The ANALYST

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February 1961

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

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Volume 86, No. 1019 February 1961

No. 92 February, 1961

THE SOCIETY FOR ANALYTICAL CHEMISTRY

BULLETIN

FORTHCOMING MEETINGS

Annual General Meeting of the Society, March 3rd, 1961

THE Annual General Meeting of the Society will be held at 2.15 p.m. on Friday, March 3rd, 1961, in the Meeting Room of the Royal Society, Burlington House, Piccadilly, London, W.1.

This will be followed at 2.45 p.m. by the Address of the Retiring President, Mr. R. C. Chirnside, F.R.I.C., who will speak on **"The Enlargement of Horizons in Analytical Chemistry."**

Biennial Dinner

THE Society will hold its Biennial Dinner (87th Anniversary) at Fishmongers' Hall, London Bridge, London, E.C.4, on Friday, March 3rd, 1961, at 7.15 p.m. for 7.45 p.m. Guests, particularly ladies, will be welcome.

Demonstration Meeting of the Society, March 29th, 1961

THE Society is holding a Meeting for the demonstration of laboratory equipment at 6 p.m. on Wednesday, March 29th, 1961, at Chelsea College of Science and Technology, Manresa Road, London, S.W.3.

Joint Meeting of the North of England Section and the Physical Methods Group, March 25, 1961

A JOINT Meeting of the North of England Section and the Physical Methods Group will be held at 2.15 p.m. on Saturday, March 25th, 1961, at the City Laboratories, Mount Pleasant, **Liverpool.**

The subject of the meeting will be **"The Analysis of Intact Samples."**

Joint Meeting of the Scottish Section with the Royal Institute of Chemistry, February 24th, 1961

A JOINT Meeting of the Scottish Section with the Royal Institute of Chemistry will be held at 7.15 p.m. on Friday, February 24th, 1961, at the Royal College of Science and Technology, **Glasgow,** C.1.

The subject of the meeting will be **"Ion-Exchange"** and the following papers will be presented and discussed—

"Applications of Ion-exchange in Inorganic Analytical Chemistry," by R. A. Wells, B.Sc., F.R.I.C.

"Ion-exchange in the Electro-plating Industry," by V. E. Gripp, B.Sc., A.R.C.S., A.R.I.C.

Ordinary Meeting of the Scottish Section, March 24th, 1961

AN Ordinary Meeting of the Section will be held on Friday, March 24th, 1961, in **Glasgow.**

The subject of the meeting will be **"Non-aqueous Titrimetry"** and the speakers will be G. R. Jamieson, B.Sc., A.R.I.C., and E. S. Lane, B.Sc., Ph.D., F.R.I.C.

Joint Meeting of the Western Section with the Bristol and District Section of the Royal Institute of Chemistry, March 2nd, 1961

A JOINT Meeting of the Western Section with the Bristol and District Section of the Royal Institute of Chemistry will be held on Thursday, March 2nd, 1961,* in **Gloucester.**

The following paper will be presented and discussed—

"Titrations in Non-aqueous Solvents," by E. Minshall, M.Sc., F.R.I.C.

Joint Meeting of the Western Section with the South Wales Section of the Royal Institute of Chemistry, March 10th, 1961

A JOINT Meeting of the Western Section with the South Wales Section of the Royal Institute of Chemistry will be held on Friday, March 10th, 1961, in **Swansea.**

The following paper will be presented and discussed—

"Vapour-phase Chromatography," by A. Verdin.

Ordindary Meeting of the Midlands Section, March 8th, 1961

AN Ordinary Meeting of the Section will be held at 6.30 p.m. on Wednesday, March 8th, 1961, at the Technical College, **Luton.**

The following paper will be presented and discussed—

"Some Newer Reagents in Analytical Chemistry," by Professor R. Belcher, D.Sc., Ph.D., F.R.I.C., F.Inst.F.

Annual General Meeting of the Midlands Section, March 14th, 1961

THE sixth Annual General Meeting of the Section will be held at 6.30 p.m. on Tuesday, March 14th, 1961, at Regent House, St. Philip's Place, **Birmingham, 3.**

Ordinary Meeting of the Midlands Section, March 23rd, 1961

AN Ordinary Meeting of the Section will be held at 7 p.m. on Thursday, March 23rd, 1961, at the Technical College, **Nottingham.**

The following paper will be presented and discussed—

"Measurement of pH and Electrode Potential for Analytical Purposes," by Dr. G. Mattock.

Annual General Meeting of the Microchemistry Group, February 24th, 1961

THE seventeenth Annual General Meeting of the Group will be held at 6.45 p.m. on Friday, February 24th, 1961, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1.

The Annual General Meeting will be followed by an Ordinary Meeting of the Group, at which an address will be given by the retiring Chairman, Mr. F. Holmes, B.Sc., A.R.I.C.

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* Please note that the date of this meeting has been altered from February 23rd.

London Discussion Meeting of the Microchemistry Group, March 22nd, 1961

THE twenty-ninth London Discussion Meeting of the Group will be held at 6.30 p.m. on Wednesday, March 22nd, 1961, at "The Feathers," Tudor Street, off Bouverie Street, Fleet Street, London, E.C.4.

Ordinary Meeting of the Physical Methods Group, February 28th, 1961

AN Ordinary Meeting of the Group will be held at 6 p.m. on Tuesday, February 28th, 1961, at the Royal College of Surgeons, London.

The subject of the meeting will be **"Physical Methods of Analysis Used in Medical Research,"** and the following papers will be presented and discussed—

"Gas Chromatography and Anaesthetic Research," by D. W. Hill, M.Sc., A.Inst.P., A.M.I.E.E.

"The Measurement of the Oxygen Tension of Blood using a Covered Platinum Electrode," by J. M. Bishop, M.D., M.R.C.P.

"Applications of Infra-red Spectroscopy to Some Problems of Medical Science," by A. E. Kellie, B.Sc., Ph.D., A.R.I.C.

The meeting will be preceded by a visit to the Research Department of Anaesthetics.

MIDLANDS SECTION

Elwell Award, 1961

ENTRIES are invited for the annual competition for the Elwell Award from any scientist not engaged in postgraduate studies, under the age of 30, working or residing in the area covered by the Midlands Section of the Society, *viz.*, south of, but including, Stoke-on-Trent and north of, but excluding, Carmarthen.

The award, consisting of a silver trophy, will be retained for one year by the candidate deemed by a panel of referees to have submitted the best paper dealing with some aspect of analytical chemistry. In addition, the successful candidate will receive a gift of scientific books.

Selected papers will be presented at a meeting of the Section during September, 1961, and the name of the successful candidate will be announced on the same evening.

The closing date for entries is Wednesday, June 7th, 1961, and the latest date for submission of papers is Friday, June 30th, 1961.

Entry forms and other particulars may be obtained from G. W. Cherry, Esq., Honorary Secretary, Midlands Section, Society for Analytical Chemistry, 48 George Frederick Road, Sutton Coldfield, Warwickshire.

COMMUNICATIONS ACCEPTED FOR PUBLICATION IN *THE ANALYST*

The following communications have been accepted for publication in *The Analyst*, and are expected to appear in the near future.

"Polarographic Determination of Dimethyl and Dibutyl Phthalates in Propellants with use of Zinc Amalgam to Overcome Interference from Nitroglycerine," by J. Townend and E. Macintosh.

"Compensation for Temperature Variations within the Cell of a Dissolved Oxygen Indicator - Recorder incorporating a Wide-bore Dropping-mercury Electrode," by A. Littlewood. (Note.)

"Automatic Determination of Penicillin in Fermentation Broth: An Improved Iodimetric Assay," by R. R. Goodall and R. Davies.

"Determination of Zinc in Metallurgical Materials by Atomic Absorption Spectrophotometry," by J. A. F. Gidley and J. T. Jones. (Note.)

"The Determination of Tin in Pure Iron, Mild Steel and Certain Low Alloy Steels by Cathode-ray Polarography," by P. H. Scholes.

"The Determination of Impurities in Chlorine Gas by Gas Chromatography," by J. Lacy and K. G. Woolmington.

"The Semi-micro Determination of Fluorine and Chlorine in Organic Compounds. Part IV. The Determination of Halogens in Gases and Volatile Liquids," by R. D. Chambers, W. K. R. Musgrave and J. Savory. (Note.)

"The Determination of Small Amounts of Amine in Aqueous Solutions," by P. J. Lloyd and A. D. Carr.

"Use of Induction Heating in Determining Carbon and Hydrogen," by Doris E. Butterworth. (Note.)

Notices

LIBRARY OF THE CHEMICAL SOCIETY

Easter Closing, 1961

THE Chemical Society Library will be closed for Easter from 1 p.m. on Thursday, March 30th, until 9.30 a.m. on Wednesday, April 5th, 1961.

EIGHTH OTTAWA SYMPOSIUM ON APPLIED SPECTROSCOPY

September 18th to 20th, 1961

THE Eighth Ottawa Symposium sponsored by the Canadian Association for Applied Spectroscopy is to be held in Ottawa on September 18th, 19th and 20th, 1961.

Papers are invited for presentation on the subjects of applied spectroscopy, including emission, ultra-violet, infra-red, X-ray and nuclear magnetic resonance work in the field of instrumental analysis.

Titles and brief abstracts of papers should be submitted before June 6th, 1961, to Roland Lauzon, Programme Chairman, Eighth Ottawa Symposium on Applied Spectroscopy, c/o Division of Pure Chemistry, National Research Council, Ottawa, Ontario, Canada.

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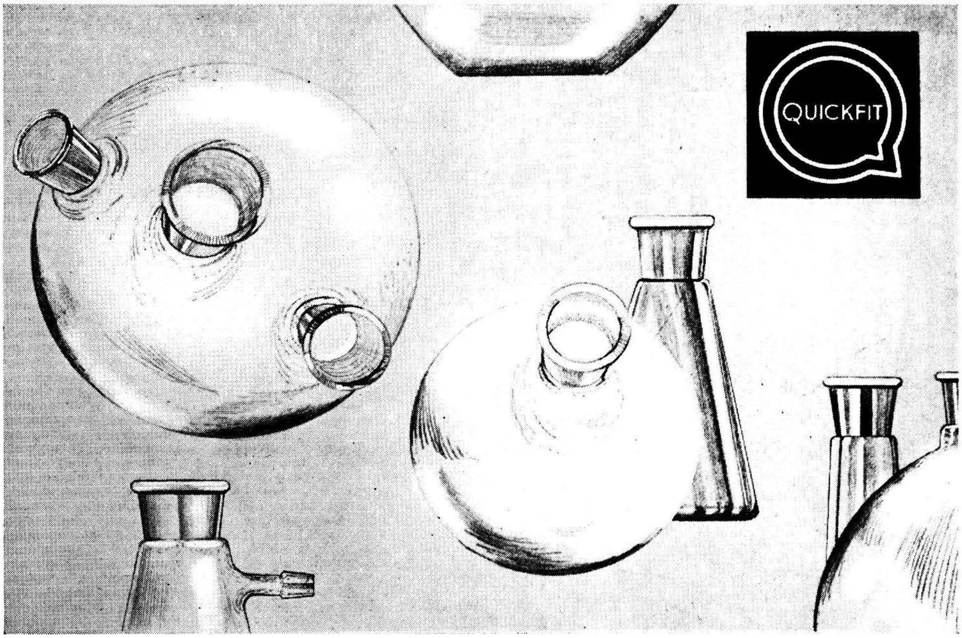
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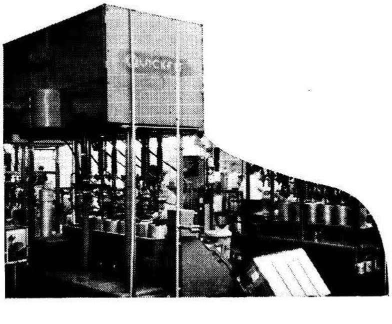

