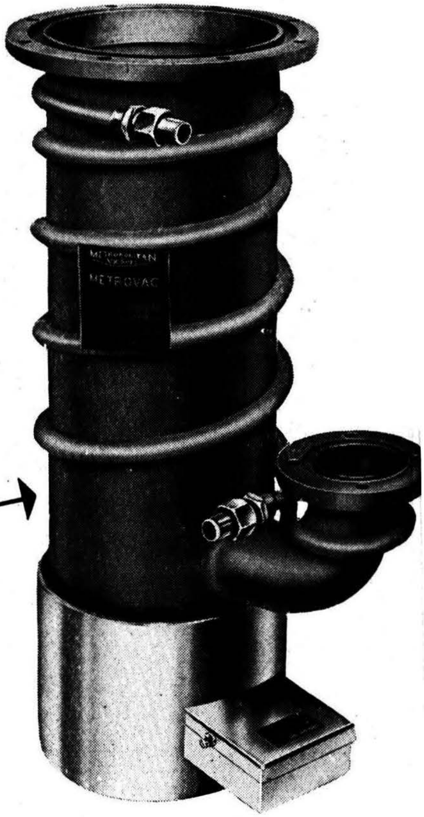

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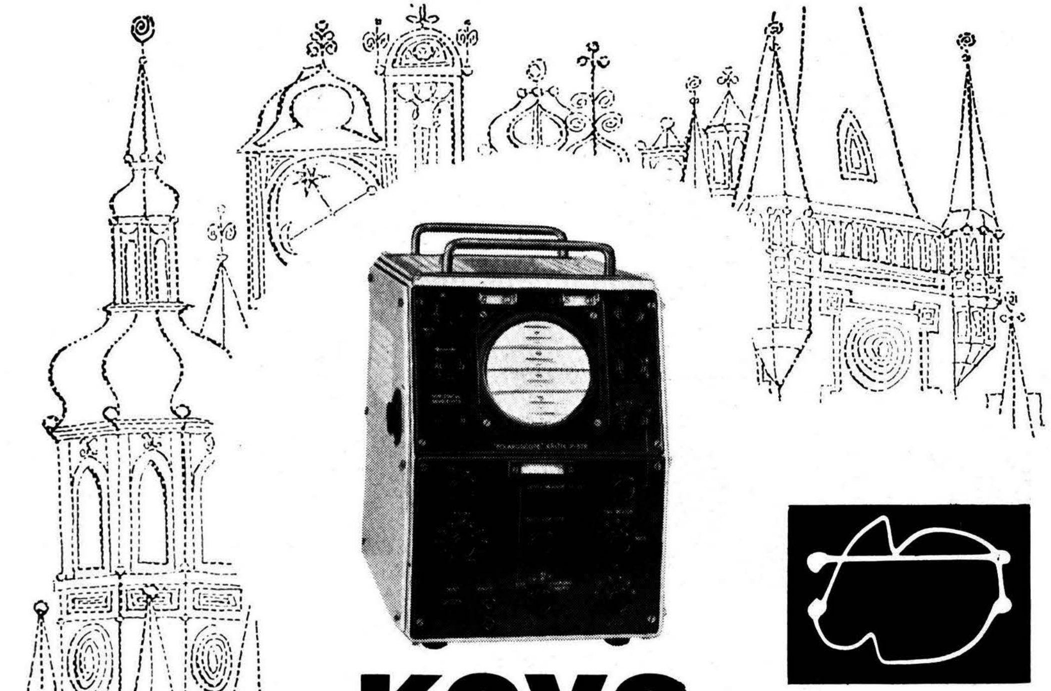

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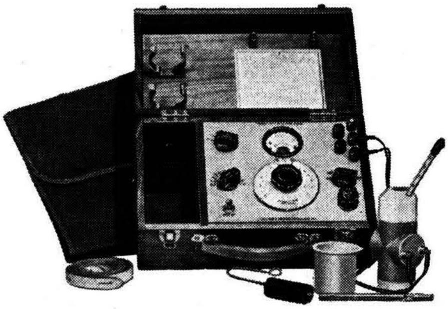

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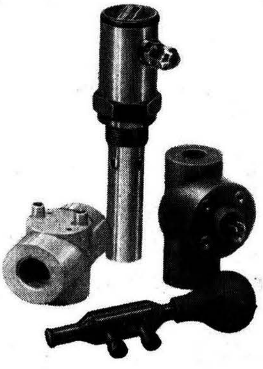

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FEBRUARY, 1960 Vol. 85, No. 1007

THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

JOINT MEETING

A Joint Meeting of the Society (organised by the Physical Methods Group) with the Oils and Fats Group of the Society of Chemical Industry was held at 7 p.m. on Wednesday, February 3rd, 1960, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President of the Society, Mr. R. C. Chirnside, F.R.I.C.

The following paper was presented and discussed: "Spectroscopic Investigations of Fats," by D. Chapman, M.Sc., Ph.D.

NEW MEMBERS

Ordinary Members

David Anthony Baxter, B.Sc. (Nott.); Francis John Carter, A.R.I.C., A.M.C.T.; Lawrence Edmond Gilchrist, B.Sc. (Liv.); Geoffrey Willoughby Goodman, B.Sc. (Lond.); Donald Peter Green, B.Sc. (Lond.); George Andrew Guthrie, M.Sc. (Manc.), A.R.I.C., F.P.S.; Ronald Albert Hendey, A.R.I.C.; Donald Harvey Jackson, B.Sc. (Lond.); Henry M. Koehler, M.S. (Chiago); Gilbert V. Manché, B. Pharm. (Malta); Cecil Stanley McRoe; Edward Jollasse Miles, B.Sc., F.R.I.C., A.M.B.I.M.; Ernest James Newman, B.Sc. (Lond.), A.R.I.C.; Ronald Leslie Noble, B.Sc., Ph.D.; Barry Edward Northam, B.Sc., Ph.D. (Birm.), A.R.I.C.; Richard Francis Phipers, B.Sc., Ph.D. (Liv.); David Islwyn Rees, M.Sc. (Wales); Richard Michael Rowley, B.Sc. (N.U.I.); Dennis Franklin Withington, B.Sc. (Birm.), A.R.I.C.

Junior Members

Cyril John Clifford, B.Sc. (Leeds), A.R.I.C.; Raj Kumar Kapur, B.Sc. (Delhi); Reinhard Schmutzler, Diplomchemiker (Wurzburg).

DEATH

We record with regret the death of

Cyril Ernest Gill.

SCOTTISH SECTION

A Joint Meeting of the Section with the Chemical Society, the Glasgow Section of the Society of Chemical Industry and the Glasgow and West of Scotland Section of the Royal Institute of Chemistry was held at 7.15 p.m. on Friday, December 4th, 1959, in the Royal College of Science and Technology, Glasgow. The Chair was taken by the Chairman of the Glasgow and West of Scotland Section of the Royal Institute of Chemistry, Dr. W. A. Caldwell, B.Sc., F.R.I.C.

The following paper was presented and discussed: "Petroleum Refining: A Chemist's View of To-day and To-morrow," by E. le Q. Herbert, B.Sc., F.H.-W.C., M.I.Chem.E., F.Inst.Pet., M.Inst.F., F.R.I.C.

MIDLANDS SECTION

An Ordinary Meeting of the Section was held at 7 p.m. on Thursday, December 17th, 1959, at the Nottingham and District Technical College, Burton Street, Nottingham. The Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P.

A discussion on "Kjeldahl Nitrogen Determinations" was opened by R. A. Savidge, A.R.I.C., and H. C. Wilkinson, M.Sc., F.R.I.C. (see summaries below).

KJELDAHL DETERMINATION OF NITROGEN

Mr. R. A. Savidge gave a short review of the development of the Kjeldahl procedure and the various modifications made by different workers. Of the three catalysts in common use, mercury was superior to copper, whereas selenium had been shown by many workers to cause loss of nitrogen.

With a view to stimulating discussion, the speaker criticised the standard procedure of the British Pharmacopoeia and the B.P. Codex.

The method described by G. Middleton and R. E. Stuckey (*J. Pharm. Pharmacol.*, 1951, **3**, 829) for calculating the acid consumption of different compounds was illustrated for carbon-rich compounds, but could not be applied to nitrogen-rich compounds, such as melamine and guanidine. The speaker particularly stressed the importance of maintaining the ratio of the volume of sulphuric acid to the weight of potassium sulphate at approximately 0·9.

He recommended W. E. Dickinson's method (*Anal. Chem.*, 1958, **30**, 992) for nitro-compounds and refractory nitrogen compounds. Dickinson's observation that zinc or thiosulphate could only be relied upon for the quantitative reduction of nitrosalicylic acid led the speaker to conclude that the Jodlbauer method (*Chem. Zent.*, 1886, **57**, 433) was contra-indicated for nitro-compounds.

Three methods were therefore recommended as most suitable for the macro-scale assay of different classes of compounds—

(*a*) the simple Kjeldahl for non-refractory materials, together with those compounds that did not char and required the addition of dextrose (*e.g.*, nicotinic acid);

(*b*) Dickinson's method for nitro compounds and refractory nitrogen compounds; and

(*c*) Jodlbauer's method to include nitrate nitrogen.

The speaker mentioned the thiosalicylic acid method of P. McCutchan and W. F. Roth (*Anal. Chem.*, 1952, **24**, 369). Dickinson's observation might account for the low results they quoted, found also by the speaker when he used this method, for pure specimens.

In conclusion, the speaker showed a table of results by different methods on several compounds.

THE DETERMINATION OF NITROGEN IN COAL AND COKE BY THE KJELDAHL METHOD

Mr. H. C. Wilkinson described the development of the semi-micro Kjeldahl method for the determination of nitrogen in coal and coke during the last twenty years. Beginning with the work of A. E. Beet and R. Belcher (*Fuel*, 1938, **17**, 53), the speaker showed how the factors affecting the estimation on the semi-micro scale were studied by various workers, and how the present British Standard methods (B.S. 1016, Part 7: 1959) for these determinations were arrived at from these contributions.

He next discussed the occurrence of nitrogen in coal and coke, making reference to the difficulties associated with the breakdown of the cyclic nitrogen compounds, which themselves were protected by surrounding carbon of various degrees of refractoriness. The necessity for a powerful catalyst to bring about this decomposition was emphasised, and, it was for this reason that a selenium catalyst was employed, due recognition being made of the fact that prolonged boiling of the digest in the presence of selenium could cause loss of ammonia.

The latter factor was unimportant when the estimation was being carried out on coal, the period of boiling being only a few minutes, but special precautions were necessary with coke, for which prolonged boiling was necessary.

It was shown how a catalyst that did not contain selenium had proved effective for use with coke, which was reduced to a finely divided state (passing 240 B.S. mesh) before treatment (H. C. Wilkinson, *Fuel*, **1958**, **37**, **116**), so reducing the effect of the surrounding carbon and rendering the nitrogenous groupings more accessible to attack. The digestion period for cokes was normally between 1½ and 3 hours.

Comparative values for nitrogen determinations on a series of coals and cokes by the Dumas - oxygen flask method and various modifications of the semi-micro Kjeldahl method were presented, and it was shown that satisfactory agreement existed between the former method and the Kjeldahl method finally developed.

BIOLOGICAL METHODS GROUP

THE fifteenth Annual General Meeting of the Group was held at 7 p.m. on Wednesday, December 9th, 1959, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Dr. J. I. M. Jones, F.R.I.C. The following Officers and Committee Members were elected for the forthcoming year:—*Chairman*—Dr. J. I. M. Jones. *Vice-Chairman*—Mr. J. S. Simpson. *Hon. Secretary and Treasurer*—Mr. K. L. Smith, Standards Department, Boots Pure Drug Co. Ltd., Nottingham. *Members of Committee*—Messrs. P. A. Andrews, S. K. Kon, J. W. Lightbown, R. F. Milton, Miss J. Stephens and Mr. R. E. Weston. Mr. W. A. Broom was appointed Hon. Recorder and Messrs. D. M. Freeland and J. H. Hamence were re-appointed Hon. Auditors.

The Annual General Meeting was followed by an ordinary meeting of the Group, at which the following papers were presensed and discussed: "Biological Methods in Forensic Toxicology," by A. S. Curry, M.A., Ph.D. (read by Dr. I. Holden); "Some Experiments on the Determination of Alcohol in Biological Fluids by the Alcohol Dehydrogenase Method," by M. F. Haisman; "Enzymes and Antibodies in Forensic Science," by S. S. Kind, B.Sc.

Obituary

CLARENCE ARTHUR SEYLER

BY the death of CLARENCE ARTHUR SEYLER on July 24th, 1959, in his ninety-third year, this Society loses yet another name from the now very small list of those whose membership dates back to the last century.

Seyler was born in London on December 5th, 1866. He was the eldest son of the late Clarence H. Seyler and a brother of Miss Athene Seyler, C.B.E., the celebrated actress. He was educated at Priory House School, Clapton, the City and Guilds Technical College, Finsbury, and University College, London. After graduating as B.Sc., he gained practical experience at the London Hospital under Dr. Charles Meynott Tidy, who was Professor of Chemistry and of Public Health at the Hospital, and also Medical Officer of Health and Public Analyst for Islington. Later he became assistant to Sir William Crookes, an experience which greatly extended the range of his own interest and knowledge in scientific matters.

In 1892, Clarence Seyler left London to become chief assistant to Dr. William Morgan, who had in Swansea one of the largest and best-equipped commercial laboratories in the country from which he conducted an extensive analytical, assaying and consulting practice. On the death of Dr. Morgan in 1895, Seyler succeeded to his practice and his appointments as Public Analyst and Agricultural Analyst for the County Borough of Swansea and the Counties of Carmarthen, Glamorgan and Pembroke. It was in this year that he was elected a member of the Society of Public Analysts—now the Society for Analytical Chemistry. During his earlier years he regularly attended the monthly meetings of the Society in London, and the many references in *The Analyst* to his contributions in the discussions of papers presented to the Society up to the year 1910 testify to his wide interests and experience. He was a member of Council of the Society during various periods ranging from 1901 to 1929.

It is perhaps not surprising, in view of his experience with Dr. Tidy (whose name will always be associated with the "oxygen absorbed" test for waters) that Seyler's early original work was concerned with some fundamental water problems. In 1894, he published in *Chemical News* the results of a critical examination of Trillich's method for determining free carbon dioxide in water using solutions of sodium hydroxide or carbonate with phenolphthalein as indicator, and three years later he read before our Society a classical paper on "The Estimation of Carbon Dioxide in Natural Waters" (*Analyst*, 1897, **22**, 312). In 1908 he contributed a paper on "The Solvent Action of Carbonic Acid upon the Carbonates of Heavy Metals" (*Analyst*, 1908, **33**, 454), and between 1908 and 1917, in collaboration with Mr. P. V. Lloyd, he published in the *Journal of the Society of Chemical Industry* a series of papers on the equilibrium between carbonic acid and the carbonates of calcium, magnesium and lithium. Following a study of the evolution method for determining sulphur in pig-iron, Seyler contributed a paper (*Analyst*, 1903, **28**, 97) in which he recorded the results of experiments he had made to ascertain the conditions required to ensure accurate results.

Having regard to the situation of Swansea in relation to the South Wales coalfield, not unnaturally Seyler soon became interested in the application of science to coal. He used to say to his friends, "Nature put these things down and it is up to us to find out why, and the order of formation." Gradually Nature's play unfolded itself to Seyler's acute mind, and in 1900 and 1901 he read his first papers on the "Chemical Classification of Coal" before the South Wales Institute of Engineers. This classification was based primarily on the carbon and hydrogen contents of the pure coal substance. In 1921 he was invited to join the Analytical Committee of the Fuel Research Board.

In 1923, by a fortunate coincidence, he had to examine simultaneously a broken iron shackle-pin and a particularly dull piece of anthracite, and this led him to apply the metallurgical method of polishing and etching to the microscopical examination of coal—a technique that proved highly successful in his hands. From this time onwards, encouraged by the Department of Scientific and Industrial Research, Seyler devoted much of his time to studying problems of coal petrology, and he published many important original papers on this subject, too numerous to list, but they include contributions to *Nature*, *Philosophical Transactions of the Royal Society*, the *Journal of the Institute of Fuel*, *Fuel in Science and Practice*, the *Proceedings of the South Wales Institute of Engineers* and the *Journal of the Society of Chemical Industry*, while some of his work is recorded in publications of the D.S.I.R.

In 1938, the University of Wales conferred on him the degree of D.Sc. (honoris causa), and three years later he was awarded the Melchett Medal of the Institute of Fuel for his work on the reflectivity of various micro-petrological constituents of coal, but of all the honours bestowed on him, the one that he treasured most was the Gold Medal awarded to him in 1931 by the South Wales Institute of Engineers and the bar that was added six years later for his papers to the Institute on "Petrology and the Classification of Coal," in which he pointed out the inter-relationship that existed between his work on the chemical composition of coal and his more recent studies on the micro-structure of coal.

The responsibilities for nearly fifty years of a busy practice combined with public appointments and the satisfaction derived from having made substantial contributions to scientific knowledge would suffice most men of 76 years, but not Clarence A. Seyler. In December, 1942, he resigned his official appointments and closed his laboratory in order to become general consultant to the British Coal Utilisation Research Association and head of the Department of Coal Systematics and Petrology at Leatherhead, where he continued his researches for another fifteen years, retiring from active work in 1957.

By his pioneering work on the chemical composition and micro-structure of coal, he gained a world-wide reputation among fuel technologists. Seyler's "Classification of Coal" is known and accepted by all who look upon coal as a material of scientific interest. In coal he could see many of the wonders and beauties of past ages, and not merely a substance from which energy can be extracted or profit acquired.

Seyler was a Fellow of the Royal Institute of Chemistry and he served on its Council during the years 1912–15 and 1924–27. He was also a Fellow of the Geological Society of London, a founder-member and Fellow of the Institute of Fuel and a Member of the Society of Chemical Industry.

It is an indication of the esteem in which he was held, both at home and abroad, that on his ninetieth birthday a plaque, carved in coal, was presented to him by Continental and British coal scientists.

But Seyler's interest was not confined to his professional work, for he was active also in humanistic studies. He was a member of the University Board of Celtic Studies, and from 1926 to 1958 a member of the Council of the National Museum of Wales. Whatever subject attracted him, whether scientific or cultural, he always applied himself to it with wholehearted enthusiasm. He was keenly interested in archaeology and he was an authority on place-names. He could speak Anglo-Saxon, and he was well-known for his work on the history of the early charters of Swansea and Gower. After he moved to Leatherhead he became a member of the Surrey Archaeological Society.

Seyler always took a great interest in photography and the theatre. He was one of the first in South Wales to own a motor-car and to take up colour photography. He had a kind and generous disposition, while his fund of knowledge, breadth of interests and his artistic temperament made him a most interesting and delightful companion.

When he retired he went to live at Abergavenny, but later he moved to Ferndown (Dorset), and he died peacefully in a nursing home at Bournemouth after an illness lasting only three days. He married Miss Ellen Richards in 1895 and he is survived by his widow and his two daughters. He was a distinguished member of our Society, a great scientist and a fine gentleman.

STANLEY DIXON

The Analytical Chemistry of Zirconium

A Review*

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FOR many years a requirement has existed for the determination of zirconium in materials such as minerals, rocks and steels. The recent availability of zirconium metal in a high state of purity has resulted in further requests for determinations of zirconium, especially from metallurgists using zirconium metal in studies on new alloy systems. In consequence, many investigations have been carried out to improve methods for determining zirconium. Since 1950, more than 140 papers have been published—42 dealing with gravimetric methods, 28 with volumetric methods, 40 with absorptiometric methods and the remainder with various other methods. Although a specialised review[1] was published in 1957, the last general review[2] of this subject was made over 7 years ago, and a re-assessment is therefore opportune. This review is presented to assist analytical chemists in making the correct choice from the available methods for solving analytical problems connected with the determination of zirconium.

GENERAL CHEMISTRY

Before describing the various analytical techniques for determining zirconium, some general data about the behaviour of this element in aqueous solutions are relevant. The normal valency of zirconium is 4, although valencies of 5, 6, 7 and 8 can be realised by co-ordination; valencies of 2 and 3 are known, but only in exceptional circumstances. Although normally quadrivalent, zirconium never exists as the Zr^{4+} ion, but always in combination with some other element, usually oxygen or fluorine, for which it has great affinity. The most stable entity is the zirconyl ion, ZrO^{2+}, which can undergo normal ionic reactions. In sulphate solutions there is evidence that zirconium is present mainly as an ionic complex containing one or more zirconium atoms bound by oxygen linkages. In faintly acid solutions hydrolysis of the zirconium can give rise to some difficulty. However, the degree of complex formation or hydrolysis depends on both time and temperature, so that a freshly prepared solution of zirconium might give different reactions from a solution that has been either set aside for some time or heated. This phenomenon must always be borne in mind, especially in the preparation of solutions for analysis. For more comprehensive information about the chemistry of zirconium, Blumenthal's[3] book should be consulted.

Hafnium invariably accompanies zirconium in its minerals, the average atomic ratio of zirconium to hafnium being about 100 to 1. Most analytical methods give results for zirconium *plus* hafnium.

METHODS OF SEPARATION

PRECIPITATION—

Several organic reagents are available for the quantitative precipitation of zirconium from solution. They include mandelic acid[4] and its derivatives,[5] benzoic acid,[6,7] *m*-nitrobenzoic acid,[8,9] tannin,[10,11] fumaric acid,[12] phthalic acid,[13] *m*-cresoxyacetic acid,[14] benzilic acid,[15] cinnamic acid,[16] salicylic acid,[17] phenoxyacetic acid[17] and diphenic acid.[18] Mandelic acid and its *p*-bromo-derivative are the most useful, since they can be used in solutions at least 5 *N* in hydrochloric or perchloric acid and effect the separation of zirconium from most other elements. They are less useful for sulphuric and hydrofluoric acid solutions containing zirconium. The other organic reagents are less selective, since they are only applicable to less concentrated acid solutions. The *p*-bromo-derivative of mandelic acid is considerably more sensitive than the unsubstituted acid and is more convenient to use. These reagents have been used for the separation of zirconium in the analysis of many different types of materials before completion of the determination gravimetrically, volumetrically or absorptiometrically. These materials include steel,[19] aluminium alloys,[20] magnesium alloys,[21] titanium alloys,[22,23] thorium alloys,[24] uranium[25] and plutonium[26]; their zirconium contents range from the parts per million level[26] to high percentages.[24]

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* Reprints of this paper will be available shortly. For details, please see p. 160.

Inorganic precipitants also have their uses. In one separation the zirconium is precipitated as barium fluorozirconate.[27] This method is applicable to fluoride solutions and is important because of the need to use hydrofluoric acid in producing complete solutions of zirconium metal and zirconium-containing alloys. By this means an excellent separation of zirconium is effected from elements such as tantalum and niobium before completion of the determination volumetrically with ethylenediaminetetra-acetic acid (EDTA). This method of separation is also widely used in the analysis of fission products for zirconium-95.[28]

The separation of zirconium by precipitation as its insoluble phosphate from sulphuric acid solutions has been in use for many years, but the limitations of this procedure in gravimetric analysis are well known. However, this method still finds applications when the presence of phosphate can be tolerated in the final determination. Vinogradov and Shpinel[29] used it for separation before determining zirconium by precipitation with 8-hydroxyquinoline and then a volumetric finish. Olsen and Elving[30] used it before titrating zirconium with cupferron to an amperometric end-point.

Precipitation with diammonium arsonate and the arsonic acids is out of favour for the separation of zirconium, with the exception of the reagent *p*-dimethylaminophenylazobenzenearsonic acid. This is a sensitive precipitant and permits the separation of microgram amounts of zirconium from common elements,[31] but there is some co-precipitation of titanium, niobium, tantalum, tungsten and thorium. Jean,[32] in work on aluminium alloys, found that interference from titanium is prevented if the precipitation is carried out from 30 per cent. v/v hydrochloric acid solutions containing succinic acid.

ION EXCHANGE—

Both cation- and anion-exchange resins have some applications to the separation of zirconium from other elements. In separations from many other elements, ion-exchange methods are less suitable than those involving mandelic acid or its derivatives. They are more satisfactory for the analysis of solutions containing a limited number of elements that can be individually separated. With a cation-exchange resin, the separation of mixtures of zirconium, titanium and thorium into the individual constituents has been reported.[33] From a column of Dowex 50 when a 1 per cent. solution of citric acid (pH 1·75) is used as eluting agent, zirconium and then titanium are eluted. For elution of the thorium, 0·052 *M* diammonium citrate (pH 4·98) must be used. The separation of zirconium from aluminium and chromium has beeen effected with the Russian cation-exchange resin KV-2 (H^+ form).[34] Zirconium is adsorbed by the resin from solutions *N* in hydrochloric acid, whereas aluminium and chromium are not. After transference of the sample to the column, washing with *N* hydrochloric acid is carried out until no more chromium or aluminium is eluted and then the zirconium is recovered in 4 *N* hydrochloric acid. In radiochemical analysis, Dowex 50 is suitable for separating zirconium-95 from niobium-95.[35] The carrier-free radionuclides are adsorbed on the column from 0·1 *N* hydrochloric acid, and niobium-95 is eluted with a mixture of 0·1 *N* hydrochloric acid and 0·3 per cent. hydrogen peroxide or *N* hydrochloric acid and 3 per cent. hydrogen peroxide. The zirconium-95 is recovered with 0·5 per cent. oxalic acid solution.

Separations of zirconium on anion-exchange resins have also been reported. Zirconium is quantitatively adsorbed on Amberlite IRA-400 from 0·05 to 0·2 *N* sulphuric acid solutions as a negatively charged sulphate complex.[36] It can then be eluted with 4 *N* hydrochloric acid and thus separated from most elements, with the exception of tin, vanadium, molybdenum, tungsten and uranium. Titration against EDTA solution to the Solochrome violet R end-point is used to determine the concentration of zirconium. In the analysis of phosphate-containing materials, sodium fluoride is added to the solution of the sample in sulphuric acid to prevent the precipitation of zirconium phosphate.[37] The zirconium is adsorbed on a column of Amberlite IRA-400 from 0·1 *N* sulphuric acid and 0·5 per cent. sodium fluoride solutions, and any titanium is eluted with 0·1 *N* sulphuric acid and 5-volume hydrogen peroxide; zirconium is recovered in 4 *N* hydrochloric acid. The separation of mixtures of zirconium, thorium and niobium into their individual constituents has also been effected from sulphuric acid solutions by anion exchange.[38] When a solution of the elements in a mixture of 0·1 *M* sodium sulphate and 0·03 *M* sulphuric acid is passed through a column of a quaternary ammonium type resin, the thorium passes through, but zirconium and niobium are adsorbed. Zirconium is then eluted with 2 *N* hydrochloric acid, and finally niobium is eluted with 4 *N* hydrochloric acid. In another method the zirconium - ascorbic acid complex is employed.[39] Zirconium is quantitatively adsorbed on Amberlite IRA-400, Dowex 1 or Dowex 2 from a 2 per cent. solution of ascorbic acid (pH 4 to 4·5) and is finally eluted in *N* hydrochloric acid. By this means a separation from iron, aluminium, chromium, alkaline earths and alkali metals is obtained, but uranium, thorium, titanium, vanadium, molybdenum and tungsten interfere.

Separations in more specialised analysis include those of zirconium from plutonium[40] and protactinium.[41] Plutonium^{IV} ions form an anionic complex in 7·2 *N* nitric acid, and the complex is retained on a column of Dowex 1; zirconium passes through. The separation of protactinium from zirconium is effected from hydrochloric acid solutions. Both elements are strongly adsorbed from solutions greater than 9 *M* in hydrochloric acid, but only weakly absorbed from solutions less than 5 *M*. At molarities between these extremes, a difference in the K_D values permits some separation to be effected. For example, at least 95 per cent. of the zirconium can be eluted with six column-volumes of 6 to 7 *M* hydrochloric acid and is accompanied by only 0·1 per cent. of the protactinium. With 8 *M* hydrochloric acid the amount of zirconium recovered is reduced to between 85 and 90 per cent. The protactinium can be eluted in a small volume of dilute hydrochloric acid.

SOLVENT EXTRACTION—

Methods in which solvent extraction is used to separate zirconium from other elements are not numerous. Several possible systems have been examined, but often lack of selectivity limits their applicability. Scadden and Ballou[42] developed the extraction of zirconium from fission products with dibutylphosphoric acid as extracting agent. Zirconium in either micro or macro concentrations can be extracted into 0·06 *M* dibutylphosphoric acid in di-*n*-butyl ether from solutions *M* in sulphuric acid, 2·5 *M* in ammonium sulphate, 0·004 *M* in oxalic acid and containing 6 per cent. of hydrogen peroxide. No niobium accompanies the zirconium, which can be recovered from the organic phase in 4 *M* hydrofluoric acid. Moore[43] separated zirconium from most other elements by extracting it from solutions 6 *M* in hydrochloric acid into 0·5 *M* thenoyltrifluoroacetone. For fission-product analysis the extraction was best carried out from 2 *M* nitric acid solutions. To obtain a complete separation from niobium and protactinium, it was necessary to add 1 per cent. of hydrogen peroxide or 0·5 to 1 *M* hydroxylamine hydrochloride to the aqueous solution.

An interesting method has been described by Young and White,[44] who extracted zirconium from either nitric or hydrochloric acid solutions into a solution of tri-*n*-octylphosphine oxide in *cyclo*hexanone. The concentration of zirconium was determined absorptiometrically after the zirconium - pyrocatechol violet complex had been formed in the organic layer. When the extraction was applied to a chloride medium containing thiocyanate ions, the only major interference was from molybdenum, titanium and hafnium and the presence of milligram amounts of phosphate and sulphate ions could be tolerated. Uranium, thorium and hafnium interfered with extraction from nitrate solutions, and only microgram amounts of phosphate and sulphate ions could be permitted. This separation is convenient for subsequent absorptiometry in the organic layer, but for other methods of determination difficulty can be foreseen in the recovery of the zirconium from the tri-*n*-octylphosphine oxide layer.

Zirconium, together with other quadrivalent and trivalent elements, can be extracted as its cupferron complex into a (1 + 1) mixture of benzene and *iso*amyl alcohol, thereby giving a separation from bivalent elements.[45] The solvent extraction of other elements, leaving zirconium in the aqueous layer, is often used in analysis. Iron[46] has been removed by extraction with ether from a hydrochloric acid solution, and niobium and tantalum[47] by extraction with *iso*butyl methyl ketone from a solution 10 *M* in hydrofluoric acid and 6 *M* in sulphuric acid.

CHROMATOGRAPHY—

The separation of zirconium from other elements by paper chromatography has received little attention. Only four papers have been published—two describe the separation of zirconium from hafnium, one from zirconium - thorium mixtures and the fourth from zirconium - titanium - thorium mixtures. The separations of zirconium from hafnium were made by using mixtures of dichlorotriethylene glycol and nitric acid[48] or *n*-pentanol, methanol and nitric acid[49] for development; the use of the latter mixture permitted the detection of 1 per cent. of hafnia in zirconia or 0·5 per cent. of zirconia in hafnia when *p*-arsonic acid was used as colour reagent. Zirconium and thorium were separated by using acetone - 5 per cent. aqueous oxalic acid as eluting agent,[50] whereas for zirconium, thorium and titanium, ethanol - hydrochloric acid - water was used, with morin as colour developer.[51]

METHODS OF DETERMINATION

GRAVIMETRIC—

From the many organic and inorganic precipitants available for zirconium, only mandelic acid[52] and tartrazine[53] are claimed to form precipitates suitable for direct weighing. When an organic precipitant is used, the precipitate is usually weighed as zirconium oxide, whereas the phosphate and arsenate methods of precipitation produce ZrP_2O_7 and $(ZrO)_2As_2O_7$,[54] respectively. In these methods, therefore, the conversion factors are not favourable for determining small amounts of zirconium.

Organic precipitants—Mandelic acid and its *p*-bromo-derivative are the most widely used precipitants in this class. In Kumins's original method,[4] the precipitate was formed by adding 50 ml of *M* mandelic acid to 50 ml of the zirconium solution adjusted to 2 *N* in hydrochloric acid. After digestion at 85° to 90° C for 20 minutes, the precipitate was separated, washed, and ignited to ZrO_2. Many workers have attempted to devise means of weighing the tetramandelate precipitate directly. Belcher, Sykes and Tatlow[55] obtained consistent but low results, and the application of a correction factor was unsuccessful, except over extremely narrow ranges of zirconium concentrations. Hahn and Baginsky[52] subsequently explained this lack of stoicheiometry on the basis of contamination of the zirconium tetramandelate precipitate with basic salts, such as $ZrO(C_8H_7O_3)_2$ and $Zr(OH)(C_8H_7O_3)_3$. They concluded that better results would be obtained by precipitating from strongly acid solutions, in which hydrolysis of zirconium is at a minimum. These workers recommended that precipitation be effected by adding mandelic acid solution dropwise to a hot solution of zirconium at least 5 *N* in hydrochloric acid. After digestion and filtration of the cooled solution through a sintered-glass crucible, the precipitate is washed successively with a saturated solution of zirconium tetramandelate, 95 per cent. ethanol and anhydrous diethyl ether. It is dried to constant weight at between 110° and 120° C. The precipitation of zirconium with mandelic acid from hydrochloric acid solutions gives excellent separation from many elements, including aluminium, antimony, barium, bismuth, calcium, cadmium, cerium, chromium, copper, iron, mercury, magnesium, nickel, thorium, tin, titanium, uranium, vanadium and zinc. The precipitation is less satisfactory from sulphuric acid solutions, and the concentration of this acid must be kept below about 2 *N*. Mills and Hermon[56] obtained complete recovery of 1 to 30-mg amounts of zirconium from 0·8 *N* sulphuric acid solutions by extending the period of digestion of the precipitate to 1 hour.

Several derivatives of mandelic acid have been examined by Oesper and Klingenberg,[5] who recommended the *p*-bromo or *p*-chloro compounds as being more suitable for the determination of zirconium. They found that these derivatives were considerably more convenient to use than was mandelic acid and that the *p*-bromomandelic acid salts of zirconium could be weighed directly. This latter claim was not supported by Belcher, Sykes and Tatlow's examination,[55] but subsequent thermogravimetric studies by Wendlandt[57] have shown that a re-examination of the precipitation conditions might be justified, as the precipitate approximately corresponds to the formula $Zr(C_8H_5O_3Br)_4$ and has greater stability than any other organic precipitate of zirconium so far examined. The fluoro- and trifluoromethyl-derivatives have been examined and found to show no improvement over *p*-bromomandelic acid.[55] Several organic reagents closely related to mandelic acid have been studied by various workers. Hahn and Joseph[58] used naphthylglycollic acid for the gravimetric determination of zirconium and obtained quantitative results on solutions up to 0·5 *N* in hydrochloric acid and up to 2·5 *N* in sulphuric acid.

Tartrazine has recently been recommended for the gravimetric determination of zirconium.[53] It has good potentialities, because the resultant precipitate can be weighed directly after drying at 110° C. A 2 per cent. aqueous solution of tartrazine is added dropwise to a zirconium oxychloride or nitrate solution at pH 1 until precipitation is complete. The final solution is heated to 80° C and then filtered. The precipitate is washed with water to remove excess of reagent, dried at 110° C and either weighed as the complex or ignited to ZrO_2. The reagent appears to be fairly selective, since only barium, thorium and mercuric ions form a precipitate, but sulphate, tartrate and citrate interfere.