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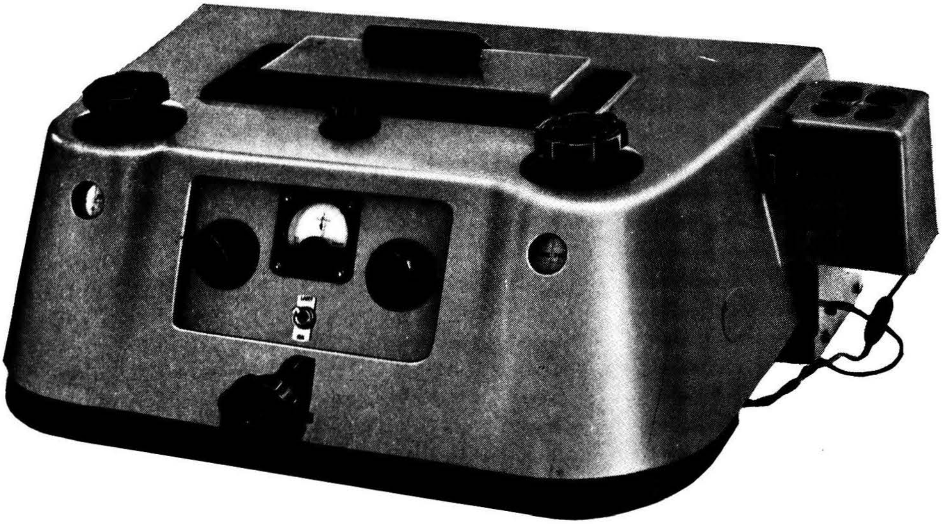

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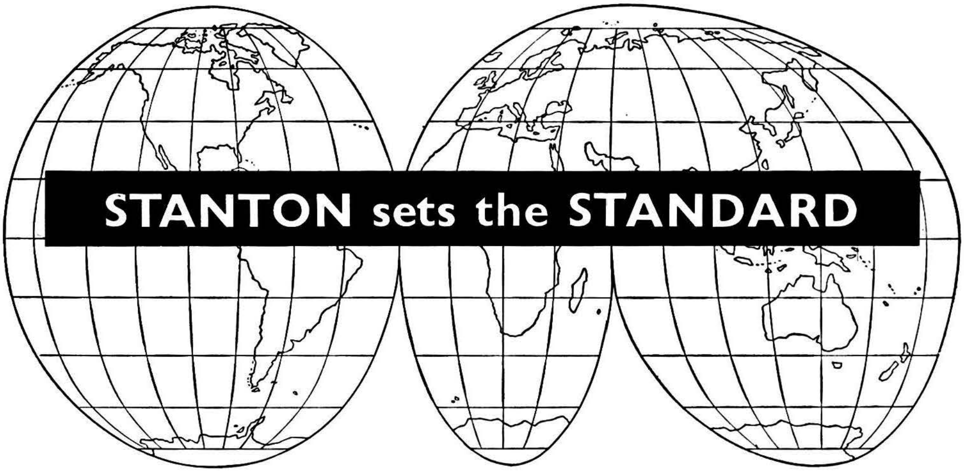

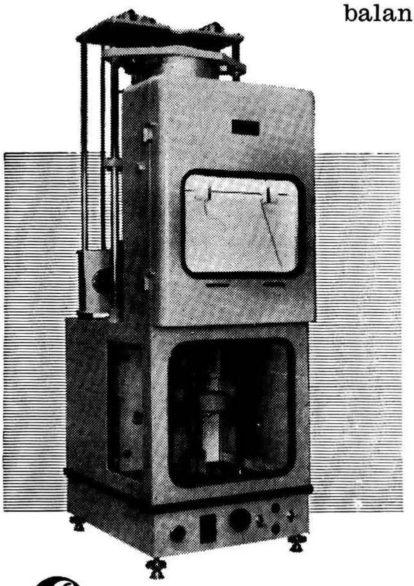

HILGER & WATTS

Atomic-absorption Spectroscopy

Atomic-absorption spectroscopy, originally developed by Dr. A. Walsh of the C.S.I.R.O., Melbourne, Australia, has certainly made its mark on the literature. We give here, as a matter of interest, some of the bibliography on the subject. We regret that we are unable to give a complete bibliography in this space or to supply reprints of these papers.

ANALYST:

The Determination of Exchangeable Sodium, Potassium, Calcium and Magnesium in Soils by Atomic-Absorption Spectrophotometry. *David, D. J.* **85,** 495 (1960)

The Application of Atomic Absorption to Chemical Analysis. A Review. *David, D. J.* **85,** 779 (1960)

Atomic-Absorption Spectrophotometry with Special Reference to the Determination of Magnesium. *Allan, J. E.* **83,** 466 (1958)

Determination of Zinc and Other Elements in Plants by Atomic-Absorption Spectroscopy. *David, J. E.* **83,** 655 (1958)

The Quantitative Determination of Some Noble Metals by Atomic-Absorption Spectroscopy. *Lockyer, R., Hames, G. E.* **84,** 385 (1959)

Determination of Calcuim in Plant Material by Atomic-Absorption Spectrophotometry. *David, D. J.* **84,** 536 (1959)

Determination of Zinc in Metallurgical Materials by Atomic-Absorption Spectroscopy. *Gidley, J. A. F., Jones, J. T.* **85,** 249 (1960)

NATURE:

Atomic-Absorption Spectrophotometric Determination of Molybdenum and Strontium. *David, D. J.* **187,** 1109 (1960)

Determination of Nickel and Cobalt by Atomic-Absorption. *Allen, J. E.* **187,** 1110 (1960)

Determination of Silver in Lead Concentrates by Atomic-Absorption Spectroscopy. *Rawling, B. S. et al.* **188,** 137 (1960)

Determination of Magnesium in Blood Serum by Atomic-Absorption Spectroscopy, *Willis, J. B.* **184** (4681), **187** (1959)

Some Atomic Reactions by Absorption Spectroscopy. *Broida, H. P., Schiff, H. I., Sugden, T. M.* **185,** 759 (1960)

Determination of Calcium in Blood Serum by Atomic-Absorption Spectrosopy. *Willis, J. H.* **186** (4720), 249 (1960)

ANALYTICAL CHEMISTRY:

Atomic-Absorption Spectroscopy. (Survey). *Robinson, J. W.* **32,** 17A (1960)

A Study of Atomic-Absorption Spectroscopy. *Menzies, A. C.* **32,** 898 (1960)

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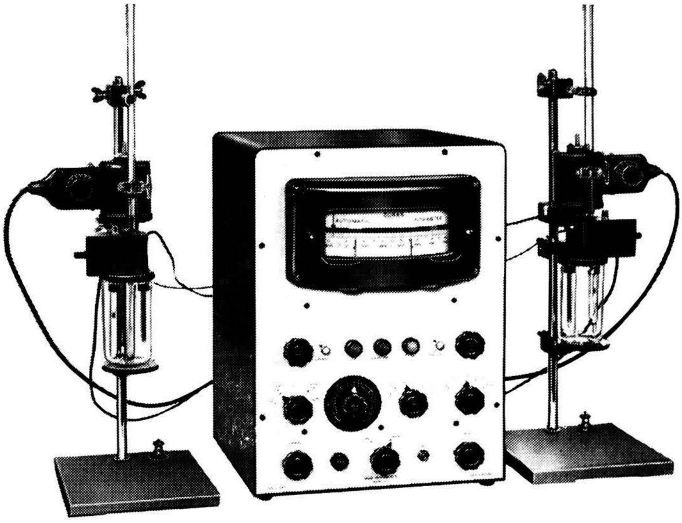

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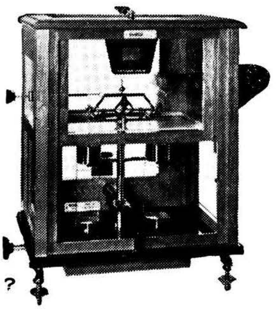

FEBRUARY, 1961 Vol. 86, No. 1019

THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

An Ordinary Meeting of the Society, organised by the Physical Methods Group, was held at 7 p.m. on Wednesday, February 1st, 1961, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Mr. R. C. Chirnside, F.R.I.C.

The subject of the meeting was "X-ray Fluorescence" and the following papers were presented and discussed: "X-ray Fluorescence Spectroscopy," by K. M. Bills; "Some Analytical Applications of X-ray Fluorescence Spectrometry," by F. Brown, B.Sc., Ph.D., A.R.I.C.

NEW MEMBERS

Ordinary Members

Edmund Hollis Amstein, B.Sc., A.R.C.S., Ph.D. (Lond.); Roy Maurice Dagnall, B.Sc. (Birm.); Patrick Paul Donovan, M.Sc., Ph.D. (N.U.I.), M.I.C.I.; Michael Freegarde, B.Sc. (Sheff.), A.R.I.C.; William Edward Hearn; John Charles Henry Jones, B.Sc. (Lond.); Ronald Mead Pearson, A.R.I.C.; Albert George Roach, Ph.D. (Manc.), B.Sc. (Wales), A.R.I.C.; Ernest Walter Summers, B.Sc. (Lond.); Victor Daniel Tyrrell, B.Sc., M.A. (T.C.D.), M.Sc. (N.U.I.).

Junior Members

Peter Edmund Arnold, A.R.I.C.; James Lewis Tomlinson.

DEATH

We record with regret the death of

Hubert Thomas Stanley Britton.

SCOTTISH SECTION

A Joint Meeting of the Scottish Section of the Society with the Chemical Society, the Society of Chemical Industry and the Royal Institute of Chemistry was held at 7.15 p.m. on Friday, December 2nd, 1960, in the Royal College of Science and Technology, George Street, Glasgow, C.1. The Chair was taken by the Chairman of the Scottish Section, Mr. A. N. Harrow, A.H.-W.C., F.R.I.C.

The following paper was presented and discussed: "Ramsay, Chemistry and the Electrical Industry," by R. C. Chirnside, F.R.I.C.

MIDLANDS SECTION

An Ordinary Meeting of the Section was held at 7 p.m. on Tuesday, January 10th, 1961, at the Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton. The Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P.

The following paper was presented and discussed: "Trace Analysis Using the Polarographic Technique," by Mrs. B. Lamb, B.Sc., F.R.I.C.

BIOLOGICAL METHODS GROUP

THE sixteenth Annual General Meeting of the Group was held at 6.30 p.m. on Thursday, December 8th, 1960, in "The Feathers," Tudor Street, London, E.C.4. 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*—Mr. J. S. Simpson. *Vice-Chairman*—Mr. W. A. Broom. *Hon. Secretary and Treasurer*—Mr. K. L. Smith, Standards Department, Boots Pure Drug Co. Ltd., Nottingham. *Members of Committee*—Mr. P. A. Andrews, Mrs. J. Gammon, Miss A. M. Jones, Dr. J. I. M. Jones, Dr. M. W. Parkes and Dr. G. F. Somers. Mr. D. M. Freeland and Dr. J. H. Hamence were re-appointed on. Auditors.

The Annual General Meeting was followed by a Discussion Meeting on "Problems in the Control of Neomycin Quality," which was opened by J. W. Lightbown M.Sc., Dip. Bact. The Chair at this meeting was taken by the new Chairman, Mr. J. S. Simpson, F.I.M.L.T.

Obituary

ARNOLD LEES

ARNOLD LEES, F.R.I.C., who passed away suddenly at his home in Southport on December 22nd, 1960, in his 71st year, was born in Ramsbottom, Lancashire, and was educated at Cockburn High School, Leeds.

His first introduction to public health chemistry was with the York Water Board. In the year 1914 he became an assistant in the laboratory of J. A. Foster, who was Public Analyst for the East Riding of Yorkshire, and in 1916 he joined an Ordnance Factory at Leeds. In 1918 he was appointed an assistant analyst on the staff of the Lancashire County Laboratory under W. Collingwood Williams and spent 37 years in that laboratory, both in Liverpool and later when it was removed to Preston, retiring in January, 1955. He was made Chief Assistant County Analyst and an Additional Public Analyst in 1938 and was appointed Deputy County Analyst in 1946. His work as an analyst was always characterised by its neatness, and he was meticulous (to use his own word) in his attention to the detail of any investigation. In collaboration with G. D. Elsdon and with J. R. Stubbs he contributed papers to *The Analyst.*

Arnold Lees was a staunch supporter of the North of England Section of the Society and never missed a meeting over a period of many years. In 1940 he became Honorary Secretary of the Section, which office he held until 1955. It was largely due to his efforts that the meetings, and particularly the Summer Meetings, were such an unqualified success. On his resignation a presentation was made to him by the then President, Dr. D. W. Kent-Jones, in recognition of his services to the Section.