Inorganic precipitants—The gravimetric determination of zirconium by a method based on the precipitation of zirconium phosphate has been available for many years.[59,60] The precipitation is carried out from solutions 3·6 *N* in sulphuric acid by adding an excess of diammonium hydrogen orthophosphate. It is thus applicable to solutions that are not ideal for precipitation by mandelic acid. The method is selective because at this acid concentration no other metal, with the exception of titanium, is precipitated. However, the zirconyl phosphate precipitate is bulky, gelatinous and inclined to carry down other elements. It is difficult to wash efficiently during filtration, and for this reason the method should be applied only to small amounts of zirconium. In recent years some efforts have been made to improve the conditions of precipitation to give a better form of precipitate. Willard and Hahn[61] claimed to have made improvements by using metaphosphoric acid as precipitant. The zirconyl phosphate was slowly deposited at room temperature after addition of metaphosphoric acid to a 3·6 *N* sulphuric acid solution containing up to 200 mg of zirconium oxide. Unfortunately, a digestion period of 12 hours or more was necessary for complete precipitation. Precipitation of zirconium by disodium hydrogen orthophosphate from a 3 to 4 *N* acid solution containing EDTA[62] is also claimed to produce a slow-forming crystalline precipitate, which does not carry down other ions, as in the normal phosphate method. Just sufficient EDTA is added to form the complex with zirconium; difficulties could otherwise occur from precipitation of EDTA. If precipitation is carried out in presence of hydrogen peroxide, interference from titanium is greatly reduced.

Gravimetric methods based on the precipitation of zirconium as arsenate[63] and basic selenite[64,65] have also been available for many years. Although the former is applicable to solutions 2 *N* in hydrochloric acid or 3·75 *N* in nitric acid, precipitation is incomplete from sulphuric acid solutions. Special treatment is necessary to convert the precipitate to zirconium oxide. This treatment includes preliminary ignition at a low temperature in a porcelain crucible to remove arsenic by sublimation and then final ignition at 1100° C in a platinum crucible. The selenite method is also applicable to dilute hydrochloric acid or nitric acid solutions, but the presence of sulphuric acid slows down the precipitation. Procedures in which mandelic acid is used as precipitant are preferable to these methods.

VOLUMETRIC—

Titration methods for determining zirconium have been revolutionised since the introduction of EDTA in analysis. Both direct and indirect procedures are available, and reasonable selectivity is obtained in these methods because they are carried out in solutions having low pH values. The stable zirconium - EDTA complex persists in acid solutions, conditions in which bivalent and many tervalent ions are not complexed. These methods are considered in this section, together with some not involving the use of EDTA.

Indirect methods involving EDTA—Methods in which the excess of EDTA over the amount required to form the complex with zirconium is titrated are preferred, as the risk of low results caused by hydrolysis of zirconium is avoided. The elements used for the titration include bismuth, iron and thorium, which form stable complexes with EDTA in solutions having pH values from 2 to 3. For visual end-point detection the use of a bismuth solution as titrant and xylenol orange as indicator is favoured, a sharp colour change from yellow to red being obtained at the end-point. Kinnunen and Wennerstrand[66] recommend the addition of excess of EDTA to a solution of zirconium, as nitrate or perchlorate, adjusted to a pH between 1 and 2 and then titration with bismuth nitrate solution. For all except the smallest amounts of zirconium, our experience shows that it is preferable to add the excess of EDTA to an acidic solution of the sample before adjusting the pH to between 1 and 3 and carrying out the titration.[24] This procedure should not be applied to chloride solutions, because of the risk of precipitating bismuth as oxychloride. However, at pH values between 2 and 3, chloride solutions can be titrated back with a thorium solution. Both fluoride and sulphate ions interfere. In other systems involving a bismuth solution as titrant, thiourea[67] or potassium iodide[68] is used to indicate the end-point. With thiourea as indicator, the titration is generally carried out at pH 2. However, the optimum pH for the titration and the thiourea concentration are closely inter-related. There is interference from iron^{III}, arsenic^{III}, thorium, titanium, tin^{II}, tin^{IV}, mercury, molybdenum, niobium, nickel, tantalum, fluoride, sulphate and phosphate ions. Some operators find difficulty in detecting the end-point clearly, as the change is from colourless to yellow. The bismuth - potassium iodide system behaves similarly and can be used over the pH range 1 to 5, depending on the concentration of iodide added.

For the determination of zirconium in sulphate solutions, a solution of ferric iron can be satisfactorily used to titrate the excess of EDTA. Salicylic acid,[69,70] tiron[71] and benzohydroxamic acid[70] are available as indicators. With salicylic acid as indicator, the titration is carried out at pH 6 and the end-point is difficult to distinguish visually, as the colour changes from brown to yellow, but this does not apply when the end-point is detected photometrically. With tiron, the titration is effected at pH 4·8 and the indicator colour changes from yellow to purple. Both these end-points suffer slightly from fading caused by the ferric iron slowly displacing zirconium from its complex with EDTA. The end-point with benzohydroxamic acid is satisfactory when determined photometrically. The titration is carried out at pH 2 to 3 and is suitable for the analysis of uranium - zirconium alloys. Even at this low pH, however, there is interference from some elements, including aluminium, bismuth, thorium, tin^{II}, tin^{IV}, titanium, uranium^{VI} and molybdenum.

When choosing a method for a particular analysis, consideration has to be given to the selectivity of the various procedures. As far as possible, methods applicable to solutions having low pH values should be used, as there is then no interference from nearly all bivalent and many tervalent metals. However, even under the best conditions interference may usually be expected from aluminium, iron^{III}, chromium^{III}, cerium^{IV}, thorium, titanium, bismuth, vanadium^{V}, niobium, tantalum, copper and nickel and also from sulphate, fluoride, phosphate, tartrate, citrate, oxalate and molybdate. The presence of highly coloured ions in solution may also cause difficulty, and oxidants and reductants in solution may affect the indicator. It is possible, however, to overcome several of these interferences by making use of masking reactions, thereby avoiding chemical separations. This technique is best illustrated by reference to Fritz and Johnson's[67] work, in which the bismuth - thiourea system was used. In this titration, interference from niobium, tantalum, sulphate and phosphate can be prevented by using ammonium tartrate, and interference from thorium and titanium is overcome by adding sulphate after the initial formation of the complex with EDTA. More generally, difficulty caused by the presence of ferric iron in complexometric titrations can be removed by reducing the iron to the ferrous state, ascorbic acid being a satisfactory reducing agent for this purpose. In the bismuth - potassium iodide system,[68] interference from fluoride ions was prevented by preferential complexation with beryllium. Difficulties caused by the presence in solution of coloured substances that do not react with EDTA can often be avoided by detecting the end-point photometrically.

Electrometric methods are available for end-point detection in back-titration procedures; Vladimirova[72] used an amperometric titration of excess of EDTA with bismuth under conditions similar to those in the bismuth - thiourea method. This titration is slower to carry out than are those in which the end-point is detected visually. A potentiometric method[73] is also available; the excess of EDTA is titrated with a solution of copper in acetate buffer solutions having pH values between 4 and 5·5 and a mercury electrode is used as the indicator electrode. In general, however, methods involving the use of indicators are to be preferred. They are applicable to the determination of zirconium in amounts varying from several milligrams to about 100 μg. Prior separation of the zirconium, if necessary, can be achieved by precipitation with mandelic acid, the separated precipitate being dissolved before titration with EDTA.[25]

Direct methods involving EDTA—Some workers have reported direct-titration procedures for zirconium, the titrations being carried out in mineral acid solutions to prevent possible losses of zirconium by hydrolysis. Körbl and Přibil[74] described a titration procedure applicable to *M* nitric acid solutions; xylenol orange was used as indicator. However, we found that this procedure gave a slow end-point and low results for zirconium.[24] Good results could be obtained for small amounts of zirconium by titrating to a preliminary end-point in *M* nitric acid, neutralising most of the free acid by careful dropwise addition of ammonia and continuing the titration to a permanent end-point. This modification reduces the selectivity of the method, and thorium, for example, which does not interfere in *M* nitric acid, causes serious interference at the lower acidity.

Russian workers have subsequently reported direct titrations in solutions approximately 2 *N* in hydrochloric acid, Eriochrome black T,[75] carminic acid[75] or 4-(4′-nitrophenylazo)-pyrocatechol[76] being used as indicator. The EDTA is standardised against a solution of zirconium containing the same amount of hafnium as is present in the sample. Solochrome violet R[77] has also been proposed as an indicator for the direct titration of zirconium in hot *N* hydrochloric acid solutions. It is reported that 1- to 50-mg amounts of zirconium in 50 ml of solution can be determined with a precision of ±1 to 0·1 per cent. and 10- to 1000-µg amounts in 10 ml of solution with a precision of ±8 to 0·6 per cent. Even under these acid conditions, iron^{III}, tin^{II}, vanadium^{V}, molybdenum, tungsten, titanium, oxidants and reductants interfere, as also do phosphate, fluoride and large amounts of sulphate and nitrate. The natural colours of copper, chromium, cobalt and nickel may mask the colour change of the indicator if these ions are present in large amounts. Interference from ferric iron can be decreased if the iron is reduced to the ferrous state by the minimum amount of stannous chloride.

Other indicators available for direct titrations are of the lake-forming type and require less acid solutions. Under these conditions there is a greater risk of zirconium being hydrolysed and the colour change at the end-point is not generally good. The titration is best carried out in cold solutions at a pH between 1·3 and 1·5 with Eriochrome cyanine R[78] as indicator, a pH between 1·5 and 2·5 with 2-*p*-sulphophenylazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (SPADNS) as indicator[79] or in approximately 0·5 *N* hydrochloric acid with Chromazurol S as indicator.[80] With the last-named indicator it is recommended that the zirconium solution be run into a known amount of EDTA solution, thus reversing the usual order. The titration with Eriochrome cyanine R as indicator can readily be changed into a back-titration procedure.

Other titration methods—Several indirect methods available do not involve the use of EDTA. Acidimetric titrations based on formation of a complex between zirconium and fluoride[81,82] or tartrate,[83] with subsequent liberation of hydroxyl ions, have been suggested. Other procedures involve the precipitation of zirconium with mandelic acid,[84] *p*-bromomandelic acid,[85] iodate[86] or 8-hydroxyquinoline,[29] solution of the precipitate after separation and subsequent titration of the anion. The *p*-bromomandelate ion is determined by oxidation with an excess of ceric ions and then titration of the excess with ferrous ions, ferroin being used as indicator. The mandelate ion is determined by oxidation with potassium permanganate. Iodate is determined in the usual way by treatment with potassium iodide and titration of the liberated iodine with sodium thiosulphate. The normal procedure is used for 8-hydroxyquinoline, *i.e.*, treatment with potassium bromide and potassium bromate and determination of the excess by titration with thiosulphate after the addition of potassium iodide.

Amperometric-titration procedures involving the use of cupferron,[30] fluoride[87] and 1-nitroso-2-naphthol[88] as titrant have been described. The cupferron method is most valuable, as it can be directly applied to fluoride solutions of zirconium and even to suspensions of zirconium phosphate. The zirconium is titrated in 10 per cent. v/v sulphuric acid solutions against 5 per cent. w/v cupferron solution, the diffusion current being measured at −0·84 volt against a saturated-calomel electrode. Little preliminary treatment of the sample is needed, but a disadvantage of the method is the instability of the cupferron solution. In the fluoride method, the zirconium is titrated at pH 2·2 in chloride solutions containing 50 per cent. of ethanol, ferric ions being present to help in the detection of the end-point. The titration with 1-nitroso-2-naphthol is carried out in acetate-buffered solutions; the titrant is stable for about 2 weeks, as compared with 1 day for cupferron solution. Several elements, including copper, cobalt, iron and palladium, are precipitated by 1-nitroso-2-naphthol and interfere. Substances known to cause interference include aluminium, calcium, chromium, gold, magnesium, titanium, zinc, sulphate, nitrate and fluoride.

ABSORPTIOMETRIC—

There has been a great increase in recent years in the number of absorptiometric methods available for determining zirconium. Before 1950, the only useful direct method was based on the coloured lake formed by zirconium with alizarin[89] or its sulphonate, although experiments had been carried out with other possible lake-forming reagents, including purpurin and quinalizarin.[89] An indirect method in which *p*-dimethylaminoazophenylarsonic acid[90] was used found application in the analysis of complex materials requiring a preliminary separation of the zirconium. In the last decade, however, the position has changed completely and there are now more than a dozen reagents forming suitable coloured complexes with zirconium. These reagents are listed in Table I, and the value of the molar extinction coefficient for each is shown wherever possible; these values are calculated from the results in the methods as described.

TABLE I

LIST OF REAGENTS FOR ABSORPTIOMETRIC DETERMINATION OF ZIRCONIUM

Reagent	Molar extinction coefficient	References*
Alizarin	7000	46, 89, 91 to 98
Alizarin blue S	3600	99
Arsenazo	—	100
Carminic acid	5000	101
Chloranilic acid	20,000 (330 mμ), 4000 (525 mμ)	26, 102, 103
Fast grey RA	10,000	104
Flavanol	22,000	105, 106
Haematin	—	107
Mandelic acid	—	108
Morin	9000	109, 110, 111
Nitroso-R salt	1400	112
Phenylfluorone	140,000	113, 114
m-Nitrophenylfluorone ..	170,000	115
Pyrocatechol violet	30,000 to 40,000	116, 117, 118
Quercetin	33,000	119
SPADNS	40,000	120
Thoronol	3000	121
Xylenol orange	34,000	122, 123

* See reference list, p. 95.

Several of the substances originally developed as indicators in EDTA titrations form stable coloured complexes with zirconium ions. Under certain conditions pyrocatechol violet forms a complex more stable than the zirconium - EDTA complex. This is convenient because this reagent can then be used for determining zirconium in solutions containing EDTA added to prevent other elements from reacting with it. Two sets of conditions have been proposed for forming the zirconium - pyrocatechol violet complex at pH 5·2. In one method[117] the complex is formed by adding the pyrocatechol violet to a zirconium solution at pH 3 before finally adjusting the pH to 5·2 with an acetate buffer. In the other method[116] colour is developed by adding the reagent to a neutral solution of the zirconium - EDTA complex and then adjusting the pH to 5·2. These different ways of using the reagent result in the formation of different complexes, and, although Flaschka and Farah's method[116] is only about half as sensitive as that described by Young, French and White,[117] the resultant complex is stable and interferences are less. The zirconium colour can be discharged by adding fluoride ions, and this effect is useful in preparing a blank reference solution. A method involving the zirconium - pyrocatechol violet complex has been developed in which a preliminary separation of the zirconium is effected by solvent extraction of its tri-*n*-octylphosphine oxide complex from chloride or nitrate media.[118] The coloured complex is formed directly in the organic medium after separation. Other indicators examined for complexometric titrations include xylenol orange,[122,123] SPADNS[120] and Fast grey RA.[104] Xylenol orange appears to be the most useful, since it is sensitive and can be used in more concentrated acid solutions (either hydrochloric or sulphuric) than can either of the other two indicators. Interferences with all these reagents would appear to be much the same.

Chloranilic acid is another satisfactory reagent for determining zirconium; it reacts in perchloric acid solution (about 2 *N*) to form a magenta complex with zirconium. There are two peaks in the absorption spectrum of this complex, at 330 and 525 mμ, the peak in the ultra-violet region being four times as sensitive as that in the visual region. Since the absorption decreases with increasing acidity and interferences are least at higher acidities, conditions must be chosen so as to compromise between these two effects. This reagent has been used for determining zirconium in steels[103] after the separation of iron, etc., by mercury-cathode electrolysis and in plutonium[26] after a preliminary precipitation with *p*-bromomandelic acid. Mandelate ions absorb light in the ultra-violet region (258 mμ) of the spectrum,[108] and the determination of zirconium can therefore be completed absorptiometrically after precipitation by mandelic acid or its derivatives; the zirconium tetramandelate precipitate is readily soluble in ammonium hydroxide. Although the selectivity of this method is high, the sensitivity is rather low.

The most sensitive reagents so far described for the absorptiometric determination of zirconium are 2:3:7-trihydroxy-9-(3′-nitrophenyl)fluorone (*m*-nitrophenylfluorone)[115] and 2:3:7-trihydroxy-9-phenyl-6-fluorone (phenylfluorone).[113,114] The zirconium - *m*-nitrophenylfluorone complex is unstable in aqueous solution and must be measured as a suspension in a medium stabilised with *cyclo*hexanol - ethanol. Sano, however, claims that for the range 0·0 to 0·15 p.p.m. of zirconium the suspension is stable for at least 3 days and that even 16 p.p.m. of zirconium gives a suspension stable for 40 minutes.[115] Titanium, germanium and tin are the most serious interfering elements and iron^{III} also causes trouble. As in most methods for determining zirconium, fluoride, phosphate and hydroxy acids interfere.

Although alizarin red S is gradually being superseded for the direct determination of small amounts of zirconium, it is finding application in difference absorptiometry. Manning and White[94] used this technique for determining milligram amounts of zirconium, and the results agreed well with those obtained gravimetrically by precipitation with mandelic acid. For routine analysis this method should be faster than the gravimetric method. Other workers[98] have applied this technique to the determination of zirconium - hafnium ratios with a good precision.

A few indirect methods are available for zirconium, one of which is based on the phosphate method of precipitation.[124] A standard phosphate solution is added to an acidified zirconium solution and the decrease in the phosphate concentration is measured by utilising the molybdophosphoric acid colour; from 1 to 80 p.p.m. of zirconium can be determined by this method. Oxalohydroxamic acid, which forms a precipitate of constant composition with zirconium, has been used in a similar method.[125] After the precipitate has been separated, it is dissolved in 10 per cent. acetic acid and its hydroxamic acid content is found by forming a coloured complex with ferric iron and completing the determination absorptiometrically. *p*-Dimethylaminoazophenylarsonic acid has been used for determining zirconium in various materials, including uranyl nitrate,[126] aluminium alloys,[32] steels and coal ash.[127] For uranyl nitrate the determination is carried out by separating the zirconium precipitate and dissolving it in a mixture of hydrofluoric and oxalic acids. This solution is made up to volume and optical-density measurements are made at 490 mμ. In the other determinations the organic reagent is added to the sample solution and any decrease in the intensity of the colour of the solution is measured. If the precipitation is carried out in a 30 per cent. hydrochloric acid solution containing succinic acid, interference from titanium is prevented.

MISCELLANEOUS—

Zirconium does not produce steps suitable for direct polarographic analysis, but an indirect method has been developed[128] in which *m*-nitrobenzoic acid is used to precipitate the zirconium from 0·2 N hydrochloric acid solutions. The precipitate is dissolved in 6 M hydrochloric acid, and the concentration of *m*-nitrobenzoate is determined by using the step at —0·2 volt against a saturated-calomel electrode in a base solution of pH 1·6 containing 0·1 N potassium chloride and 0·0075 per cent. of gelatin as a maximum suppressor.

Radioactivation analysis has been used by Hudgens and Dabagian[129] to determine zirconium in mixtures with hafnium. When irradiated in a pile, zirconium-94 gives rise to zirconium-95, which decays to niobium-95. The niobium-95 is then separated from the other radionuclides and counted. A standard zirconium sample is irradiated beside the unknown, and, by a series of calculations, the zirconium content of the unknown can be found. As little as 2 p.p.m. of zirconium in hafnium may be determined. Zirconium - hafnium ratios have also been determined by emission-spectrographic[130,131,132] and X-ray fluorescence methods.[133,134]

Spectrographic methods have been described for determining zirconium in silicate rocks,[135] steels[136] and uranium alloys.[137] In the method for silicate rocks, barium chloride is used to reduce differential evaporation and to increase the sensitivity of detection of zirconium. X-ray fluorescence methods have also been applied to the determination of zirconium in ores and minerals.[138,139]

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A Spectrographic Method for the Analysis of High-purity Acids*

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A method has been developed for determining trace impurities in high-purity acids, such as are required in semiconductor technology or for the analysis of semiconductor materials. After chemical concentration as sulphates the impurities, with copper added as an internal standard, are dried on a graphite electrode and excited by d.c. arc in an atmosphere of argon and oxygen. The sensitivity for most of the seventeen elements investigated is about 0·02 μg. The recovery after chemical concentration and the reproducibility of the spectrographic technique have also been studied; results obtained on samples of four acids (hydrochloric, nitric, hydrofluoric and acetic) are reported and discussed.

ONE of the main problems of the analyst when determining trace elements by chemical methods is the magnitude of the reagent blank value, which must be kept small compared with the amount of trace element being determined. When sub-microgram amounts are being dealt with, as in semiconductor analysis, the magnitude of this blank value assumes an over-riding importance, since many reagents of analytical grade are less pure than the material being analysed. This difficulty has sometimes been circumvented by using methods for which no chemical pre-treatment of the sample is needed (*e.g.*, direct spectrographic analysis or solid-source mass spectrography) or by using radiochemical-activation methods in which contamination of the sample after activation is of no consequence. Direct spectrographic methods have the advantage that many impurity elements can be recorded simultaneously, but, since the trace elements are diluted some millions of times with the parent material, the sensitivity of the method is limited. Spectrographic analysis is nevertheless capable of giving high sensitivity (about 19^{-9} g for some elements), provided that a chemical concentration procedure can be used to remove the parent material. It is then an attractive method for analysing samples falling within the intermediate range of purity, *i.e.*, 0·01 to 10 p.p.m.

An attempt was therefore made to develop some simple chemical concentration procedure that would separate at one and the same time many elements in a form suitable for spectrographic examination. The intention was to concentrate the trace impurities in a small volume of a sulphuric acid solution that could be dried on a graphite electrode and excited. It was foreseen that such a procedure could be used for determining the concentration of many metals yielding non-volatile sulphates and would also be applicable not only to the liquid etchants that are important in semiconductor technology, but also to solid materials, provided that the base material could be removed and the impurities concentrated in the presence of sulphuric acid.

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EXPERIMENTAL

PREPARATION OF STANDARDS—

A series of standard solutions was prepared and used to investigate the spectrographic procedure described on p. 101. A master solution containing, as their sulphates, the elements listed in Table II (except lead) was first prepared from AnalaR and Specpure materials. The solution contained 50 µg of each element per 0·1 ml of *N* sulphuric acid. A solution of copper sulphate containing 0·05 g of copper per 1 ml of *N* sulphuric acid was prepared from Specpure copper for the purpose of adding copper as internal standard. Copper was used as internal standard because it could readily be determined separately, either spectrographically or by other means, and because at the concentration chosen it provided a useful selection of internal-standard lines.

Ten standards with concentrations ranging from 0·005 to 5·0 µg of each element per 0·1 ml were prepared by successive dilutions of the master solution with *N* sulphuric acid. To each aliquot before dilution was added sufficient copper to give a final concentration of 1·0 mg per 0·1 ml of standard solution. A supplementary set of eight standards containing 0·1 to 1·0 µg of lead per 0·1 ml was also prepared.

All solutions were stored in silica or polythene flasks.

PREPARATION OF ELECTRODES—

High-purity graphite was used. The upper electrode was 6 mm in diameter, pointed to an 80° cone. The shape and dimensions of the lower electrode, on which the solution was dried, are shown in Fig. 1. It is known that undercutting, as shown at (*b*), assists in maintaining a high temperature at the impregnated head and therefore ensures complete volatilisation of the sample in a comparatively short exposure time.[1] This was confirmed for our experimental conditions by means of the falling-plate technique. Pre-arcing the electrodes removes surface contamination and renders them porous. The dimensions of the electrodes and the pre-arcing conditions employed are determined by the degree of porosity required, which in turn depends upon the amount of solution to be absorbed. If the dimensions of the electrode at (*a*), Fig. 1, are too small or the pre-arcing conditions are too severe, the porosity may extend through the neck to the base of the electrode. Conversely, if the porous layer is too thin the solution dries on the top and sides of (*a*) in the form of an encrustation, which may be mechanically dispersed by the initiating spark. In both instances sensitivity is reduced. In the procedure finally adopted, 0·1 ml of solution was transferred to the electrode, and the optimum conditions for absorbing this amount were obtained by pre-arcing electrodes of the dimensions shown at 4 amps for 4 seconds. The pre-arcing period was used to obtain a spectrographic record of impurities, and any pair of electrodes showing contamination were

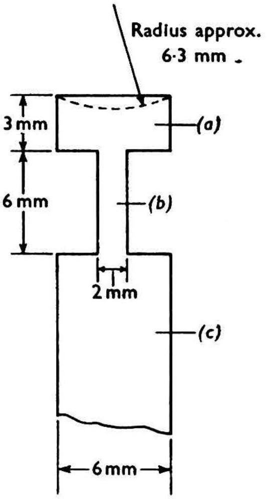

Fig. 1. Lower electrode

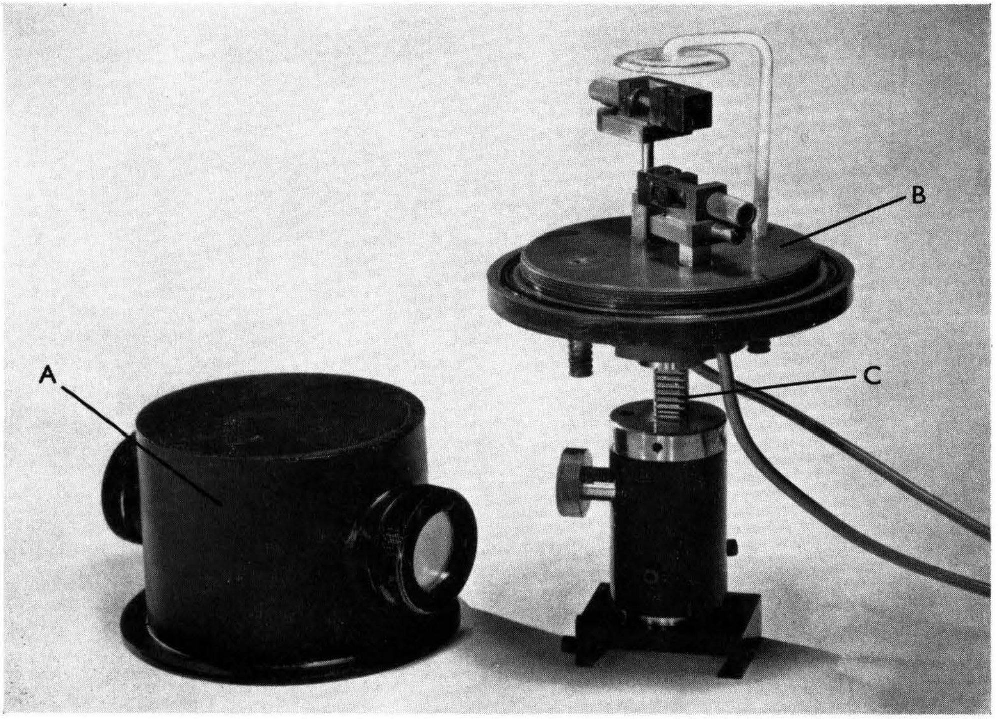

Fig. 2. Excitation chamber

[To face page 98.

discarded. The upper and lower electrodes were retained in pairs, the lower electrode being re-heated before use to a uniform temperature by placing it in a suitably drilled steel block kept at about 130° C by means of an electric hot-plate.

EXCITATION IN CONTROLLED ATMOSPHERE—

In order to excite samples in a controlled atmosphere a chamber (see Fig. 2) had been constructed that could be evacuated and the air replaced by a gas or mixture of gases at normal, high or low pressures. This chamber was used in the investigation described here. It consisted of a copper cylinder, A, with one end closed and the other fitted with a sealing flange, which could be screwed on to a threaded insulating base, B, carrying the electrode holders and inlet and outlet ports. The chamber had two diametrically opposed windows; the one facing the spectrograph slit was made of optically flat quartz. An O-ring seal in the base ensured a gas-tight joint, and a Pyrex-glass hood (not used in this investigation) above the electrodes facilitated the removal of fumes. The complete chamber was supported on a specially designed mount that fitted the Hilger Barfit and could be adjusted to the desired height by a rack-and-pinion device, C.

By using the gas-control system (see Fig. 3) the flow of gases could be regulated by taps T_1 and T_2 and measured by the calibrated rotameters, R_1 and R_2.

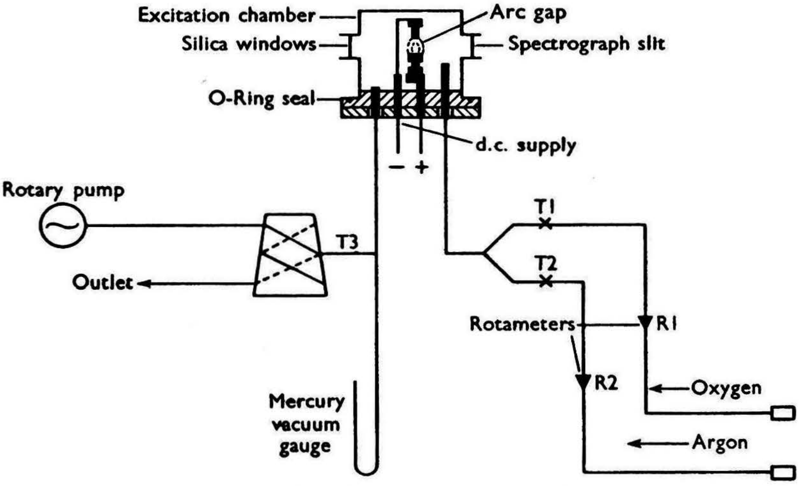

Fig. 3. Controlled-atmosphere system

CHEMICAL CONCENTRATION—

A 10-ml portion of sample to which 1 ml of 0·1 *N* sulphuric acid had been added was slowly evaporated to dryness on a silica hot-plate. For the blank test, 1·0 ml of 0·1 *N* sulphuric acid was similarly treated. The dry crucible was removed from the hot-plate, and 1·0 ml of Specpure copper sulphate solution containing 1·0 mg of copper in 0·1 *N* sulphuric acid was added from a silica pipette. (It was convenient to prepare this solution from the original copper sulphate solution by adding to 10 ml of the latter 40 ml of *N* sulphuric acid and diluting to 500 ml.) The crucible was warmed, and by tilting and slowly rotating it, the residue on the sides was dissolved. The sides were washed down with a fine jet of de-ionised water, and the solution was again evaporated to dryness. A 0·1-ml portion of de-ionised water was added, the solution was warmed, and the residue was dissolved. This was found to be best accomplished by rotating the crucible and drawing the solution up the sides with a platinum micro-spatula. The solution was transferred dropwise to the heated electrode in order to prevent it running down the sides, the spatula being used to facilitate this operation. The solution was allowed to dry after the addition of each drop. After transferring as much as possible to the electrode, the crucible was washed by the addition of 0·05 ml of de-ionised water, which was transferred to the electrode as previously described. The operation was standardised as far as possible, the time permitted to elapse from the addition of the first

TABLE I

SPECTROGRAPHIC CONDITIONS

Spectrograph	Hilger E 478
Waveband	2700 to 4300 A
Slit width	10 μ
Slit length	3 mm
Source to slit distance ..	30 cm
Upper electrode	80° pointed graphite
Lower electrode	As shown in Fig. 1. (Positive)
Gap width	3 mm
Source	12-amp d.c. arc (spark initiated) in controlled atmosphere—(1 + 1) argon - oxygen mixture
Exposure time	15 seconds
Plate	Kodak B10
Development	D19b at 20° C for 3 minutes
Step-sector spectrum ..	Fe - Fe arc, 5 amps; 10.15 seconds at 38 cm

TABLE II

LINE PAIRS

Line pair					
Element	Copper	Iron line	Index value, μg	Range, μg	Notes
Fe II 2755·74	I 2768·9	2767·52	3·0	0·2 to 5·0	
Mg 2779·8			2·0	0·2 to 5·0	
Mn 2798·3			0·25	0·02 to 0·5	(1)
Mg II 2802·7			0·025	0·005 to 0·5	
Cr II 2835·6	I 2858·2		0·3	0·1 to 5·0	
Mn 2933·06	I 2882·9		8·0	0·2 to 5·0	
Ni I 3050·8	I 3160·0	3125·66	0·085	0·05 to 0·5	
Bi I 3067·7			0·045	0·01 to 0·5	(2)
Al I 3082·1			0·09	0·05 to 1·0	
Mo 3170·3			0·10	0·02 to 0·5	
Ni I 3050·8	I 3128·67		1·15	0·2 to 5·0	
Bi I 3067·7			1·12	0·2 to 5·0	
Al I 3082·1			1·35	0·2 to 5·0	
Be II 3130·42			0·015	0·005 to 0·2	
Mo 3170·3			2·60	0·2 to 5·0	
Ti II 3222·8	I 3223·4	3233·98	2·05	0·2 to 5·0	
In I 3256·1			0·8	0·05 to 5·0	
Cd I 3261·0			2·0	0·2 to 5·0	
Be I 3321·3	I 3319·7	3370·79	0·3	0·05 to 2·0	
Zn I 3345·0			2·0	0·2 to 5·0	
Zr II 3391·95			1·5	0·2 to 5·0	
Zn I 3345·0	I 3375·7		0·25	0·10 to 5·0	
Ti (3) 3361·2			0·07	0·02 to 0·3	(3)
Zr II 3391·95			0·25	0·05 to 1·0	
Ni I 3414·77	I 3413·3	3447·28	0·10	0·01 to 1·0	(4)
Co I 3453·51	3454·7		0·13	0·01 to 2·0	
Fe I 3581·2	I 3545·0	3545·64	0·02	0·2 to 1·0	(5)
Cr I 3593·5			0·08	0·02 to 0·5	(6)
Pb I 3683·47	3676·9	3686·00	0·36	0·05 to 2·0	
Ga I 4172·1	I 4177·8	4181·76	0·17	0·02 to 1·0	
Cr I 4254·3	I 4249·0	4260·5	0·2	0·02 to 0·2	

(1) Self-reversal gives a non-linear working curve above 0·5 μg.
(2) Working curve is non-linear below 0·1 μg owing to OH-band interference.
(3) Double line Ti 3361·213 - Ti 3361·26 above 0·3 μg.
(4) Zirconium greater than 2·0 μg interferes with the nickel line.
(5) Most sensitive iron line, but the blank limits the sensitivity to 0·2 μg.
(6) Alternative to Cr 4254·3, which is near the edge of the plate.

drop to the removal of the electrode to the electrode holder being not less than 5 minutes. The sample was then arced as described below.

All platinum-ware was thoroughly cleaned by boiling in hydrochloric acid and washed with de-ionised water; every precaution was taken to reduce risk of contamination. A sample and blank determination were carried out simultaneously.

SPECTROGRAPHIC PROCEDURE—

After the sample electrode had been transferred to the lower-electrode holder a counter electrode was placed in the upper holder. The analysis gap was adjusted to 3 mm, and aligned on the optical axis by an optical-projection method. The chamber top was screwed on to the sealing ring and evacuated to approximately 0·5 mm of mercury. The two-way tap, T_3 (see Fig. 3), was then closed and T_2 was opened to fill the chamber with argon. With T_3 turned to the outlet position, T_1 and T_2 were adjusted to give a steady flow of 1·5 litres per minute of a (1 + 1) mixture of argon and oxygen. This rate of flow was maintained during the arcing of the sample, which was for 15 seconds at 12 amps. A step-sector spectrogram was recorded on each plate. Details of the spectrographic conditions are shown in Table I.

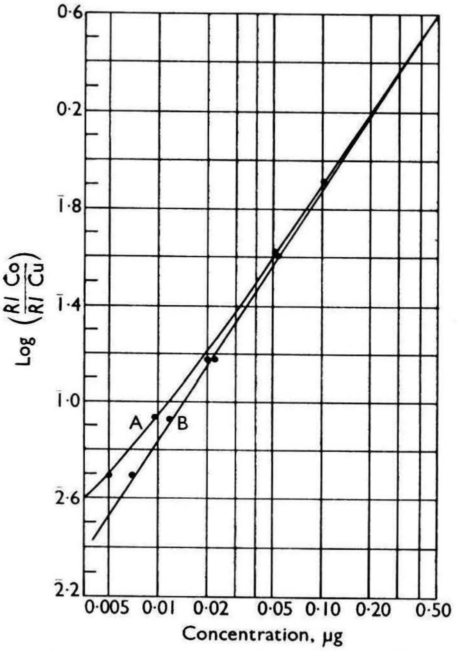

Fig. 4. Working curve for cobalt with Co. 3453·51 - Cu 3454·7 line pair: curve A, uncorrected; curve B, corrected for blank value of 0·002 μg

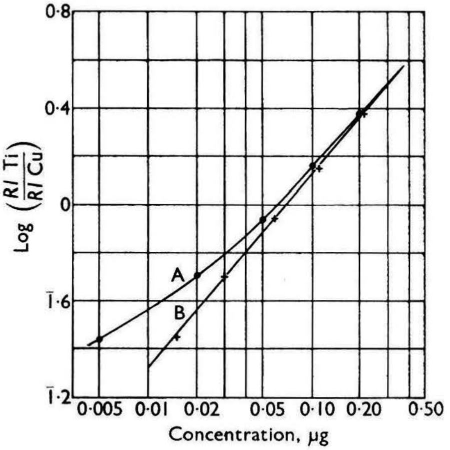

Fig. 5. Working curve for titanium with Ti 3361·2 - Cu 3375·7 line pair: curve A, uncorrected; curve B, corrected for blank value of 0·01 μg

The spectrograms were measured on a Hilger non-recording microphotometer. Galvanometer-deflection readings were obtained for the impurity line, its copper internal-standard line and their adjacent backgrounds. These values were converted to Seidel densities—log(1/T − 1)—and the relative intensities were obtained from a characteristic curve derived at the appropriate wavelength. After making background corrections, log(*RI* impurity/*RI* Cu) was calculated and converted to micrograms of impurity from previously prepared working curves (see p. 102). The line pairs used to cover the range of concentrations present in the standards are shown in Table II. Table II includes index values, which are given to assist in the identification of the line pairs, and also the iron lines used to obtain the characteristic curves, although any form of plate calibration may be used.

PREPARATION OF WORKING CURVES—

Spectrograms were prepared by transferring 0·1-ml portions of the standard solutions on to heated electrodes. The solutions were transferred dropwise, each drop being allowed to dry before the addition of the next, and the total drying time was standardised at 5 minutes after addition of the first drop. The standard was then excited, and the log *RI* ratios were obtained as previously described. Working curves were constructed by plotting these ratios against micrograms of the impurity element. Corrections for residual blank value were made when necessary by the method of successive approximations. These blank values were below the lower limits shown in Table II, column 5. Typical working curves are shown in Figs. 4 and 5, which also illustrate the method of correcting for blank value.

TEST OF THE METHOD

REPRODUCIBILITY—

The reproducibility of the spectrographic procedure (excluding that for lead) was assessed from replicate exposures of standard solutions. The tests were limited to four standards in the lower microgram range, since it was considered that the impurities in the samples would lie within this range. The reproducibility would probably be better at higher concentrations, at which the effect of background and blank would be less significant. Standards were exposed between four and eight times, each exposure being on a different plate. The standard deviation[2] and the coefficients of variation are shown in Table III.

TABLE III

REPRODUCIBILITY TESTS

	Standard containing 0·2 μg of element		Standard containing 0·1 μg of element		Standard containing 0·05 μg of element		Standard containing 0·02 μg of element	
Element	Standard deviation, μg	Coefficient of variation, %	Standard deviation, μg	Coefficient of variation, %	Standard deviation, μg	Coefficient of variation, %	Standard deviation, μg	Coefficient of variation, %
Magnesium	0·025	12·5	0·015	15	0·005	10	0·005	25
Manganese	0·020	10	0·010	10	0·006	12	0·005	25
Chromium	0·020	10	0·015	15	0·015	30	0·005	25
Bismuth	0·015	8·5	0·010	10	0·007	14	0·005	25
Nickel	0·015	8·5	0·005	5	0·007	14	0·004	20
Molybdenum	0·030	15	0·010	10	0·008	16	0·005	25
Beryllium	0·025	12·5	0·015	15	0·005	10	0·003	15
Titanium	0·020	10	0·005	5	0·005	10	0·005	25
Cobalt	0·010	5	0·005	5	0·006	12	0·003	15
Gallium	0·010	5	0·015	15	0·008	16	0·003	15
Indium	0·040	20	0·030	30	0·025	50	—	—
Zirconium	0·030	15	0·025	25	0·025	50	—	—
Zinc	0·020	10	0·015	15	—	—	—	—
Iron	0·030	15	—	—	—	—	—	—

It can be seen that, for the first ten elements, the reproducibility is satisfactory, the coefficient of variation for the range 0·2 to 0·05 μg (with the exception of that for chromium at 0·05 μg) being between 5 and 16 per cent., and at the 0·02-μg level between 15 and 25 per cent. Of the remaining elements zinc gives satisfactory reproducibility down to its limit of determination, namely 0·1 μg, whereas indium and zirconium give less satisfactory reproducibility below 0·2 μg, because the choice of lines is restricted to those of low density. The limit of sensitivity for iron was 0·2 μg and hence no figures are given below this value. No results are given for aluminium because adventitious contamination of some electrodes vitiated the tests, although subsequent work has indicated that reproducibility is satisfactory at the 0·05-μg level.

RECOVERY FROM EVAPORATION—

To test the reliability of the chemical procedure, standard additions of the impurities were made at concentrations equivalent to 0·01 and 0·1 p.p.m. to each of four specially purified acids, *i.e.*, nitric, hydrochloric, hydrofluoric and acetic. It was desirable to determine the recovery at two different concentration levels; further, a preliminary examination had indicated that the concentration of some elements was such (>0·03 p.p.m.) that reliable results would not be obtained from the addition of only 0·01 p.p.m. The amounts of elements recovered were calculated by deducting from the results on the "prepared" acids the amounts already determined in the untreated acids. The recoveries, based on single determinations, are shown in Table IV.

TABLE IV

RECOVERY OF IMPURITIES

	Element recovered (0·1 p.p.m. added) from—				Element recovered (0·01 p.p.m. added) from—			
Element	nitric acid, p.p.m.	hydrochloric acid, p.p.m.	hydrofluoric acid, p.p.m.	acetic acid, p.p.m.	nitric acid, p.p.m.	hydrochloric acid, p.p.m.	hydrofluoric acid, p.p.m.	acetic acid, p.p.m.
Magnesium ..	0·105	0·085	0·102	0·075	0·012	—	—	—
Manganese ..	0·135	0·105	0·115	0·115	0·010	0·011	0·012	0·012
Chromium ..	0·070	0·110	0·090	0·090	0·008	0·011	0·008	0·012
Bismuth ..	0·115	0·130	0·105	0·130	0·009	0·012	0·010	0·012
Aluminium ..	0·085	0·090	0·095	0·105	—	—	—	—
Nickel ..	0·100	0·115	0·095	0·095	0·009	0·008	0·008	0·011
Molybdenum	0·075	0·085	0·080	0·070	0·008	0·012	0·008	0·007
Beryllium ..	0·075	0·100	0·085	0·080	0·009	0·012	0·009	0·010
Indium ..	0·105	0·120	0·105	0·095	—	—	—	—
Zinc	0·140	0·100	0·105	0·115	—	—	—	—
Titanium ..	0·085	0·105	0·080	0·070	0·012	0·011	—	0·007
Zirconium ..	0·065	0·120	0·075	0·065	0·006	0·011	0·005	0·005
Cobalt ..	0·090	0·115	0·095	0·095	0·009	0·010	0·010	0·011
Iron	0·130	0·105	0·100	0·140	—	—	—	—
Gallium ..	0·105	0·115	0·095	0·105	0·013	0·013	0·013	0·015
Cadmium ..	0·120	0·100	0·075	0·090	—	—	—	—

As the recovery values are obtained from the difference between two results an error of around 25 per cent. is considered to be acceptable on these single determinations.

APPLICATION OF THE METHOD

As an example of the application of the method to a specific problem the results obtained on two sets of four acids are shown in Table V. One set of samples (A) was taken from specially purified acids and the other set (B) from analytical-reagent grade acids taken from stock.

TABLE V

ANALYSIS OF ACIDS

	Concentration of element found in nitric acid—		Concentration of element found in hydrochloric acid—		Concentration of element found in hydrofluoric acid—		Concentration of element found in acetic acid—	
Element	A, p.p.m.	B, p.p.m.	A, p.p.m.	B, p.p.m.	A, p.p.m.	B, p.p.m.	A, p.p.m.	B, p.p.m.
Magnesium ..	0·007	0·07	0·03	0·085	0·07	0·06	0·042	0·1
Manganese ..	<0·002	0·025	0·0025	0·065	0·003	0·003	<0·002	0·1
Chromium ..	0·012	0·025	<0·002	<0·002	0·003	<0·002	<0·003	0·002
Bismuth ..	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002
Aluminium ..	0·025	0·7	0·075	0·5	0·055	0·08	0·035	0·19
Nickel ..	0·002	0·015	0·005	<0·002	<0·002	0·002	<0·002	0·0025
Molybdenum	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002
Beryllium ..	<0·0002	<0·0002	<0·0002	<0·0002	<0·0002	<0·0002	<0·0002	<0·0002
Indium ..	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002
Zinc	0·025	0·07	0·04	0·035	0·023	0·28	0·065	0·082
Titanium ..	<0·002	0·004	0·006	0·1	0·3	0·08	0·003	0·005
Zirconium ..	<0·005	<0·005	<0·005	0·005	<0·005	<0·005	<0·005	<0·005
Cobalt ..	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002
Iron	0·055	0·043	0·14	0·3	0·26	0·38	0·075	0·05
Lead	0·015	0·15	0·025	0·295	0·35	0·27	<0·015	<0·015
Gallium ..	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002	<0·002

The results show that the impurity contents of the specially prepared nitric, hydrochloric and acetic acids are, with the exceptions of zinc and iron, considerably lower than those of the acids taken from stock. For hydrofluoric acid, however, the titanium concentration is higher in the specially prepared acid than in that of analytical-reagent grade; the only marked increase in purity being with reference to zinc. The hydrofluoric acid was subsequently distilled in platinum. This produced material of greater purity, which on analysis gave 0·015 p.p.m. of aluminium, <0·01 p.p.m. of zinc, 0·004 p.p.m. of titanium and <0·02 p.p.m. of lead.

The zinc and lead contents of the specially prepared hydrofluoric acid were determined in an independent laboratory by square-wave polarography. The means from several determinations were 0·018 and 0·36 p.p.m. (w/v), respectively, which are in good agreement with spectrographic figures.

CONCLUSION

The sensitivity obtainable depends primarily on the weight of sample taken. This can readily be increased when dealing with acids, although a longer time will thereby be required for evaporation and consequently the danger of adventitious contamination increases. When applying the method to the analysis of other materials, an increase in the weight of sample taken will necessitate the use of a larger volume of acid for its solution, and the limiting factor for some elements is therefore likely to be the purity of the acid itself.

The sensitivity of the method for any element, with due regard for the recovery from the chemical concentration, is probably best judged from a knowledge of the minimum weight of the element that can be determined with reasonable precision. Under the conditions of the proposed method these minimum weights are—

(*a*) 0·01 µg of magnesium, beryllium and cobalt;
(*b*) 0·02 µg of manganese, chromium, bismuth, molybdenum, nickel, titanium and gallium;
(*c*) 0·1 µg of aluminium, zirconium, zinc, lead and indium;
(*d*) 0·2 µg of iron (this figure would be lower were it not for the high blank value).

The minimum detectable amounts are less than these figures, sometimes by a substantial factor.

Finally, it should be noted that in attempting to determine many elements from one exposure, the choice of wavelength region has to be a compromise. This may result in the optimum sensitivity for some elements not being attained, since it is unlikely that the most sensitive lines for all of them will lie in the selected region.

We thank Dr. C. A. Parker for much helpful discussion and the Superintendent of the Admiralty Materials Laboratory for permission to publish this paper.

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DISCUSSION

MR. C. WHALLEY asked if the authors would give more details of the size and shape of the vessels used for the final evaporation. He also asked how critical was the temperature at which the evaporation took place, and whether the evaporation was carried out on a water bath. Finally, he enquired whether there was any danger of the formation of water-insoluble sulphates.

MR. OLFIELD replied that the platinum crucibles used were of normal size—approximately 37 mm in diameter and 40 mm deep, with a capacity of 30 ml. The evaporation was carried out on a silica hotplate, which was maintained at about 130° C. The procedure was standardised as far as possible, 10 ml of solution requiring about 4 hours for evaporation. The formation of water-insoluble sulphates was avoided by working in acid solutions. To ensure this, the second evaporation was taken only to the point of incipient fuming, so that in the addition of the final 0·1 ml of de-ionised water a solution of approximately normal sulphuric acid was formed.

The Colorimetric Micro-determination of Copper in Water: A Survey of Available Methods*

By B. TUCK and E. M. OSBORN

(*Central Electricity Generating Board, Yorkshire Division, Divisional Chemical Laboratory, Skelton Grange Power Station, Leeds* 9)

An evaluation of the available colorimetric methods for the direct micro-determination of copper has been carried out. The presence of interfering substances, such as iron, nickel and zinc, and of hydrazine and volatile amines, *e.g.*, *cyclo*hexylamine and morpholine, was investigated. The method involving use of 2:2′-diquinolyl is recommended; it is rapid, accurate and unaffected by the above-mentioned substances.

THE formation and deposition of metals and metallic oxides is considered to play a major role in boiler corrosion, particularly in areas where heat transfer is high. These depositions are carried into the boiler by solution of iron and copper in the feed-water system.

The recent advent of extra-high-pressure boilers has emphasised the need for feed waters of high purity. The Feed Water Standards Panel of the Central Electricity Generating Board has recommended[1] that, for boilers operating at 1500 lb per sq. inch or over, the concentration of copper and iron in feed waters should together not exceed 10 μg per litre.

A revision of analytical techniques was necessary to permit these impurities to be rapidly and accurately determined at these extremely low concentrations and has proved the desirability of using direct methods instead of prior concentrations by ion-exchange techniques.

Since the presence of copper in feed water indicates that active corrosion is occurring in the system, its rapid and accurate determination in the range 1 to 10 μg per litre has become a matter of great significance.

Of the five methods described, the first three, namely those involving use of sodium diethyldithiocarbamate, bis*cyclo*hexanone oxalyldihydrazone and oxalyldihydrazide, required prior concentration by ion-exchange methods to produce sufficient copper to be determinable.

This was carried out as described below—

Eight to ten litres of the condensate under examination were passed through a bed of Zeo-Karb 225 in the hydrogen form, approximately 1 cm in diameter and 4 to 5 cm deep, contained in a polythene column and supported by a disc of Whatman No. 541 filter-paper. A flow rate of about 2 litres per hour for a period of 4 to 5 hours was used. The resin was treated with 5 *N* hydrochloric acid and washed with water to produce a total effluent of 100 ml. Copper was normally determined in 25 ml of this effluent.

The presence of impurities, *viz.*, iron, nickel and zinc, and feed-line dosing chemicals —*cyclo*hexylamine, morpholine and hydrazine—has also been considered in this evaluation for subsequent use in power-station laboratories.

SODIUM DIETHYLDITHIOCARBAMATE METHOD

Sodium diethyldithiocarbamate forms sparingly soluble compounds with certain metals; the copper compound, when extracted by organic solvent, is suitable for the colorimetric determination of that metal.

REAGENTS—

All reagents should be of recognised analytical grade.

Bromine water, saturated.

Citric acid solution, 20 *per cent., aqueous.*

Ammonia solution, sp.gr. 0·880.

Sodium diethyldithiocarbamate solution, 0·1 *per cent., aqueous.*

Carbon tetrachloride.

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* Presented at the meeting of the Society on Wednesday, November 4th, 1959.

PROCEDURE—

Oxidise 25 ml of effluent from the ion-exchange column by adding 0·5 ml of bromine water, and boil until colourless. Add 2 ml of citric acid solution, make alkaline with ammonia solution, and add 2 ml of sodium diethyldithiocarbamate solution. Extract the brown colour produced with four 10-ml portions of carbon tetrachloride, combine the extracts, and make up to 50 ml in a calibrated flask. Measure the colour with a Spekker absorptiometer (Ilford No. 601 violet filter), and read the copper concentration from a graph prepared from the following figures—

Amount of copper present, µg ..	Nil	10	20	30	40
Absorptiometer-drum reading ..	1·000	0·915	0·822	0·720	0·618

TESTS FOR INTERFERENCE—

Interference was evident from iron, nickel and zinc, although interference from the last-named element was not expected; the results are shown in Table I. Experience showed that, although the concentration of nickel in boiler-feed water was only about 10 per cent. of the copper concentration, zinc was often present in amounts approximately equal to or greater than those of copper.[2]

TABLE I

RECOVERY OF COPPER BY THE SODIUM DIETHYLDITHIOCARBAMATE METHOD IN PRESENCE OF IRON, NICKEL AND ZINC

The absorptiometer-drum reading in absence of copper was 1·000

Amount of copper present, µg	Amount of iron present, µg	Amount of nickel present, µg	Amount of zinc present, µg	Absorptiometer-drum reading	Amount of copper found, µg
20	—	—	—	0·824	20
	20	5	5	0·805	22
50	—	—	—	0·485	50
	—	15	—	0·400	56
	—	—	30	0·433	53
	—	30	30	0·398	56
	—	—	30	0·455	52

The colour is not stable in the presence of light[3]; diffuse daylight causes fading within 1 hour.

BIS*cyclo*HEXANONE OXALYLDIHYDRAZONE METHOD

This method is based on procedures described by Nilsson[4] and by Wetlesen and Gran,[5] with modifications.[6] The reagent is stated to be highly sensitive for both cupric and cuprous copper. A blue complex is produced with copper in alkaline solution (pH 7 to 10).

REAGENTS—

Ammonium citrate solution, 10 *per cent., aqueous*—Prepare from analytical-reagent grade material.

Neutral red indicator solution, 0·05 *per cent., aqueous.*

Ammonia solution, sp.gr. 0·880—Analytical-reagent grade.

*Bis*cyclo*hexanone oxalyldihydrazone solution,* 0·5 *per cent., in* 50 *per cent. ethanol.*

PROCEDURE—

To 25 ml of effluent from the ion-exchange column add 0·5 ml of ammonium citrate solution, 1 drop of neutral red indicator solution and then ammonia solution dropwise until the colour is yellow. Dilute the solution almost to the mark in a 50-ml calibrated flask, and add 1 ml of bis*cyclo*hexanone oxalyldihydrazone solution. Dilute to the mark, mix well, and set aside for 30 minutes. Measure the colour produced with a Spekker absorptiometer (Ilford No. 606 yellow filter), and read the copper concentration from a graph prepared from the following figures—

Amount of copper present, µg ..	Nil	10	20	30	40	50
Absorptiometer-drum reading ..	1·000	0·882	0·705	0·558	0·412	0·265

Tests for interference—

The coloured complex is stable for some time. Slight interference was noted in presence of nickel and zinc (see Table II). Sandell[7] states that lead, nickel and zinc interfere.

The complex appears to be insoluble in all organic solvents and so cannot be concentrated by extraction.

Table II

Recovery of copper by the bis*cyclo*hexanone oxalyldihydrazone method in presence of iron, nickel and zinc

The absorptiometer-drum reading in absence of copper was 1·000

Amount of copper present, µg	Amount of iron present, µg	Amount of nickel present, µg	Amount of zinc present, µg	Absorptiometer-drum reading	Amount of copper found, µg
25	—	—	—	0·613	25
	100	—	—	0·639	24·5
	50	—	25	0·607	27
	—	25	—	0·603	27
10	—	100	—	0·878	8·5
	50	10	—	0·847	10·5
	50	10	10	0·853	10

The method is simple and has been used frequently in this laboratory when prior concentration has been carried out by ion exchange.

If larger amounts (from 5 to 10 mg) of other cations are present the volume of ammonium citrate solution used should be increased to 5 ml.[8]

Oxalyldihydrazide method

This method was described by Gran,[9] after a suggestion by Nilsson that the colour obtained in the reaction might be more intense and less sensitive to changes in pH than that obtained with bis*cyclo*hexanone oxalyldihydrazone.

Reagents—

Neutral red indicator solution, 0·05 per cent., aqueous.

Ammonia solution, sp.gr. 0·880—Analytical-reagent grade.

Formaldehyde or acetaldehyde solution, 40 per cent., aqueous.

Oxalyldihydrazide solution—Dissolve equimolecular weights of diethyl oxalate and hydrazine hydrate separately in five volumes of ethanol, and mix the solutions. (In less than 1 hour a nearly quantitative yield is obtained.) Wash the product with a little ethanol, recrystallise from boiling water, and prepare a saturated aqueous solution.

Procedure—

Add 1 drop of neutral red indicator solution to 25 ml of effluent from the ion-exchange column, and make just alkaline with ammonia solution. Add 4 ml of oxalyldihydrazide solution and then 10 ml of formaldehyde or acetaldehyde solution, dilute to 50 ml, mix well, and set aside for 30 minutes. Measure the colour produced with a Spekker absorptiometer (Ilford No. 606 yellow filter for the blue formaldehyde complex or Ilford No. 605 yellow-green filter for the violet acetaldehyde complex).

A calibration graph for the acetaldehyde modification can be prepared from the following figures—

Amount of copper present, µg ..	Nil	5	10	20	30	40
Absorptiometer-drum reading ..	1·000	0·922	0·835	0·668	0·510	0·360

Tests for interference—

Colour is most intense in the pH range 5 to 10, and the presence of phosphate is said to depress the colour intensity.[5] The colours produced with formaldehyde and acetaldehyde are stable for many hours. It can be seen from the results in Table III that excessive amounts of nickel and, to a lesser extent, iron depress the colour intensity.

The better procedure is that involving use of acetaldehyde; it is superior to determination by using bis*cyclo*hexanone oxalyldihydrazone.[9]

NEOCUPROINE METHOD

This method is specific for cuprous copper and involves the formation of a yellow-brown cuprous complex, which is extracted by chloroform. The procedure was described by Gahler[10]; he did not mention purification of reagents, but this was found to be necessary.

TABLE III

RECOVERY OF COPPER BY THE OXALYLDIHYDRAZIDE METHOD (ACETALDEHYDE MODIFICATION) IN PRESENCE OF IRON, NICKEL AND ZINC

The absorptiometer-drum reading in absence of copper was 1·000

Amount of copper present, µg	Amount of iron present, µg	Amount of nickel present, µg	Amount of zinc present, µg	Absorptiometer-drum reading	Amount of copper found, µg
20	—	—	—	0·670	20
	100	—	—	0·690	18·8
	50	—	20	0·675	19·8
	—	20	—	0·685	19·3
10	—	—	100	0·832	10·3
	—	100	—	0·862	8·5
	50	10	—	0·836	10·1
	50	10	10	0·852	9·6

REAGENTS—

Neocuproine solution—Prepare a 0·1 per cent. solution of 2:9-dimethyl-1:10-phenanthroline in ethanol.

Chloroform—Analytical-reagent grade.

Hydroxylamine hydrochloride solution—Prepare a 10 per cent. aqueous solution of analytical-reagent grade hydroxylamine hydrochloride, add 5 ml of neocuproine solution, and extract with three 20-ml portions of chloroform. Store the purified solution in a polythene bottle.

Sodium citrate solution—Prepare a 30 per cent. aqueous solution of analytical-reagent grade sodium citrate, add 10 ml of hydroxylamine hydrochloride solution and 5 ml of neocuproine solution, and extract with three 20-ml portions of chloroform.

PROCEDURE—

Place 400 ml of the sample in a 500-ml separating funnel, reduce by adding 2 ml of hydroxylamine hydrochloride solution, and form the complex by adding 10 ml of sodium citrate solution (the pH of the solution should be about 6). Add 2 ml of noeocuproine solution, and extract the pale-yellow colour of the cuprous complex in 10 ml of chloroform. By pipette, place 5 ml of ethanol in a 25-ml calibrated flask, and slowly run in the chloroform layer, agitating the flask to ensure thorough mixing. (This is necessary because the neocuproine may be precipitated, so producing a cloudy solution.) As the partition coefficient of the complex between chloroform and water is high, only a further 5-ml portion of chloroform is required to complete the extraction. Dilute the contents of the flask to the mark with chloroform, and measure the colour with a Spekker absorptiometer (Ilford No. 60 = 1 violet filter). Note that the final dilution is with chloroform; the use of ethanol, as recommended by Gahler,[10] produced precipitation.

The readings obtained with two series of standard solutions were—

Amount of copper present, µg	Nil	2	4	7	10	12
Absorptiometer-drum reading (first series)	1·000	0·960	0·935	0·888	0·840	0·808
Absorptiometer-drum reading (second series)	1·000	0·966	0·937	0·890	0·845	0·814

TESTS FOR INTERFERENCE—

It was decided to examine the effect of iron on the colour produced by copper, although Smith and McCurdy[11] stated that cuprous copper was the only cation to form a complex. Ratios of ten parts of iron to one part of copper produced no adverse effect whatsoever.

Amounts of cyanide greater than 1 mg should not be present, and the recovery of copper in presence of sulphide is only 37 per cent. Perchlorate, phosphate, fluoride and ammonium ions do not interfere. Luke and Campbell[12] have tested the effects of fifty-seven cations; none was found to interfere.

Vol. 85, 1960: February, p. 108.

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with chloroform, and measure the colour with a Spekker absorptiometer (Ilford No. 601

2:2′-DIQUINOLYL METHOD

The use of 2:2′-diquinolyl has been reported,[13,14,15] and the procedure described below was found to be suitable.

REAGENTS—

Tartaric acid solution, 50 per cent., aqueous—Prepare from analytical-reagent grade tartaric acid.

Hydroxylamine hydrochloride solution, 10 per cent., aqueous—Prepare from analytical-reagent grade hydroxylamine hydrochloride, and store in a polythene bottle.

Sodium hydroxide, 5 N—Prepare from analytical-reagent grade sodium hydroxide.

2:2′-Diquinolyl solution, 0·05 *per cent., in amyl alcohol.*

Sodium sulphate, anhydrous—Analytical-reagent grade.

Amyl alcohol—Analytical-reagent grade.

NOTE—It was necessary to remove traces of copper from the hydroxylamine hydrochloride and tartaric acid solutions in a manner similar to that described for hydroxylamine hydrochloride and sodium citrate solutions under "Neocuproine Method."

PROCEDURE—

Place 400 ml of the sample in a 500-ml separating funnel, and add 2 ml each of tartaric acid and hydroxylamine hydrochloride solutions. Adjust the pH to between 5 and 6 by using 5 *N* sodium hydroxide and a narrow-range indicator paper (this is critical in that no coloured complex will form below pH 4 or above pH 7). Form the lilac-coloured complex by adding 10 ml of 2:2′-diquinolyl solution (an excess produces a milky cloud). Extract the complex in two 20-ml portions of amyl alcohol, dry the combined extracts by swirling with anhydrous sodium sulphate, and filter into a 50-ml calibrated flask. Dilute to the mark with amyl alcohol, and measure the colour produced with a Spekker absorptiometer (Ilford No. 604 green filter).

A calibration graph was prepared from the following figures—

Amount of copper present, µg ..	Nil	2	4	6	8	10
Absorptiometer-drum reading ..	1·000	0·989	0·978	0·967	0·957	0·947

TESTS FOR INTERFERENCE—

Iron, nickel and zinc do not interfere in the determination. The absorptiometer-drum reading in presence of 6 µg of copper was 0·967; the readings for 6-µg amounts of copper in presence of 100 µg of iron, nickel and zinc were 0·966, 0·966 and 0·967, respectively.

In addition to interfering metals, boiler-feed waters may contain any of several chemicals added to reduce corrosion potentialities. These include hydrazine, used as an oxygen scavenger, volatile amines, such as *cyclo*hexylamine and morpholine, which increase the pH and in effect act as carbon dioxide scavengers, and filming amines, which cause dropwise condensation to occur and so reduce the possibility of corrosive action. Hydrazine, when used, is added to the extent of approximately 0·02 to 0·05 p.p.m. and will reduce copper and iron to states of lower valency; it does not interfere with the determination.

The effects of *cyclo*hexylamine and morpholine on the neocuproine and the 2:2′-diquinolyl methods were tested separately. At a concentration of 10 mg per litre, about five times that found in a normal feed-water system, neither amine had any effect on the determination of copper.

CONCLUSIONS

The sodium diethyldithiocarbamate method has been shown to lack sensitivity and selectivity; its use is not recommended.

The bis*cyclo*hexanone oxalyldihydrazone and oxalyldihydrazide methods are easy to carry out and can be recommended for determining larger amounts of copper than are normally found in this type of system or if the sample is previously concentrated by ion exchange.

Use of the above-mentioned methods necessitates preliminary ion-exchange techniques, and the result is an average figure over the period of the test; this is obviously less satisfactory than a series of spot tests carried out over the same period and producing individual results.

This led to the adoption of the neocuproine method, which was superseded by the 2:2′-diquinolyl method. The latter is preferred because of its superior colour, lilac as against yellow, because it is much easier to carry out and because reproducibility is excellent near the zero point on the calibration graph.

The presence of any of the substances encountered in boiler-feed water, including hydrazine and volatile amines, causes no interference with the more sensitive methods.

We thank the Divisional Controller, Yorkshire Division, Central Electricity Generating Board, for permission to publish this paper.

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DISCUSSION

MR. C. WHALLEY asked if the lecturer would give more details about the sensitivity of the neocuproine method compared with the diethyldithiocarbamate procedure. He had never found any increase beyond a factor of about 2 with the two methods. He asked if the greater sensitivity found by the authors was due to variations in the extraction procedure.

MR. TUCK replied that they had found that, with neocuproine, 0·002 p.p.m. could be determined, but only about 0·02 p.p.m. with sodium diethyldithiocarbamate. This excluded the consideration of interference in the latter method by other metals present.

DR. N. EVERS said that new methods for the determination of copper frequently appeared in *Analytical Abstracts* and many of them were claimed to be superior to existing methods, but it was comparatively rare to find a paper in which different methods were assessed impartially. The paper just presented was therefore most valuable.

MR. TUCK thanked Dr. Evers for his kind remarks, and added that, although there were many methods for determining small amounts of copper, those examined probably represented a fair cross-section.

The Separation and Determination of Free Purines, Pyrimidines and Nucleoside in Cod Muscle

By N. R. JONES

(*Department of Scientific and Industrial Research, Torry Research Station, Aberdeen*)

A procedure is described for the quantitative separation of purines, pyrimidines and nucleoside present in extracts of cod muscle. After the removal of nucleotide at pH 6·5 by a strongly basic anion-exchange resin in the formate form, the purines, etc., are exchanged on to a similar resin in chloride form at pH 11 to 12. They are then eluted by a gradient of increasing chloride and tetraborate concentrations, and diminishing pH, for evaluation by ultra-violet spectrophotometry.

THE nitrogenous extractives and volatile substances in fish muscle are major flavouring constituents, and, in recent years, it has been established that their changes provide objective indexes of the freshness of fish.[1] Work in this laboratory[1,2,3] has indicated that the catabolism of nucleotides in cod muscle is of considerable technological importance. More recently, Saito, Arai and Matsuyoshi[4] have described an evaluation of a combined fraction of hypoxanthine and inosine, separated from nucleotides chromatographically, as a measure of the degradation of adenine nucleotide and hence of freshness. In our experience, the determination of hypoxanthine alone has been of greater value than the simpler combined measurement, and the presence or absence of other purines has been found to give an indication of the physiological condition of the fish before death. A satisfactory and reasonably rapid procedure for complete analysis was therefore required.

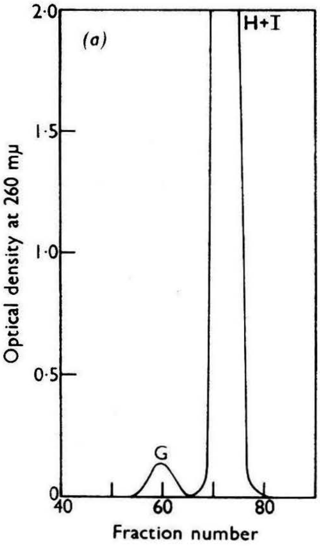
Chromatography appeared to be the most suitable method of analysis. Cohn[5] reported separations of synthetic mixtures of purines and pyrimidines and of mixtures of ribonucleosides[6] on anion-exchange resins. Saito and Arai[7] separated a crude fraction containing both hypoxanthine and inosine from extracts of carp muscle by stepwise elution from a similar resin system. This paper describes separations of hypoxanthine from other purines and pyrimidines and inosine (hypoxanthine riboside) by a rapid system of gradient elution from an anion-exchange resin. No attendance on the column to change eluting agents is necessary and interfering nucleotide is removed in a preliminary operation.

EXPERIMENTAL

Naturally occurring purines, pyrimidines and nucleosides other than adenosine are anionisable to a degree whereby they may be exchanged for chloride on strongly basic anion-exchange resins at pH 11 to 12. At this pH, however, the nucleotides occurring in muscle extracts are unstable, and systems for nucleoside and base analysis cannot be safely subjected to such alkalinity. Nucleotides have therefore been removed from the extracts in a preliminary step by ion exchange on Dowex 1 (formate) at pH 6·5. The resin was used in this form in preference to the chloride form because less resin was required, there being no interference from the chloride ion in the extracts.

The nucleotide-free extracts were adjusted to pH 11 to 12 with ammonia and were then passed through a column of Dowex 1 (chloride), on which the purines, etc., were held. Initially they were eluted by a gradient of increasing chloride concentration and decreasing pH, as it was hoped that van der Waals forces between the resin particles and the pentose moiety might retard the passage of inosine sufficiently to effect a separation from hypoxanthine, which has an almost identical p*K*.[8,9] This hope was not realised, but it was found that the presence of tetraborate, forming a relatively strong acid by its complex with the ribose of inosine, was effective (see Figs. 1*a* and 1*b*).

Separations of a synthetic mixture of purines, pyrimidines and inosine and of a nucleotide-free extract are shown in Fig. 2, optical-density measurements on the fractions being made at an arbitrary 260 mμ. In practice only a single nucleotide, inosine, has been detected in separations of cod-muscle extracts by this procedure. The homogeneity of the inosine peak has been established from a comparison of the absorption at 248 mμ (approximately the maximum of hypoxanthine derivatives in acid) and the bound-ribose concentration estimated as described by Meijbaum.[10] An average ratio of 1 equivalent of hypoxanthine to 0·98 equivalent of ribose was obtained from 10 samples of fish in different stages of spoilage. The purities of the other peaks were determined by reference to known ultra-violet absorption data; all peaks other than that of hypoxanthine were uncontaminated. Indications were obtained in some separations that, although there was no inflexion indicative of the presence of adenine on the hypoxanthine peak, 1 to 4 per cent. of the former base was present in some samples. This was estimated by solving the simultaneous equations—



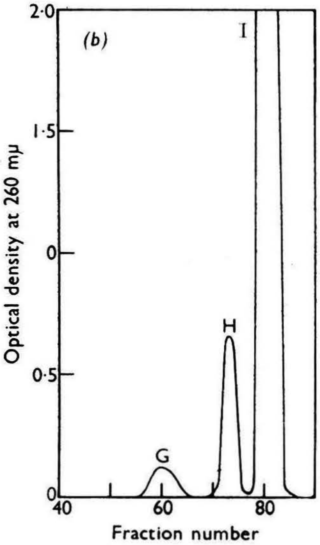


Fig. 1(*a*). Chromatographic separation of the purine constituents of cod muscle in the absence of tetraborate: G, guanine; H, hypoxanthine; I, inosine

(Extract equivalent to 5 g of muscle was separated; the mixing vessel contained 200 ml of 0·2 *N* ammonium hydroxide - 0·025 *N* hydrochloric acid and the reservoir contained 0·05 *N* hydrochloric acid)

Fig. 1(*b*). Chromatographic separation of the purine constituents of cod-muscle extract in the presence of tetraborate: G, guanine; H, hypoxanthine; I, inosine.