He was passionately fond of sport, particularly cricket and football. He was a member of Lancashire County Cricket Club and he made a point every year of attending the Scarbrough Cricket Festival, where he enjoyed the company of his many friends. During his last ten years he was President of an amateur football club in his home town. He was also a Committee member of the Northern Section of the Lancashire Amateur League, a member of Council of the Lancashire Amateur League and Area Representative of the Lancashire Football Association, Amateur Committee. In his retirement, therefore, he gave his services to sport as wholeheartedly as he had given them to the North of England Section of the Society during his professional career.

Arnold Lees had many friends in his profession and in the world of sport. He was an exemplary father dearly loved by all his family. He leaves a widow and two sons; the latter have both taken up careers in chemistry.

GEO. H. WALKER

Analytical Chemistry of Beryllium

A Review*

By L. E. SMYTHE and R. N. WHITTEM
(*Austrailian Atomic Energy Commission Research Establishment, Sydney, New South Wales, Australia*)

SUMMARY OF CONTENTS

BEFORE 1939, the analytical chemistry of beryllium dealt mainly with the analysis of beryllium ores, a limited number of beryllium compounds and a few useful alloys with such metals as aluminium (introduced in 1918) and copper (introduced in 1926). During the past 20 years new uses have been found for beryllium in the electrical, chemical and metal industries and, more recently, in the field of atomic energy. The increasing use of beryllium and its compounds led to the recognition, in the early 1940's, of beryllium disease causing respiratory illness and certain kinds of skin reactions. Investigations of this disease and the control of occupational levels of beryllium required the development of methods for detecting small traces of beryllium in a variety of materials (see Table I). Accurate analytical methods were also required for the whole range of macro to micro amounts of beryllium. Although a Russian[1] review was published in 1957 and a specialised review[2] in 1958, many papers have appeared in the literature during the past 3 years. This review is presented to assist analytical chemists with a coverage of the more recent methods.

MATERIALS REQUIRING CHEMICAL ANALYSIS

Materials that may require examination are listed in Table I.

GENERAL CHEMICAL AND RADIOCHEMICAL METHODS

General chemical and radiochemical methods for determining beryllium may be conveniently grouped under nine headings. This grouping, although convenient for review purposes, is not rigid, since an analytical procedure might involve a combination of methods.

GRAVIMETRIC—

Gravimetric procedures for determining beryllium are based on the formation of compounds insoluble under certain conditions; some of the more "insoluble" beryllium compounds are listed in Table II.

It should be noted that the exact compositions of many of the compounds listed in Table II are unknown and that this is a limitation to their use in accurate gravimetric methods. The literature of beryllium is overburdened with compounds that have been assigned formulae simply from the chemical analysis of the solid phases—mixed crystals, residues from evaporation or indefinite gummy precipitates obtained under various conditions.[3] For example, the halides of beryllium are hydrolysed by water, and, by careful

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* Reprints of this paper will be available shortly. For details, please see p. 142.

TABLE I

BERYLLIUM-CONTAINING MATERIALS

Material	Constituents determined
Beryllium ores (generally $3BeO.Al_2O_3.6SiO_2$)	Be, Al, Si, K, Na, Fe, Ni, Li, Mg, Cr, Mn, Ca, etc.
Beryllium metal (commercial or high-purity powder, flake or fabricated)	*Metals*—Al, Fe, Si, Ca, Mg, Cu, Mn, Cr, Ni, Cd, B, lanthanides, etc. *Non-metals*—O, H, N, C, halogens, He, ^{3}H, etc.
Beryllium oxide and hydroxide	As for beryllium metal
Beryllium alloys	As for beryllium metal, but larger amounts of alloying elements such as Th, U, Pu, etc.
Beryllium compounds (carbide, sulphate, halides, organo-metallic, etc.)	Mainly major constituents, *e.g.*, carbide, sulphate, halogen, etc.
Air	Traces of Be or Be compounds
Water (or effluent)	
Filter-paper smears or swabs	
Biological materials	
Soils	
Miscellaneous (*e.g.*, filter elements)	

NOTE—Beryllium metal, alloys or compounds will contain active constituents after irradiation in high-flux materials-testing reactors. Radiochemical analysis is necessary in such instances.

manipulation of the evaporation residues, products of almost any degree of basicity can be prepared. It follows that many compounds of beryllium cannot be prepared by methods involving the use of aqueous solutions.

Owing to lack of many insoluble beryllium compounds of definite composition, the most common and reliable method for determining beryllium gravimetrically involves precipitation of beryllium hydroxide and subsequent ignition to the oxide.[2,4,5,6] The method is comparatively straightforward, although appropriate health precautions should be taken with ignited beryllium oxide.[7] Because of the colloidal nature of beryllium hydroxide, the results of gravimetric determinations are likely to be high, owing to adsorption and occlusion of impurity elements and compounds. Special precipitation procedures are used involving precipitation of beryllium hydroxide from near-neutral solution. Appropriate separation procedures are required in the presence of aluminium, silica, the hydrogen sulphide group, iron, titanium, zirconium, lanthanides, chromium, tungsten, vanadium and thorium.

TABLE II

INSOLUBLE BERYLLIUM COMPOUNDS

Compound	Notes
Beryllium hydroxide, $Be(OH)_2$*	Amorphous powder or gel
Beryllium oxide, hydrate, $BeO.xH_2O$*	Decomposes on heating giving BeO
Beryllium oxide, BeO	Stable to above 2000° C
Beryllium sulphate, $BeSO_4$	Hydrate ($.4H_2O$) is soluble
Sodium fluoroberyllate, Na_2BeF_4*	
Potassium fluoroberyllate, K_2BeF_4*	
Barium fluoroberyllate, $BaBeF_4$*	
Beryllium carbonate, basic, $[BeCO_3 + Be(OH)_2]$*	No normal carbonate
Beryllium ammonium phosphate, $BeNH_4PO_4$*	
Beryllium - cobalt complex, $[(H_2O)_2Be_2(CO_3)_2(OH)_3][Co(NH_3)_6].3H_2O$*	
Beryllium acetate, $Be(C_2H_3O_2)_2$*	
Beryllium acetylacetonate, $Be(C_5H_7O_2)_2$	
Beryllium - tannin complex*	
Beryllium - quinaldine complex	
Beryllium - oxine complex	
Beryllium - naphthaldehyde complex	
Beryllium - mercaptobenzothiazole complex	
Beryllium stearate, $Be(C_{18}H_{35}O_2)_2$	

* Exact composition unknown.

Other gravimetric methods based on the isolation of insoluble beryllium compounds of rather indefinite composition (see Table II) require close control and careful assessment of interfering elements. These methods include isolation of beryllium as the beryllium - cobalt-ammine complex,[8,9] barium fluoroberyllate,[10,11] beryllium mercaptobenzothiazole,[12] beryllium naphthaldehyde,[13] ammonium beryllium phosphate,[14] the beryllium - tannin complex[4] or as its complexes with benzylamine, triethanolamine or oxine.[15]

Gravimetric methods are suitable for determining milligram to gram amounts of beryllium. With careful control the precision and accuracy are to approximately 0·1 to 1 per cent.

VOLUMETRIC—

Unfortunately there are few specific reactions that can be used for the volumetric determination of beryllium. A reliable volumetric procedure suitable for microgram to milligram amounts of beryllium would be invaluable. One volumetric method for beryllium[2,16,17] is based on formation of the extremely stable complex BeF_4^{2-}. If an excess of alkali fluoride (*e.g.*, potassium or sodium fluoride) is added to a suspension of beryllium hydroxide, the reaction proceeds almost quantitatively in accordance with the equation—

$$Be(OH)_2 + 4F^- \rightarrow BeF_4^{2-} + 2OH^-$$

The free base liberated is proportional to the beryllium present and can be titrated with standard hydrochloric acid. However, it should be noted that, because the reaction is not strictly stoicheiometric, it is necessary to use an empirically determined titre for beryllium for the standard hydrochloric acid.

Another volumetric method is that in which quinalizarin is used to detect the end-point.[4] Iron interferes in this method and is removed by reducing the mixture with hydrogen and selectively dissolving the iron in hydrochloric acid. The quinalizarin reagent is used in a colour-comparison test in the presence of sodium hydroxide. Several modifications of this method have been described, and it is said to be suitable for amounts of beryllium in the microgram to milligram range.

Other volumetric methods for beryllium include the salicylate - fluoride method,[18] 8-hydroxyquinaldine with a volumetric finish,[19] indirect complexometric titration of beryllium with ethylenediaminetetra-acetic acid (EDTA),[20,21] potassium iodate - sodium thiosulphate hydrolysis method,[22] titration of beryllium oxine with potassium bromate[23] and bismuth oxychloride titration.[24]

Volumetric methods for determining beryllium are possibly the least satisfactory of the chemical methods and their reliability under various conditions cannot be stated with any certainty.

COLORIMETRIC AND FLUORIMETRIC—

Several reliable colorimetric and fluorimetric methods are available for beryllium. Most of these are suited to determining microgram to low milligram amounts of beryllium. For example, a fluorimetric method for determining beryllium in which morin (2′,4′,3,5,7-pentahydroxyflavone) reagent is used is said to have a detection limit of 0·004 µg and is precise to 0·8 per cent. on 0·2 µg at the 95 per cent. confidence level.[25] The procedure and precautions to be observed to achieve this precision (*e.g.*, control of temperature, concentrations of morin, sodium hydroxide, salts, etc.) are rather time-consuming. However, with simple fluorimetric equipment and without any special precautions, measurements can easily be made at levels down to 0·1 µg. Although good colorimetric methods for beryllium are also available, fluorimetric methods appear to have greater sensitivity and are more suitable for the microgram range. The colorimetric methods involve use of adsorption indicators or formation of suitable stoicheiometric complexes.

Fluorimetric methods reported in the literature include morin preceded by selective electrolysis[26] or selective extraction,[27] 8-hydroxyquinaldine and successive extraction with final fluorimetric determination,[28,29] quinizarin (1,4-dihydroxyanthraquinone),[30] 1-amino-4-hydroxyanthraquinone[30] and a rapid routine method for determining sub-microgram and microgram amounts of beryllium in filter-paper.[31]

Colorimetric methods involve use of chrome azurol S,[32,33] 8-hydroxyquinaldine,[29] Eriochrome cyanine R,[34] aluminon (ammonium aurintricarboxylate),[35,36] chrome blue K (also known as mordant blue 31 or 4-sulpho-2-hydroxyphenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid),[37] gossypin (a glycoside of the flavanol gossypetin),[38] neothorin (arsenazo),[39] thoron [1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid],[40,41] alberon (Solochrome brilliant blue B),[33] miscellaneous hydroxyquinones,[42] salicylic acid,[43] beryllon II [8-hydroxynaphthalene-3′, 6′-disulphonic acid-(1-azo-2′)-1′, 8′-dihydroxynaphthalene-3′, 6′-disulphonic acid, di- or tetra-sodium salt],[14,44,45] quinalizarin (1,2,5,8-tetrahydroxyanthraquinone),[4,46] hapthazarin (5,6-dihydroxy-1,4-naphthaquinone),[47] 4-(*p*-nitrophenylazo)-orcinol,[48] zenia (*p*-nitrobenzeneazo-orcinol),[49] curcumin (diferuloylmethane),[4,50] molybdophosphoric acid,[51] Naphthochrome green G,[52] Naphthochrome azurine 2B,[53] quinizarin,[30,54] 5-sulphosalicylic acid,[55] 1-amino-4-hydroxyanthraquinone[30] and acetylacetone.[56]

A wide choice of colorimetric reagents for beryllium is therefore available. Generally, the choice of reagent is governed by the material to be analysed and the interfering elements. Masking agents, solvent extraction, ion exchange, chromatography and electrochemical separation have all been used in conjunction with a colorimetric finish. Currently available colorimetric methods are not generally applicable in the sub-microgram range, and the lower limit for normal spectrophotometric precision is approximately 10 μg, with an upper limit in the milligram range.

ION EXCHANGE—

Ion exchange has not been extensively used in the determination of microgram amounts of beryllium. Some promising methods have recently been reported, and it is likely that ion-exchange methods will receive more attention. The new ion-exchange chelating resins containing such groups as iminodiacetate, *e.g.*, Dowex A1 chelating resin (The Dow Chemical Co., Midland, Michigan, U.S.A.), or the sodium diallyl phosphate complexing resins[57] may prove promising as the basis of new analytical procedures. The ion-exchange separation of beryllium with salicylate analogues has been studied by Schubert, Lindenbaum and Westfall[58] and might also form the basis of an analytical procedure. It was shown that beryllium can be selectively eluted from a cation-exchange resin with sulphosalicylic acid (0·02 to 0·1 M) at pH 3·5 to 4·5. The ions Cu^{2+}, UO_2^{2+} and Ca^{2+} are not removed under these conditions; however, at pH 4·5 to 4·7 the ion UO_2^{2+} is eluted. At pH values above 6 in the presence of sulphosalicylic acid, beryllium is strongly adsorbed by an anion-exchange resin. The separation of milligram amounts of beryllium can be carried out on a cross-linked polystyrene cation-exchange resin, such as Amberlite IR-112 or Zeo-Karb 225, in the presence of a complexing agent.[59]

When a buffer solution (pH 3·5 to 5·0) containing beryllium, aluminium, chromium, titanium and a slight excess of EDTA is passed through the resin in the ammonium form, only beryllium is adsorbed. The beryllium can be eluted with ammonium chloride solution and determined by a suitable method. Belyavskaya and Fadeeva developed a method[60] for the quantitative separation of beryllium from copper and nickel; they used SBS cation-exchange resin in the ammonium form. The separation was carried out in ammoniacal medium (containing ammonium carbonate) at pH 8·5 to 9·0 and subsequent elution was with ammonium carbonate solution; full details were not available to us. Another method for determining milligram amounts of beryllium in beryl was described by Nadkarni, Varde and Athavale[61]; beryllium was separated from iron, aluminium and titanium by ion exchange. After fusion with sodium fluoride, digestion with sulphuric acid and addition of EDTA, the solution at pH 3·5 was passed through a cation-exchange resin (Amberlite IRA-120 or Zeo-Karb 225) in the sodium form. Beryllium was retained and the iron and aluminium complexes passed through. The beryllium was then eluted and determined gravimetrically, as BeO. Ion exchange has been used for the concentration of beryllium from sea water.[56] Only 10 ml of Dowex 50-X8 resin (200 to 400 mesh) converted to the ferric form and hydrolysed with ammonia were required for 50 litres of sea water.

The standard deviation of results by ion-exchange methods for beryllium in the milligram range appears to be about 5 per cent., and these methods cannot as yet be recommended for sub-microgram amounts of beryllium.

SOLVENT EXTRACTION—

Only a limited number of different solvent-extraction systems have been used in the determination of beryllium. Extraction systems based on chelate formation appear to be the most promising for analytical purposes. Six-membered ring systems including beta-diketones and hydroxycarbonyls have proved valuable. Little work, however, has been carried out on analytical ion-association extraction systems in which beryllium may be contained in the cationic or anionic member of the ion pair.

Analytical methods based on the solvent extraction of beryllium as acetylacetonate have received the most attention.[62 to 68] The method has been applied to metallurgical analysis,[65] to radiochemical analysis[64] and in conjunction with masking agents.[66,69] Most finishes after this extraction are colorimetric. Other solvent-extraction methods for determining beryllium include a fluorimetric method involving semi-micro purification of the beryllium solution by extraction with ethyl acetate and diethyldithiocarbamate[27]; sodium hydroxide and sodium sulphide[46]; 8-hydroxyquinaldine and chloroform[70]; separation as basic acetate and extraction with chloroform[71]; extraction with thenoyltrifluoroacetone.[72,73]

Solvent-extraction methods for beryllium are applicable from microgram to macro amounts. Under carefully controlled conditions recoveries of 95 per cent. and higher can be achieved. In the microgram range the standard deviation is 5 to 10 per cent., with a lower extraction limit of about 1·0 μg.

CHROMATOGRAPHIC—

Chromatographic methods for determining beryllium have not yet gained wide acceptance. The disadvantages of such methods for beryllium include (*a*) lengthy procedures, (*b*) close control is required, (*c*) results are mostly semi-quantitative and (*d*) the range of concentrations is restricted.

An electrochromatographic method for beryllium has been described by Majumdar and Singh.[74] The migration sequences of beryllium and seven other elements were determined in various electrolytes; separations were possible with some mixtures containing up to four constituents. A semi-quantitative determination of beryllium, lithium and boron in minerals by partition chromatography has been described,[75] but cannot be recommended for routine use. Amounts of beryllium between 10 and 90 μg have been separated from uranium and titanium by paper chromatography, a mixture of isopropyl alcohol, acetylacetone and hydrochloric acid being used as solvent.[76] After separation, the ions were detected with an ethanolic solution of quercetin and a solution of potassium ferrocyanide, and the planimetric method was used for quantitative evaluation of the separated spots. Values of R_F for beryllium, uranium and titanium were also reported. The average error in the analysis of a (1 + 1) mixture of beryllium and uranium did not exceed ± 10 per cent. The determination of beryllium after separation by paper chromatography has been described by Elbeih and Abou-Elnaga,[77] who used visual comparison of the oxine complex under ultra-violet illumination.

POLAROGRAPHIC—

Published work on the polarographic determination of beryllium is limited.[78] Recently, Venkataratnam and Raghava Rao stated[79] that, in an 0·5 M lithium chloride supporting electrolyte at pH 3·4, the diffusion current at the first stage of reduction remained proportional to the concentration of beryllium in solution up to 8×10^{-3} M. Earlier workers, however, have failed to detect any "steps" for the reduction of beryllium from aqueous solutions of its salts.[80] Proximity of the hydrogen steps resulting from hydrolysis of Be^{2+} ions plus the need for accurate pH control is likely to cause difficulties in measuring step height. A more promising field of investigation would be polarographic methods based on the reduction of beryllium - organo complexes of the hydroxyazo type or amperometric methods.[81,82]

RADIOCHEMICAL—

Several interesting radiometric-titration, tracer,[56] photo-neutron and activation methods for beryllium have been described. Neutron-activation methods for impurities in beryllium are referred to in the next section.

A promising method, based on earlier work by Gaudin and Pannell[83] and by Aĭdarkin and his co-workers[84] has been further developed by Milner and Edwards.[85] The method is based on measuring the photo-neutron flux produced when samples containing beryllium are irradiated with photons from an antimony-124 source. The method is rapid, interferences are small (with the exceptions of boron, cadmium, samarium and gadolinium) and, under the best conditions, the lower limit of detection is less than 0·002 per cent., as BeO. Radiometric-titration procedures involving use of phosphorus-32[86,87] and iron-59[88] have been described. The phosphorus-32 method is said to be suitable for determining milligram amounts of beryllium in alloys and concentrates. Beryllium, as sulphate, is added to a buffer solution at pH 5 to 5·5 and is titrated with 0·1 M diammonium hydrogen orthophosphate (containing phosphorus-32) of activity 20,000 to 30,000 counts per minute per ml. At intervals, 0·5-ml aliquots are withdrawn, spun in a centrifuge and counted, and the equivalence point is found graphically. The precision of current radiometric procedures is not as good as those of colorimetric and fluorimetric methods. Beryllium has been determined[88] in beryl by using radioactive iron-59. A preliminary oxalate precipitation is involved, and the procedure in its present form does not appear to be suitable for microgram amounts of beryllium. A beryllium-hazard detector in which polonium-210 alpha particles are used has been described.[89] A 2·6-curie polonium-210 source provides a flux of alpha particles, to which samples of beryllium dust on filter-paper are exposed. The gamma-ray yield of the reaction $^{9}\mathrm{Be}(\alpha, n, \gamma)^{12}\mathrm{C}$ is used to measure the beryllium content. The method is applicable in the range 0·2 to 100 μg of beryllium and a determination can be completed in 5 to 10 minutes. The method, however, necessitates a large capital cost for the source and detection equipment and cannot be recommended for routine use.

DETERMINATION OF IMPURITIES IN BERYLLIUM—

Considerable attention has been devoted to the determination of impurities in beryllium, and nearly all the analytical methods described in this review, with the addition of methods such as vacuum fusion extraction, have been applied. Despite the demand for improved analytical methods, few analyses have been carried out on beryllium with very low levels of impurities such as oxygen, hydrogen and nitrogen. In fact, the solid solubility limits for oxygen, hydrogen and nitrogen have apparently never been determined.[90] It is doubtful if ultra-high-purity beryllium has ever been prepared and submitted to comprehensive analysis.

A comprehensive review dealing with methods for the detection of twenty-one components in beryllium has been published,[2] but no such review covers the literature of the past 2 years. Conventional methods have been used for detecting common anions, such as chloride and sulphate, in beryllium compounds. Spectrographic methods have been extensively used for determining metallic impurities in beryllium and beryllium compounds and are detailed later. Vacuum fusion extraction procedures have been extensively used for determining hydrogen, oxygen and other gases in beryllium. A wide variety of chemical and radiochemical methods has also been used. Some of the more important papers are summarised in Table III.

SPECTROMETRIC METHODS

EMISSION—

The major advantages of emission spectrometry are specificity, high sensitivity, rapid processing of large numbers of samples and the relatively small samples. Against this, limitations are imposed by the empirical nature of the method when quantitative results are required. For every form and composition of sample, it is necessary either to have a range of standard samples or to carry out more or less extensive sample preparation to ensure that standards and samples can be directly compared. Even when this is done, spectrographic analyses for major elements show a considerably higher standard deviation than do most other methods. Thus, although many spectrographic techniques have been described for determining beryllium in beryl,[134,135,136] it is our opinion that this determination is preferably carried out by conventional "wet" chemical methods. This section will therefore deal with methods for determining traces of beryllium and its compounds and with methods for determining traces of impurities in beryllium and beryllium oxide.

Determination of very small amounts of beryllium—Several techniques have been described for determining traces of beryllium in various materials, for example, plutonium,[137] thoria,[138] bismuth - uranium alloys[139] and plants.[140] The major effort, however, appears to have been directed to meet the requirements of speed and sensitivity limits set for environmental monitoring by smears, air-sampling, etc., reviewed recently by Brooks.[141] A wide variety of techniques has been used, the highest sensitivity claimed being obtained by the cathode-layer technique. In this method,[135,142,143] the sample, as a powder or a solution dried on the graphite cathode, is arced at 10 to 15 amps, and only light originating very near the cathode is allowed to enter the spectrograph. A limiting sensitivity of 2×10^{-11} g of beryllium has been claimed.[143]

Conventional d.c. arc techniques, in which the sample is placed on the anode and light from all the gap is admitted to the spectrograph have also been described.[144,145] Thallium was used as internal standard in both these methods, and Landis and Coons[145] claimed that, by adding barium chloride as carrier, higher sensitivity and reproducibility were obtained over the range 0·002 to 0·1 μg of beryllium. Another d.c. arc technique is the "iron-flux" method used by Garton, Webb and Sayer,[146] who covered the range 0·005 to 4 μg of beryllium with a single exposure.

Spark techniques have also been described. Fred, Nachtrieb and Tomkins[147] were able to detect 0·002 μg of beryllium with a copper spark. Davis, Parker and Webb[148] used a condensed spark between graphite electrodes, on one of which the sample, collected on a paper pad, was glued; with a direct-reading spectrograph, these workers were able to detect 0·003 μg of beryllium. Aluminium was used as internal standard, aluminium sulphate solution being placed on the pad (by pipette) before sparking.