(Conditions as for Fig. 1(*a*), except that the reservoir contained 0·05 *N* hydrochloric acid - 0·01 *M* sodium tetraborate)

$$E_{248} = 10{\cdot}8x + 8{\cdot}9y$$
$$E_{260} = 7{\cdot}35x + 13{\cdot}0y$$

where E_{248} and E_{260} are the optical densities of the bulked fractions of the peak at 248 and 260 mμ in 2 *N* hydrochloric acid, x and y are the molar ratios of hypoxanthine and adenine, respectively, and the constants are the millimolar extinctions of the bases at the two wavelengths.[11] However, estimations of such low concentrations of adenine are of doubtful significance, as the molar extinctions reported by different workers vary appreciably.

An investigation of the material not held on Dowex 1 (chloride) at pH 11 has established that adenosine is normally absent from extracts of cod muscle. Levels higher than 0·4 mg per 100 g of tissue have not been recorded.

The peak after that of inosine in separations of extracts contains no purine or pyrimidine residue. The absorption at 260 mμ represents the "tail" of an "end-group" absorption that increases steadily with decrease in wavelength.

METHOD

APPARATUS—

Dowex 1 (*formate*) *column assembly*—A 100-ml separating funnel leads through a rubber or ground-glass seal into a glass column, 4 cm × 1·8 cm, fitted at its lower end with a glass-wool plug. The column contains a 2-cm bed of Dowex 1 (formate).

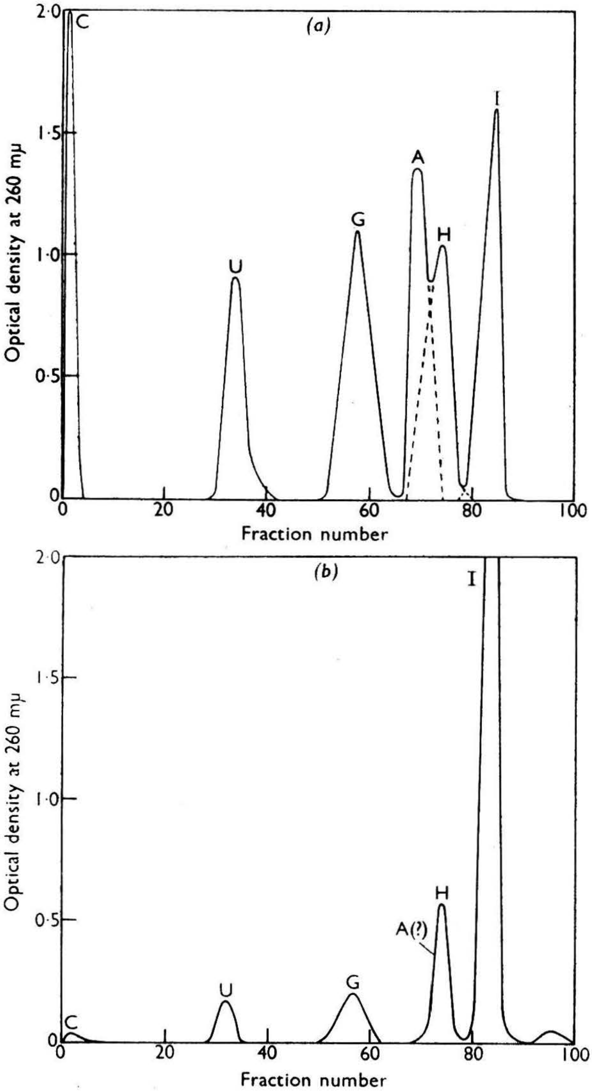


Fig. 2. Separation of cytosine (C), uracil (U), guanine (G), adenine (A), hypoxanthine (H) and inosine (I) from:

(*a*) a synthetic mixture

(*b*) an extract equivalent to 5 g of cod muscle (see "Method")

Dowex 1 (*chloride*) *column assembly*—A 500-ml separating funnel (the reservoir) leads into a 250-ml conical flask (the mixing vessel) fitted near the base with a right-angled side-tube, 3 mm in diameter and about 15 cm long. The mixing vessel contains a glass-sheathed stirrer bar and is placed on a small magnetic-stirrer motor. For flexibility a 5-cm length of polythene tubing is interposed between the side-arm of the mixing vessel and a 4-cm length of glass tubing, which leads through a rubber stopper into a glass column, 15 cm × 1·3 cm. The column is fitted with a two-way tap at the base, and a glass-wool plug is inserted immediately above the tap, so giving a minimum of dead space. A small right-angled side-arm is fitted to the column 3 cm from the top. A short length of rubber tubing is attached, and both this and the polythene tubing are fitted with screw-clips. The column contains an 8-cm bed of Dowex 1 (chloride).

Fraction collector—To collect 5-ml fractions.

Buchner funnel and flask—The flask is chilled in ice. The Whatman No. 1 filter-paper in the funnel is washed before use with dilute hydrochloric acid and with water to remove material absorbing at 260 mμ.

REAGENTS—

Perchloric acid, 0·6 M.

Hydrochloric acid, concentrated.

Ammonium hydroxide, 2 N.

Potassium hydroxide, 5 N.

Reservoir solution—A solution of 0·05 *N* hydrochloric acid containing 0·01 *M* sodium tetraborate, $Na_2B_4O_7$.

Mixing vessel solution—A 0·2 *N* solution of ammonium hydroxide containing 0·02 *N* hydrochloric acid.

Dowex 1–8x (*formate*)—Suspend Dowex 1–8x (chloride), 200 to 400 mesh (obtained from Howe & Co. Ltd., 46 Pembridge Road, London, W.11) in water, and pour into the detached column until a sedimented bed 2 cm deep is obtained. Wash the bed with ten times its volume of a solution containing 6 *N* formic acid and 1 *M* sodium formate, a similar volume of 88 per cent. w/v formic acid[12] and then with water until the effluent is free from acid. Do not allow the column to run dry.

Dowex 1–8x (*chloride*)—Suspend the commercial resin in water, and pour the slurry into the detached column until an 8-cm bed has separated. Wash the bed with fifty times its volume of 6 *N* ammonium hydroxide, with water until the effluent is free from ammonia, with twenty times its volume of 2 *N* hydrochloric acid and again with water until free from acid. Repeat the cycle of ammonia and acid washing. This procedure is necessary to remove from the resin material absorbing at 260 mμ. Do not allow the column to run dry.

PROCEDURE—

Extraction—Dissect 6 to 10 g of muscle, and homogenise into 2 volumes of chilled 0·6 *N* perchloric acid. Filter the mixture rapidly at 0° C, and immediately adjust the pH of the filtrate to 6·5 by carefully adding 5 *N* potassium hydroxide. Do not allow the pH to rise above this value, as there is a danger that the nucleotides may break down. After 30 minutes at 0° C, remove any potassium perchlorate that has crystallised.

Removal of nucleotides—Run an aliquot equivalent to 5 g of tissue through the column of Dowex 1 (formate). Wash with water until the optical density of the effluent has decreased to 0·01 at 260 mμ. The effluent and washings contain the nucleoside, purine and pyrimidine fractions.

Separation of purines, pyrimidines and nucleosides—Adjust the pH of the effluent and washings from the Dowex 1 (formate) column to between 11 and 12 with 2 *N* ammonium hydroxide. Run the combined effluent and washings through the column of Dowex 1 (chloride) from a separating funnel. Wash with water containing 2 drops of 2 *N* ammonium hydroxide per 50 ml until the optical density of the effluent has decreased to 0·01 at 260 mμ. Attach the column to the assembly, and, with the polythene connection closed, pour 200 ml of a solution of 0·2 *N* ammonium hydroxide containing 0·02 *N* hydrochloric acid into the mixing vessel. Attach the reservoir to the assembly, and fill it with the solution of 0·05 *N* hydrochloric acid containing 0·01 *M* sodium tetraborate. Start the stirrer. Open the reservoir stopcock and the polythene connection, and, by means of the screw-clip on the side-arm of the column, release sufficient air to break the air-lock between the column and the mixing vessel. Open the column stopcock, and start the collector. Collect ninety 5-ml fractions over 2 to 16 hours, as convenient. Measure their optical densities at 260 mμ to establish the positions of the peaks, and combine the fractions of individual peaks. Add hydrochloric acid to 2 *N*, and make optical density measurements at the appropriate absorption maxima for evaluation against the known molar extinction coefficients.[11] This procedure is preferable to calculations based on the direct evaluation of the concentrations in the fractions from their absorptions at 260 mμ, as the pH (and hence the extinction coefficient) may change appreciably from the front to the tail of a large peak. Also, the combination of fractions allows the dilution of large peaks to a concentration at which Beer's law applies.

RESULTS

The peaks obtained during the separations of a synthetic mixture and of an extract of cod muscle are shown in Fig. 2, and Table I shows the recoveries when 1-μmole amounts of the different bases were added to an extract of muscle.

TABLE I

RECOVERY OF ADDED BASES FROM COD-MUSCLE EXTRACT

Extracts equivalent to 5 g of muscle from a fish stored in ice for 8 days were separated

			Base found per 5 g of muscle—		
Base	Absorption maximum, mμ	Molar extinction coefficient ($\times 10^{-3}$)	in absence of added base, μmole	in presence of 1 μmole of added base, μmole	Recovery, %
Cytosine	276	10·0	0·04, 0·04	1·07, 1·04	102
Uracil	260	8·2	0·29, 0·31	1·26, 1·30	98
Guanine	275	7·35	0·91, 0·94	1·89, 1·95	100
Adenine* ..	262	13·15	0·05, 0·06	1·10, 1·12	105
Hypoxanthine* ..	248	10·8	3·41, 3·49	4·45, 4·51	103
Inosine	251	10·9	18·0, 18·4	19·2, 19·4	110

* Estimated by using the simultaneous equations on p. 112.

CONCLUSIONS

The proposed method provides a reasonably accurate and rapid procedure for separating and determining the purines, pyrimidine and nucleoside present in cod muscle. Its use for other tissues should be preceded by an investigation of a peak running in the position of inosine to establish that it is not contaminated with other nucleosides. As batches of resin vary slightly in their chromatographic behaviour, it is also desirable to carry out a trial run with pure bases to establish the exact positions of the peaks before analysis.

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A Method for the Quantitative Micro-determination of Diphenyl

Quantitative Determination of Diphenyl in Paper Wrappers

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A colorimetric method is described for the micro-determination of diphenyl. With concentrated sulphuric acid, traces of formaldehyde and ferric iron, diphenyl gives an intense blue colour. If certain conditions are fulfilled, the reaction conforms to the Beer - Lambert law up to 14 μg of diphenyl per 5 ml of reagents. The method is suitable for determining diphenyl in paper wrappers.

SINCE wrappers impregnated with diphenyl have so far been the most effective means of preventing rotting in citrus fruits, it was considered important to devise a method for the reliable determination of the diphenyl content of paper used for wrapping.

Many investigations have been carried out in recent years in attempts to devise a method for determining small amounts of diphenyl in wrappers and fruits. The colorimetric[1,2,3] and spectrophotometric[4,5,6,7,8,9] methods used are rather laborious and almost invariably necessitate the use of costly apparatus, which is not available in most laboratories.

The proposed method based on a colour reaction is simple and rapid and permits the determination of extremely small amounts of diphenyl with the use of an ordinary absorptiometer.

In this paper the reaction is discussed and a description is given of a method for determining diphenyl in wrappers.

EXPERIMENTAL

When pure concentrated sulphuric acid and traces of formaldehyde and ferric iron are added to extremely small amounts of diphenyl dissolved in an organic solvent, such as ethanol, glacial acetic acid, acetone, diethyl ether or methanol, a blue-coloured solution is immediately obtained. The intensity of colour increases with the amount of diphenyl.

The colour changes slowly to violet. When the solution is heated or 37 per cent. formaldehyde is added this change of colour is greatly speeded up. Dilution with distilled water, 95 per cent. ethanol or glacial acetic acid results in disappearance of the colour. When tap-water is added, the colour changes to violet and then soon disappears.

SPECIFICITY OF THE COLOUR REACTION—

The effects of the reagents and their combination were tested with diphenyl and its derivatives and with some other aromatic hydrocarbons (see Table I). Benzidine does not give a colour reaction with any of the reagents used. Traces of formaldehyde do not generally affect the colour obtained with sulphuric acid alone. On addition of ferric iron, intense colours are produced in all instances except that of diphenyl in acetic acid (the feeble green colour is most probably caused by formaldehyde present as impurity in the acetic acid). The subsequent addition of formaldehyde brings about a change of colour with diphenyl and its derivatives. The blue-green colour of fluorene turns clear blue when the solution is heated or set aside for a long time. The instantaneous, intense blue colour occurs solely with diphenyl.

SENSITIVITY OF THE REACTION—

The reaction can be employed for the determination of extremely small amounts of diphenyl and also of *o*-phenylphenol, sodium *o*-phenylphenate and fluorene. Amounts of the order of 1 μg of these compounds, with 5 ml of reagents, produce colours sufficiently intense to be discernible visually.

The other hydrocarbons listed in Table I give insufficiently distinct colours, even when larger amounts are used.

CONDITIONS OF REACTION—

Solvent—Chloroform ensures the best extraction of diphenyl from wrappers; however, in this solvent the colour reaction proceeds slowly, and the colour of the mixture obtained is not suitable for measurement. When sufficient glacial acetic acid is added, *e.g.*, 9 volumes to 1 volume of chloroform, the blue solution is obtained.

Mineral acid—The colour reaction takes place only in the presence of concentrated sulphuric acid; there is no reaction with hydrochloric or nitric acid.

The maximum amount of sulphuric acid required is about 3 volumes to 1 volume of solvents. In order to ensure the instantaneous development of full colour intensity when 5 ml of sulphuric acid are used, it is advisable to limit the total volume of solvents—chloroform and acetic acid—to 0·2 ml.

Ferric iron—Ferric oxide, ferric chloride and ferric sulphate bring out the blue colour. The colour is obtained with extremely small amounts of ferric iron, of the order of 1 μg per 10 μg of diphenyl, but it develops slowly and does not attain maximum intensity. With larger amounts of ferric iron the blue colour is produced immediately and soon reaches full intensity. A relatively large excess of ferric iron does not interfere with the reaction. Ferrous iron and cupric copper give no reaction.

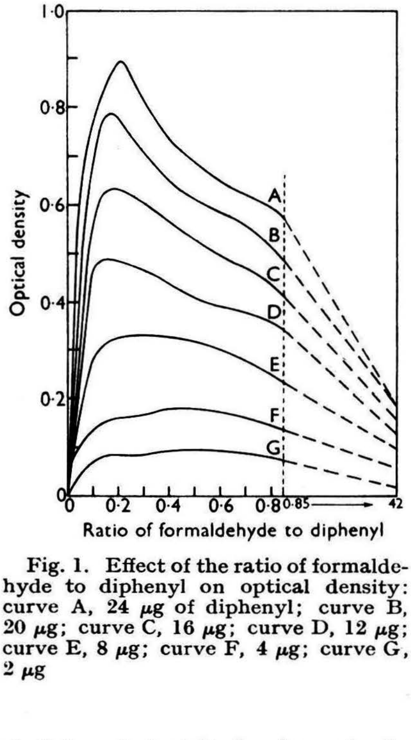


Fig. 1. Effect of the ratio of formaldehyde to diphenyl on optical density: curve A, 24 μg of diphenyl; curve B, 20 μg; curve C, 16 μg; curve D, 12 μg; curve E, 8 μg; curve F, 4 μg; curve G, 2 μg

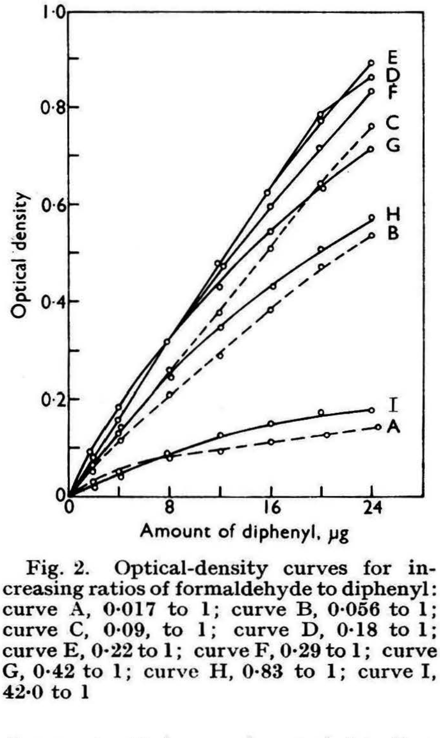


Fig. 2. Optical-density curves for increasing ratios of formaldehyde to diphenyl: curve A, 0·017 to 1; curve B, 0·056 to 1; curve C, 0·09, to 1; curve D, 0·18 to 1; curve E, 0·22 to 1; curve F, 0·29 to 1; curve G, 0·42 to 1; curve H, 0·83 to 1; curve I, 42·0 to 1

Ferric iron seems to act as an oxidising agent. In fact, the blue colour is also obtained when ferric iron is replaced by traces of other oxidising agents, such as potassium permanganate or potassium dichromate. The colour disappears, however, with an excess of these reagents.

Formaldehyde—When proceeding as described for the construction of the standard graph (see p. 119), but adding increasing amounts of formaldehyde to a given amount of diphenyl (see Fig. 1), the colour intensity increases rapidly, and, after reaching a maximum, decreases gradually. For all amounts of diphenyl the maximum is attained when the ratio of formaldehyde to diphenyl is approximately 0·18 to 1. Only when this ratio is between 0·09 and 0·22 to 1, *i.e.*, between one and two molecules of formaldehyde for every two molecules of diphenyl, does the reaction proceed in accordance with the Beer - Lambert law (see Fig. 2).

ORDER AND MODE OF INTRODUCING REAGENTS—

To ensure the appearance of the characteristic colours listed under D in Table I, formaldehyde and ferric iron must be added quickly after the sulphuric acid. If sulphuric acid, or the reagents B or C, is allowed to react for a few minutes alone with the hydrocarbons, then the addition of the other reagents—formaldehyde or ferric iron—has no effect on the colours obtained with reagents A, B or C. Only the acetic acid solution of diphenyl, which is colourless with sulphuric acid and formaldehyde, becomes slowly purple on addition of ferric iron, but in no instance does the characteristic colour indicated in column D develop. It is probable that blocking of the hydrocarbons by sulphonation prevents the appearance of the coloured derivatives.

TABLE I

ACTION OF SULPHURIC ACID, TRACES OF FORMALDEHYDE AND FERRIC IRON ON VARIOUS AROMATIC HYDROCARBONS

All results apply to 50 to 100 μg of hydrocarbon in 0·1 ml of solvent

Aromatic hydrocarbon	With 95 per cent. ethanol as solvent				With glacial acetic acid as solvent			
	A	B	C	D	A	B	C	D
Diphenyl ..	Pink	Pink	Violet-red	Intense blue	Colourless	Colourless	Greenish	Intense blue
o-Phenylphenol ..	Pink	Pink	Dark green	Brownish pink	Colourless	Colourless	Dark green	Brownish pink
Sodium *o*-phenylphenate ..	Raspberry-red	Pink	Reddish violet	Brownish pink	Colourless	Colourless	Green	Brownish red
Benzidine ..	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Fluorene ..	Pink	Violet-red	Olive-green	Bluish green	Colourless (greenish?)	Colourless (blue?)	Dark green	Blue-green
Naphthalene	Yellow	Yellow	Plum-violet	Plum-violet	Colourless	Colourless	Plum-violet	Plum-violet
Anthracene	Orange-red	Red	Greyish pink	Greyish pink	Brown	Brown	Greyish pink	Greyish pink
Phenanthrene	Pink	Pink	Olive-green	Blue-green	Yellow	Yellow	Olive-green	Olive-green
Benzene ..	Yellow	Yellow	Orange	Orange	Yellow	Yellow	Orange	Orange
Phenol ..	Colourless	Orange	Yellow	Lilac-red	Colourless	Colourless	Greenish	Greenish

A = 2 ml of pure concentrated sulphuric acid added.
B = A and 5 μg of formaldehyde added.
C = A and 250 μg of ferric iron added.
D = A, 5 μg of formaldehyde and 250 μg of ferric iron added.

To prevent any previous action of sulphuric acid on diphenyl, sulphuric acid with ferric iron should be added to a diphenyl solution already containing formaldehyde.

METHOD

It has been found convenient to prepare the chloroform solutions of diphenyl in a way such that 1 ml should contain about 800 μg of diphenyl. The ratio of formaldehyde to diphenyl has been fixed at 0·187 to 1.

APPARATUS—

Absorptiometer—A Hilger absorptiometer, type H810, with 6-inch × $\frac{5}{8}$-inch tubes was used.

Test-tubes, 150 *mm* × 16 *mm*.

Graduated tubes—Ten-millilitre tubes, with ground-glass stoppers.

Micropipettes—Curved tip 0·1 and 0·2-ml pipettes, graduated at 0·001-ml intervals.

REAGENTS—

All reagents should be of recognised analytical grade.

Standard diphenyl solution—Dissolve 80 mg of pure diphenyl in chloroform, and make up to 100 ml.

Acetic acid reagent—Mix 1 ml of 37 per cent. formaldehyde solution with glacial acetic acid to make 100 ml. Determine colorimetrically the amount of formaldehyde impurity present in the glacial acetic acid, and then add the necessary amount of the prepared solution to obtain an acetic acid reagent containing 16·6 mg of formaldehyde per litre. Check the formaldehyde content of the reagent as described below.

Prepare a standard solution containing 16·6 mg of formaldehyde per litre of water by mixing 1 ml of 37 per cent. formaldehyde with distilled water to make 100 ml; then dilute a 4·5-ml portion of this solution to 1 litre. Place 0·0, 0·5, 0·10 and 0·15 ml of the standard solution and 0·05, 0·10 and 0·15 ml of acetic acid reagent in separate test-tubes; add 5 ml of chromotropic acid reagent—500 mg of chromotropic acid in 100 ml of diluted sulphuric acid (4 + 2·8)—to the contents of each test-tube. Place the test-tubes in boiling water for 15 minutes, and then cool, and determine the optical densities at 610 mμ, an orange filter being used. Set the absorptiometer to zero against the first test-tube. Equal amounts of acetic acid reagent and standard solution should show the same optical densities.

Sulphuric acid reagent—Prepare a stock solution by dissolving 50 g of ferric sulphate in 950 ml of diluted sulphuric acid (1 + 8·5).

For use, mix 5 ml of stock solution with 95 ml of concentrated sulphuric acid; prepare daily.

Chloroform.

Bone charcoal powder (not absorbing diphenyl).

PREPARATION OF STANDARD GRAPH—

Mix 1 ml of the standard solution of diphenyl with 9 ml of acetic acid reagent in a graduated 10-ml tube. Each 0·1 ml of this mixture contains 8 μg of diphenyl. Place at the bottom of separate test tubes 0·025, 0·05, 0·10, 0·15, 0·20, 0·25 and 0·30 ml of this diphenyl mixture (see Note). Gradually add 5 ml of sulphuric acid reagent to the contents of each test-tube. After introducing a small amount, mix vigorously until full colour intensity is obtained; then add the rest of the reagent, mixing thoroughly. The colour obtained should be clear; any secondary colour, such as grey or violet, indicates failure of the test. Wait a few minutes until gas bubbles have disappeared, and then measure the optical densities with an orange filter at 610 mμ. Set the absorptiometer to zero with the sulphuric acid reagent alone.

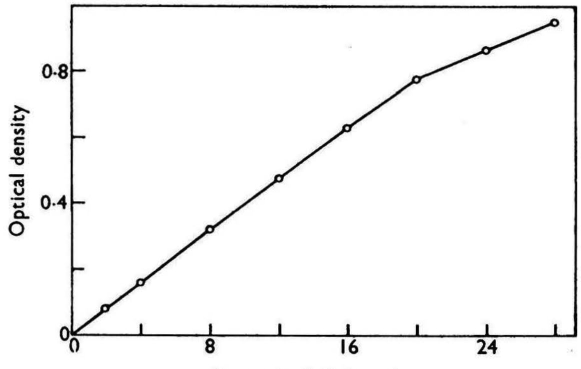


Fig. 3. Standard graph

The standard graph (see Fig. 3) shows that the Beer - Lambert law is obeyed up to 14 μg of diphenyl in 5 ml of reagent. The standard graph was found to be reproducible at different times and with various solutions of diphenyl.

NOTE—The differences in the final volumes caused by adding increasing amounts of diphenyl solution and acetic acid reagent are slight and can be ignored. Inclusion of supplementary amounts of chloroform and acetic acid would complicate the procedure and result in an unwarranted change in the amount of formaldehyde. The use of small volumes of sulphuric acid reagent gives unsatisfactory results.

PROCEDURE—

Extraction of diphenyl with chloroform may be carried out with or without heating.

Hot extraction—Place one or several diphenyl-impregnated wrappers in a Soxhlet extraction apparatus. Extract diphenyl with chloroform for 1 hour. Collect the chloroform extract quantitatively, and note its volume.

Cold extraction—Place one or several diphenyl-impregnated wrappers in a flask having a ground-glass stopper. Add an exactly measured amount of chloroform (50 to 100 ml). Close the flask, and shake for 20 minutes.

Purification of the extract—Withdraw a portion of the extract, mix with a little bone charcoal powder, and filter.

Calculation of required volume of extract—To calculate the volume of extract containing about 800 μg of diphenyl, place 0·01-ml portions of the extract in three test-tubes, and add 0·09, 0·14 or 0·19 ml of acetic acid reagent. Add 5 ml of sulphuric acid reagent to the contents of each test-tube. Measure the optical densities of the colours obtained.

If the contents of the three test-tubes have about the same optical density, calculate approximately the volume required.

TABLE II

RECOVERY OF DIPHENYL

Diphenyl present, mg	Diphenyl found, mg	Difference, mg	Error, %
20	20·1	+0·1	+0·5
25·6	25·62	+0·02	+0·07
29·8	31·5	+1·7	+5·7
40	40	0	0
50	47·5	−2·5	−5·0
103·6	101·25	−2·35	−2·25
200	192	−8·0	−4·0

TABLE III

RECOVERY OF DIPHENYL FROM IMPREGNATED PAPER WRAPPERS

Method of extraction	Diphenyl added, mg	Diphenyl found, mg	Difference, mg	Error, %
Hot	0·0	0·0	0·0	0·0
Cold	0·0	0·0	0·0	0·0
Hot	5·12	5·17	+0·05	+1·0
Cold	6·90	7·20	+0·30	+4·0
Hot	6·90	6·75	−0·15	−2·0
Cold	10·0	10·8	+0·8	+8·0
Hot	12·0	12·2	+0·2	+1·6
Cold	12·0	12·2	+0·2	+1·6
Cold	77·0	77·5	+0·5	+0·6

If the optical density increases with the amount of acetic acid reagent, take less than 0·01 ml of extract, for instance 0·005 or 0·0025 ml, until the optical densities obtained with increasing amounts of acetic acid reagent are about the same. Calculate the required volume of extract.

Determination of diphenyl—Place an aliquot of extract containing approximately 800 μg of diphenyl in a 10-ml graduated tube. If necessary, add chloroform to make up the volume to 1 ml, or reduce the volume to 1 ml. To evaporate excess of chloroform, put the extract into the 10-ml graduated tube—not more than 5 ml at a time—and keep the tube in water at 70° C in a way such that the level of chloroform is always above the level of water. Make sure that there is always at least 1 ml of solution in the tube. When the aliquot of extract has been adjusted to 1 ml, add 9 ml of acetic acid reagent. Determine the optical densities corresponding to 0·05, 0·10 and 0·15 ml of the mixture as described for the construction of the standard graph, and calculate the amount of diphenyl in the wrappers.

ACCURACY OF THE METHOD

Determinations were made on chloroform solutions of known diphenyl content and on wrappers impregnated with known amounts of diphenyl (see Tables II and III). It can be seen that deviations are small and remain within the limits of experimental error.

Determinations were also made of diphenyl contained in two halves of the same sheets of wrappers furnished by a manufacturer (see Table IV). There is generally good agreement between the values obtained for corresponding halves. The slight differences may be due to irregularities during the manufacture of the paper.

TABLE IV

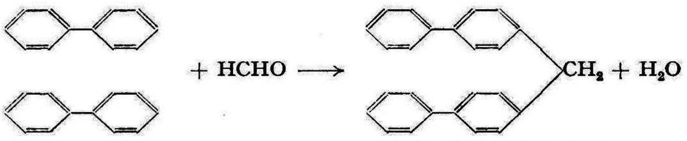
DETERMINATION OF DIPHENYL IN PAPER WRAPPERS

	Diphenyl found in—	
Wrapper sample No.	first portion, mg	second portion, mg
1	20·6	20·0
2	22·3	23·1
3	22·0	20·0

DISCUSSION OF THE METHOD

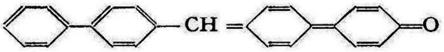
It would appear that for the characteristic colour reaction to take place both *para* positions of diphenyl must be free. The blocking of these positions by $-NH_2$ (benzidine) or one of them by sulphonation prevents the appearance of the blue colour.

It may be assumed that the formation of the blue colour takes place according to the mechanism proposed by Feigl[10] and that, in the reaction reported here, bis(*p*-diphenyl)methane is formed.



Bis(*p*-diphenyl)methane

This product would give, on oxidation, a *para*-quinonoidal blue-coloured derivative.



According to Weiler,[11] bis(*p*-diphenyl)methane is obtained when formaldehyde and traces of sulphuric acid react with diphenyl dissolved in acetic acid. Bis(*p*-diphenyl)methane dissolves in sulphuric acid and imparts to it a blue colour.[11]

The intense blue colour obtainable with diphenyl immediately and with fluorene on heating is probably due to the formation of the same compound, since equimolecular amounts of diphenyl and fluorene have yielded colours of equal intensity.

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A Field Method for Determining Total Air-borne Lead

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A field test is described for determining small amounts of total air-borne lead in industrial atmospheres; it can be carried out on the sample used for determining lead fume by Dixon and Metson's staining method. The sample is collected on a test paper, which is then treated in a graduated sample tube with cold dilute nitric acid containing hydrogen peroxide to dissolve the lead dust and disintegrate the paper. Measured amounts of ammoniacal cyanide - metabisulphite - citrate solution and a solution of dithizone in carbon tetrachloride are successively added, and the lead dithizonate is extracted at pH 11. The colour of the lower layer is compared with aqueous colour standards or permanent glass colour standards.

CONSIDERABLE differences often exist in the toxic effects produced by exposure to atmospheres containing relatively fine and relatively coarse air-borne particles of a metal or metallic compound. For this reason it is desirable to find a means of differentiating chemically between these two size groups. Unfortunately, no simple terms appear to exist that will distinguish the two groups on grounds of size alone. For want of better, the terms fume and dust are used here and elsewhere[1] to denote, respectively, fine and coarse air-borne particles. Lead fume, which, strictly speaking, should owe its origin to a condensation process, is composed of lead oxide or, more rarely, lead particles of mean diameter well below 1 μ. Lead dust is regarded as consisting of particles of lead compounds, predominantly of greater diameter than 1 μ, capable of temporary suspension in air and usually of mechanical origin. This classification has the drawback that lead dust may contain an extremely small fraction, comparable in particle size and nature with lead fume, that on analysis by field test would in fact be reported as lead fume. If, however, this "pseudo-fume" behaves on inhalation similarly to true lead fume, this drawback may not be serious in practice.

We have recently described a field method for determining lead fume[1] in the presence of moderate amounts of lead dust, and stated that there was also a need for a field method for determining total air-borne lead. A field method for determining total air-borne lead, which is designed to be used in conjunction with the previous method, is now described. The sample of air-borne lead is collected on a test paper, the amount of lead fume is determined by measurement of the colour intensity developed on the paper, and the total lead is then determined by treatment of the same test paper by a wet method. The lead-dust content can then be obtained by difference if required.

EXPERIMENTAL

As it was a requirement of the method for total air-borne lead that the determination was to be carried out on the sample used for the determination of lead fume, it was obvious that the starting point would have to be the 1-cm diameter circle of test paper containing the coloured lead complex of tetrahydroxyquinone or largely undissolved lead dust or both. The first problem was evidently to devise a method of converting all the lead into a soluble form. Secondly, if the criteria of a field method were to be observed,[2] the test procedure would have to be simple in form and preferably independent of technical services.

METHOD OF DISSOLVING LEAD DUST—

The most suitable solvent for lead dust was found to be a cold 5 per cent. aqueous solution of nitric acid containing 0·05 per cent. of hydrogen peroxide. Particles up to 20 μ in diameter of the following substances were found to dissolve completely after 2 minutes' shaking: metallic lead; lead suboxide, monoxide and dioxide; red lead; white lead; lead chromate, tartrate, silicate, borate, iodide, chloride, fluoride and arsenate; normal and basic forms of lead phosphate, phosphite and stearate; and calcium plumbate. Lead sulphide and lead sulphate required 5 minutes' shaking before solution was complete, but basic lead sulphate was more readily soluble.

DETERMINATION OF LEAD—

The acidic solution of lead nitrate was shaken with ammoniacal cyanide - metabisulphite - citrate solution, a variant of the composite reagent frequently used in the determination of lead by the dithizone method. This reagent contains (*a*) ammonium hydroxide, which brings the pH of the sample to 11, (*b*) potassium cyanide, with which most metals form complexes that are retained in the aqueous phase during the subsequent extraction with dithizone solution (lead, bismuth, thallium and stannous tin alone form complexes preferentially with dithizone), (*c*) ammonium citrate, which prevents or delays precipitation of phosphates, etc., on the addition of ammonium hydroxide and (*d*) metabisulphite; a sulphite is normally added to reduce any oxidants that might decompose the dithizone, and in the proposed method metabisulphite serves the additional purpose of decomposing excess of hydrogen peroxide. The colorimetric determination of the lead was carried out by a modification of Snyder's high- pHtechnique.[3,4] A solution of dithizone in carbon tetrachloride was shaken with the aqueous sample solution, and the colour of the lower layer, containing the lead - dithizone complex in carbon tetrachloride, was compared with those of a series of standard aqueous cobalt salt solutions.[5]

Snyder used chloroform as the solvent for dithizone in his one-colour extraction process and claimed that the free dithizone remaining in the chloroform layer was insignificant in amount.[4] Gage[6] pointed out that the substitution of carbon tetrachloride for chloroform resulted in a much more complete transfer of free dithizone from the organic to the aqueous layer provided that the optimum concentration of dithizone was used.

The use of carbon tetrachloride in place of chloroform has the further advantages that carbon tetrachloride solutions of dithizone are in general more stable than chloroform solutions and that carbon tetrachloride solutions of lead dithizonate, unlike chloroform solutions, match the easily prepared cobalt salt standard colour solutions.