TABLE III

SUMMARY OF METHODS FOR DETERMINING IMPURITIES IN BERYLLIUM AND ITS COMPOUNDS

Impurity determined	Literature reference*	Remarks
Oxygen (as BeO) in Be	91	Chemical method (methanol - Br_2); error ±0·01 per cent., as BeO
	92	Chemical method (HCl)
Oxygen in Be	93	Activation method (^{16}N measured); relative error ±5 per cent.
	94, 95	Micro vacuum fusion; coefficient of variation 15 to 20 per cent. at 0·01 per cent. level
Helium and tritium in Be	96, 97	Fusion and extraction
Free carbon in Be	98	Solution, ignition and gasometric finish
Combined carbon in Be	99	Solution and gasometric finish
Fluorine in Be	100	Absorptiometric method
Oxygen in BeO and Be	101	Chemical method ($CuSO_4$)
Chlorine in BeO and Be	102	Chemical method
Combined nitrogen in Be	94, 95	Vacuum fusion method
	103	Chemical method (Kjeldahl)
	104	Chemical method (diffusion)
Beryllium oxide in BeF_2	105	Chemical method
Fluorine in Be compounds	106	Chemical method
Lanthanides in Be	107	Chemical method (oxalate)
Various metals in Be	108, 109, 110	Spectrographic methods
Copper in Be	111, 112, 113	Absorptiometric methods
Silicon in Be	112, 114	Absorptiometric methods
Manganese in Be	115, 116, 117	Absorptiometric methods
Iron in Be	118, 119	Absorptiometric methods
Chromium in Be	120	Absorptiometric method
Nickel in Be	121, 122, 123, 124	Absorptiometric and volumetric methods
Tungsten in Be	125	Absorptiometric method
Cadmium in Be	126	—
Uranium in Be	127, 128	X-ray fluorescence spectroscopy
Silicon in Be compounds	129	Absorptiometric method
Free Be and carbide-C in Be	130, 131	Chemical methods
Iron in Be compounds	132	Chemical methods
Various impurities in Be	133	Activation analysis
—	2	Review of various methods

* See reference list, p. 91.

Solution methods have been described. Feldman[149] and Owen and his co-workers[150] used a porous-cup - spark technique in which the sample was fed into the discharge by percolation through the thin base of a hollow graphite electrode. A closely allied technique is the rotating-disc method in which the lower electrode is a rotating disc of graphite partly immersed in the sample solution. This has been used by Smith and his co-workers[151] and by the U.K. Atomic Energy Authority.[152] The latter workers used scandium as internal standard and, by choosing various beryllium and scandium lines, covered the range 0·03 to 50 μg of beryllium.

Since air and smear samples are usually collected on filter-paper, most of the techniques mentioned above involve considerable chemical pre-treatment, such as wet ashing and separation of interfering elements. Since these determinations are most usually carried out for Health Physics purposes, it seems to us that speed is more important than accuracy, especially when "spills" give rise to suspected contamination. Accordingly, in these laboratories, smear- and air-sample analyses are carried out by a modification of the method described by Davis, Parker and Webb,[148] in which the filter-paper samples are glued to graphite electrodes 10 mm in diameter. A pulsed-arc discharge is used, with the sample as cathode and a blunt graphite anode 6 mm in diameter; the gap is 4 mm. Results are reported in the range <0·01 to >2 μg of beryllium by making visual comparison with standards prepared by drying solutions of beryllium sulphate on similar filter-papers. If a stock of machined electrodes is maintained, a batch of twenty samples can be processed by one operator in about 90 minutes. The main disadvantage of the method is that results may vary appreciably with different physical forms and chemical compositions of the beryllium contamination. However, as the biological effects vary far more with the particle size and chemical state of the beryllium, the method is regarded as acceptable for Health Physics control. The speed of the method is invaluable in assessing the spread of contamination after a "spill."

Churchill and Gillieson[153] introduced a technique for the continuous monitoring of air for beryllium by drawing a constant flow of air across a spark gap. The light from the spark was dispersed by a grating monochromator set for the beryllium doublet at 3130 A and was continuously recorded by means of a photomultiplier, d.c. amplifier and circular-chart recorder. An improved version of this monitor has been described[154] in which integration over a short time was used rather than continuous recording. Other refinements were higher dispersion to improve sensitivity, background correction and periodic standardisation (involving a discharge between beryllium - copper electrodes to generate particles of beryllium oxide). It was claimed that, by re-designing the spark gap and using a pulsed-arc discharge axially in the air stream, rather than a condensed spark across it, results were independent of the particle size and chemical composition of the beryllium aerosol. A similar instrument is being constructed in these laboratories. Here, very high dispersion is used, since it has been found that titanium interferes if the monochromator "window" is set to admit both lines of the beryllium doublet at 3130 A. Our monochromator has a band pass of 0·1 A, sufficient to resolve one beryllium line from titanium. A number of the refinements made by Webb, Webb and Wildy[154] have been omitted, since we require specificity and sensitivity to changes in concentration, rather than absolute accuracy. Recently, commercially constructed automatic monitors have become available. One of these[155] is based on the rotating-disc technique[151] and will automatically process up to sixty samples at the rate of six per hour. The other[156] involves a filter tape that is directly excited in a spark, providing a result every minute.

Determination of traces of impurities in beryllium and its compounds—Over the last two decades, the requirements for determining impurities in beryllium and its compounds have varied as pure forms of beryllium have become available. Arc methods are used almost exclusively; in general, all samples are converted to beryllium oxide before arcing. A typical early example is the method described by Lee Smith and Fassel,[157] who used a 16-amp arc and a barium hydroxide - graphite mixture as a "spectroscopic buffer" for determining aluminium, calcium, chromium, iron, magnesium, manganese and silicon, mostly in the range above 100 p.p.m.

The carrier-distillation method originally developed for determining impurities in uranium[158] has been used for determining silver, cadmium, molybdenum, lead, zinc, lithium and calcium,[2] but the limits of detection were not stated. With lanthanum as carrier, Zaïdel and his co-workers[159] detected gadolinium, europium and samarium in beryllium down to 0·1 p.p.m. Zaïdel and others[138] have also described an interesting method for determining very small amounts of boron in beryllium oxide. A 30-mg sample of oxide is heated *in vacuo* and volatile impurities are collected on a copper electrode, which is then sparked.

Recently, Karabash and his co-workers[71] have described a chemico-spectrographic method for determining twenty-five elements as impurities in beryllium and beryllium oxide. The sample (2 g) is converted to basic beryllium acetate and is then extracted with chloroform until about 5 per cent. of the beryllium remains in the aqueous layer, which is then separated, evaporated to dryness and converted to oxide. The oxide is then arced in a graphite cup at 12 amps. Detection limits are given as—

5 p.p.m. for Zn,
3 p.p.m. for Ca and Al,
2 p.p.m. for Ba, Ti, Fe, Sb, Te, In and Tl,
1 p.p.m. for Mg, Mo, Co, Ni, Sn, Pb and Na,
0·5 p.p.m. for V, Cr, Bi and Ga,
0·3 p.p.m. for Cu,
0·2 p.p.m. for Ag,
0·1 p.p.m. for Mn and
0·05 p.p.m. for Cd.

X-RAY METHODS—

When X-ray techniques are considered for analytical problems in the beryllium field, the most notable factor is the very low absorption and scattering of X-rays by beryllium atoms. This means that the sensitivity of detection of beryllium metal is poor. On the other hand, the sensitivity of detection of impurities in beryllium metal is fairly high, particularly if thick specimens can be used.

An example, now being examined in these laboratories, is the determination of beryllium oxide in beryllium, which is usually present in the range 0·3 to 1 per cent. Since the solubilities of oxygen and beryllium oxide in beryllium are likely to be very low, it is expected that this technique will give results for total oxygen in beryllium if the metallurgical history of the sample is such as to favour reasonable crystallite size for the beryllium oxide.

X-ray fluorescence methods for many impurities are also feasible and are very sensitive. Qualitatively, chromium, copper, iron, lead, manganese, nickel, vanadium, zinc and zirconium have been detected[128] in MTR shim rod; uranium was estimated at the 500 p.p.m. level. At present, we are examining a method for determining iron in beryllium and in beryllium oxide. It is planned to extend this to other common impurities, *e.g.*, chromium, copper, manganese, nickel, zinc and uranium.

MASS SPECTROMETRY—

Mass spectrometry is not generally applicable to the determination of beryllium, since beryllium and most of its compounds are insufficiently volatile for application of the usual gas-phase techniques. The use of stable-isotope dilution methods involving solid sources has not been reported, perhaps because of the difficulty of obtaining supplies of beryllium-10.

However, mass spectrometry in conjunction with vacuum fusion has been used in Canada[96] and in England[97] for determining gases formed in beryllium by (*n*, 2*n*) reactions; the gases found were ^{4}He, ^{3}He, $^{1}H_2$ and $^{3}H_2$. The British workers found a large and variable content of $^{1}H_2$, which may be attributable to the reduction, during vacuum fusion, of water adsorbed on the specimens or to radiolysis of water occluded in the specimens.

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Spectrophotometric Measurements of Theaflavins and Thearubigins in Black Tea Liquors in Assessments of Quality in Teas*

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The theaflavins and thearubigins formed as a result of enzymic oxidations of polyphenols during the fermentation process in tea manufacture determine the colour of a tea liquor and are associated with some of the other liquor characters recognised by tea tasters. A spectrophotometric method for determining theaflavin is described. This method also yields an approximation of the total thearubigin content, and the ratio of optical-density values for thearubigins at 380 and 460 mμ provides a further parameter giving an indication of whether lightly or deeply coloured thearubigins predominate.

As a result of the fermentation process in tea manufacture the liquor of black tea develops certain characters not present in green or unfermented teas. Among the terms used by tasters to describe these characters are colour, strength, quality and briskness. It has been shown that these characters, measured organoleptically, are influenced by the extent to which fermentation has taken place, and, further, that colour and strength are correlated with the polyphenol oxidase activity and total polyphenol content of the plucked shoots from which the tea was manufactured.[1,2] It follows that some, at least, of the liquor characters of a black tea are due to the presence of polyphenolic enzymic oxidation products.

The main polyphenolic oxidation products found in black tea extracts are the thearubigins.[3,4] These are a complex mixture of substances derived largely, if not entirely, from two parent substances, 1-epigallocatechin and its gallic acid ester. These substances are not polymers, as previously thought, in fact they are probably mainly dimeric. They have fairly strongly acidic properties and in tea liquors considerable proportions of them are present as potassium and calcium salts. Although no pure substances have been isolated from the thearubigin mixture, some separation into fractions has been achieved. S I and S II fractions differ in their solubility relationships and in their chromatographic behaviour.[3] The absorption spectrum of the S II fraction is similar to that of the S I fraction; it nevertheless shows significantly greater absorption in the visible region, but not in the ultraviolet region.[5]

The other oxidation products detected in black tea include theaflavin and theaflavin gallate, a bis-flavanol and its mono- and di-galloyl esters and several trace substances.[3 to 8] The theaflavin and theaflavin gallate have been isolated as pure substances and rather tentative structures have been suggested. The bis-flavanols show a single absorption band ($\lambda_{max.} = 280$ mμ)[5] and contribute nothing towards the colour. Contributions by the trace substances may be disregarded, so that colour in tea liquors may be considered as due to

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theaflavins and thearubigins alone. Determination of these two groups of substances should therefore give a precise method of measuring the colour of a tea liquor, and such measurements might also be expected to be correlated with some of the other liquor characters.

The method developed for determining theaflavins and thearubigins depends on the fact that the theaflavins are almost quantitatively extracted from a tea liquor by one extraction with either ethyl acetate or isobutyl methyl ketone. These solvents do not extract thearubigins of the S II type, but there is a partial extraction of the free-acid forms of the S I type thearubigins. Potassium and calcium salts are not extracted. The thearubigins extracted by ethyl acetate or isobutyl methyl ketone are soluble in aqueous sodium hydrogen carbonate, whereas the theaflavins are insoluble. Complete separation of theaflavins and thearubigins is therefore effected by shaking the ethyl acetate or isobutyl methyl ketone extract with aqueous sodium hydrogen carbonate.

Theaflavin and its gallate have well defined absorption maxima at 380 and 460 mμ.[5,8] Either of these wavelengths is suitable for direct spectrophotometry in the extract washed with sodium hydrogen carbonate, as no other substances are present that absorb at these wavelengths. The fall in optical density, which results from the washing with sodium hydrogen carbonate, affords a method of determining the extractable thearubigins.

Direct spectrophotometric determination of residual thearubigins in the aqueous layer after extraction with ethyl acetate or isobutyl methyl ketone is not possible, as a high proportion of the thearubigin molecules is present as anions, which are more deeply coloured than the free acids. Addition of excess of aqueous oxalic acid reduces the colour intensity to that of the free acids, and spectrophotometry is possible after this acidification.

METHOD

PREPARATION OF THE TEA EXTRACT—

In the traditional technique of tea tasting a weighed sample of tea is infused with boiling water for from 5 to 10 minutes in a porcelain pot fitted with a lid. The resulting liquor is decanted into a porcelain cup. This method was not sufficiently reproducible for analytical purposes and it was necessary to modify it; the modified method is described below.