Although extraction of the lead dithizonate at pH 11 in one operation is not so accurate as the more usual repeated extraction at pH 9 to 9·5,[7] it was found to be adequate for the purposes of a field test. As far as could be judged by the visual colorimetric method employed, practically complete recovery of the lead was achieved, and any free dithizone retained in the carbon tetrachloride layer was insufficient to affect the colour of the lead dithizonate solution.

The small circle of test paper containing the original sample of lead was completely disintegrated during the process of solution, and the fragments remained in the upper aqueous layer or at the liquid interface, leaving the lower carbon tetrachloride layer clear. If a lead fume determination had been previously carried out, the tetrahydroxyquinone reagent originally present in the test-paper circle was automatically destroyed during the subsequent treatment.

METHOD

APPARATUS—

The apparatus used for sampling, *viz*, pump, test-paper holder (a suitable form of holder is made by Messrs. Siebe, Gorman, Surbiton, Surrey) and test papers, was identical to that previously described.[1]

Test tubes—Six matched stoppered tubes of lead-free glass, about 5 inches long and ¾-inch internal diameter. The sample tube is graduated at 2·5, 5 and 17·5 ml.

REAGENTS—

Ammonium citrate solution, 25 *per cent. w/v, aqueous.*

Potassium cyanide solution, 10 *per cent. w/v, aqueous*—This solution should be at least 2 days old, so that traces of sulphide may become oxidised.

Ammonium hydroxide, sp.gr. 0·880.

Sodium metabisulphite solution, 10 *per cent. w/v, aqueous.*

The above-mentioned reagents should be rendered lead-free, the first three by the methods described by the Analytical Methods Committee of the Society for Analytical Chemistry,[7] or they can be purchased lead-free.

Sodium metabisulphite solution should be prepared and rendered lead-free as described below.

Dissolve 25 g of sodium (or potassium) metabisulphite in 150 ml of water, adjust to pH 9 by adding ammonium hydroxide, and extract with 10-ml portions of dithizone in chloroform until the extract is no longer red, but faintly blue. Remove the traces of excess of dithizone by extraction with chloroform. Remove the chloroform by filtration, and dilute the filtrate to 250 ml with water.

Ammoniacal cyanide - metabisulphite - citrate solution—Mix 325 ml of ammonium hydroxide, 30 ml of potassium cyanide solution, 60 ml of sodium metabisulphite solution and 20 ml of ammonium citrate solution with 565 ml of water.

Store the solution in borosilicate-glass or polythene bottles. It is stable for at least several months.

Nitric acid - hydrogen peroxide solution—Mix 5 ml of lead-free concentrated nitric acid with 95 ml of water. Add 0·2 ml of 30 per cent. w/v analytical-reagent grade hydrogen peroxide. The acid can be purchased lead-free or purified by distillation.

Dithizone solution—Dissolve 40 mg of analytical-reagent grade dithizone in 1 litre of analytical-reagent grade carbon tetrachloride. Shake the solution vigorously with an approximately 0·1 *M* aqueous solution of sulphur dioxide. Reject the aqueous layer. Keep the dithizone solution in a dark bottle (a "squeeze" type of polythene bottle is convenient) covered with a layer of the aqueous solution of sulphur dioxide.[8] This solution can be preserved for at least several months if stored in a cool place.

Standard colour solutions—Prepare an aqueous solution of cobalt chloride or sulphate containing 15·0 g of cobalt per litre. Take 0·55, 1·90, 3·30, 6·30 and 7·70 ml of this solution, and dilute each to 10 ml. These standards represent, respectively, the blank, 0·2, 0·4, 0·8 and 1·0 mg of lead per cubic metre of air for a 15-litre sample of air.

These cobalt solutions are similar in tint to the sample solutions.[5,9] The rather better matching obtained by the addition of extremely small amounts of blue and yellow salts to the cobalt solutions was not considered worthwhile in view of the greater complication in the preparation of the standard colour solutions.

If desired, Lovibond permanent glass colour standards can be used in place of the standard colour solutions. Messrs. Tintometer Ltd., Salisbury, England, manufacture a disc containing coloured-glass standards for use in the determination of both lead fume[1] and total air-borne lead by means of a comparator provided with a specially designed graduated sample tube.

PROCEDURE—

Take the sample of air-borne lead exactly as described previously.[1]

Cut out the 1-cm circle of test paper containing the lead sample. The area of collected lead will be purple if the lead fume has been determined; if this determination has not been carried out the area of exposure can be roughly indicated in pencil before inserting the test paper into the holder.

Transfer nitric acid - hydrogen peroxide solution to the sample tube up to the 2·5-ml mark, and add the circle of test paper. Replace the glass stopper, and shake vigorously for a few minutes to disintegrate the paper and dissolve the lead dust. Add ammoniacal cyanide - metabisulphite - citrate solution up to the 17·5-ml mark, insert the stopper, and shake for a few seconds. Pour dithizone solution carefully through the aqueous layer until it rises to the 5 ml mark. Insert the stopper, shake for 1 minute, and set aside until the layers separate. Compare the colour of the lower lead dithizonate layer with those of the standard colour solutions in order to determine the total lead content of the sample. Colorimetric comparison is facilitated by the use of diffused light and by screening the upper yellow aqueous layer.

RESULTS

Samples of various types of air-borne lead were taken by the proposed procedure. The circle of test paper was bisected and the lead content of one-half was determined visually by the field method. For comparative purposes the lead content of the dithizonate solutions was also determined spectrophotometrically.

It was desired to confirm the results by the field method by means of an independent fundamental method. The spectrochemical method is insufficiently precise for amounts below about 10 μg of lead. It was not possible to use a larger sample, as was done in checking the field method for lead fume,[1] since homogeneity of sample could not be proved by the development of a uniform stain. Accordingly, the other half of the test paper was analysed by X-ray fluorescence spectrometry, which does not destroy the sample, and, with the more concentrated samples, also by spectrochemical examination. The results are shown in Table I.

DISCUSSION OF THE METHOD

RANGE—

The standard sample in the determination of lead fume is 15 litres, and the same sample is also used for the determination of lead dust. With this sample, the method is not precise below $\frac{1}{15}$ mg or above 1 mg of lead dust per cubic metre. (The threshold toxic limit of lead is 0·2 mg per cubic metre.) Greater sensitivity can be attained by increasing the volume of sample, a device that cannot be employed in the determination of lead fume, because carbonaceous matter in the air may obscure the stain obtained with tetrahydroxyquinone. Similarly, a smaller volume of sample will increase the range of the method at the upper limit.

TABLE I

COMPARISON OF FIELD, X-RAY FLUORESCENCE AND SPECTROGRAPHIC METHODS

Sample	Lead found by field method— visually, µg	spectrophotometrically, µg	Lead found by X-ray fluorescence spectrometry, µg	Lead found by spectrographic method, µg
Basic lead sulphate	3	2·6	3·0	—
Litharge	5	4·7	5·5	—
Lead stearate	6	5·6	5·0	—
Lead metal	9	8·2	7·5	—
Dibasic lead phosphite	12	11·0	12·5	10
Lead suboxide	12	11·5	—	11
Red lead	12	12·0	—	10

INTERFERENCE BY OTHER CONSTITUENTS OF DUST—

The possible constituents of industrial dusts are legion, and it would not be safe to assume non-interference in the field test by unknown major constituents of a dust without thorough investigation. Usually, however, the potential sources of non-plumbic dust components in an industrial process in which lead is used are known. Bismuth, thallium and stannous tin would, if dissolved in the treatment of the sample, be extracted with lead to form coloured dithizonates. The colour of the bismuth salt is faint compared with that of lead, and bismuth would not seriously interfere unless present in great excess. It is unlikely that a tin compound would dissolve in the nitric acid - hydrogen peroxide mixture, but thallium, which gives a fairly intensely coloured dithizonate, would seriously interfere in the determination of lead. The presence of relatively large amounts of alkaline phosphates does not appear to interfere.

Alkaline-earth phosphates, which can seriously interfere in the determination of lead in foodstuffs, etc.,[10] have no effect when present in the amounts likely to be found in a sample of atmospheric dust. If iron is present in amounts greater than 20 times the equivalent of the threshold toxic limit for lead (0·2 mg of lead per cubic metre), the apparent lead content is reduced. If the presence of large amounts of iron is suspected, 2 to 3 ml of lead-free 20 per cent. w/v hydroxylamine hydrochloride solution[11] should be added with the ammoniacal cyanide - metabisulphite - citrate solution before addition of the dithizone solution

Methods were previously described[1] for eliminating stain on the test paper due to cadmium, zinc and antimony. Test papers so treated could obviously not be used for the determination of total air-borne lead, and a fresh sample for this purpose would have to be taken.

CONCLUSIONS

The methods described can be used to determine on one sample lead fume and total lead, or both separately. The procedure is within the scope of comparatively unskilled workers and requires neither heat nor technical services, although the use of an electric pump relieves the tedium of operating a hand pump. The differentiation between fume and dust cannot always be effected, *e.g.*, fume cannot be determined in an atmosphere grossly contaminated with dust, and, as already mentioned, particles of the same size range and nature as fume, but of mechanical origin, would be reported as fume.

The use of the two field methods described may help to establish whether cases of lead poisoning are due to exposure to atmospheres of fume or of dust.

This work was carried out on behalf of the Committee on Tests for Toxic Substances in Air and the Ministry of Labour and National Service.

We thank Mr. H. L. Bolton of this Laboratory for arranging confirmatory lead determinations by X-ray fluorescence spectrometry and spectrography. This paper is published by permission of the Department of Scientific and Industrial Research.

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A Method for Obtaining Weighed Micro Samples of Moisture- or Oxygen-sensitive Compounds

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The standard method for enclosing a micro sample of liquid in a capillary tube is to seal the tube by means of the flame from a micro bunsen burner. This method is not satisfactory for readily hydrolysable compounds, owing to the presence of water vapour both in the atmosphere and in the products of combustion from the coal gas. A method is described whereby the whole sampling procedure is carried out in a dry box and the capillary tube is electrically sealed.

FROM time to time the need arises for weighed micro samples of compounds sensitive to oxygen or moisture, such as are present in the atmosphere. The need for a suitable procedure was particularly urgent in this laboratory in connection with investigations on the methylchlorosilanes. It was realised that methods based on the sealing of capillaries with a micro bunsen burner would be unsuitable and it was therefore decided to adapt a commercially available glove-box in order to carry out manipulations. The box chosen, with a "posting box" fitted on the left-hand side, is shown in Fig. 1. A special drying system was fitted up in order to dry the nitrogen used to purge the box, which also housed subsidiary equipment, including apparatus for sealing the capillary electrically.

THE DRY BOX—

A glove-box was purchased from H. & E. Lintott Ltd. and a posting-box was attached to its left-hand side to facilitate insertion and withdrawal of subsidiary apparatus and samples (see Fig. 1). Gloves for manipulating apparatus inside the box are shown hanging from the two front ports. The box is purged with dry nitrogen by passing the gas slowly through, so that a slight positive pressure is maintained in the box. Preliminary experiments with various drying agents, including charcoal and liquid air, finally led to the choice of concentrated sulphuric acid in a sintered-glass bubbler. A tower containing Linde molecular sieves inserted in the gas line after the scrubbers acted as a trap for sulphuric acid spray. As a

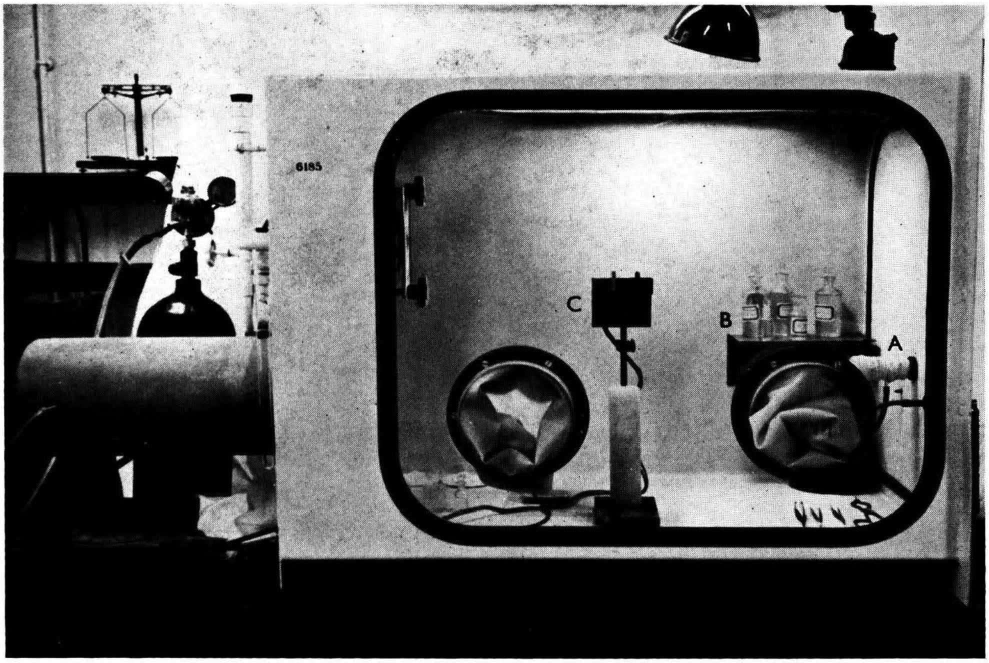
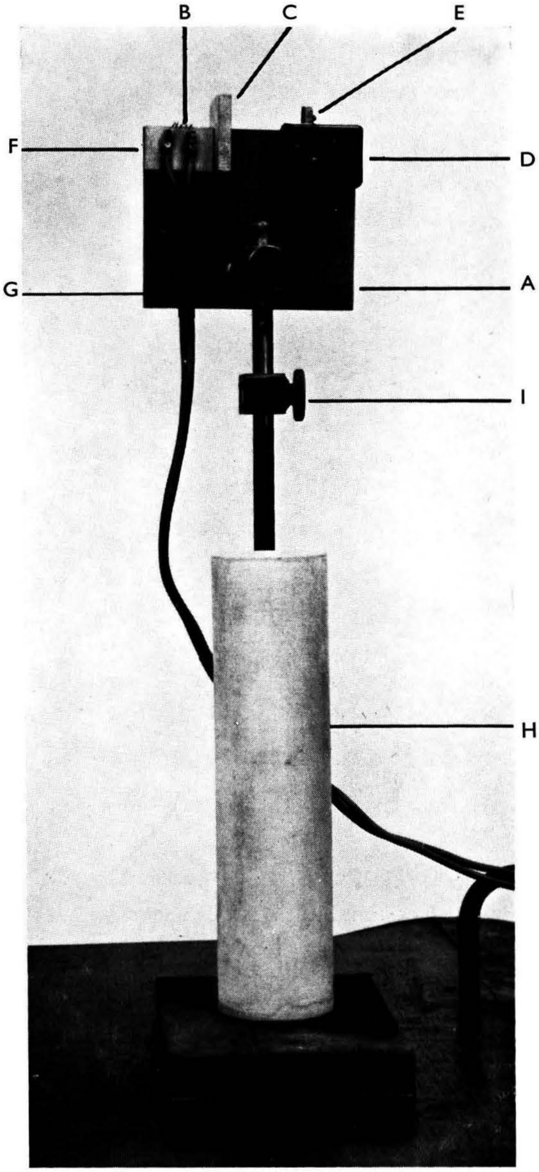


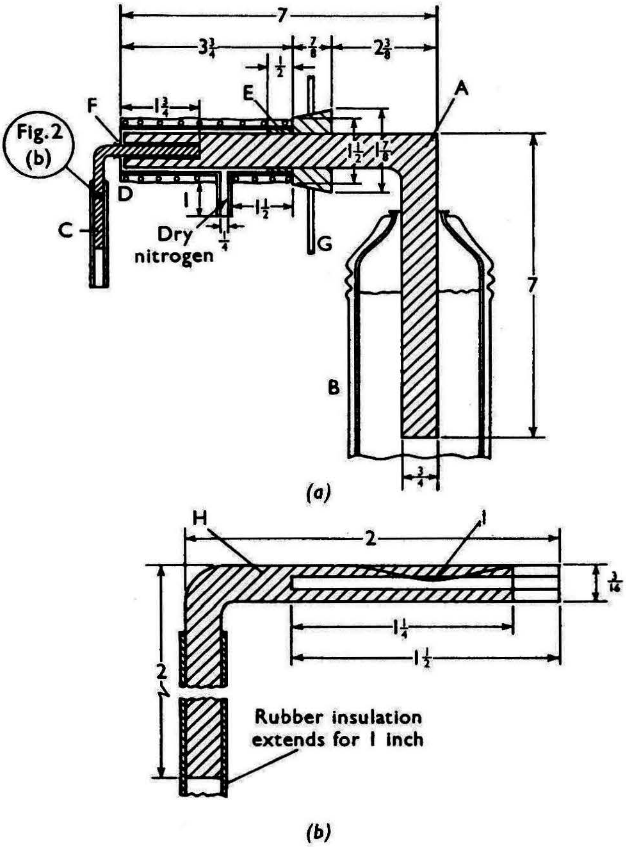
Fig. 1. Glove-box modified for use as a nitrogen dry box: A, cold source; B, sample shelf; C, capillary-sealing device



A = Tufnol backplate.
B = Hardened-platinum coil (coil diameter = 0·12 inch; No. of turns = 4; wire diameter = 0·035 inch).
C = Sindanyo heat-insulating block.
D = Bakelite guide.
E = Brass retaining clip.
F = Ceramic mount.
G = Adjustable bearing (allowing back-plate to be rotated through 90°).
H = Polythene block to support sample flasks.
I = Capillary clip (can be raised and lowered).

Fig. 4. Sealing equipment

further precaution to ensure that the atmosphere inside the box remained dry, a number of dishes containing phosphorus pentoxide were placed on the floor of the box. It was found to be necessary to maintain a slow stream of nitrogen through the box for about 10 weeks in order to reduce the moisture content to a level such that the dew point of the atmosphere in the box was of the order of —60° C. This was considered to be sufficiently dry for the subsequent manipulations of the samples; the deposition of moisture was only just detectable on the end of the aluminium rod (see Fig. 2*a*) after a few hours' exposure, cooling being effected by a mixture of Drikold and acetone. To some extent the porosity of the rubber gauntlets imposed a limit to the degree of dryness in the box, but it is considered that an improvement might be effected by using gauntlets made from a synthetic material having porosity lower than that of rubber.



A = Aluminium rod.
B = Thermos flask for Drikold - acetone mixture.
C = Rubber insulation.
D = Glass sheath, 1-inch i.d., with asbestos-cord lagging.
E = Rubber seal.
F = ¼-inch hole in glass sheath.
G = ⅛-inch wall of dry box.
H = Brass rod.
I = Hairspring in 5/64-inch diameter hole.

Fig. 2. (*a*) Cold source; (*b*) brass rod for cooling capillaries (all dimensions are in inches)

A number of minor alterations were carried out to the box itself; holes were made to permit the introduction of leads for the nitrogen supply, and a small hole, closed by means of a rubber stopper, was made in the side of the box to facilitate the removal of the sealed capillary tubes, so avoiding unnecessary use of the posting box. Samples were stored on a small metal shelf fitted to the rear panel of the box (see Fig. 1), thus effecting economy of space on the floor of the box. Wooden apparatus and fitments were avoided in order to minimise dangers of water contamination.

SUBSIDIARY EQUIPMENT—

Various equipment is needed for the capillary-sealing process. This includes a preheater (see Fig. 3), which permits an open capillary tube to be heated to about 200° C before withdrawing a sample. To the right of the box (see Fig. 1) a vacuum flask containing Drikold can just be seen. An aluminium rod dips into the flask and is bent at right angles so that the end passes through a hole in the side of the box (see Fig. 2*a*). In this way the aluminium rod serves as a cold source for certain manipulations of the capillary tubes. The exposed end of the aluminium rod is screened with a glass tube; this tube serves as a jacket through which nitrogen passes to prevent condensation of traces of residual moisture that may be present in the box.

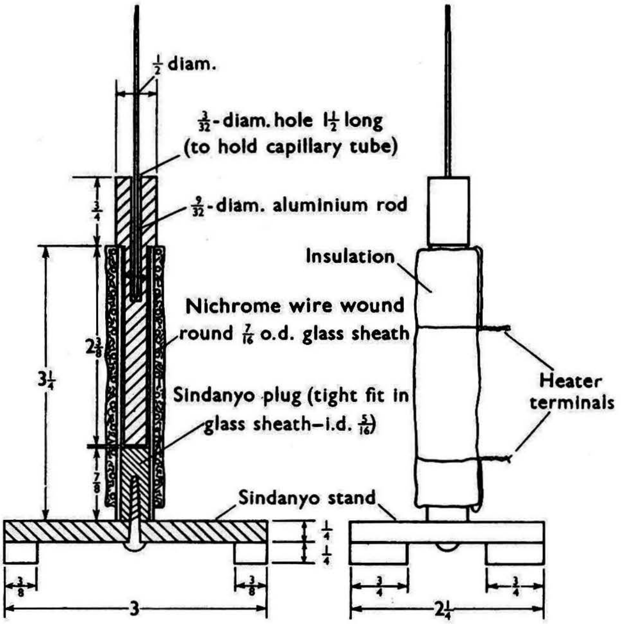


Fig. 3. Preheater (for details of electrical connections, see Fig. 5, p. 129; all dimensions are in inches)

Fig. 2*b* shows a brass rod having a hole drilled in one end into which a capillary tube can be inserted and held firm by a spring. The brass tube can be cooled to about −60° C by inserting it in the end of the aluminium rod, which has been drilled in order to accommodate it to a depth of about 3 inches. A piece of rubber tubing placed over the exposed end of the brass rod permits it to be easily handled.

A polythene cylinder (see Figs. 1 and 4) acts as a support for the sample, and behind the cylinder is a Tufnol plate supporting a platinum coil on which the capillary is electrically sealed. A Bakelite block used as a guide is so placed in relation to the coil that the capillary can be aligned to lie horizontally in the centre of the coil after passing through a heat-insulating Sindanyo block (see Fig. 4). A brass clip holds the capillary in position by gripping the brass holder (Fig. 2*b*). The Tufnol plate can be swivelled through 90° so that the capillary lies either horizontally or vertically. The upright rod supporting the Tufnol plate holds a spring clip, which is used to hold the capillary tube while it is filled with sample.

The platinum coil is constructed from platinum containing 10 per cent. of rhodium (obtained from Engelhard Industries Ltd., code No. SR10) and readily withstands continuous use at temperatures of over 1000° C. By using a suitable electrical system, the temperature of the coil is arranged so that the capillary can either be maintained at a low heat, from

300° to 400° C, or heated for a prescribed period at about 1000° C. The electrical arrangement of the power supply for heating and sealing the capillaries is shown in Fig. 5. When S1 is closed, thereby operating relay RL1, contacts RL1.1 are closed, thus completing the mains circuit to T2, which applies a variable preliminary heating current to the heating coil via T1. This current can be maintained for as long as S1 is kept closed. Interlocking contacts, RL1.2 and RL1.3, by opening when S1 is closed, prevent simultaneous operation of the sealing cycle.

When S2 is closed, thereby operating relay RL2, contacts RL2.1 and RL2.3 are closed, and the latter starts the timing unit controlling the sealing cycle. Any predetermined sealing time from 0·1 to 10 seconds can be chosen by adjustment of the timing unit. Interlocking contacts RL2.2 and RL2.4 open and prevent simultaneous operation of the preliminary-heating circuit.

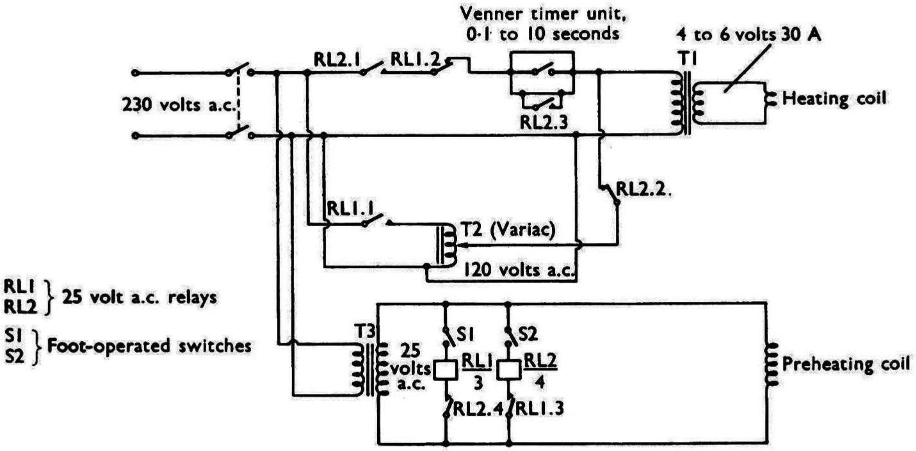


Fig. 5. Power supply for ampoule-sealing unit

The preheating coil (see Fig. 3), permanently connected to T3, is used to warm up the capillary before it is filled and sealed.

FILLING A CAPILLARY TUBE—

The filling process is normal micro-analytical technique, except that all operations are carried out with gloved hands inside the dry box. The usual type of capillary tube is sealed at one end and drawn out more finely at the other end to about half of its original diameter. The sealed end is inserted into the heater shown in Fig. 3. Meanwhile the sample for analysis is removed from the shelf of the cabinet and placed on the polythene block (see Fig. 4). The capillary is removed from the heater and placed vertically above the sample in the spring clip attached to the support rod shown in Fig. 4. By turning a knurled screw attached to the spring clip, the capillary is readily lowered into or raised from the sample bottle. The capillary is rapidly lowered into the sample, and the brass sleeve—previously cooled in the aluminium rod—is simultaneously placed over the end of the capillary. The capillary is raised from the sample almost immediately, it being ensured that sufficient sample has entered. The brass sleeve holding the capillary is removed from the clip and inverted so that the capillary points upwards and the other end is then tapped gently on the floor of the box so that the "plug" of sample falls to the bottom of the capillary tube.

SEALING A CAPILLARY TUBE—

The brass tube holding the capillary is fitted under the clip on the Bakelite guide (see Fig. 4) so that the fine end of the capillary lies centrally inside the platinum coil and the remainder is shielded from the coil by the Sindanyo heat-insulating block. After turning the Tufnol plate so that the coil lies horizontally, the electrical power unit is switched on so that the coil is heated to almost dull-red heat, thereby removing any liquid from the end of the capillary by volatilisation. This procedure is essential in order to avoid carbon formation due to lack of oxygen in the box; if formed, carbon would prevent efficient sealing at the subsequent stage. This final stage involves heating the coil to about 1000° C by using the appropriate relay with the timing unit arranged for about a 6-second period of heating. The sealed capillary is readily removed via the small hole in the side of the box, having previously ensured that the pressure inside the box is slightly above atmospheric.

We thank Mr. T. R. Prentice, of the Research Department, for the design of the electrical sealing system.

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The Determination of Traces of Selenium in Tellurium

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A method is described for the determination of concentrations greater than 0·5 p.p.m. of selenium in tellurium. If necessary, selenium can be concentrated into not more than 0·5 g of tellurium by utilising the fact that it is more readily reduced in 2 to 2·5 *N* hydrochloric acid solution than is tellurium. Selenium is determined colorimetrically with 3:3′-diaminobenzidine. When the selenium content of the tellurium is greater than about 7 p.p.m. the determination can be carried out directly.

In work on the purification of tellurium, a method was required for determining traces of selenium in the element or its compounds. Until recently such a determination has usually been based on reduction to the element.[1] A considerable advance was made when Hoste[2] proposed the use of 3:3′-diaminobenzidine as a colorimetric reagent for quadrivalent selenium. Hoste and Gillis[3] subsequently showed the reaction to be highly specific, and Cheng[4] developed a modification that increased the sensitivity by permitting extraction of the colour into an immiscible solvent. Although milligram amounts of tellurium do not interfere with the determination, the effect of major amounts does not seem to have been considered hitherto.

EXPERIMENTAL

ATTACK ON THE TELLURIUM SAMPLE—

The diaminobenzidine reagent reacts only with quadrivalent selenium, and any selenium in the tellurium must therefore be converted to this form. Since selenium compounds are more readily reduced and less easily oxidised than the corresponding tellurium compounds,[1] it is unlikely that any selenium in tellurium will be present in other than elemental form. Oxidation with nitric acid will conveniently convert both selenium and tellurium to the quadrivalent form only. The action of nitric acid on selenium produces selenious acid; with tellurium, however, basic tellurium nitrate is formed. Unless a considerable excess of nitric acid is used the basic nitrate is likely to be precipitated, and this may retard further attack on the tellurium unless the mixture is well stirred.

EFFECT OF QUADRIVALENT TELLURIUM ON DETERMINATION OF QUADRIVALENT SELENIUM—

The chief limitation on the amount of tellurium that can be tolerated in the determination of selenium appears to be that set by the low solubility of tellurium compounds under the analytical conditions. Hydrolysis of the basic nitrate on dilution can lead to the precipitation of tellurium dioxide, and to avoid this the nitrate is dissolved in sodium hydroxide solution, sufficient citric acid solution then being added to form the water-soluble complex. Under these conditions the presence of up to 0·5 g of tellurium can be tolerated, as can be seen from the results shown below for the recoveries found when 15·5-μg portions of quadrivalent selenium were added to solutions containing different amounts of purified tellurium; the selenium content of the tellurium was about 0·15 p.p.m.

Tellurium present, g ..	0·0	0·002	0·01	0·05	0·1	0·5
Selenium^{IV} found, μg ..	15·2	15·9	15·8	15·2	15·5	15·5

When more than 0·5 g of tellurium is present, precipitation of the citric acid complex begins when the pH of the solution is increased to the value necessary for the extraction of the piazselenol colour into toluene. This, therefore, is the largest amount of tellurium tolerable under the specified conditions.

CONCENTRATION OF SELENIUM INTO A SMALL AMOUNT OF TELLURIUM—

When the selenium content of the tellurium is low, it may be necessary to take a weight of sample greater than 0·5 g in order to have enough selenium for a satisfactory determination. The tellurium in excess of the tolerable amount must therefore be removed, and this can be achieved by reducing a suitable solution so that only a small proportion of the tellurium is precipitated as the element. For this separation nitrate ions must be removed from the solution, as they slowly react with the hydrazine and so make it difficult to control the extent of precipitation. This removal is achieved by heating to fumes with sulphuric acid, but care must be taken in this operation, as a small but definite loss of selenium has been noticed when the heating has been purposely prolonged or made unduly vigorous. However, under normal conditions no loss occurs; this was confirmed by Gorsuch,[5] who showed that, at tracer level, there was no loss of selenium, provided that reducing conditions did not prevail.

The tellurium dioxide formed is directly soluble in hydrochloric acid, but even with 8 *N* acid at room temperature there is some loss of selenium from such a solution, presumably as the volatile chloride. This can be overcome by dissolving the tellurium dioxide in sodium hydroxide solution and adding the calculated amount of concentrated hydrochloric acid to give a final solution 2 *N* in this acid, allowance having been made for the conversion of tellurium to $TeO_2.4HCl$. It is necessary to make allowance for this conversion of tellurium, as otherwise some dioxide appears during the subsequent precipitation by hydrazine dihydrochloride solution. After this reduction with a small amount of hydrazine, the precipitate of selenium and tellurium is separated by filtration and dissolved in nitric acid, and quadrivalent selenium determined as before.

To check the completeness with which selenium, together with a little tellurium, was precipitated, a solution containing radioactive quadrivalent selenium-75 was prepared from Specpure selenium that had been irradiated for 1 week at pile factor 10. Aliquots representing 8·4 and 50·4 µg of selenium were added to the product of the reaction between 1 g of tellurium and diluted nitric acid (1 + 1), and the mixtures were treated as described under "Procedure for Determining Selenium Contents Between 0·5 and 10 p.p.m." After the precipitates had been separated, sufficient 6 *N* sodium hydroxide was added to the filtrates to dissolve the hydrated tellurium dioxide. This was necessary to prevent loss of selenium in the subsequent evaporation to 25 ml. The amounts of selenium present were determined by counting the final solution in a Geiger - Müller tube; for the 8·4 and 50·4-µg additions of selenium, activities equivalent to less than 1 (the limit of detection) and 1·1 µg, respectively, were found.

Similar additions of quadrivalent selenium were made to 10-g amounts of tellurium, but in these experiments the large amounts of salts in the filtrates precluded evaporation to a volume at which reasonable sensitivity could be expected from a Geiger - Müller counter. Since the more ready reduction of selenium has been established, it was considered sufficient to precipitate a little of the tellurium in the filtrate from the first precipitation and to seek radioactivity in solutions of this second precipitate. In neither experiment was the activity equivalent to as much as 0·5 µg of selenium (the limit of detection for 10-ml portions of solution).

It would seem, therefore, that the precipitation of selenium under the given conditions is practically complete.

METHOD

REAGENTS—

Unless otherwise stated, all reagents should be prepared from analytical-grade materials.

Citric acid solution, 40 per cent. w/v.
Ammonia solution, diluted (1 + 1).
Nitric acid, diluted (1 + 1).
Sodium hydroxide, approximately N *and* 6 N.
Hydrochloric acid, concentrated and approximately N.
Sulphuric acid, diluted (1 + 1).

3:3′-Diaminobenzidine dihydrochloride solution, 0·5 *per cent. w/v, aqueous*—The reagent obtained from L. Light and Co. Ltd. was used.

Hydrazine dihydrochloride solution—Prepare a saturated aqueous solution (approximately 37 per cent. w/v) of laboratory-reagent grade hydrazine dihydrochloride.

Toluene—Redistil toluene having a low sulphur content.

Standard quadrivalent selenium solution—Dissolve 0·1650 g of re-sublimed selenium dioxide in 500 ml of dilute nitric acid (1 + 99), and dilute 5 ml of the solution to 500 ml with de-ionised water. This solution contains 2·35 μg of quadrivalent selenium per ml.

Tellurium—Prepare tellurium having an extremely low selenium content by reducing, with an excess of hydrazine dihydrochloride solution, telluric acid that has been purified by ion exchange.[6]

PREPARATION OF STANDARD GRAPH FOR QUADRIVALENT SELENIUM—

Take 0·5, 1·0, 3·0, 5·0, 7·0 and 10·0-ml portions of standard quadrivalent selenium solution (or suitable aliquots to cover the range up to 25 μg of selenium), and dilute each to 25 ml with water. To each solution add 10 ml of citric acid solution, and adjust the pH to between 2·7 and 2·9 with diluted ammonia solution (use a pH meter). Add 2 ml of 3:3′-diaminobenzidine dihydrochloride solution, swirl to mix, and set aside for 1 hour. Adjust the pH to between 8·0 and 8·2 with diluted ammonia solution, and transfer to a 100-ml separating funnel. Shake vigorously for 1 minute with 15·0 ml of toluene, discard the aqueous layer, and filter the toluene layer through a plug of filter-paper into a 4-cm glass spectrophotometer cell. Measure the optical density at 420 mμ with a Unicam SP600 spectrophotometer against a reagent blank prepared in the same way from 25 ml of water. For use with 1-cm cells, take 5·0, 10·0, 15·0 and 25·0-ml portions of standard selenium solution, and continue as described above.

The maximum deviations from linearity for 4- and 1-cm cells were 0·5 and 2·5 μg of selenium, respectively.

SIMPLIFIED PROCEDURE FOR DETERMINING SELENIUM CONTENTS ABOVE ABOUT 7 p.p.m.—

Weigh up to 0·5 g of finely divided tellurium into a 100-ml beaker, and dissolve in 15 ml of diluted nitric acid (1 + 1), warming and stirring if necessary. Evaporate just to dryness, and dissolve the residue in 25 ml of *N* sodium hydroxide. Add 10 ml of citric acid solution, adjust the pH to between 2·7 and 2·9 with hydrochloric acid, and continue as described for the standard graph.

PROCEDURE FOR DETERMINING SELENIUM CONTENTS BETWEEN 0·5 AND 10 p.p.m.—

Weigh 1 to 10 g of finely divided tellurium into a 400-ml beaker, and carefully add 100 ml of diluted nitric acid (1 + 1). Heat on a hot-plate for 1 hour, with frequent stirring, add 4 ml of diluted sulphuric acid (1 + 1), and evaporate until fumes of sulphur trioxide are evolved, again with frequent stirring. Dissolve the residue in as little 6 *N* sodium hydroxide as possible, noting the volume used, and add sufficient concentrated hydrochloric acid to neutralise the sodium hydroxide, to allow for conversion to $TeO_2.4HCl$ and to give a solution 2 *N* in this acid. Add 2 ml of hydrazine dihydrochloride solution, heat just to boiling-point, and set aside on a hot-plate at 40° to 60° C for 3 hours.

Draw the supernatant liquid through a sintered immersion filter (porosity No. 2), and wash the precipitate three times with water. Dissolve the precipitate in 10 ml of diluted nitric acid (1 + 1), and evaporate just to dryness. Dissolve the residue in 25 ml of *N* sodium hydroxide, and determine quadrivalent selenium as before.

RESULTS

The recovery of quadrivalent selenium added to the tellurium - nitric acid mixture as soon as the initial vigorous reaction had subsided was investigated. When the simplified procedure was used for small amounts of quadrivalent selenium added to about 0·5-g portions of purified tellurium, the results were—

Selenium added, μg	0·0	1·5	3·0	4·4	5·9
Selenium found, μg	0·0	1·5	3·3	4·3	6·0

When the selenium was added to about 10-g portions of purified tellurium, the results were—

Selenium added, μg	0·0	3·1	6·2	9·3	12·4	15·5
Selenium found, μg	1·7	4·8	7·4	10·3	13·2	17·1

Reagent blank values by these procedures are not large. In the simplified procedure the value of the blank is about 1·5 µg of selenium. When up to 10 g of tellurium are analysed, considerably larger amounts of reagents are used and the blank value is in the range 2·0 to 4·6 µg of selenium. However, these figures represent the limitation on the lower limits for selenium determination, which must be placed at about 3 p.p.m. by the simplified procedure and 0·5 p.p.m. by the full procedure.

As represented by divergences in the above results, the accuracy when 4-cm cells are used is better than ±1 µg of selenium.

CONCLUSION

The proposed method for determining traces of selenium in tellurium is considerably more sensitive than any available hitherto and is simple to perform.

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The Separation and Determination of Traces of Quadri- and Sexavalent Selenium in Telluric Acid

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A method is proposed for separating traces of quadri- and sexavalent selenium in the presence of much telluric acid. In nearly neutral solution, the addition of hydrazine solution in suitable amount will reduce to the element all the quadrivalent selenium, together with a small proportion of the tellurium. Repetition of the separation in a solution 2·1 to 2·5 *N* in hydrochloric acid reduces all the sexavalent selenium, again with a small proportion of the tellurium. In each instance the selenium is converted to selenious acid, which is determined colorimetrically with 3:3′-diaminobenzidine.

When more than about 17 g of telluric acid must be taken as sample, in order to ensure the presence of a suitable amount of selenium in each valency state, an ion-exchange method is proposed for removing most of the telluric acid before separating the two forms of selenium.

TELLURIC acid is usually prepared by a fairly vigorous oxidation process, and it might therefore be considered that any selenium present in the tellurium would be oxidised to selenic acid. During work on the determination of sexavalent selenium in telluric acid, it was found that some of the selenium behaved in a manner different from that expected of the sexavalent form and that this behaviour could only be caused by the presence of quadrivalent selenium as impurity. The presence of selenium in both valency states had therefore to be considered, and it was desirable that each of these forms should be determined separately. This seemed to be impossible by any of the established methods, with the possible exception of chromatography,[1] but it is doubtful whether this technique is sufficiently sensitive or accurate. In the work described here, the two forms of selenium are separated by differences in the conditions under which they can be reduced to the element. Oxidation of the element to the quadrivalent state then permits it to be determined colorimetrically with 3:3′-diaminobenzidine,[2] provided that the amount of accompanying quadrivalent tellurium does not exceed about 0·5 g.[3]

EXPERIMENTAL

DETERMINATION OF QUADRIVALENT SELENIUM IN TELLURIC ACID—

3:3′-Diaminobenzidine cannot be used directly for the determination of quadrivalent selenium in telluric acid because the latter causes extensive oxidation of the reagent. The products of oxidation are insoluble in toluene, into which the selenium colour is extracted, and would not normally interfere with the determination. However, in presence of much telluric acid the rate of oxidation of the reagent is too fast to permit any appreciable formation of the piazselenol colour. The oxidation can be suppressed by complexing the telluric acid with a large excess of a "poly-ol," such as glycerol or mannitol, but the resulting large volume of solution renders the method inconvenient. It is therefore necessary to separate the selenium from the sexavalent tellurium, and this is conveniently done by reducing the quadrivalent selenium to the elemental state with hydrazine. Under similar conditions selenium compounds are more easily reduced than are those of tellurium, and hence, by limiting the amount of reductant, all the selenium can be reduced and only a small amount of the tellurium is co-precipitated.

The effect of acidity on this reduction has been studied over the range 0·0 to 2 *N* in hydrochloric acid. An 11·8-µg amount of quadrivalent selenium was added to a solution containing about 2 g of purified telluric acid, and the acidity was adjusted to the required value. Precipitation was carried out by adding 2 ml of a saturated solution of hydrazine dihydrochloride, this amount being sufficient to precipitate all the selenium and less than 0·5 g of tellurium. The results, which indicate that the recovery of selenium is independent of the acidity within the range examined, were—

Acidity, *N*	0·0	0·4	0·8	1·2	1·6	2·0
Selenium recovered, µg ..	11·9	11·6	10·5	10·9	11·0	12·2

The values for acidity include the hydrochloric acid combined with the hydrazine; for zero acidity, the precipitant was neutralised with ammonia solution before being allowed to react with the telluric acid.

DETERMINATION OF SEXAVALENT SELENIUM IN TELLURIC ACID—

3:3′-Diaminobenzidine is not suitable for the determination of sexavalent selenium,[4] nor does there appear to be any other sensitive colorimetric reagent. Conversion to the quadrivalent state is therefore necessary, and it would seem that reduction to the element and re-oxidation would be the most satisfactory course, as it would permit the removal of any tellurium in excess of the amount that can be tolerated.

The influence of acidity on the reduction of sexavalent selenium to the element by hydrazine was examined; contrary to the behaviour of quadrivalent selenium, recovery from the selenic state was markedly dependent on the hydrochloric acid concentration in the solution from which precipitation occurred. The conditions were the same as those used in studying the effect of acidity on the reduction of quadrivalent selenium, except that the amount of sexavalent selenium added to each 2 g of purified telluric acid was 9·8 µg; the results were—

Acidity, *N*	0·0	0·8	1·2	1·6	2·0	2·1	2·3	2·5	2·9
Selenium recovered, µg ..	0·2	3·0	4·1	5·8	8·9	9·3	9·6	10·1	9·6

Recovery is therefore complete in solutions at least 2·1 *N* in hydrochloric acid.

SEPARATION OF QUADRI- AND SEXAVALENT SELENIUM IN TELLURIC ACID—

The above sets of results reveal a possible method for separating the two forms of selenium in telluric acid. Reduction in neutral solution by a limited amount of hydrazine should precipitate a little tellurium and all the quadrivalent selenium initially present. After removing the precipitate and acidifying the filtrate to produce a solution 2·1 to 2·5 *N* in hydrochloric acid, a second reduction should precipitate a little more tellurium together with the selenium reduced from the sexavalent condition.

In order to study the separation and to see how complete it might be, experiments were undertaken in which radioactive selenium-75 in the quadri- and sexavalent forms was used.

For quadrivalent selenium, Specpure elemental selenium was irradiated for 1 week at pile factor 10 and dissolved in diluted nitric acid (1 + 1), and the solution was suitably diluted. In solutions containing 2 g of telluric acid and 19·5 μg of added inactive sexavalent selenium, precipitation of less than 0·5 g of tellurium was made from almost neutral solution in presence of 8·6 and 50·6 μg of activated quadrivalent selenium. In each experiment the filtrate was evaporated to 25 ml and any activity in the solution was sought by counting in a Geiger - Müller tube. In neither solution was there detectable activity, the limit of detection being 0·5 μg of selenium.

These experiments were repeated with 15-g amounts of telluric acid. It was not possible to determine any residual radioactivity in the filtrates, for the amount of material in solution was too great to permit evaporation to a volume sufficiently small to provide a low enough level for the limit of detection of the selenium tracer. The experiments with 2 g of telluric acid showed that most of the quadrivalent selenium was precipitated with the first small amount of tellurium; any remaining quadrivalent selenium should be precipitated when a second small amount of tellurium is reduced. Consequently, in the experiments with 15 g of telluric acid, a second precipitation was carried out and the precipitate was dissolved, this solution then being tested for radioactivity; in no experiment was any detected, the limit of detection again being 0·5 μg of selenium.

For sexavalent selenium, AnalaR sodium selenate was irradiated for 1 week at pile factor 10 and stored for 2 weeks before use to allow sodium-24 (half-life 15 hours) to decay. Since evidence had earlier been obtained that some reduction to quadrivalent and to elemental selenium occurred in the pile, the selenate was treated to re-oxidise these forms to the sexavalent state. It was then dissolved in about 25 ml of water, an equal volume of nitric acid was added, and the solution was boiled. Potassium permanganate solution was added in slight excess to the cooled solution, which was then diluted to give a final solution containing 5·0 μg of sexavalent selenium per ml.

The completeness of precipitation of sexavalent selenium from a solution 2·3 *N* in hydrochloric acid and containing 2 g of telluric acid and 15·6 μg of inactive quadrivalent selenium was tested in presence of 7·5 and 50 μg of activated sexavalent selenium. An initial precipitation of less than 0·5 g of tellurium from almost neutral solution was made to remove quadrivalent selenium. The precipitate was separated by filtration and dissolved to give 10 ml of solution. The solution of the precipitate formed in presence of 50 μg of activated sexavalent selenium showed activity equivalent to 1·2 μg of selenium, but the solution of the other precipitate showed no detectable activity; the detection limit represented 0·5 μg of selenium.

The filtrates from the first precipitations were evaporated to about 25 ml and made 2·3 *N* in hydrochloric acid, and a further precipitation was made from each. This should have carried down most of the sexavalent selenium. The filtrates were neutralised to prevent loss of selenium as chloride, evaporated to 25 ml and counted. In neither solution was there any detectable activity; the lower limit for the detection of activity in this volume of solution was equivalent to 1 μg of selenium. Within the limits of detection mentioned, therefore, separation of sexavalent selenium was complete.

When the initial solution contained 15 g of telluric acid, the same principle was used as for quadrivalent selenium, and activity was sought in solutions of the precipitate formed in neutral solution and in solutions of second precipitates from 2·3 *N* hydrochloric acid. For additions of 7·5 and 50·0 μg of activated sexavalent selenium in presence of 15·5 μg of the inactive quadrivalent form, the activity was less than the detection limit of 0·5 μg of selenium for the precipitate from neutral solution. The only measurable activity was from the second precipitation from hydrochloric acid solution when 50 μg of sexavalent selenium had been added; activity equivalent to 0·9 μg of selenium was found.

Under a wide range of conditions, therefore, the separation of sexa- and quadrivalent selenium from each other and the recovery of both forms from macro amounts of telluric acid are complete.

No difficulty was encountered in carrying out the separation and determinations when only a few grams of telluric acid were taken as sample. However, when about 15 g of telluric acid were taken, difficulty sometimes occurred in the reduction from the acid solutions, probably owing to the formation of H_2TeCl_6. This was overcome by increasing the amount of precipitant used, thereby increasing the amount of tellurium precipitated nearer to the limit tolerable in the selenium determination (0·5 g). It was also helpful if the solution was allowed only just to attain boiling-point during the precipitation.

When still larger amounts of telluric acid must be taken in order to have a reasonable amount of selenium for each determination, a preliminary ion-exchange separation of selenium on the acetate form of a strongly basic anion-exchange resin is desirable. Selenium can be completely recovered from a telluric acid solution having a pH of 2·6 to 2·8 by passage through a column of Amberlite IRA-400 resin in the acetate form.[5] If the column is eluted with 3 *M* sodium chloride without preliminary washing, the effluent contains the selenium and sufficient telluric acid to permit the precipitations of selenium *plus* tellurium to be carried out.

DETERMINATION OF TOTAL SELENIUM IN TELLURIC ACID—

For the purer grades of telluric acid, only a determination of total selenium is usually required. It has just been shown that sexavalent selenium is completely precipitated, together with a small proportion of the tellurium, by reduction of telluric acid from a solution 2·3 *N* in hydrochloric acid. The results on p. 134 suggest that quadrivalent selenium is completely precipitated under these conditions, and this was confirmed by using activated quadrivalent selenium. The experiments described above, in which radioactive selenium-75 was used to show that quadrivalent selenium was completely precipitated from neutral solutions of telluric acid, were repeated with solutions 2·3 *N* in hydrochloric acid. No radioactivity was detected in the filtrates after concentration to a small volume. Reduction in solutions having this acidity therefore serves to precipitate selenium completely from both quadri- and sexavalent states.

METHOD

REAGENTS—

Unless otherwise stated, all reagents should be prepared from analytical-grade materials.

Telluric acid—Analytical-reagent grade telluric acid has a variable content of selenium, sometimes as much as 70 p.p.m. Remove this selenium by passing a solution of telluric acid through a column of Amberlite IRA-400 resin in the acetate form.[5] (Convert the resin to the acetate form by treatment with a large excess of 3 *M* sodium acetate and then extensive washing with water.)

Hydrazine dihydrochloride solution—Prepare a saturated aqueous solution (about 37 per cent. w/v) of the laboratory-reagent grade material.

3:3′-*Diaminobenzidine dihydrochloride solution*, 0·5 *per cent. w/v, aqueous*—The reagent obtained from L. Light and Co. Ltd. was used.

Sodium hydroxide, N.

Ammonia solution, diluted (1 + 1).

Hydrochloric acid, concentrated.

Nitric acid, concentrated and dilute (1 + 99).

Sodium chloride, 3 M.

Standard quadrivalent selenium solution—Dissolve 0·1650 g of re-sublimed selenium dioxide in dilute nitric acid, and dilute to give a solution containing 2·35 μg of selenium per ml.

Standard sexavalent selenium solution—Initially, about 25 g of a 40 per cent. w/w solution of laboratory-reagent grade selenic acid were diluted to 1 litre. The concentration of selenium in this solution was determined gravimetrically after reduction by excess of hydrazine dihydrochloride solution in about 2·1 *N* hydrochloric acid solution.[6] Three such determinations gave values of 5·53, 5·50 and 5·51 g of selenium per litre, and suitable dilution gave a solution containing 2·76 μg of selenium per ml.

Later, a 0·4561-g portion of analytical-reagent grade sodium selenate decahydrate was dissolved in 1 litre of water, and 10 ml of this solution were diluted to 500 ml to give a solution containing 1·95 μg of selenium per ml.

PROCEDURE FOR SEPARATING AND DETERMINING QUADRI- AND SEXAVALENT SELENIUM—

For weights of telluric acid up to 17 *g*—Weigh a suitable amount of telluric acid, dissolve in water, and dilute to give from 50 ml of solution for 2 g of sample to 250 ml of solution for 17 g. To this solution add a volume of saturated hydrazine dihydrochloride solution varying from 2 ml for 2 g of sample to 4 ml for 17 g of sample, heat to boiling-point, and set aside on a hot-plate at 40° to 60° C for 3 hours. (After this, it is usually convenient to allow the precipitate to settle overnight.) Draw the supernatant liquid through a sintered immersion filter (porosity No. 2), and wash the precipitate three times with water. Reserve the filtrate and washings. Dissolve the precipitate in 5 ml of concentrated nitric acid, and determine the amount of quadrivalent selenium present as described previously.[3]

Evaporate the combined filtrate and washings, if necessary, to about 100 ml. Add 23 ml of concentrated hydrochloric acid to give a solution just over 2·1 N in this acid. Add a suitable volume of saturated hydrazine dihydrochloride solution, varying from 2 ml for 2 g of sample to 6 ml for 17 g, heat almost to boiling-point, and set aside for 3 hours on the hot-plate. Cool, separate the precipitate of tellurium as before, and determine the selenium produced by reduction from the sexavalent state.

For weights of telluric acid greater than 17 *g*—Dissolve a suitable amount of sample in water to provide a solution containing not more than 100 g of telluric acid per litre, and adjust the pH to between 2·6 and 2·8 with acetic acid. Pass the solution at 10 ml per hour through a 200-mm × 5-mm column of Amberlite IRA-400 ion-exchange resin in the acetate form previously conditioned by passage of 3 M sodium acetate adjusted to a pH between 2·6 and 2·8 with a few drops of acetic acid. Elute immediately with 200 ml of 3 M sodium chloride, and finally wash the column with three 25-ml portions of water. Add 4 ml of saturated hydrazine dihydrochloride solution to the effluent, and boil to precipitate selenium reduced from the quadrivalent state, together with some tellurium. Separate the precipitate, and determine selenium as before.

Evaporate the filtrate and washings to about 300 ml, add 65 ml of concentrated hydrochloric acid and 4 ml of saturated hydrazine dihydrochloride solution. Boil, and treat the precipitate in the usual way to determine selenium reduced from the sexavalent state.

PROCEDURE FOR DETERMINING TOTAL SELENIUM—

Depending on whether the weight of sample is greater or less than about 17 g of telluric acid, an initial concentration of selenium by ion exchange, as described above, will be necessary. Treat the sample solution or the effluent from the ion-exchange column as described in the appropriate section under "Procedure for Separating and Determining Quadri- and Sexavalent Selenium," but omit the first precipitation of tellurium. Determine the total selenium in the tellurium obtained by a single precipitation from hydrochloric acid solution.

RESULTS

Some typical figures for the recovery of added quadri- and sexavalent selenium in presence of various amounts of telluric acid are shown in Table I. Since the object of the investigation was to extend the determination of selenium in tellurium to the lowest possible limit, 4-cm cells were used in the spectrophotometer and no attempt was made to locate the upper limit for quantitative recovery of selenium. It can be seen that, for the solutions containing 25 g of telluric acid, batch No. 1 contained more sexavalent selenium than did batch No. 2.

Table II shows results for the recovery of added selenium by the procedure for determining total selenium.

It is not possible to obtain directly a figure for a complete reagent blank value in these procedures, as in absence of telluric acid there can be no precipitate of tellurium *plus* selenium. Further, attempts to carry out this precipitation in presence of only a small amount of telluric acid (less than 0·2 g), thereby greatly reducing the amount of selenium from this source, were not successful, as a considerable increase in the amount of reductant used was necessary to produce a suitable amount of tellurium precipitate. The blank is therefore only determinable on those reagents used after the precipitation and is in the range 1·2 to 1·7 μg of selenium. Selenium in the hydrazine dihydrochloride or in any hydrochloric acid added to the solution before precipitation should be included in the blank, but in fact appears as part of the selenium content of the telluric acid. However, this effect is in general small, and the results in Table I show that, for 17 g of telluric acid, it is less than 0·5 μg for each valency state of selenium.

When the ion-exchange separation is used, involving about 30 g of sodium chloride per separation, the largest error may be expected to arise, as any selenium in the sodium chloride will appear as being present in the telluric acid. Attempts were therefore made to

TABLE I

RECOVERY OF ADDED SELENIUM FROM TELLURIC ACID

	Amount added		Amount found	
	Quadrivalent selenium, µg	Sexavalent selenium, µg	Quadrivalent selenium, µg	Sexavalent selenium, µg
Solution containing 2 g of purified telluric acid—				
	0·0	0·0	0·2	0·3
	1·6	2·0	1·5	2·0
	1·6	5·9	2·0	6·0
	3·1	3·9	3·3	4·2
	4·7	2·0	4·5	2·1
	4·7	5·9	4·9	5·9
Solution containing 17 g of purified telluric acid—				
	0·0	0·0	0·2	0·4
	2·4	2·8	2·7	2·9
	4·7	2·8	4·8	3·3
	4·7	5·5	5·2	5·4
	7·1	8·3	7·9	8·5
	11·8	13·8	12·9	13·6
Solution containing 25 g of telluric acid—*				
Batch No. 1	0·0	5·5	1·7	9·9
	2·4	2·8	4·2	7·2
	4·7	0·0	6·0	3·6
	4·7	5·5	6·2	9·7
Batch No. 2	0·0	8·3	1·7	10·5
	2·4	11·0	4·0	13·6
	7·1	0·0	7·8	1·8
	9·4	2·8	10·8	4·6

* In experiments with this solution, most of the telluric acid was separated by ion exchange.

TABLE II

RECOVERY OF ADDED SELENIUM, AS TOTAL SELENIUM, FROM TELLURIC ACID

The selenium was added to a solution containing 15 g of purified telluric acid

Quadrivalent selenium added, µg	Sexavalent selenium added, µg	Total selenium added, µg	Selenium found, µg
0·0	0·0	0·0	1·5
0·8	1·0	1·8	3·0
1·6	0·0	1·6	3·1
0·0	2·0	2·0	3·5
3·1	2·0	5·1	6·4
3·1	5·9	9·0	10·0

TABLE III

EFFECT OF SODIUM CHLORIDE ON RECOVERY OF SELENIUM ADDED TO SOLUTION OF 2 g OF TELLURIC ACID

Selenium added, µg	Selenium found in absence of sodium chloride, µg	Selenium found in presence of 30 g of sodium chloride, µg	Selenium introduced by sodium chloride, µg
Quadrivalent selenium—			
0·0	0·4	1·2	0·8
3·1	2·9	3·2	0·3
7·8	8·0	8·5	0·5
Sexavalent selenium—			
0·0	0·5	1·2	0·7
5·9	5·8	6·6	0·8
9·8	10·1	10·6	0·5

compare the recoveries of standard amounts of quadri- and sexavalent selenium in presence of about 2 g of telluric acid and in absence and presence of 200 ml of 3 *M* sodium chloride. The results, which are shown in Table III, were not entirely conclusive, as the amount of each valency state of selenium found in the sodium chloride was less than the measurable portion of the reagent blank value. However, it seems probable that 200 ml of 3 *M* sodium chloride contain about 0·5 μg of each valency state of selenium, and the results in Table I for the solution containing 25 g of telluric acid are higher than the true values by this amount.

As the measured reagent blank value may be up to 1·7 μg of selenium, it is desirable that at least this amount of selenium should be present in each determination.

CONCLUSION

The proposed procedures are suitable for determining as little as 1·7 μg of selenium in either valency state (or as total selenium when only total selenium is determined). Since the only limit on the size of the telluric acid sample is placed by the capacity of the resin column for selenium, no final lower limit for the determination of selenium in telluric acid can be stated. Weights of sample up to 25 g have been treated.

The work described was carried out as part of the research programme of the National Chemical Laboratory, and this paper is published by permission of the Director of the Laboratory.

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A Polarographic Determination of Trace Amounts of Lead in Zirconium and Its Alloys

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A method has been developed for determining lead (<100 p.p.m.) in reactor-grade zirconium and zirconium alloys. The procedure involves a preliminary separation of the lead - diethyldithiocarbamate complex and subsequent determination of the metal by using a cathode-ray polarograph. The recommended procedure is satisfactory over the range 20 to 100 p.p.m. of lead, and, by simple modifications, both limits can be extended.

Iron and molybdenum interfere, but interference by amounts up to at least 1 and 2·5 per cent., respectively, can be overcome by a preliminary extraction with diethyl ether from acid solution.

MOST specifications for reactor-grade zirconium state that the concentration of lead must not exceed 100 p.p.m., and this has necessitated the provision of a reliable analytical procedure covering the range from about 10 to 100 p.p.m. of lead in zirconium and its alloys.

One of the more widely used procedures for determining small amounts of lead in metallurgical products depends on extraction of lead dithizonate with chloroform from an aqueous solution. Extraction at two different pH levels is usually necessary in order to overcome the effects of interfering elements, and the lead is subsequently determined absorptiometrically.[1] Such a procedure has been recommended for determining lead in zirconium,[2] but the method is time-consuming and reagent blank values are relatively high (equivalent to about 40 p.p.m. of lead, based on the examination of a 0·5-g sample).

Many methods have been described for the polarographic determination of lead in miscellaneous materials,[3,4] indicating that well defined waves, corresponding to reversible reductions, can be obtained in a wide range of base electrolytes. A direct polarographic method for determining lead in zirconium has been recommended,[5] but this procedure was unsatisfactory because of interference when alloying elements were present, especially copper and molybdenum.

It is known that lead diethyldithiocarbamate can be extracted with chloroform from an ammoniacal tartrate - cyanide solution[6]; the only other metals known to react are bismuth, thallium and cadmium. A method involving this principle has recently been applied to the determination of trace amounts of lead and bismuth in cast iron,[7] the determination being completed polarographically in presence of an acidified tartrate base electrolyte.

This procedure was therefore chosen as a basis for the development of a method for determining trace amounts of lead in zirconium and its alloys.

EXPERIMENTAL

Borosilicate glassware was used throughout the experimental work.

POLAROGRAPHY—

In preliminary experiments to establish the sensitivity of the polarographic method, dilute nitric acid (1 + 99) was used as the base electrolyte and a standard lead solution (1 ml ≡ 0·01 mg of lead) in nitric acid was prepared. Solutions containing 0·0 to 0·05 mg of lead in 5·0 ml of dilute nitric acid (1 + 99) were examined on a K1000 cathode-ray polarograph (Southern Instruments Ltd.). This instrument has a graticule in front of the screen calibrated horizontally from 0 to 500 mV and vertically from 0 to 5 μA. A sensitivity control (scale factor) makes it possible to read currents from 0·025 to 125 μA full scale. The capillary of the dropping-mercury electrode has a nominal bore of 0·05 mm and is 15 cm long; it is intended to cover a drop-time of one in 5 to 10 seconds, the weight of 1 drop being 7·35 mg (measured in 1·0 *N* potassium chloride).

The mercury reservoir was adjusted to give a drop-time of 7 seconds, and the solutions were transferred, in turn, to the polarographic cell. Each solution was de-oxygenated by bubbling argon through it for 10 minutes. When a start potential of —0·5 volt was used, the polarograms had well defined waves with a peak potential at —0·76 volt against a mercury-pool anode. With a scale factor (sensitivity setting) of 0·5, a wave height of 8 graticule divisions was obtained for the solution containing 0·01 mg of lead (equivalent to 20 p.p.m., based on a 0·5-g sample). This sensitivity was adequate for the range of lead contents to be determined; if necessary, the procedure could be extended to smaller amounts of lead simply by adjusting the scale factor of the instrument.

Wave heights were shown to be proportional to the amounts of lead added; typical polarograms are shown in Fig. 1.

EXTRACTION OF LEAD DIETHYLDITHIOCARBAMATE—

In preliminary tests, solutions containing 0·0 to 0·05 mg of lead were separately added to a mixture of dilute sulphuric and citric acids. Each solution was neutralised with ammonium hydroxide and a slight excess of this reagent was then added. After 5 ml of a 0·4 per cent. solution of sodium diethyldithiocarbamate had been added, the complex was extracted with three 10-ml portions of chloroform. The combined extracts were evaporated to dryness, nitric and perchloric acids were added, and the solution was again evaporated to dryness. The residue was dissolved in 5·0 ml of dilute nitric acid (1 + 99), and the solution was examined polarographically as described above. The results were identical with those obtained previously, thereby confirming that lead diethyldithiocarbamate can be completely extracted.

Solutions containing 0·0 to 0·05 mg of lead were then added to 0·5-g samples of commercially pure zirconium, the metal being subsequently dissolved in a mixture of sulphuric and fluoroboric acids. Each solution was oxidised with nitric acid and boiled to expel nitrous fumes, and citric acid solution was added to form a complex with the zirconium. Ammonium hydroxide was added in slight excess, the solution was transferred to a separating funnel, and potassium cyanide solution was added to form complexes with interfering metals, particularly copper. Sodium diethyldithiocarbamate solution was added, the lead complex was extracted with three 10-ml portions of chloroform, and the combined extracts were treated as described previously. The results were identical with those obtained formerly, thereby indicating that the procedure would be suitable for determining lead in zirconium over the range 20 to 100 p.p.m.; the reagent blank was equivalent to 7·5 p.p.m. of lead. Similar tests over a period of several weeks showed that the slope of the graph was slightly variable, presumably because of small variations in factors controlling the polarographic diffusion current, *e.g.*, temperature and rate of flow of mercury; a control test containing, say, 50 p.p.m. of lead, should therefore be carried out with each batch of determinations. In further tests, results were low and erratic when the amount of lead present exceeded about 120 p.p.m.; this was attributed to precipitation of lead, either as sulphate in acid solution or hydroxide in ammoniacal solution. When the amount of lead present is greater than 100 p.p.m., it is necessary to use a smaller weight of sample.

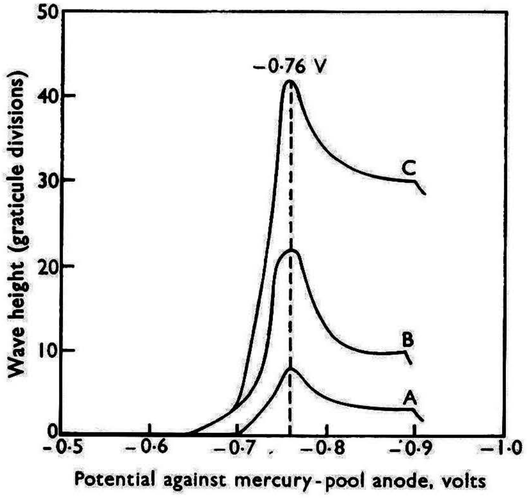

Fig. 1. Typical polarograms for lead: curve A, 0·01 mg of lead; curve B, 0·03 mg of lead; curve C, 0·05 mg of lead. (Scale factor, 0·5)

EFFECT OF CONCENTRATION OF REAGENTS—

Tests on solutions containing 0·5 g of commercially pure zirconium and 0·03 mg of lead showed that, after neutralisation, increase in the amount of ammonium hydroxide, sp.gr. 0·925, over the range 2 to 5 ml had no significant effect on the determination, but, above 5 ml, results gradually decreased as the ammonium hydroxide concentration increased; this was attributed to incomplete extraction of the complex.

Variation in the amount of potassium cyanide solution (20 per cent.) from 2·5 to 12·5 ml had no significant effect, and in subsequent tests the volume of this reagent added was 5 ml.

Increases in the amount of citric acid solution (60 per cent.) over the range 2 to 10 ml had a negligible effect. Less than about 2 ml was insufficient to react with the amounts of zirconium present, and zirconium hydroxide was precipitated when ammonium hydroxide was subsequently added.

EFFECT OF OTHER METALS—

Tests on solutions containing 0·5 g of zirconium and the equivalent of 60 p.p.m. of lead established that no significant interference was caused by the presence of at least 2·5 per cent. of copper, 2 per cent. of tin, 0·5 per cent. of nickel, 0·2 per cent. of chromium, 0·1 per cent. of zinc, 0·05 per cent. of manganese, 0·02 per cent. of cobalt or 0·01 per cent. of cadmium.

Concentrations of iron up to about 0·2 per cent. did not interfere, provided that the chloroform extraction was made immediately after the sodium diethyldithiocarbamate solution had been added, but concentrations above about 0·2 per cent. caused low results; Rooney[7] attributes this interference to oxidation of the sodium diethyldithiocarbamate by ferric iron. Interference by up to at least 1 per cent. of iron was overcome by means of a preliminary extraction of iron with diethyl ether from a mixture of hydrochloric and sulphuric acids. Tests on solutions containing from 0·01 to 0·5 per cent. of molybdenum and the equivalent of 40 p.p.m. of lead showed that molybdenum is partly extracted by chloroform and produces a wave immediately in front of the lead wave. In presence of more than about 0·1 per cent. of molybdenum, sufficient of this element was extracted to distort the lead wave and prevent accurate measurement of its height (see Fig. 2). A preliminary extraction of an acidic solution with ether, as described under "Procedure," prevented interference from up to at least 2·5 per cent. of molybdenum. When the lead content is low (10 p.p.m. or less) the effect of molybdenum is proportionally greater, and an ether extraction is necessary for concentrations of molybdenum above about 0·02 per cent.

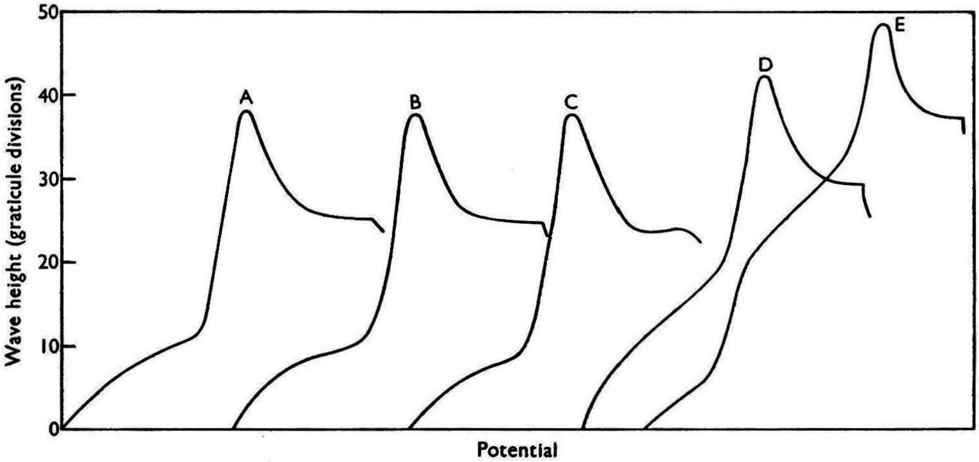

Fig. 2. Effect of different concentrations of molybdenum on wave produced by 0·02 mg of lead (equivalent to 40 p.p.m. in 0·5-g sample): curve A, 0·01 per cent.; curve B, 0·05 per cent.; curve C, 0·1 per cent.; curve D, 0·2 per cent.; curve E, 0·5 per cent. (Start potential, –0·5 volt; scale factor, 0·25)

METHOD

APPARATUS—

The use of borosilicate glassware is recommended.

REAGENTS—

Standard lead solution—Dissolve 0·5 g of high-purity lead in 50 ml of diluted nitric acid (1 + 1), add 50 ml of nitric acid, sp.gr. 1·42, and dilute to 500 ml in a calibrated flask. Dilute 10 ml of this solution to 1 litre.

$$1 \text{ ml} \equiv 0{\cdot}01 \text{ mg of lead.}$$

Sodium diethyldithiocarbamate solution, 0·4 per cent.—Dissolve 0·4 g of the reagent in about 60 ml of water, add 2 ml of ammonium hydroxide, sp.gr. 0·925, and dilute to 100 ml. Extract with two 10-ml portions of chloroform, and discard the organic layers. This solution must be freshly prepared.

Potassium cyanide solution, 20 per cent.—Dissolve 20 g of potassium cyanide in water, and dilute to 100 ml. To this solution add 5 ml of 0·4 per cent. sodium diethyldithiocarbamate solution, extract with 10-ml portions of chloroform until the organic layer remains colourless, and discard the organic layers. This solution must be freshly prepared.