Weigh 9 g of tea into a 500-ml Erlenmeyer flask placed on a boiling-water bath. Bring 375 ml of distilled water to the boil, and pour it on to the tea. Allow extraction to continue for 10 minutes, without letting the temperature fall below 85°C. Filter through a plug of cotton-wool, and allow to cool just to room temperature.

PROCEDURES FOR PARTITION AND SPECTROPHOTOMETRY—

Shake 50 ml of the cooled, well shaken, filtered extract with 50 ml of isobutyl methyl ketone, taking care to avoid the formation of an emulsion. Allow the layers to separate, and dilute a 4-ml portion of the isobutyl methyl ketone layer to 25 ml with methanol (solution A). Dilute a 2-ml portion of the aqueous layer to 10 ml with water and then to 25 ml with methanol (solution B).

Shake 25 ml of the isobutyl methyl ketone layer vigorously for 30 seconds with 25 ml of a 2·5 per cent. aqueous solution of sodium hydrogen carbonate. Allow the layers to separate, and discard the aqueous layer. Dilute 4 ml of the washed isobutyl methyl ketone layer to 25 ml with methanol (solution C).

Add 2 ml of a saturated aqueous solution of oxalic acid and 6 ml of water to a 2-ml portion of the aqueous layer left from the first extraction with isobutyl methyl ketone, and dilute to 25 ml with methanol (solution D).

Measure the optical densities, E_A, E_B, E_C and E_D, of solutions A, B, C and D, respectively, in 1-cm cells at 380 and 460 mμ with a Unicam SP500 or similar spectrophotometer.

NOTES—The two layers obtained from a 1 + 1 mixture of isobutyl methyl ketone and water are nearly equal in volume. With isobutyl methyl ketone there is no danger of the volumes of the layers being affected by partial saponification of the organic solvent, as might occur with ethyl acetate, particularly if recovered solvents are used.

In the preparation of solutions B and D from the aqueous phase from the first partition, it is essential that the methanol content should not exceed 60 per cent. otherwise a cloudiness may develop, owing to precipitation of pectins.

If the sodium hydrogen carbonate contains more than a small amount of sodium carbonate, theaflavins may be lost by alkaline autoxidation during washing of the isobutyl methyl ketone extract. Analytical-reagent grade sodium hydrogen carbonate should therefore be used, and the solution should be freshly prepared. To minimise the possibility of losses by autoxidation the period of shaking must be as short as possible, and one layer should be completely removed from the other immediately after they have separated. Under normal conditions solution C is stable, but the measurement of its optical density should not be delayed.

In routine determinations of theaflavin and thearubigins no use is made of the E_B values. However, the E_B/E_D ratio has a particular significance, which will be referred to in subsequent publications.

EVALUATION OF THEAFLAVIN CONTENT—

There is always considerably more theaflavin gallate than theaflavin in a tea, so that little error will be introduced by expressing total theaflavins as theaflavin gallate.

The optical densities, E_C, at 380 and 460 mμ are converted into a percentage of anhydrous theaflavin gallate by multiplying by the factors 2·25 and 6·69, respectively. These factors are applicable only when the conditions of extraction, partition and spectrophotometry are as described above, and are calculated from the optical-density values for theaflavin gallate shown in Table I. It is assumed that the theaflavin gallate used for standardisation purposes is the dihydrate of molecular weight 892·7.[8]

NOTE—The ratio of optical densities at 380 and 460 mμ should be 2·98 to 1. If the ratio is appreciably greater than this, incomplete removal of thearubigins by sodium hydrogen carbonate is indicated. A lower value would suggest that the ratio of theaflavin to theaflavin gallate was greater than usual (see Table I).

EVALUATION OF THEARUBIGIN CONTENT—

Any factor for converting optical density into a percentage of thearubigin must be somewhat arbitrary, as we are dealing with a variable and rather complex mixture of substances, none of which has been isolated in a pure state. A further complication is introduced by the uncertainty as to the degree of hydration of the thearubigins.

It is apparent from Table I that the optical densities for the S I and S II fractions differ appreciably at 460 mμ, but do not differ much from each other at 380 mμ. The average value of $E_{1\,cm}^{0.02\%}$ at 380 mμ for the two fractions is 0·733. Optical densities at 380 mμ obtained for these two fractions with four other teas were—

Sample No.	1	2	3	4
Optical density of S I fraction ..	0·712	0·655	0·658	0·739
Optical density of S II fraction ..	0·734	0·796	0·720	0·810

The acceptance of 0·733 as an average value of $E_{1\,cm}^{0.02\%}$ at 380 mμ for total thearubigins is therefore unlikely to lead to any considerable error, and, if this average value is assumed, the percentage of extractable thearubigins in a tea is, for the conditions of extraction, partition and spectrophotometry described above, approximately $7{\cdot}06\ (2E_D + E_A - E_C)$. The results must be accepted with certain reservations, but they are of the expected order of magnitude.

THE E_{380}/E_{460} RATIO FOR THEARUBIGINS—

The ratio of the values for $2E_D + E_A - E_C$ at 380 and 460 mμ in different teas has varied from 3·6 to 8·2. This indicates that the mixture of thearubigins in teas is by no means constant. If it is assumed that thearubigins have approximately the same optical densities at 380 mμ, the variation in this ratio gives some indication of the average intensity of colour (at 460 mμ) of the thearubigins. A high ratio implies relatively light colour, and a low ratio a correspondingly deeper colour. As will be apparent from Table I, the more deeply coloured S II fraction has a lower ratio than the corresponding S I fraction.

TABLE I

$E_{1\,cm}^{0.02\%}$ VALUES FOR THEAFLAVIN, THEAFLAVIN GALLATE AND THEARUBIGIN FRACTIONS

The absorption spectra of the theaflavins and the thearubigin fractions were plotted over the range 220 to 600 mμ. The resulting absorption curves and optical densities at certain wavelengths have been published previously[5,8]

Sample	$E_{1\,cm}^{0.02\%}$ value at— 380 mμ	460 mμ	Ratio E_{380}/E_{460}
Theaflavin	3·400	1·235	2·75
Theaflavin gallate	2·225	0·747	2·98
Thearubigins (fraction S I) ..	0·717	0·138	5·20
Thearubigins (fraction S II) ..	0·750	0·233	3·20

This ratio is a useful extra parameter in describing the thearubigins of a tea, for thearubigin content is not necessarily proportional to depth of colour, particularly if the E_{380}/E_{460} ratio is high.

With nearly all Assam teas this ratio falls between 3·6 and 4·4 (average 4·0). A rough estimate of the percentage of thearubigin in such teas is given by $4 \times 7{\cdot}06\ (2E_D + E_A - E_C)$ when optical densities are measured at 460 mμ. In the earlier stages of this investigation measurements were carried out at 460 mμ only, but, so long as the teas originated from Assam, the optical densities could be used to give an approximation of their thearubigin contents.

RESULTS

Many commercial and experimentally manufactured teas have been analysed by the proposed procedure and detailed results will be reported elsewhere. Typical results are considered below. Those in Table II give some idea of the range of values obtained.

TABLE II

REPRESENTATIVE ANALYSES OF COMMERCIAL TEAS

Thearubigin contents in brackets were calculated from optical densities at 460 mμ

Sample	Theaflavin content, %	Thearubigin content, %	Ratio E_{380}/E_{460}	Taster's remarks
N.E. India—				
Good quality (C)	0·78	(8·9)	—	Golden colour, strong
Medium quality (C)	0·68	(7·6)	—	Bright
Poor quality (C)	0·36	(7·1)	—	Coloury, dull, common
Assam O.F. grade (C)	0·70	13·1	4·24	—
Assam B.P. grade (CTC)	1·45	16·7	3·64	Very bright, golden
Duars O.F. grade (C)	0·58	7·6	4·38	—
Duars (Legg cut)	1·08	14·7	4·57	Hard, bright colour, with rich colour
Ceylon—				
P.F. grade (C)	0·92	14·6	8·25	Bright, golden
B.O.P.F. grade (C)	0·81	17·1	7·33	Rich, very coloury
Nyasaland—				
B.O.P. grade (C)	0·42	13·6	6·00	Dull
Kenya—				
B.P. grade (C)	0·34	8·5	—	Thin, grey
Argentine—				
P.F. grade (C)	0·23	15·0	4·53	Very thick, dull, muddy

C = Conventional manufacture. CTC = C.T.C. manufacture.

The thearubigin content of a tea is always considerably higher than the theaflavin content, but, as theaflavins are much more intensely coloured (see Table I), their contribution to total colour is a decidedly significant one. In assessing tone of colour, the taster is influenced more by the theaflavin content than the thearubigin content, and in conventionally manufactured teas the preferred liquor colours are associated with theaflavin contents of 0·75 per cent. or more.

Conventional methods of manufacture, particularly in N.E. India, have to some extent been replaced by other methods (C.T.C. and Legg cut) in which the leaf receives a more thorough bruising, resulting in a quicker and more extensive fermentation. Analyses of such teas show increased theaflavin and thearubigin contents and an increase in the ratio of theaflavin to thearubigin. This accounts for the increased "brightness" and greater depth of colour normally associated with these methods of manufacture.

Table II also shows the different E_{380}/E_{460} ratios obtained for thearubigins. These are lowest in teas originating from N.E. India.

Theaflavin and thearubigin contents are also affected by fermentation conditions, as indicated in Table III. It will be noted that the theaflavin content reaches a maximum level comparatively early in the fermentation process, and that, in the later stages of fermentation, thearubigin contents increase slowly at the expense of the theaflavins. As the liquor characters of strength, briskness and quality are affected by variations in the duration of fermentation,[1] it is considered probable that these particular characters are determined, to some extent at least, by the theaflavin and thearubigin contents.

TABLE III

EFFECT OF DURATION OF FERMENTATION ON THEAFLAVIN AND THEARUBIGIN CONTENTS OF C.T.C. MANUFACTURED TEAS

Each result is an average from six separate experimental manufactures

Fermentation time, hours	1	2	3	4	5
Theaflavin content, %	1·61	1·46	1·34	1·27	1·17
Thearubigin content, %	13·0	16·2	16·6	16·7	17·1

CONCLUSIONS

We are of the opinion that the measurement of theaflavins and thearubigins, coupled with the E_{380}/E_{460} ratio for thearubigins, represents the best available method for determining colour in tea liquors. In view of the probable association of these variables with other liquor characters, it might be thought that these methods would serve as a basis for a chemical evaluation of the market value of a tea. This, however, is too optimistic a view. Quality in tea is not determined by polyphenolic oxidation products alone, for there are other important factors, among which caffeine and the volatile substances responsible for aroma may be mentioned. Market valuations are also affected by such factors as appearance and keeping properties on storage. The replacement of traditional methods of tea tasting by chemical analysis is not yet therefore in sight, but it is claimed that the methods described above should prove extremely useful in supplementing a taster's report. Analytical results, unlike a taster's evaluation, are not affected by market fluctuations, and are much more suitable when it is desirable to maintain records of the properties of teas manufactured. The analytical method may also be expected to be developed as a means of control during manufacture.

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The Volumetric Determination of Dixanthogen

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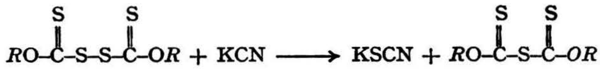
A convenient method for determining dixanthogen has been developed; it is based on the quantitative reaction of dixanthogen with potassium cyanide to form xanthogen monosulphide and potassium thiocyanate. Xanthogen monosulphide and the excess of cyanide are removed, and the thiocyanate is determined iodimetrically after conversion to cyanogen bromide. The method is applicable to the determination of dixanthogen in mixtures also containing xanthate.