PROCEDURE—

For each batch of samples carry out both a blank determination on the reagents and control tests on solutions containing the equivalent of 25 and 50 p.p.m. of lead (based on a 0·5-g sample).

Place 0·5 g of sample (see Note) in a 150-ml beaker, and add 20 ml of dilute sulphuric acid (1 + 4) and 1 ml of fluoroboric acid. Warm gently to assist solution, oxidise with nitric acid, sp.gr. 1·42, added dropwise, and boil gently for 1 minute. Cool, add 5 ml of 60 per cent. citric acid solution and ammonium hydroxide, sp.gr. 0·925, until the solution is neutral to litmus paper, and then add 2 ml of ammonium hydroxide in excess. Cool, transfer the solution to a separating funnel, and add 5 ml each of 20 per cent. potassium cyanide solution and 0·4 per cent. sodium diethyldithiocarbamate solution.

TABLE I

LEAD CONTENTS FOUND BY THE PROPOSED METHOD

For lead contents less than 20 p.p.m. the scale factor of the instrument was adjusted to give increased sensitivity

Sample No.	Description of sample	Lead added, p.p.m.	Lead found, p.p.m.
1	Commercially pure zirconium	Nil	9, 9, 10, 11
2	Commercially pure zirconium	Nil	4
		20	23, 26, 24
		40	44, 42, 46
		60	64, 67, 63, 59, 60, 63, 64, 64
3	Zircaloy 2*	Nil	7, 6, 7
4	Zircaloy 2*	Nil	17
		20	37, 39, 36
		40	57, 55, 57
		60	78, 75, 76
5	Zirconium + 0·5 per cent. each of copper and molybdenum	Nil	20
		20	40, 41, 38
		40	60, 58, 62
		60	78, 82, 82
6†	Zirconium + 0·5 per cent. each of copper and molybdenum	Nil	43, 43, 46, 44, 43, 41, 44, 45, 42

* This alloy contained zirconium *plus* 1·5 per cent. of tin, 0·12 per cent. of iron, 0·1 per cent. of chromium and 0·05 per cent. of nickel.

† The standard deviation of the results for this sample was 1·5 p.p.m.

Without delay extract with three separate 10-ml portions of chloroform, and transfer the chloroform layers to a 50-ml beaker. Evaporate the combined extracts just to dryness, add 3·0 ml each of nitric acid, sp.gr. 1·42, and perchloric acid, sp.gr. 1·54, and then heat gently until the solution has evaporated to dryness.

Cool, dissolve the residue in 5·0 ml of dilute nitric acid (1 + 99), and transfer the solution to a polarographic cell. Bubble argon through the solution for 10 minutes to remove dissolved oxygen, and then develop the polarogram with a start potential of —0·5 volt against a mercury-pool anode. (If a Southern Instruments cathode-ray polarograph, model K1000, is used a scale factor (sensitivity setting) of 0·5 is usually suitable for lead contents from 20 to 100 p.p.m.; for less than 20 p.p.m. of lead, adjust the scale factor accordingly.)

The peak potential for lead under these conditions is about —0·76 volt.

Calculate the lead content of the sample by reference to the wave heights found for the control solutions.

NOTE—For lead contents exceeding 100 p.p.m. use a smaller weight of sample. For alloys containing more than 0·2 per cent. of iron or more than 0·1 per cent. of molybdenum, or both, dissolve the sample in 20 ml of dilute sulphuric acid (1 + 9) and 0·5 ml of fluoroboric acid, oxidise with a slight excess of nitric acid, sp.gr. 1·42, and evaporate until fumes of sulphur trioxide are evolved. Cool, add 40 ml of diluted hydrochloric acid (1 + 1), transfer to a separating funnel, and extract with one 40-ml and then four successive 25-ml portions of diethyl ether. Discard the ether extracts, add 5 ml of 60 per cent. citric acid solution, and continue as described above.

APPLICATION OF THE METHOD

The proposed method was applied to solutions of commercially pure zirconium and zirconium alloys containing the equivalent of 20 to 60 p.p.m. of added lead; recoveries were all satisfactory. Replicate determinations were made on typical samples and reproducible results were obtained (see Table I); the standard deviation at the 40 p.p.m. level was about 1·5 p.p.m.

CONCLUSIONS

The proposed procedure is suitable for determining 20 to 100 p.p.m. of lead in zirconium, Zircaloy 2 and a zirconium alloy containing 0·5 per cent. each of copper and molybdenum. Smaller amounts of lead can be readily determined by adjusting the scale factor of the cathode-ray polarograph. When the lead content is above 100 p.p.m., a smaller weight of sample must be used.

This relatively simple procedure is recommended for use on a control basis. About twelve determinations can be completed by one analyst in a normal working day.

The standard deviation of the method at the 40 p.p.m. level is about 1·5 p.p.m.

We thank Mr. W. T. Elwell, Division Chief Analyst, for helpful suggestions and assistance in the preparation of this paper.

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A Polarographic Method for Determining Nitrite in Meat-curing Brines

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A polarographic method for determining nitrite is described; it is based on the formation of 1-nitroso-2-naphthol from nitrite and 2-naphthol. The nitroso compound is reduced at the dropping-mercury electrode. The completeness of the reaction, the effect of interfering substances, the reproducibility and the recovery have been investigated.

THE polarographic determination of nitrite is usually carried out by acidifying the solution and measuring the nitroso wave. This is a convenient method for relatively pure solutions and has been used by Ingram[1] for determining nitrite in brines. We have used it for analysing pump-brines, but for protein-contaminated solutions such as cover-brines the method is less satisfactory, especially at low concentrations of nitrite.

During the development of a method for determining nitrate,[2] the formation of nitroso compounds was observed when nitrite was present during the nitration reaction, and this investigation was started with the aim of developing a method for the polarographic determination of nitrite by means of the nitroso reaction. As the half-wave potentials of nitroso compounds show little specificity, interference from nitroso compounds formed from substances already present in the solution need not be feared.

The reagent used is a solution of 2-naphthol in sodium hydroxide, which, when acidified in presence of sodium nitrite, results in the formation of 1-nitroso-2-naphthol (1:2-naphthoquinone-1-oxime); this compound shows a well defined reduction wave. Some aspects of the polarography of 1-nitroso-2-naphthol were studied by Kolthoff and Langer[3] in connection with the amperometric titration of cobalt.

The half-wave potential at pH 9·9 (—0·33 volt) seemed to be the most desirable, as a solution of pH 9·7 is easily obtained by neutralising a hydrochloric acid solution with ammonia. Above a certain concentration, small variations in the total amount of ammonia present have little effect on the pH.

During the progress of this work an interesting paper by Peach was published[4]; he used the nitroso reaction for the identification and colorimetric determination of nitrites with resorcinol. Nitrosoresorcinol and 1-nitroso-2-naphthol should be equally suitable for the polarographic determination of nitrite.

EXPERIMENTAL

FORMATION OF 1-NITROSO-2-NAPHTHOL—

The reagents described below were used to study the reaction between nitrite and 2-naphthol. A measured volume of standard sodium nitrite solution, 0·5 ml of 2-naphthol reagent solution and 0·25 ml of 19 per cent. hydrochloric acid were placed in each of a series of 10-ml calibrated flasks. The flasks were placed in an ice - water mixture to ensure that the reaction took place at a low temperature. The reaction was allowed to proceed for a definite time, at the end of which 5·0 ml of ethanol and then 1·0 ml of ammonia solution were placed in each flask, and the contents of the flasks were allowed to attain room temperature. The mixtures were immediately diluted to volume with water, and polarograms were recorded between 0·0 and —0·5 volt with a dropping-mercury cathode and a mercury-pool anode.

The diffusion current so obtained increased with the reaction time and became constant after about 45 minutes. In subsequent experiments the reaction was allowed to proceed for at least 1 hour. The relationship between diffusion current and initial nitrite concentration was linear between 0·005 and 0·15 per cent. of sodium nitrite.

COMPLETENESS OF NITROSO REACTION—

The diffusion current produced by a known concentration of analytical-reagent grade 1-nitroso-2-naphthol was compared with that produced by the 1-nitroso-2-naphthol formed when a known amount of nitrite was allowed to react with 2-naphthol. The solutions used in this series of experiments were identical with respect to buffer concentrations, etc. It was found that the reaction was about 90 per cent. complete at concentrations between 0·008 and 0·08 per cent. of sodium nitrite.

INTERFERING SUBSTANCES—

The only interfering substances expected to be present in some brines were proteins. It was found that the presence of proteins caused a decrease in the amount of nitrite, as measured by the diffusion current after reaction with 2-naphthol. This interference was overcome by heating the solution in a bath of boiling water and separating the precipitated proteins by filtration, nitrite then being determined in the filtrate.

METHOD

APPARATUS—

A photographic recording Heyrovský-type polarograph manufactured by Laboratorni Pristroje, Prague, Czechoslovakia, was used.

REAGENTS—

2-Naphthol reagent solution—Dissolve 2 g of sodium hydroxide in about 50 ml of water, add 2 g of 2-naphthol, and dilute to 100 ml with water.

Hydrochloric acid, 19 *per cent.*—Dilute 1 volume of hydrochloric acid, sp.gr. 1·19, with 1 volume of distilled water.

Ammonia solution, 12 *per cent.*—Dilute 1 volume of ammonia solution, sp.gr. 0·910, with 1 volume of distilled water.

Sodium acetate solution, saturated, aqueous.

Ethanol, 96 *per cent.*

Standard nitrite solution—Dissolve 0·2 g of sodium nitrite in water, and dilute to 100 ml in a calibrated flask.

PROCEDURE FOR COVER-BRINES—

Place 20 to 40 g of sample in a 50-ml calibrated flask, add 0·20 ml of sodium acetate solution, mix well, and heat in a bath of boiling water for 30 minutes. Allow the contents of the flask to attain room temperature, dilute to the mark with water, and filter. Place 2·00 ml of filtrate in each of two 10-ml calibrated flasks, and in one of the flasks also place 0·50 ml of standard sodium nitrite solution. Stand the flasks in an ice - water mixture, and add 0·50 ml of 2-naphthol reagent solution and 0·25 ml of 19 per cent. hydrochloric acid to the contents of each, mixing thoroughly after each addition. After 1 hour, place 5 ml of ethanol and 1·0 ml of ammonia solution in each flask, and dilute to the mark with water. Record a polarogram of each solution between —0·1 and —0·5 volt against the mercury-pool anode, and correct the diffusion current for the reagent blank value. Calculate the concentration of nitrite in the sample from the increase in diffusion current caused by the addition of the standard nitrite solution.

Note that, at extremely low concentrations of nitrite, it is better to correct for the blank value as follows. Place 2·00 ml of the filtrate or sample in a 10-ml calibrated flask, and add 1 drop of a 10 per cent. solution of urea and 0·25 ml of 19 per cent. hydrochloric acid. After 30 minutes, add 0·50 ml of 2-naphthol reagent solution, and continue as described above. The addition of urea and hydrochloric acid destroys nitrite, and the blank value so obtained is more reliable than that for the reagents alone, since all the variables present in the sample, except nitrite, are also present in the blank solution.

PROCEDURE FOR PUMP-BRINES—

Place 20 to 40 g of sample in a 50-ml calibrated flask, dilute to the mark with water, and filter if the solution is not clear. Continue as described under "Procedure for Cover-brines," beginning at "Place 2·00 ml of filtrate. . . ."

DISCUSSION OF RESULTS

The standard-addition method was used in order to account for the many variables present in such complex mixtures as meat-curing brines.

In order to study the reproducibility of the method, a sample of cover-brine containing 0·175 per cent. of added sodium nitrite was analysed six times; the mean value found was 0·1752 per cent. of sodium nitrite with a standard deviation of 0·0014, *i.e.*, the coefficient of variation was 0·80 per cent. The results of some recovery experiments are shown in Table I.

TABLE I

RECOVERY OF SODIUM NITRITE FROM COVER-BRINE

Original sodium nitrite content, %	Sodium nitrite added, %	Sodium nitrite found, %	Recovery of added nitrite, %
0·046	0·200	0·250	102·0
0·026	0·050	0·074	97·5
0·048	0·125	0·172	99·2
0·048	0·075	0·123	100·0

The minimum concentration of sodium nitrite that could be determined by the proposed method was 0·0075 per cent.

I thank Mr. B. Krol and Dr. P. Hirsch-Ayalon for their interest in this work and Miss J. Jongerden for carrying out many of the experiments.

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Notes

A FIELD METHOD FOR THE DETERMINATION OF SULPHUR DIOXIDE IN AIR

A PREVIOUSLY described method for the approximate determination of sulphur dioxide in air[1] depends on the reaction between the gas and starch - potassium iodide - potassium iodate test paper. This test is not specific for sulphur dioxide, and, unless strict control is exercised during the preparation of the test paper, the stains produced may not be uniform; this makes their comparison with a standard colour chart difficult.

Gandolfo[2] used test papers impregnated with ammoniacal zinc nitroprusside for determining small amounts of sulphur dioxide in foodstuffs by allowing the gas liberated by acid to diffuse past a strip of the test paper. However, for reasons stated elsewhere,[3] it is better in quantitative determinations to draw the gas through the test paper, and a method involving this technique is described here. The use of the reagent supported on silica gel did not provide a sufficiently sensitive method.

METHOD

APPARATUS—

Aspirator—A rubber-bulb hand aspirator of capacity approximately 120 ml.

Test-paper holder—A suitable holder has been described previously.[4]

Insufflator—An all-glass spray type similar to that used in the determination of lead fume[5] is satisfactory.

Filter-papers—Postlip No. 633 extra-thick white filter-paper in strips 1-inch wide.

REAGENTS—

Sodium nitroprusside solution—A 10 per cent. w/v aqueous solution of analytical-reagent grade sodium nitroprusside.

Zinc sulphate solution—A 6 per cent. w/v aqueous solution of analytical-reagent grade zinc sulphate heptahydrate.

Ammonia solution, sp.gr. 0·880.

PREPARATION OF TEST PAPERS—

To 5 volumes of sodium nitroprusside solution add, with stirring, 5 volumes of zinc sulphate solution, and dissolve the precipitated zinc nitroprusside by adding 1 volume of ammonia solution. Thoroughly soak strips of filter-paper in this solution, allow the superfluous liquid to drain off, and dry the papers at a temperature not exceeding 40° C in an atmosphere free from chemical fumes. Store the dried test papers in a stoppered container in the dark. Freshly prepared test papers should be pale pink, although they may acquire a pale greenish blue tint at the edges after prolonged storage. This change in colour does not affect their performance.

PROCEDURE—

Hold a piece of dried test paper 5 to 6 inches from the jet of the insufflator, and spray with water for 6 seconds (see Note). Fix this moistened test paper in the holder, and attach the holder to the aspirator with a piece of rubber tubing. Draw a 360-ml sample of air through the paper at a rate not exceeding 6 ml per second. Remove the test paper from the holder, and compare the brick-red stain produced if sulphur dioxide is present with a standard stain chart or with a disc of standard tints (obtainable from Tintometer Ltd., Salisbury, Wilts.) in order to determine the concentration of the gas.

NOTE—The spraying of the test papers immediately before use can be avoided by adding glycerol to the solution from which they are prepared, provided that the zinc nitroprusside is dissolved by adding solid ammonium acetate instead of ammonia solution. However, it was found that papers so prepared failed after about 4 weeks' storage. It has been observed that, although dry zinc nitroprusside kept in the dark appears to be stable indefinitely, ammoniacal solutions of the compound decompose from the outset to yield a precipitate of zinc ferricyanide; it is possible that this decomposition occurs in the moist papers during storage.

DISCUSSION OF THE METHOD

STANDARD STAINS—

Standard atmospheres containing sulphur dioxide were prepared by Cummings and Redfearn's method,[6] and stains produced by these atmospheres were copied by means of water colours in order to prepare a standard stain chart. A series of five colours, representing 1, 2·5, 5, 10 and 20 p.p.m. of sulphur dioxide in a 360-ml sample, was found to be adequate. Tints representing the same series are provided on the disc mentioned above.

SPECIFICITY—

Hydrogen chloride present in concentrations exceeding 150 p.p.m. was found to produce a slight discoloration of the test paper. Hydrogen sulphide at a concentration of 15 p.p.m. gave a just-discernible stain. Carbon disulphide at concentrations up to at least 500 p.p.m. yielded no stain.

SCOPE—

With a 360-ml sample the range of concentrations of sulphur dioxide determinable with an accuracy to within about ±20 per cent. is 1 to 20 p.p.m. Concentrations outside these limits can be measured by increasing or decreasing the size of the sample. The stains are stable for about 2 hours.

This Note is published by permission of the Department of Scientific and Industrial Research, and we thank Dr. B. E. Dixon for helpful advice and Mr. D. S. Williams for practical help.

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THE MICRO-DETERMINATION OF ENDRIN

THE use of a boron trifluoride reagent in the determination of small amounts of dieldrin has been described.[1] Endrin appears to undergo a similar isomerisation to a polycyclic ketone,[2] although Cookson and Crundwell[3] favour a formula involving the formation of an additional ring during the re-arrangement.

It was hoped that the reaction conditions used in the method for dieldrin[1] might be directly applicable to the determination of endrin. However, the optimum time of heating was found to be 30 minutes, as shown by the results for 100 μg of endrin—

Time of heating at 78° C, minutes	10	30	60	120
Absorption at 440 mμ (2-cm cell)	0·310	0·310	0·275	0·275

The optimum temperature was found to be 40° C; the results, for 100 μg of endrin, were—

Temperature, °C	20	40	60
Absorption at 440 mμ (2-cm cell)	0·360	0·365	0·345

The sensitivity of the method is only approximately half that of the method for dieldrin, a similar amount of which would have given an absorption of 0·840 in a 2-cm cell.

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THE SEPARATION OF TOTAL RARE EARTHS AND THORIUM FROM SOME MULTIPLE-OXIDE MINERALS

A FAVOURED stage in the separation of (total) rare earths in mineral analysis is that involving precipitation in dilute hydrofluoric acid to give the insoluble fluorides of magnesium, calcium, scandium, strontium, barium, rare earths and thorium. The presence of alkalis, however, renders the rare-earth fluorides appreciably soluble owing to the formation of alkali - rare-earth double fluorides, and it is clear that the method cannot be used after an alkali attack on the mineral (or on an alkali-containing mineral such as pyrochlore). Many multiple-oxide minerals will dissolve in concentrated mineral acids (albeit more or less slowly), but some resist even hot hydrofluoric acid - aqua regia mixture. The titanium-rich mineral davidite is often unattacked by acids, as also are tantalum-rich niobate - tantalates such as yttrotantalite and tanteuxenite. For such minerals the sulphur dichloride - chlorine method of decomposition[1,2] is ideal, and it is highly advantageous in the partial analysis of the many acid-soluble rare-earth niobate - tantalates. The method and its merits have been known for nearly 50 years, but it seems to have enjoyed only limited popularity with mineral analysts. We have recently used it for obtaining rare earths from a variety of minerals and think that a note endorsing its scope might be useful.

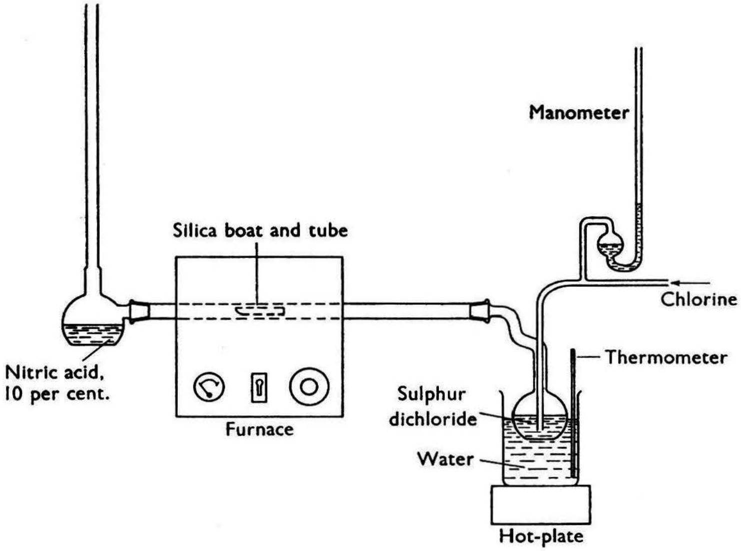

Fig. 1. Apparatus for separating rare earths and thorium

About 1 g of ground mineral (150 mesh) is weighed into a silica boat, 10 cm × 1 cm, and introduced into a silica tube, 60 cm × 2·8 cm, held in a furnace (see Fig. 1). Chlorine is bubbled at the rate of 250 ml per minute through a flask of sulphur dichloride kept at 40° to 50° C. The temperature of the furnace is raised to 500° C over a period of 20 minutes and kept at this temperature for 1 hour. Titanium, niobium and tantalum often begin to volatilise from the sample as soon as the temperature reaches 400° to 430° C to give a thick cloudy vapour, which condenses in the flask containing 50 ml of 10 per cent. nitric acid. Contemporaneously, a pale yellow sublimate collects on the inside of the silica tube away from the furnace. Any iron in the sample volatilises at a higher temperature than do titanium, niobium and tantalum; its presence is confirmed by a dark red-brown film coating the inside of the tube near the furnace. If after 1 hour at 500° C the mineral is not attacked, the temperature is increased to 550° C. The residue in the boat contains all the sodium, magnesium, aluminium, silicon, potassium, calcium, scandium, strontium, yttrium, barium, lanthanons and thorium originally present in the mineral; titanium, niobium and tantalum are completely absent, and there is considerably less iron than in the original mineral—it is sometimes sensibly absent. Uranium divides itself between residue and condensed sublimate. If no sodium or potassium was originally present, the residue can be dissolved in nitric acid (to oxidise uranium to uranyl) and treated with dilute hydrofluoric acid to precipitate fluorides of the alkaline earths, scandium, the rare earths and thorium. Rare earths with thorium are separated from these fluorides after solution in perchloric acid by precipitation with methyl oxalate, a modification[3] of Gordon, Vanselow and Willard's method[4] being used.

A titanium-poor and alkali-free niobate - tantalate (probably a samarskite or yttrocolumbite) was analysed for rare-earth oxides (RE_2O_3) *plus* thoria six times after a conventional mineral acid attack; the results were 15·21, 15·37, 15·44, 15·53, 15·59 and 15·63 per cent. by weight (mean 15·46 per cent., standard deviation ±0·16 per cent.). The same mineral was decomposed by the sulphur dichloride - chlorine method and analysed for rare-earth oxides *plus* thoria; the results were 14·78, 14·80, 15·19, 15·23, 15·32 and 15·42 per cent. by weight (mean 15·12 per cent., standard deviation ±0·27 per cent.). The conventional method had a coefficient of variation of just over 1 per cent. compared with that for the sulphur dichloride - chlorine method of just under 2 per cent. and an average yield of 2½ per cent. higher. The difficulty of removing all the residue from the silica boat after sulphur dichloride - chlorine decomposition may partly account for this small difference.

The method has been found most satisfactory for obtaining rare earths (and the limited amount of thoria) from davidite, which has a low rare-earth oxide content (4 to 12 per cent.) and high titania and iron contents (up to 60 per cent. and up to 20 per cent., respectively). The yield from the davidite-like mineral from Tete, Mozambique, was 6·23 per cent. of rare-earth oxides *plus* thoria compared with 5·67 per cent. obtained by Ryan and Maple (see Bannister and Horne[5]), who used a sodium peroxide attack and then separations by old-established methods. On the other hand, we have looked for rare earths in three previously analysed Australian davidite-like minerals reported to contain no rare earths[6] and found 6·73, 5·69 and 2·41 per cent. of rare-earth oxides *plus* thoria in the three different types; it was confirmed that the thoria content of the separated rare-earth oxides *plus* thoria was low.

Rare-earth minerals that are attacked by the sulphur dichloride - chlorine method include davidite, members of the euxenite - polycrase series, members of the fergusonite - formanite series, samarskite, tanteuxenite, yttrotantalite and yttrotungstite. The multiple-oxide minerals ilmenite and ilmenorutile are also attacked; this may be turned to advantage in the determination of magnesium oxide (and alumina) in these minerals.

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THE DETECTION OF OXIDISED STARCHES

IT it difficult to distinguish between oxidised starches and unmodified starches by either the colour reaction with iodine or examination under the microscope. However, Schoch and Maywald[1] have described a method in which the increased dye-absorbing power of an oxidised starch compared with that of an unmodified one is utilised. The identification of the oxidised starch depends on visual comparison under a miscroscope. In order to put the method on a quantitative basis and to indicate more easily the degree of dye absorption, the method described below was devised.

METHOD

Transfer 0·5 g of starch to a 200-ml calibrated flask with water, add 10 ml of a 0·1 per cent. aqueous safranine solution, and dilute to about 190 ml with water. Set aside for 1 hour, with frequent swirling, and then dilute to the mark with water. Shake, and then spin in a centrifuge until the suspension clarifies. Dilute 10 ml of the clear supernatant liquid to 50 ml with water. At the same time, prepare a series of standard solutions by taking 10-, 7·5-, 5·0- and 2·5-ml portions of a solution containing 10 ml of 0·1 per cent. safranine solution in 200 ml of water and diluting each to 50 ml; these standard solutions represent 100, 75, 50 and 25 per cent. of dye, respectively. Measure the amount of dye in the sample preparation by comparing its colour with those of the standards. This can be done visually if only an estimate is required; alternatively, a suitable comparator can be used. If a spectrophotometer is available, more accurate results can be obtained by measuring the optical densities of all the solutions at 515 to 520 mμ, water being used as reference solution.

RESULTS

Table I shows some typical results found for maize and potato starches.

TABLE I

TYPICAL RESULTS FOR VARIOUS STARCHES

Starch	Dye unabsorbed, %	Range of results, %
Unmodified starches—		
Maize	83	80 to 90
Potato	60	55 to 70
Thick-boiling oxidised starches—		
Maize	46	—
Potato	37	—
Thin-boiling oxidised starches—		
Maize	3	—
Potato	2	—

Any of the other dyes suggested by Schoch and Maywald[1] can be used instead of safranine, with suitable alterations in the dilutions and absorption wavelength.

The proposed method has been used for the routine examination of starches as an aid to their classification into modified and unmodified starches. Differences in moisture content have been ignored.

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MODIFICATIONS TO THE BROMIDE-DISTILLATION METHOD FOR DETERMINING ARSENIC

THE bromide-distillation method described by Magnuson and Watson[1] for the micro-determination of arsenic in biological materials was adapted by Bartlet, Wood and Chapman[2] for determining arsenic in fruits and vegetables. Maren[3] used the method in studying the pharmacology of arsenical drugs, but occasionally encountered positive blanks and aberrant high values, which he ascribed to insufficient acid being carried over during the distillation. Magnuson and Watson depended on the amount of hydrobromic acid distilled in 4 minutes to give the correct conditions of acidity for forming the molybdenum-blue colour; they stated that the range for colour development was 1·0 to 5·0 milli-equivalents of distilled acid. Maren showed that the permissible lower limit of acidity was 2·1 milli-equivalents of halogen acid and recommended the addition of a further 1 milli-equivalent of acid together with the ammonium molybdate solution. Bartlet, Wood and Chapman concluded that the low acidity of the distillate reported by Maren was caused either by an excess of water in the distillation flask or by insufficient heat. These workers found that the amount of water placed in the distilling flask with the sample aliquot was critical when the distillation time was 4 minutes. To avoid these difficulties they continued distillation until thin fumes appeared in the lower chamber of the trap; these fumes appeared between 4 and 9 minutes after the potassium bromide solution had been added.

When this modified bromide-distillation method was used in this laboratory for an extensive survey of arsenic residues on apples, it was found that the amount of acid distilled could not be adequately controlled and that recoveries of arsenic were unacceptable. However, if the final acidity of the distillate is controlled by preliminary neutralisation and then addition of a known amount of acid, accurate results can be obtained. This modification removes the necessity for any specific type of heater for the distillation. Recoveries of arsenic were further improved by increasing the amount of potassium bromide solution added, and complete colour formation was ensured by increasing the concentration of the hydrazine sulphate solution from 0·05 to 0·10 per cent.

METHOD

REAGENTS—

In addition to the potassium bromide solution, molybdenum colour reagent and standard quinquivalent arsenic solution specified previously,[2] the reagents required are—

Sodium hydroxide, 5 N.

Hydrazine sulphate solution, 0·10 *per cent. w/v, aqueous.*

Indicator papers—Accutint indicator papers, wide range B, obtained from Anachemia Chemicals Ltd., Montreal, were used; other similar indicator papers could be used.

PROCEDURE—

Carry out the prescribed procedure[2] to the point at which the distillate is transferred through the top of the trap to a 25-ml beaker, but add 3·0 ml of potassium bromide solution through the dropping funnel instead of 2·0 ml, as specified. Rinse the trap with three 2-ml portions of water, and combine the rinsings with the distillate. Add 5 *N* sodium hydroxide dropwise until the distillate is neutral. (Check by mixing the solution with a drawn-out glass rod after each addition of alkali and touching an indicator paper with the point of the rod; the first appearance of a green colour, usually after from 6 to 12 drops of 5 *N* sodium hydroxide have been added, indicates that the solution is neutral.) Transfer to a 25-ml calibrated flask, add 3·0 ml of 1·0 *N* hydrochloric acid, and form the colour with ammonium molybdate and hydrazine sulphate solutions, as described for the standards.[2] Measure the optical density at 840 mμ with a spectrophotometer.

RESULTS

Some results for the recovery of arsenic by the proposed procedure are shown in Table I. "Average variation" refers to the average of differences between "added" and "recovered" arsenic. It was judged that recovery was best when the amount of arsenic added was from 10 to 25 μg; all sample aliquots were therefore chosen to contain as close to 15 μg of arsenic as possible.

TABLE I

RECOVERY OF ADDED ARSENIC BY PROPOSED METHOD

Amount of arsenic added,	Range of recoveries (highest minus lowest)		Average variation		Number of determinations
μg	μg	%	μg	%	
5·0	0·4	8·0	+0·28	+4·57	7
10·0	0·6	6·0	−0·18	−1·80	5
15·0	0·4	2·7	−0·20	−1·35	6
20·0	0·5	2·5	−0·78	−3·90	5
25·0	0·9	3·6	−0·99	−3·94	7
30·0	1·6	5·3	−1·97	−6·53	3

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Apparatus

A SIMPLE SEPARATING APPARATUS FOR SOLVENT EXTRACTIONS WITH SOLVENTS LIGHTER THAN WATER

WHEN extracting from a liquid—usually an aqueous solution—into a lighter solvent, it is necessary, with a conventional separating funnel, to transfer the heavier liquid to a beaker before removing the solvent. The aqueous layer must then be returned to the separating funnel if, as often happens, the extraction has to be repeated with fresh solvent. This is obviously an inconvenient operation and, as the volume of the aqueous phase is increased by the washing required for each transference, the degree of extraction may be adversely affected. Alternative forms of apparatus have been devised[1] to avoid these difficulties, but they are complicated and not always commercially available.

The apparatus shown in Fig. 1 can be assembled from a polythene bottle and stopper or sleeve, a glass stopcock and a laboratory clamp.

An extraction is made in the manner described. The aqueous solution and solvent are transferred to the bottle, the stopcock is inserted, and the bottle is shaken. After the layers have separated, the bottle is placed in the clamp and the solvent is forced up through the stopcock until the interface is flush with the top of the borehole. (A fine control of the height of the liquid can be exercised by tightening the clamp until the interface reaches the stopcock and then lightly touching the bottle with a finger.) The stopcock is then closed, and the solvent is expelled from the end of the tube by tilting the bottle and giving it a slight shake. A fresh portion of solvent for a further extraction can be introduced by opening the stopcock and releasing the clamp.

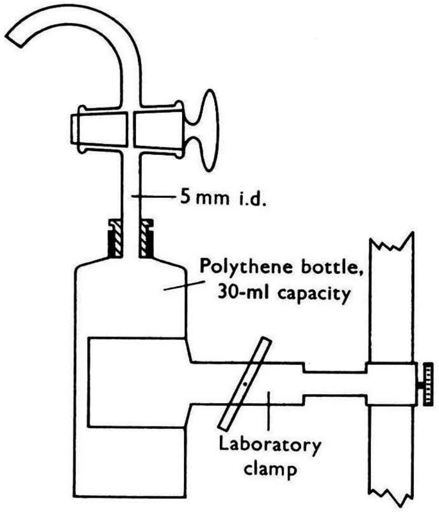

Fig. 1. Apparatus for solvent extractions

Certain features of the apparatus are important. The bottle should be of the thin-walled type, not only so that the separation of the phases may be clearly observed but also to avoid exerting undue pressure on the clamp. A little lubricating grease applied to the thread of the clamp is benficial. In order to achieve a clear-cut separation, the stem of the stopcock should not protrude beyond the end of the stopper or sleeve, and the latter should closely fit the neck of the bottle at its lower end. As a polythene bottle can only be collapsed to half its volume, the heavier solution should occupy half or more of the capacity of the bottle. Hence, if the volume of the aqueous solution is to remain fixed, a bottle to suit the volume of the aqueous layer must be chosen. It also follows that the ratio of the volume of the aqueous layer to that of the solvent layer must be 1 to 1 or less; such ratios, fortunately, are the most commonly used.

The apparatus can be used in inorganic analysis for extractions with solvents less dense than the aqueous solution, for which a glass separating funnel is normally used. The extraction of interfering amounts of iron from fairly concentrated hydrochloric acid solution with amyl acetate before the determination of chromium with diphenylcarbazide is an example of this application.

Several solvents, including amyl acetate, diethyl ether, *iso*butyl methyl ketone, ethyl methyl ketone, ethyl acetate and *iso*octane, were kept in polythene bottles overnight, and the solvents were then evaporated in a beaker; no perceptible residue was found. A set of bottles has been in daily use for several weeks for the above-mentioned extraction of iron and has been unaffected by either the amyl acetate or the hydrochloric acid. If a solvent extracts traces of organic matter from the polythene, this organic matter can be oxidised by heating with a mixture of perchloric and nitric acids—a procedure often used to oxidise non-volatile organic impurities derived from the solvent. The solvent is often discarded and the aqueous layer is used; contamination of the organic layer is then not objectionable.

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APPARATUS FOR THE ROUTINE DETERMINATION OF THE OXYGEN CONTENT OF BERYLLIUM METAL BY ACTIVATION

IN an earlier paper[1] we described the determination of oxygen in beryllium by irradiation with 14·5 MeV neutrons; the transfer of the sample to a counter after irradiation and the recording of the counter output were done manually. With the increase in demand for analyses by this method, it became necessary to do these operations automatically.

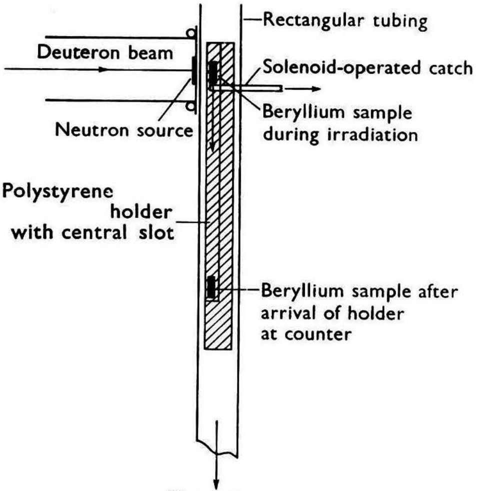
Rectangular tubing
Deuteron beam
Solenoid-operated catch
Beryllium sample during irradiation
Neutron source
Polystyrene holder with central slot
Beryllium sample after arrival of holder at counter
To counter

Fig. 1. Apparatus for transferring sample to counter after irradiation

The samples were passed along a 15-foot length of rectangular tubing, of the type used for wave guides, to a shielded counter. Compressed air or, when applicable, free fall under gravity was used to move the samples.

Some difficulty was experienced in finding a material suitable for the sample holder, which when irradiated, should not produce any short-lived activity similar to that from the sample.

Most materials contained too much oxygen, and even polythene, polystyrene and reactor-grade graphite contained more oxygen than did the beryllium to be analysed. This problem was solved by using a polystyrene holder, 6 inches long, which allowed the beryllium sample to move from one end to the other between the time of irradiation and the time that the sample arrived at the counter. The part of the holder close to the counter therefore had little activity, as it had been some distance from the neutron source. The sample and holder were supported during irradiation by a catch, and this was withdrawn by a solenoid actuated at the same time as a shutter cut off the deuteron beam (see Fig. 1).

A gas-flow proportional counter having a thin window was used to detect the nitrogen-16 activity. Pulses from the counter were fed through a pre-amplifier and a main amplifier into a time sorter, a unit producing pulses of increasing voltage with time. In these experiments the time sorter was set to give an increase in output-pulse height of 0·1 volt per second after being triggered by the same switch that released the sample from the neutron source. The output of the time sorter was fed into a 100-channel pulse analyser having a channel width of 0·25 volt. Each channel was thus, in effect, a scaler for 2·5 seconds. After the irradiation the counts in each channel were noted and corrected for background, and a decay curve was plotted. This curve was analysed graphically to give the nitrogen-16 component.

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Book Reviews

CHOLESTEROL. By DAVID KRITCHEVSKY. Pp. xii + 291. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1958. Price $9.75; 78s.

The Compleat Analyst asks not only "How?" but also "Why?"—and indeed he must do so, for on the answer to the second question may turn his choice of method, according to the degrees of specificity, precision and accuracy, for example, essential to a test's objective.

Such thoughts may well arise in the mind of any clinical biochemist or chemical pathologist —to give but two of his various possible descriptions—on reading Dr. Kritchevsky's wide-ranging and critical survey of all the known and some of the suspected facts about cholesterol. This is perhaps the most mysterious, if only because also one of the most ubiquitous, of the more complex compounds occurring, and occurring only, in animal organisms. Since we do not know what cholesterol is in the body for—if you prefer a less teleological turn of phrase, since we do not know what cholesterol does in the body—why should it be necessary to have available methods for its determination in blood and other tissues, and anyhow how "good" should these methods be? And as witness to my statement of agnosticism, let me quote Dr. Kritchevsky himself (p. 194) —"Clearly the problem of the metabolic effects of dietary fat and cholesterol is not simple, nor is it near solution." This, moreover, is only part of the whole cholesterol problem.

To neither of the analyst's questions can this book, admirable as it is in many ways, provide any kind of direct answer, perhaps because Dr. Kritchevsky does not consider them to fall strictly within his remit, but also doubtless because the answer to one of them at least is still to seek.

The book is divided into seven chapters and also has a most useful appendix, in which are tabulated many physical constants and analytical values, both for cholesterol itself and for some of its more interesting derivatives, notably its esters and ethers. The first four chapters deal with the chemistry (1), biosynthesis (2), absorption and transport (3) and metabolism (4) of cholesterol; chapter 5 is entitled "Cholesterol in Disease States" and chapter 6 "The Blood Cholesterol."

The analyst, having in these first six chapters duly brushed up, or acquired, the essential fundamental knowledge, comes now to Chapter 7. This is about the determination of cholesterol, despite its mistitle—"Analysis of Cholesterol"—for it is surely the cholesterol-containing material that is analysed, not the cholesterol. Those who hope for re-assurance that current methods will determine the cholesterol, the whole cholesterol and nothing but the cholesterol, the ideal analytical goal, won't get it. They will find confirmed what many of them probably know and the rest may well suspect, namely, that of the two main techniques hitherto in use one is a pretty unspecific colour reaction, based on the use of concentrated sulphuric acid at that (the Liebermann-Burchard test) and the other a precipitation with digitonin, itself probably often a substance of doubtful homogeneity, originally discovered by Windaus, who also found that other steroid substances may show the same property. The same absence of specificity applies to the more recently introduced colorimetric methods involving a reaction with—of all things—ferric chloride. Thus whether even a combination of two or more tests can distinguish cholesterol from chemically related substances likely to occur with it in animal tissues, or from some or all of the vegetable steroids that may accompany the animal steroids in the diet of omnivores, such as man, is a question not asked directly in this chapter or elsewhere in the book. Moreover, the author's mild comment that none of the reactions with strongly acidic substances "is specific for cholesterol, but several have been adapted to serve as quantitative methods" would seem to give at any rate part of the game away.

Intermediary metabolites in both the anabolism and the catabolism of cholesterol, which we know, largely from work with isotopes, to be almost entirely endogenous in origin, may or may not be included in, for example, figures for "blood cholesterol content" by any of the methods to-day accepted as "standard." So to the analyst all arguments about the connection—causal, correlative or casual—between levels of "blood cholesterol" and conditions such as atherosclerosis and cardiac disease must of necessity appear somewhat academic, not to say futile, in view of the legitimate doubts he must harbour about all the figures for "cholesterol content" reported in the literature or in the records of the hospital laboratory. Isn't it high time that some one took a good and critical look at the basic analytical problem?

A. L. BACHARACH

VOLUMETRIC ANALYSIS. VOLUME III. TITRATION METHODS: OXIDATION - REDUCTION REACTIONS. By I. M. KOLTHOFF and R. BELCHER. With the co-operation of V. A. STENGER and G. MATSUYAMA. Pp. ix + 714. New York and London: Interscience Publishers Inc. 1957. Price $15.00; 115s.

In the preface to this third volume of *Volumetric Analysis* Professor Kolthoff offers an explanation for the lapse of time after the publication of the second volume and for the change in authorship, and makes the comment that the actual authorship is somewhat difficult to define. Professor Belcher now replaces Dr. Stenger as a senior author, and Drs. Stenger and Matsuyama become co-operators.

A list of chapter headings will indicate the scope of the new volume. These are Reactions, Indicators, and General Techniques in Oxidation - Reduction Titrations, Potassium Permanganate as a Volumetric Reagent, Oxidimetry with Permanganate, Oxidimetry with Ceric Salts, Potassium Dichromate as Oxidising Titrant, Iodimetry; Reagents and their Standardisation, Iodometric Determination of Inorganic Substances, Iodometric Determination of Organic Compounds, Determination of Water with Karl Fischer Reagent, Potassium Iodate as Oxidising Titrant, Oxidation of Organic Compounds with Periodate, Potassium Bromate as a Titrimetric Reagent, Oxidation with Hypohalites, Titration with Iron^{II}, Titanium^{III} and other Strong Reducing Agents, and finally Miscellaneous Titrants.

The whole field of oxidation - reduction titrations is thus covered and it is covered well, but some mention might have been made of Snethlage's detailed study of the standardisation of sodium thiosulphate solutions by means of potassium dichromate, of Harvey's work on the determination of tin in its concentrates and ores and of ferrous propylenediamine sulphate as a replacement for Mohr's salt as a standard substance.

References to the original literature are given in support of the text at appropriate places at the foot of the page, a disposition that is much more convenient for the reader than the modern fashion of collecting references at the end of a chapter. There are over 2350 of them, and they form a valuable feature of the book.

Experimental procedures for many determinations, often amplified by useful notes and critical comments, are also given, but the occurrence of an ambiguity such as "5 per cent. hydrochloric acid," as sometimes happens, may force the reader to refer to the original paper before a determination can be satisfactorily made.

Other blemishes will, no doubt, be removed when a new edition comes to be written. Chemical equations on pages 62, 141, 163, 185, 187 and 365 and the formula of the ferric-8-hydroxyquinoline complex (p. 560) need correction, "cupric" (p. 348, note 2) should be "cuprous," the statement (p. 92) that bismuth amalgam yields tungsten (V) does not agree with Table III, p. 19, where tungsten (III) is given, "rutile," a titanium mineral, is probably meant for "nitrile" (p. 94), which it is not, "heated" (p. 234, line 26) should be "treated," for heating would surely spoil the determination, and the statement, p. 602, that the reaction between manganous, dichromate, and arsenite ions "can only proceed quantitatively to the right if the trivalent manganese produced is complexed with hydrofluoric acid" should be extended to include metaphosphoric acid (cf. p. 603), which acts as well as, if not better than, hydrofluoric acid. Finally, a few misprints, which in a volume of this size are practically inevitable, have found their way into the text.

This third volume, like its predecessors, undoubtedly forms a valuable contribution to the literature of analytical chemistry. Every analyst will find it indispensable, and those chemists whose work involves an occasional titration will need it as a book of reference. The three volumes constitute the most comprehensive survey of volumetric analysis that has so far appeared in the English language. Even so, as a survey it is not complete, for it so happens that the way in which the work was planned and written has meant that virtually no part of the wide field opened up by the application of ethylenediaminetetra-acetic acid to volumetric analysis has been covered. It seems as though, in order to round off his work, Professor Kolthoff will have to sponsor a fourth volume for which the complexones and their analytical application provide the theme.

L. S. THEOBALD

ELECTROPHORESIS: THEORY, METHODS AND APPLICATIONS. Edited by MILAN BIER. Pp. xx + 563. New York and London: Academic Press Inc. 1959. Price $15; 107s. 6d.

THE PRINCIPLES OF ELECTROPHORESIS. By RENÉ AUDUBERT and SERGE DE MENDE. Translated by A. J. POMERANS. Pp. viii + 142. London: Hutchinson & Co. (Publishers) Ltd. 1959. Price 25s.

The last 10 years have seen a rapid expansion of electrophoretic techniques from the original field of proteins and other ionic macro-molecular compounds into almost all branches of chemistry, no doubt owing to the introduction of paper electrophoresis, which not only often replaced the far more complicated and costly free- or moving-boundary electrophoresis for research and routine uses, but also made feasible the convenient analysis of a wide variety of compounds having low molecular weights.

The flood of papers that followed the wide adoption of electrophoretic methods invariably contained results and observations of mixed value and interest. It requires the knowledge and critical faculty of the practising expert to sort the wheat from the chaff and thus to present the reader with material that he can accept as reliable and helpful to his future investigations.

Too much time is wasted in laboratories in vainly trying to repeat experiments or procedures quoted even in books by authors of repute and therefore assumed to be of practical use. The fact is that few, if any, authors could possibly have tested all the procedures described for practicability, reproducibility and general usefulness. This point would then support the recent trend of having a book on a fairly large subject written by several contributors, each one an expert in his chosen but restricted field, and edited by a person of sufficient over-all knowledge of the subject to fuse the individual efforts into one comprehensive, logically connected series of chapters covering, if possible, the whole subject; in itself not a mean task.

Dr. Bier is to be congratulated on having achieved this. His book is the nearest to a standard work on the theory and practice of electrophoresis that has ever been written, covering in great detail the now classical moving-boundary electrophoresis, paper electrophoresis, zone electrophoresis in various types of supporting media and other kinds of electrophoretic methods. His task was no doubt made easier by the fine choice of his associates.

The introductory chapter by A. Tiselius, who put moving-boundary electrophoresis on the scientific map just over 20 years ago and gave paper electrophoresis a tremendous impetus nearly a decade ago, provides the historical and basic information with master-like lucidity and brevity. There are two chapters dealing with the fundamental aspects, one on electrical potentials in colloidal systems, by J. Th. G. Overbeek and J. Lijklema, and the other on acid - base equilibria of proteins, by the late K. Linderstrøm-Lang and S. O. Nielsen.

Although the mathematical treatment of some electrokinetic phenomena may be beyond the capacity of many chemists, a great deal in these chapters will be extremely useful for the understanding of the basic principles of electrophoresis. There are four chapters on moving-boundary electrophoresis; two by L. G. Longsworth on theory and practice, one by R. A. Brown and S. N.

Timasheff on applications to protein systems and one by D. H. Moore on clinical and physiological applications of electrophoresis. Paper electrophoresis is well covered by two chapters, one by Ch. Wunderly, confined to theory and practice of paper electrophoresis of proteins and other similar macro-molecular compounds, and the other by Th. Wieland on applications of zone electrophoresis, embracing all compounds except proteins, with particular reference to recent high-voltage techniques and to paper as the supporting medium. In a chapter on zone electrophoresis in various types of supporting media (except paper), H. G. Kunkel and R. Trautman deal extensively with carrier substances, such as powdered cellulose, starch, gels and poly(vinyl chloride) resins in troughs, sheets and columns. A chapter on preparative electrophoresis without supporting media, by M. Bier, and one on the electrophoresis of viruses, bacteria and cells and the microscope method of electrophoresis (a rather clumsy heading), by C. C. Brinton, jun., and M. A. Lauffer, add some interesting information to the main theme, the former surveying methods such as density-gradient electrophoresis, electro-decantation, electrophoresis convection and forced-flow electrophoresis and the latter dealing with the theory and results on viruses, bacteria and cells obtainable by a microscope method based on electrophoresis. With so much information collected from such a variety of fields by several contributors, it is not surprising that a certain amount of overlapping can be found, especially in chapters on proteins and zone and paper electrophoresis, in spite of the editor's obvious efforts to the contrary. This, however, should not detract from the real value of the book, which is of generally high standard.

The book by Audubert and de Mende is a more modest effort, written as an introduction to both the moving-boundary method and electrophoresis in paper and other supporting media, perhaps trying to cover too much at the cost of appearing too sketchy on various subjects. The first four chapters on the general properties of electrolytes, colloidal systems, electrokinetic potential and electrophoresis and determination of particle mobilities provide the basic information on the physico-chemistry of electrophoresis in a lucid and comprehensive style. There follow a chapter on the moving-boundary method, a chapter on electrophoresis in a supporting medium (giving useful information on the theoretical background of the technique), a chapter on the techniques of paper electrophoresis, a short chapter on preparative electrophoresis in a supporting medium (describing, mainly, continuous-sheet and cellulose-column methods) and, finally, a chapter on some applications of electrophoresis (surprisingly omitting amino acids and amines, but unnecessarily describing at length radioactive-tracer techniques). The main criticism is that the book is already outdated, since it is based on the literature of only up to 1954. This applies particularly to paper- and other zone-electrophoretic techniques, which have greatly progressed since then.

Some obvious mistakes, such as sulphate instead of sulphide in Fig. 77 and on p. 106 and the reversal of the photometer tracing in Fig. 78, should have been avoided. Polyhydric alcohols (p. 138) would be the more correct name. The procedure described for fatty acids (p. 137) would be found hard to repeat. It is perhaps natural that a preponderance of French equipment is illustrated in preference to other better-known designs. The book will certainly be helpful as a clear and intelligent introduction to the expanding field of electrophoresis; however, despite the great difference in price, Bier's volume seems to be the better value. D. GROSS

MICROANALISIS ELEMENTAL ORGANICO. By Dr. J. B. NIEDERL and Dr. J. A. SOZZI. Pp. xviii + 285. Buenos Aires: The Authors. 1958. Gratis.

This is a disappointing book. In the introduction, one is led to expect a new text, but the principal changes from the old, well known and valued "Niederl and Niederl" are in the language, in omissions of material present in the earlier book and in the addition of a minor section on the qualitative analysis of organic compounds.

The book is intended for students rather than practising micro-analysts. Detailed procedures are given for the determination of carbon, hydrogen, nitrogen, halogens, metals and molecular weights; other analyses are barely mentioned. Heavy emphasis is laid on the classical methods. Simplified and rapid methods widely adopted in recent years—for example, the oxygen-flask technique and the use of external absorbers for nitrogen oxides in the determination of carbon and hydrogen—are generally ignored. Even dry-combustion methods for sulphur and halogens are only referred to.

The book will probably serve a useful purpose in the South American countries, where few texts exist on this subject, but it seems to possess little of interest to English-speaking readers.

A. M. G. MACDONALD

CONTRIBUTI TEORICI E SPERIMENTALI DI POLAROGRAFIA. Volume IV. Supplemento a "La Ricerca Scientifica." Pp. 361. Padova, Italy : Centro di Studio per la Polarografia. 1959. Price 2500 Lire.

This volume contains review and original articles relating to the activities during 1957 and 1958 of the Polarographic Research Centre of the Italian National Research Council at Padua. Professor G. Semerano, the director of the Institute and a pioneer of polarography in Italy, has edited the volume and contributed articles reviewing the original work done at the Institute between 1952 and 1958 and describing the summer schools in polarography held at Bressanone between 1953 and 1958. The other papers, of which many have been contributed by visiting lecturers from other laboratories in France, Germany, Italy, the U.S.A. and the United Kingdom, describe recent developments in theoretical and applied polarography and, to a limited extent, in other modern analytical techniques, such as radioactivation analysis. Most of the papers are written in Italian; the others appear in the lecturer's native language. J. E. PAGE

Publications Received

PRINCIPLES OF NUTRITION. By EVA D. WILSON, KATHERINE H. FISHER and MARY E. FUQUA. Pp. xii + 483. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1959. Price $6.00; 48s.

MILK TESTING. By J. G. DAVIS, D.Sc., Ph.D., F.R.I.C., M.I.Biol., F.R.S.H. Second Edition. Pp. xiv + 309. London: Dairy Industries Ltd. 1959. Price 30s.

ADVANCES IN MASS SPECTROMETRY. Edited by J. D. WALDRON. Pp. xvi + 704. London, New York, Paris and Los Angeles: Pergamon Press Ltd. 1959. Price 120s.

Proceedings of a Joint Conference organised by the Hydrocarbon Research Group, Institute of Petroleum, and A.S.T.M. Committee E.14 and held in the University of London, 24th–26th September, 1958.

PERFUMES, COSMETICS AND SOAPS, WITH SPECIAL REFERENCE TO SYNTHETICS. Volume II. A Treatise on the Production, Manufacture and Application of Perfumes of All Types. By WILLIAM A. POUCHER, F.P.S., F.R.P.S. Seventh Edition. Pp. xii + 453. London: Chapman & Hall Ltd. 1959. Price 75s.

CHEMICAL PROCESS PRINCIPLES. Part II. Thermodynamics. By OLAF A. HOUGEN, KENNETH M. WATSON and ROLAND A. RAGATZ. Second Edition. Pp. lvi + 505–1072. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1959. Price $9.75; 78s.

BRITISH VETERINARY CODEX 1953: SUPPLEMENT 1959. Published by direction of the Council of the Pharmaceutical Society of Great Britain. Pp. xviii + 134. London: The Pharmaceutical Press. 1959. Price 35s.

FOOD POISONING. By ELLIOT B. DEWBERRY, M.B.E. Fourth Edition. Pp. xvi + 411. London: Leonard Hill (Books) Limited. 1959. Price 45s.

AUTOMATIC TITRATORS. By J. P. PHILLIPS. Pp. viii + 225. New York and London: Academic Press Inc. 1959. Price $6.00; 48s.

REPORT OF THE PROCEEDINGS OF THE TWELFTH SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS, WASHINGTON, D.C., U.S.A., 1958. Pp. viii + 130. Keston, Kent. I.C.U.M.S.A., 1959. Price 25s.

Obtainable from Hon. Secretary, I.C.U.M.S.A., Tate & Lyle Research Laboratories, Westerham Road, Keston, Kent.

XV CONGRESSO INTERNACIONAL DE QUIMICA PURA E APLICADA (*Quimica Analitica*): Actas do Congresso (8 *a* 16 *de Setembro de* 1956). Volume II. Pp. 1048. Lisbon: General Secretary of the XVth International Congress of Pure and Applied Chemistry, Instituto Superior Technico. 1957. Price, together with volumes I and III, 320 Escudos.

EXTRACTIVE METALLURGY. By JOSEPH NEWTON. Pp. viii + 532. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1959. Price 78s.; $9.75.

COSMETIC SCIENCE. Edited by A. W. MIDDLETON, Ph.D., F.R.I.C. Pp. xxvi + 327. London: Butterworths Scientific Publications. 1959. Price 60s.

Proceedings of the Congress organised by the Society of Cosmetic Chemists of Great Britain, held at University College, London, 15–17 April, 1959.

REPRINTS FROM *THE ANALYST*

Recommended Methods of Assay of Crude Drugs: The Determination of the Capsaicin Content of Capsicum and its Preparations

REPRINTS of the Recommended Methods prepared by the Joint Committee of The Pharmaceutical Society and The Society for Analytical Chemistry on Methods of Assay of Crude Drugs are available from the Assistant Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1 (not through Trade Agents); price to members of The Society for Analytical Chemistry, 1s. 6d.; to non-members, 2s. 6d. each. Remittances made out to The Society for Analytical Chemistry MUST accompany orders.

The first reprint in this series to become available is—

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"Gas Chromatography and its Analytical Applications," by B. A. Rose (October, 1959). Price 5s.

"Zone Melting, with Some Comments on its Analytical Potentialities," by E. F. G. Herington (December, 1959). Price 5s.

"The Analytical Chemistry of Zirconium," by G. W. C. Milner and J. W. Edwards (this issue; available shortly). Price 5s.

Reprints of earlier Review Papers are still available as follows—

"The Analysis of Synthetic Detergents," by W. B. Smith (February, 1959). Price 2s. 6d.

"The Infra-red Analysis of Solid Substances," by G. Duyckaerts (April, 1959). Price 2s. 6d.

"X-Ray Fluorescence Analysis," by F. Brown (June, 1959). Price 2s. 6d.

"Ferrous Metallurgical Analysis," by B. Bagshawe (August, 1959). Price 5s.

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THE Editor welcomes Papers and Notes for insertion in *The Analyst*, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

A copy of the current Notice to Authors, last published in full in *The Analyst*, 1959, **84**, 123, can be obtained on application to the Editor, *The Analyst*, 14 Belgrave Square, London, S.W.1. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment.

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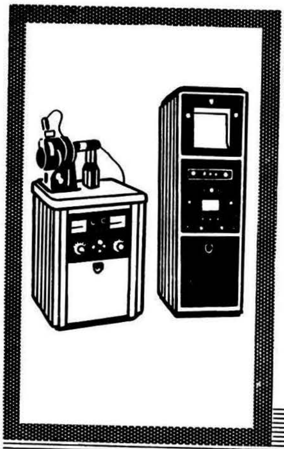

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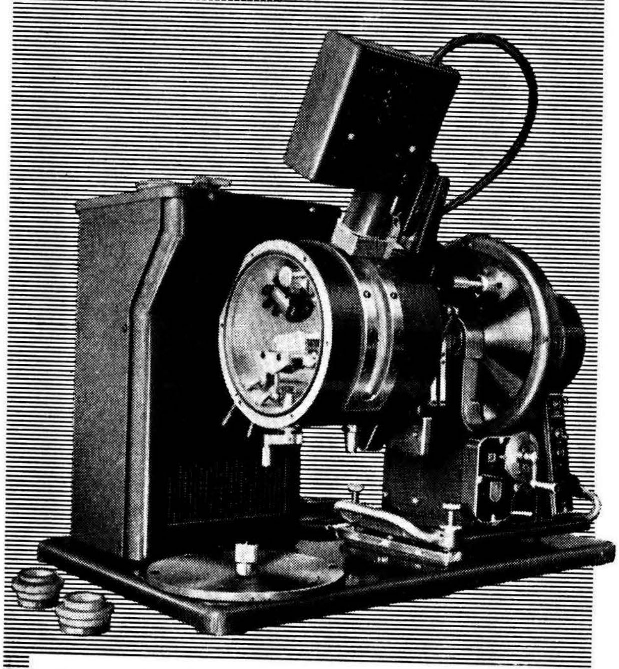

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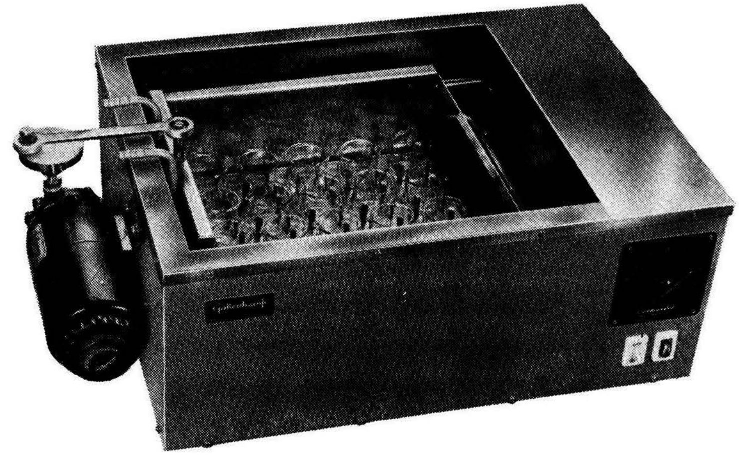

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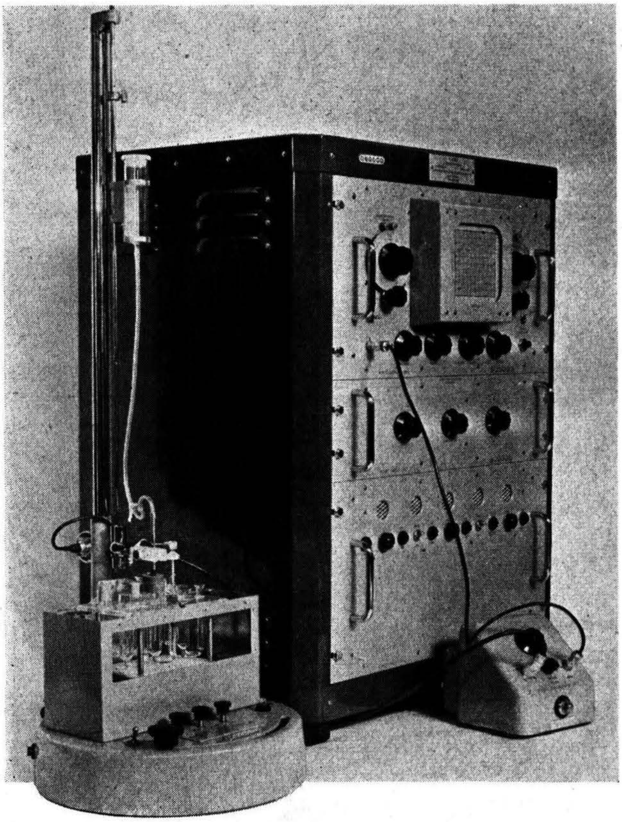

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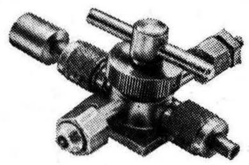

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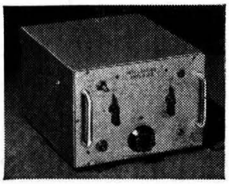

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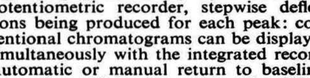

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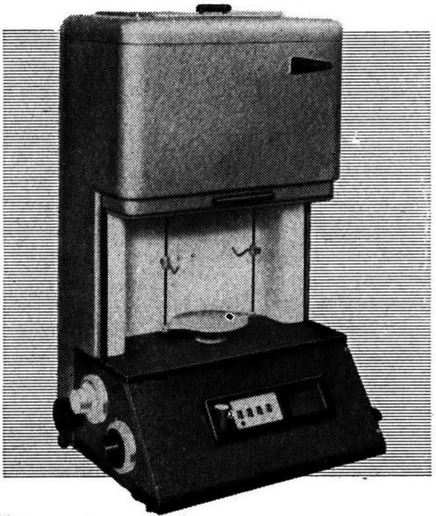

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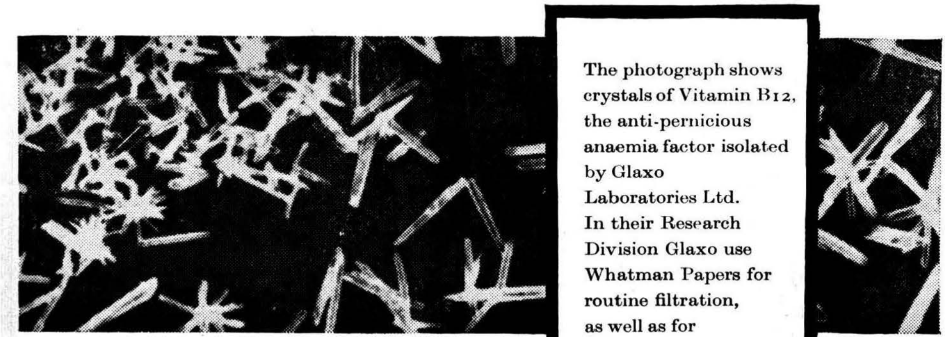

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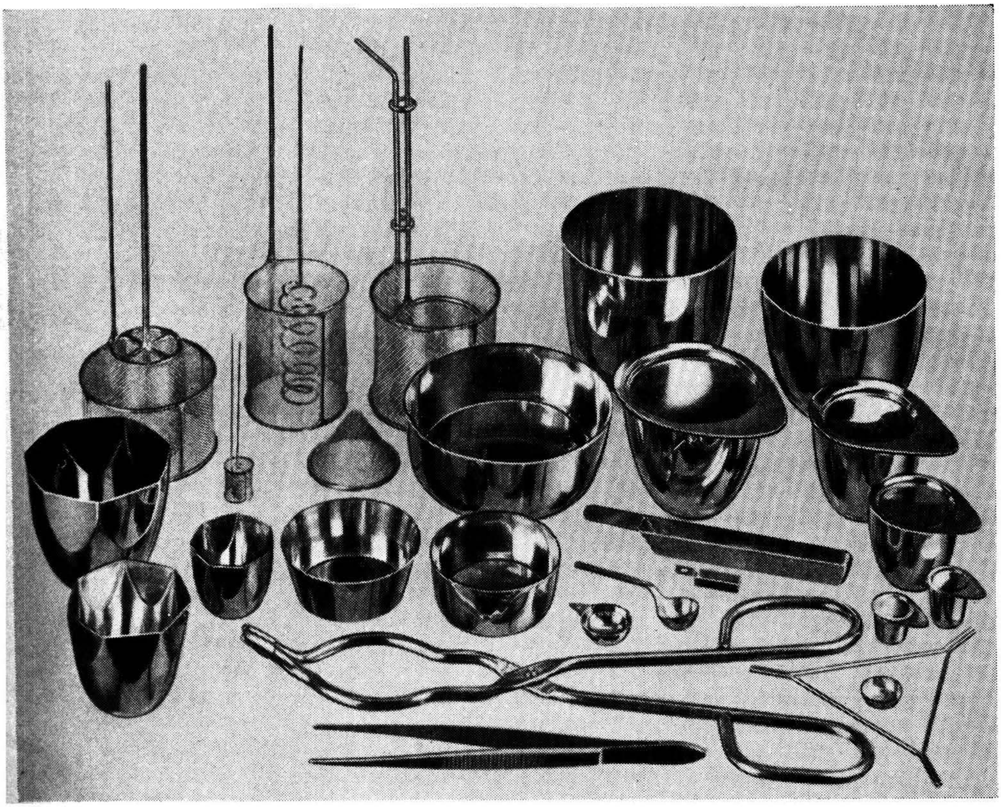

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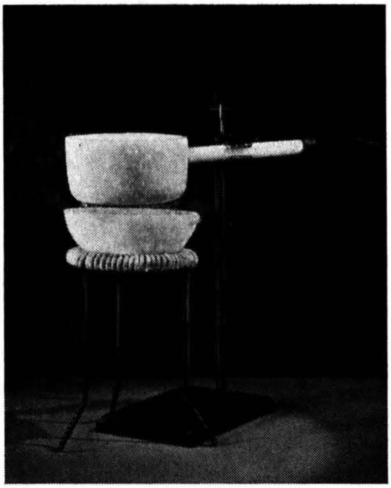

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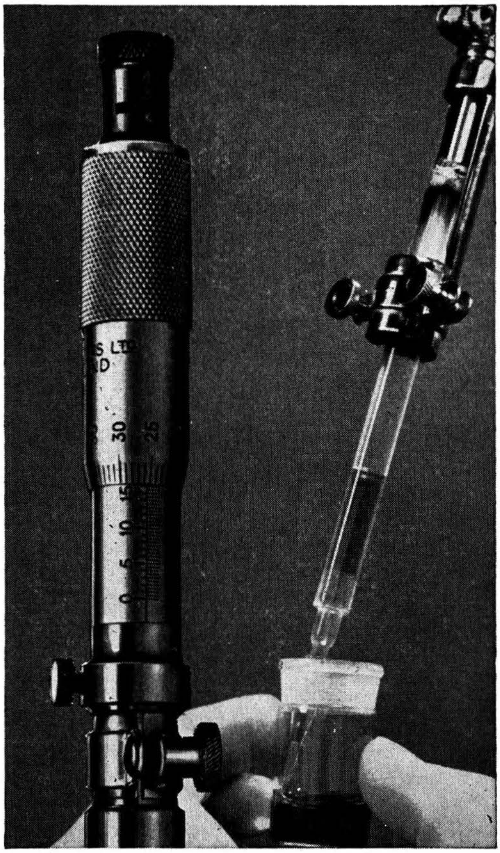

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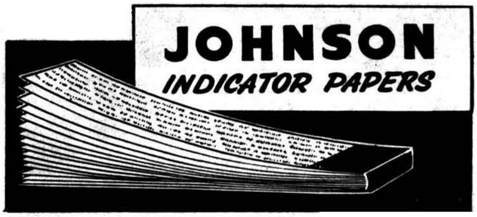

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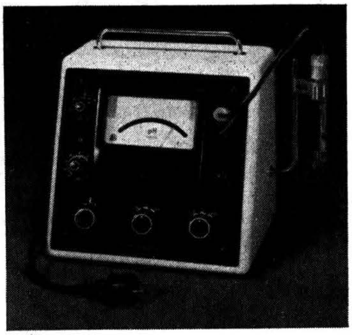

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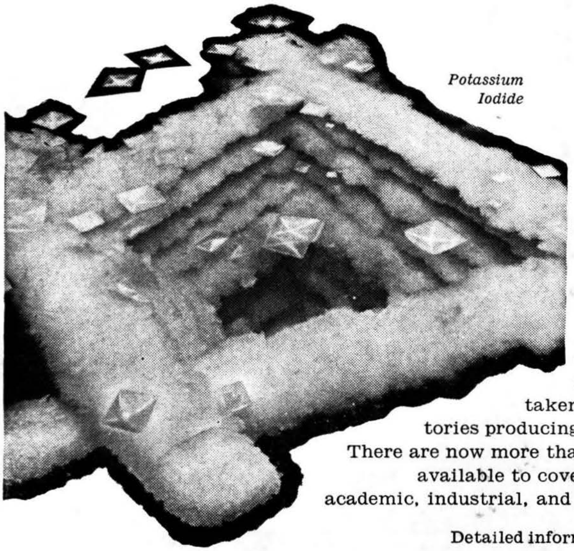

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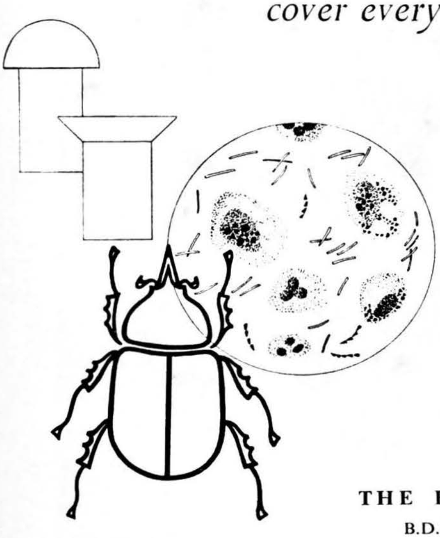

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