DURING work on the kinetics of the oxidation of xanthate to dixanthogen, it was necessary to determine the dixanthogen formed by the reaction. A search of the literature for a suitable method was unsuccessful, and attempts were, therefore, made to determine dixanthogen by utilising the reaction reported by Whitby and Greenberg.[1] According to these workers, potassium cyanide reacts with dixanthogen to form xanthogen monosulphide and alkali thiocyanate, the reaction being represented by the equation—



$$RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}OR + KCN \longrightarrow KSCN + RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}OR$$

A similar reaction has recently been used by Chatterjee, Banerjee and Sircar[2] to determine thiuramdisulphide, but their method of determination is complicated. We have simplified this determination by adopting Schulek's method[3] for determining thiocyanate (after the removal of xanthogen monosulphide and the excess of cyanide). In this method, thiocyanate is allowed to react quantitatively with bromine to form cyanogen bromide in accordance with the equation—

$$SCN^- + 4Br_2 + 4H_2O \longrightarrow CNBr + 7Br^- + SO_4^{2-} + 8H^+$$

The cyanogen bromide is then allowed to react with potassium iodide to liberate iodine, the reaction being represented by the equation—

$$CNBr + 2I^- \longrightarrow CN^- + Br^- + I_2$$

and this iodine is titrated with standard thiosulphate solution; the amount of dixanthogen originally present is then calculated.

METHOD

REAGENTS—

Unless otherwise stated, all reagents were of recognised analytical grade.

Potassium cyanide solution, 2 per cent. w/v.

Ammonium nitrate solution, 10 per cent. w/v.

Bromine water, 5 per cent. w/v.

Sodium thiosulphate, 0·05 N.

Orthophosphoric acid, 17 per cent.—Dilute 1 volume of 88 per cent. orthophosphoric acid with 4 volumes of water.

Xanthates—Prepare potassium isopropyl-, n-butyl- and isopentylxanthate by Foster's method,[4] and purify as described by Dewitt and Roper.[5] The purity of the xanthates so prepared is greater than 99 per cent. as determined by the iodine method.[6]

Di-n-butyl dixanthogen solution—Oxidise a concentrated aqueous solution of n-butylxanthate by adding a concentrated solution of iodine, as described by Whitby and Greenberg.[1] Extract the dixanthogen formed with light petroleum (boiling range 40° to 60° C), and evaporate the extract at room temperature by means of a current of air. Di-n-butyl dixanthogen is obtained as a yellow oil [sulphur found (Carius method), 42·39 per cent.; $C_{10}H_{18}O_2S_4$ requires 42·98 per cent. of sulphur]. Prepare a 1 to 1·5 per cent. w/v solution of the dixanthogen in acetone.

PROCEDURE—

Place 10 ml of di-n-butyl dixanthogen solution in a conical flask, and add 5 ml of 10 per cent. ammonium nitrate solution, 10 ml of 2 per cent. potassium cyanide solution and 10 ml of acetone. Heat the mixture at 40° to 50° C for about 25 minutes in a fume cupboard to ensure that the reaction between dixanthogen and cyanide is complete. Cool, transfer to a separating funnel, and shake well with 15 ml of benzene to extract the xanthogen monosulphide formed; repeat the extraction with a further 15 ml of benzene to ensure complete removal of the monosulphide (this is judged by the disappearance of the yellow colour of the solution). Transfer the aqueous solution to the original conical flask, add 10 ml of 17 per cent. orthophosphoric acid, and heat on a bath of boiling water in a fume cupboard for about 30 minutes to remove hydrocyanic acid.

Cool the solution, and add bromine water dropwise until a yellow colour stable for at least 5 minutes is obtained. Remove the excess of bromine by adding small amounts of ferrous sulphate, with stirring, until the yellow colour disappears. Add 3 g of potassium iodide and then a little sodium hydrogen carbonate, insert a stopper in the neck of the flask, shake well, and set aside in the dark for 10 minutes. Titrate the liberated iodine with

0·05 N sodium thiosulphate; use starch as indicator. Calculate the amount of dixanthogen present in the original solution from the titre (after correction for the blank value).

1 ml of N sodium thiosulphate ≡ 0·14925 g of di-n-butyl dixanthogen.

DISCUSSION OF THE METHOD

Solutions containing di-n-butyl dixanthogen were analysed by the proposed method; the results, which show that good accuracy is attainable, were—

Dixanthogen present, g ..	0·1397	0·1397	0·1397	0·1397	0·1185	0·1185	0·1011	0·1011
Dixanthogen found, g ..	0·1409	0·1402	0·1402	0·1395	0·1188	0·1180	0·1010	0·1008
Error, g	0·0012	0·0005	0·0005	−0·0002	0·0003	−0·0005	−0·0001	−0·0003

In this work, the use of orthophosphoric acid has many advantages. It assists in converting potassium cyanide to hydrocyanic acid, which can be easily removed by boiling. Further, since orthophosphoric acid is a weak acid, the cyanogen bromide formed is stable in the solution. Also, orthophosphoric acid combines with the yellow ferric ions, thereby rendering the solution colourless.

Removal of dixanthogen monosulphide from the solution is essential or the titration of the liberated iodine will be unreliable. The use of ammonium nitrate solution enhances the extraction of dixanthogen monosulphide by the non-aqueous solvent and so improves the accuracy of the method.

DETERMINATION OF DIXANTHOGEN IN MIXTURES ALSO CONTAINING XANTHATE—

It is well known that a xanthate is oxidised to the corresponding dixanthogen when exposed to the atmosphere. Further, an old or exposed sample of xanthate is invariably associated with the corresponding dixanthogen. It was, therefore, thought desirable to determine a dixanthogen in a mixture also containing xanthate; such mixtures were accordingly prepared. The xanthate was determined by Hirschkind's method[7] and the dixanthogen by the proposed method. In Hirschkind's method, the xanthate is quantitatively converted (by a mineral acid) to an unstable xanthic acid, which immediately dissociates into carbon disulphide and the corresponding alcohol. The amount of xanthate present can be calculated from the amount of mineral acid consumed. The procedure used is described below.

> Mix 10 ml of an ethanolic solution of isopropyl- or isopentylxanthate with 10 ml of dixanthogen solution (in acetone) in a conical flask, and determine the xanthate by Hirschkind's method.[7] (Use 0·05 N sulphuric acid, and determine the excess of acid by titration with 0·05 N alkali; calculate the amount of xanthate present from the acid consumed.) Add 15 to 20 ml of acetone to the contents of the flask to obtain a clear solution, and then determine the dixanthogen by the proposed method.

TABLE I

AMOUNTS OF XANTHATE AND DIXANTHOGEN FOUND IN PREPARED MIXTURES

Components of mixture	Xanthate present, g	Dixanthogen present, g	Xanthate found, g	Dixanthogen found, g
Potassium isopropylxanthate and di-n-butyl dixanthogen ..	0·0447	0·1146	0·0445, 0·0445	0·1151, 0·1151
Potassium isopentylxanthate and di-n-butyl dixanthogen ..	0·0637	0·1027	0·0635, 0·0635	0·1029, 0·1036

Table I shows the results found when this method was applied to two prepared mixtures; it can be seen that both xanthate and dixanthogen were determined with good accuracy.

We thank Professor M. R. A. Rao for his keen interest in the work.

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The Semi-micro Determination of Fluorine in Organic Compounds

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A method is described for determining fluorine in organic compounds; it is based on colorimetric determination of fluoride ions resulting from combustion by the oxygen flask method. The determination depends on the formation of a blue complex between fluoride ions and the cerium^{III} chelate of alizarin complexan. The influence of the type of glass of which the combustion flask is constructed has been quantitatively examined.

A SPOT test involving use of the cerium^{III} complex of alizarin complexan (1,2-dihydroxyanthraquinon-3-ylmethylamine-*NN*-diacetic acid) for detecting fluoride has been described by Belcher, Leonard and West.[1] Subsequently, these workers devised a sub-micro method for determining fluorine in organic compounds, based on the same reaction.[2] More recently, the theoretical basis of the method and the nature of the chelates involved have been described,[3] and the purpose of this paper is to describe the application of the principle to the semi-micro determination of fluorine in organic compounds.

EXPERIMENTAL

The method investigated consists in decomposing the sample by the flask combustion method,[4] a flask constructed of glass essentially free from boron and aluminium being used (see "Results and Discussion of the Method," p. 103), and then colorimetrically determining fluoride in the resulting solution. In the colorimetric reaction used, fluoride does not exert its usual bleaching effect on the dye - metal complex, but itself enters the structure. The blue colour of the fluoride-containing complex ($\lambda_{max.}$ = 565 mμ) is completely distinguishable from either the yellow of the free dye ($\lambda_{max.}$ = 423 mμ) or the red of its cerium^{III} chelate ($\lambda_{max.}$ = 495 mμ).[3] The wavelength chosen for the colorimetric determination (610 mμ) corresponds to the maximum difference between the absorption spectra of the fluoride-containing complex and the cerium^{III} chelate.

METHOD

APPARATUS—

The combustion apparatus consists of a 500-ml Erlenmeyer flask constructed of suitable glass. Into the stopper is fused one end of a length of platinum wire, 1 mm in diameter, to the free end of which is attached a piece of 36-mesh platinum gauze, 1·5 cm × 2 cm, to act as sample holder.

Optical densities were measured in 4-cm cells with a battery-operated Unicam SP600 visual-range spectrophotometer.

REAGENTS—

Alizarin complexan, 0·0005 M—Transfer 0·385 g of alizarin complexan to a 2-litre calibrated flask by means of 20 ml of recently prepared 0·5 N sodium hydroxide, and set aside for 5 minutes, with occasional swirling, to ensure complete solution. Dilute to about 1500 ml with water, add 0·2 g of hydrated sodium acetate, and adjust the pH to about 5 (thin layer of solution pink) by careful addition of 1 N hydrochloric acid. Dilute to the mark, and filter into a brown-glass bottle. This solution is stable for at least 4 months.

Cerous nitrate, 0·0005 M—Standardise approximately 0·02 M cerous nitrate by titration against standard ethylenediaminetetra-acetic acid solution at pH 6 with xylenol orange as indicator. To a suitable volume of this solution (about 50 ml) add 0·2 ml of concentrated nitric acid, 0·1 g of hydroxylamine hydrochloride and sufficient water to produce 2 litres, and filter.

Acetate buffer solution, pH 4·6—Dissolve 150 g of hydrated sodium acetate in about 600 ml of water, add 75 ml of glacial acetic acid, dilute to 1 litre with water, and filter.

Standard fluoride solution, 5 *μg per ml*—Dissolve about 22 mg (accurately weighed) of dried analytical-reagent grade sodium fluoride in water, and adjust the volume to 2 litres. Store in a polythene container.

PREPARATION OF CALIBRATION GRAPH—

In each of a series of 100-ml calibrated flasks place 50 ml of distilled water, an accurately measured volume between 2 and 8 ml of standard fluoride solution, 10 ml of alizarin complexan solution and 3 ml of acetate buffer solution. Mix each solution thoroughly, add 10 ml of 0·0005 M cerous nitrate, dilute to the mark with distilled water, and set aside, protected from direct light, for 1 hour. At the same time, prepare a blank solution in similar fashion by omitting the standard fluoride solution. Measure the optical densities of the test solutions against the blank in 4-cm cells at 610 mμ, and plot a graph of optical density against amount of fluoride present.

PROCEDURE—

Accurately weigh an appropriate amount of the sample (5 to 25 mg) on a strip of filter-paper approximately 3 cm × 4 cm (Whatman No. 1 grade is suitable) that has been folded into three along its length. Enclose the sample in the paper, insert a narrow strip of filter-paper to act as a fuse, and fix it in the platinum-gauze sample holder. Place 20 ml of water in the combustion flask, fill the flask with oxygen, ignite the fuse, and immediately insert the stopper. Carefully tilt the flask, and, when combustion is complete, set it aside for 10 minutes, with intermittent shaking. Quantitatively transfer the liquid to a 250-ml calibrated flask, dilute to the mark, and treat an aliquot expected to contain about 25 μg of fluoride by the procedure described for colour development under "Preparation of Calibration Graph." At the same time, prepare a standard colour from 5 ml of standard fluoride solution to serve as a check on the calibration graph.

Liquid samples can be satisfactorily decomposed by burning in a small gelatin or, preferably, methylcellulose capsule containing approximately 30 mg of powdered cellulose.

For solutions derived from the combustion of sulphur-containing compounds, boil gently for about 10 seconds with 1 ml of 100-volume hydrogen peroxide, neutralise to phenolphthalein with 1 N sodium hydroxide, and then add 1 ml in excess; boil to destroy excess of peroxide, cool, and adjust the pH to about 4 with 1 N hydrochloric acid.

EFFECT OF FOREIGN IONS

A qualitative survey of ions likely to interfere with the reaction has already been carried out.[1] The results of a quantitative evaluation of some of the more common of these ions are shown in Table I, from which it can be seen that aluminium and iron cause serious interference. Ions likely to be present as a result of the oxygen flask method of combustion of organic compounds exert a negligible effect, with the exception of phosphate, interference from which becomes significant if a large excess is present.

TABLE I

INFLUENCE OF SELECTED IONS ON DETERMINATION OF FLUORIDE

Ion	Amount of ion causing 10 per cent. decrease in colour produced by 26 μg of fluoride, μg	Mole ratio of interfering ion to fluoride
Aluminium	7	0·19
Ferric iron	8*	0·105
Citrate	93	0·36
Phosphate	1000	7·7
Sulphate	16,500	123
Chloride	315,000	6490

* Ferric iron forms a violet chelate that absorbs strongly at 610 mμ and hence causes an increase in colour.

RESULTS AND DISCUSSION OF THE METHOD

Calibration graphs prepared as described above are linear over the range 10 to 30 μg of fluoride, but above this range the sensitivity decreases, owing to the smaller excess of reagent. For this reason, test solutions should contain about 25 μg of fluoride. The slope of the calibration graph is positive, in contrast to those obtained by conventional bleaching methods, and the sensitivity is such that 1 μg of fluorine causes a change in optical density of about 0·014. This sensitivity is inversely affected by the concentration of acetate in the buffer solution. However, a decrease in the concentration of the buffer, although it increases the sensitivity, impairs the reproducibility.

TABLE II

FLUORINE CONTENTS FOUND BY PROPOSED METHOD AFTER COMBUSTION IN A SILICA FLASK

Sample No.	Compound	Number of determinations (n)	Theoretical fluorine content, %	Mean fluorine content found (y), %	Standard deviation of a single determination* (S), %	Standard deviation as percentage of mean fluorine content found
1	*p*-Fluorobenzoic acid, $F{\cdot}C_6H_4{\cdot}COOH$ (M.A.R. grade)	14	13·56	13·55	0·157	1·16
2	Trifluoroacetanilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CF_3$ (micro-analytical standard)	16	30·14	30·10	0·382	1·27
3	*m*-Trifluoromethylbenzoic acid, $CF_3{\cdot}C_6H_4{\cdot}COOH$ (micro-analytical standard)	15	29·98	30·00	0·248	0·83
4	Triamcinolone, $C_{21}H_{27}O_6F$	31	4·81	4·81	0·059	1·22
5	9-Fluorohydrocortisone, $C_{21}H_{29}O_5F$	5	4·98	4·89	0·035	0·72
6	Hydroflumethiazide, $C_8H_8N_3O_4S_2F_3$	10	17·20	17·27	0·058	0·34
7	Bendrofluazide, $C_{15}H_{13}O_4N_3S_2F_3$	9	13·58	13·48	0·142	1·05
8	Polytetrafluoroethylene, $(CF_2)_n$	7	76·0	75·8	0·80	1·05
9	Research compound, $C_6F_7H_2NO$	14	56·12	55·30	0·85	1·53
10	Research compound, $C_{10}F_{21}SO_3Na$	7	64·2	62·4	0·36	0·58
11	*p*-Fluorophenyl-*p*-chlorobenzyl sulphone, $C_{13}H_{10}O_2SClF$	4	6·68	6·69	0·041	0·62
12	Research compound, C_8F_{16} (perfluorocyclohexylethane)	9	76·0	72·42	0·79	1·1
13	Research compound, $[CF_3{\cdot}C_6H_4P:(C_2H_5)_2]_2AgI$	9	16·22	15·63	0·23	1·47
14	Research compound, $[CF_3{\cdot}C_6H_4P:(C_2H_5)_2]CdI_2$	6	9·50	9·15	0·056	0·61
15	1-Fluoro-2,4-dinitrobenzene, $C_6H_3O_4N_2F$	4	10·22	10·39	0·089	0·86
16	Fluorobenzene, C_6H_5F	8	19·80	19·69	0·192	0·98
17	Research compound, $CF_2ClCHCl_2$	6	22·45	21·96	0·127	0·58

* Calculated from the expression $S = \sqrt{\Sigma\,(x - y)^2/(n - 1)}$, in which x is the result of an individual determination.

The proposed method has been applied to a wide range of compounds, and the results obtained (with the use of a silica flask for combustion) are shown in Table II. Most of these results were satisfactory, but certain of the research compounds gave low results. Sample

TABLE III

COMPARISON BETWEEN RESULTS FOR FLUORINE AFTER COMBUSTION IN FLASKS OF DIFFERENT MATERIALS

Compound	Theoretical fluorine content, %	Fluorine content found after combustion in— silica flask, %	boron-free-glass* flask, %	borosilicate-glass flask, %
Triamcinolone	4·81	4·81	4·79	4·68
p-Fluorobenzoic acid	13·56	13·55	13·47	13·03
m-Trifluoromethylbenzoic acid	29·98	30·00	29·95	28·81
Polytetrafluoroethylene	76·0	75·8	75·9	72·1
Hydroflumethiazide	17·20	17·27	—	16·71

* This glass contained 3 per cent. of alumina.

No. 10 was reported to be difficult to decompose by fusion with an alkali metal, but the precision of the results obtained by the flask method points to complete combustion. Samples Nos. 12 and 17 were volatile and non-inflammable.

It was noted in the initial stages of this work that the use of borosilicate-glass combustion flasks gave consistently low results. Combustions were subsequently carried out in silica and in boron-free-glass flasks, and some comparative results are shown in Table III. It is considered that boron-free-glass flasks are suitable for routine determinations, although the results obtained are slightly lower than those found when silica flasks are used. This is probably due to the presence of a small amount of aluminium and is consistent with Rogers and Yasuda's observations.[5]

Our work has confirmed Rogers and Yasuda's contention that decomposition of the $-CF_3$ group by flask combustion is complete; we have not found it necessary to use oxidation aids, such as sodium peroxide,[6] potassium chlorate[2] or potassium nitrate.

We thank Dr. A. M. G. Macdonald of Birmingham University for supplying a number of the research compounds listed in Table II.

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The Analysis of Lead Tannate and Related Chelates by an Amperometric Method

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An amperometric method for analysing lead tannate and related complexes is described. The method is based on a reversal of the normal amperometric procedure, an aqueous ethanolic suspension of the complex being titrated with dilute nitric acid. The results agree well with those by the standard gravimetric procedure. The analysis is rapid and only small amounts of material are required.

LEAD tannate, prepared from the reaction of lead acetate with black wattle (*Acacia mollissima* Willd) tannin, has been examined in this laboratory as a possible pigment for primer paints. It was therefore important to determine with accuracy the lead content of this complex.

When a water-soluble lead salt is analysed amperometrically, lead ions are removed from solution by precipitation[1]; a plot of current against volume of precipitant added yields an L-shaped graph. Since lead tannate is insoluble in water and cannot be analysed by this procedure, it was thought that a reversal of the method might yield results. Thus, if lead tannate were suspended in an aqueous solution and lead ions, instead of being removed from the solution, were liberated by the action of dilute nitric acid, then (*i*) the diffusion current should increase linearly with the increase in concentration of lead ions, (*ii*) when all the lead tannate has been decomposed (*i.e.*, at the equivalence point), the concentration of the lead ions, and hence also the diffusion current, should remain constant and (*iii*) a plot of current against volume of nitric acid added should give an inverted L-shaped graph.

The experimental results completely substantiated these predictions, and, to check the validity of the method, two reference compounds (lead catecholate and lead pyrogallolate) were also examined.

Method

A manual polarograph and the conventional ancillary apparatus are used. Since a relatively large volume of acid is necessary for complete decomposition of the complexes, the dilution effect is corrected for by multiplying the measured values of the current by the factor $\frac{V+v}{V}$, where V denotes the original volume of the solution titrated and v the volume of reagent added at any point. Reaction is complete when the diffusion current becomes constant; in practice, there is a slight decrease in the observed values, owing to the dilution effect.

REAGENTS—

Lead acetate solution, 10 *per cent. w/v, aqueous.*

Nitric acid, approximately 0·2 N.

Black wattle tannin—De-gummed by the acetone-precipitation method.

PROCEDURE—

Prepare the chelate by adding an excess of lead acetate solution to an aqueous solution of the phenol. Separate the resulting precipitate by filtration, and dry under vacuum. Accurately weigh between 0·2 and 0·3 g of the dried lead complex, and suspend in a mixture of 20 ml of water and 5 ml of ethanol in a 150-ml beaker. Set up the standard apparatus for an amperometric determination, and bubble nitrogen through the solution for 10 minutes. Adjust the capillary to give 3 to 5 drops of mercury per second, and apply a potential of −1·2 or −1·0 volt against the saturated-calomel electrode.

Run in approximately 0·2 N nitric acid from a burette in 0·1-ml portions at first and in 1·0-ml portions as the reaction proceeds beyond the end-point. Stir the solution thoroughly, by means of the gas-inlet tube, after each addition of acid. Plot a graph of current against volume of nitric acid added. (The points should lie along two straight lines, which intersect at the end-point.)

RESULTS

In Table I results by the proposed method for the lead contents of lead catecholate, pyrogallolate and tannate are compared with those found by the standard gravimetric method; the range of the proposed procedure is also indicated. Typical titration curves for the three complexes are shown in Fig. 1.

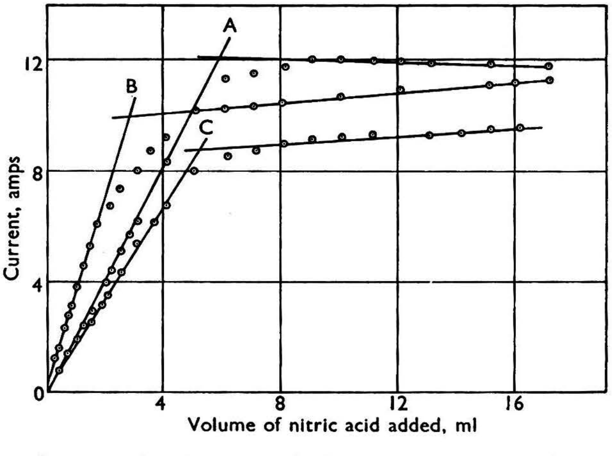

Fig. 1. Titration curves for lead complexes: curve A, lead catecholate (66·74 per cent. of lead); curve B, lead tannate (21·64 per cent. of lead); curve C, lead pyrogallolate (51·48 per cent. of lead)

From the Ilkovic equation, the relationship i_d/C, in which C is the concentration and i_d the diffusion current, should be constant.[2] It was found that, within the range 10 to 13 μ moles of lead per litre, the diffusion current was proportional to concentration.

The accuracy of the proposed method is shown by the fact that the results differ only slightly from those found by the standard gravimetric procedure.

TABLE I

COMPARISON OF RESULTS BY PROPOSED AND GRAVIMETRIC METHODS

Sample	No. of determinations by proposed method	Lead content found by—		Theoretical lead content, %
		proposed method (mean), %	gravimetric method, %	
Lead catecholate, $C_6H_4O_2Pb$	3	65·77 ± 1·20	65·44	65·72
Lead pyrogallolate, $C_6H_3(OH)O_2Pb$ or $C_{12}H_6(OH)_4O_2Pb$	3	51·34 ± 0·94	52·60	62·54 or 45·30*
Lead tannate	5	21·44 ± 0·60	21·09	—

* The structure of lead pyrogallolate is not known.

CONCLUSIONS

Amperometric analysis of the chelates is rapid; a determination can be completed in less than 1 hour. Further, only small amounts (about 0·2 g) of sample are required. There is no reason why the method should not be extended to the analysis of materials other than lead chelates. Experiments on litharge showed promise, and, with slight modifications, the method should be an asset in the analysis of pigments.

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The Separation of Vanadium and Chromium from Iron by Extraction of Ferric Chloride with Di-isopropyl Ether

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A modified procedure for separating vanadium^{IV} and chromium^{III} from iron^{III} is described; it involves extraction with di-isopropyl ether from 8 to 9 M hydrochloric acid in the presence of sulphur dioxide. The use of sulphur dioxide allows all precautions for avoiding the formation of peroxides to be omitted and obviates the uncertainty attendant upon the usual method of reducing vanadium^{V} with hydrochloric acid. Reduction of ferric iron by sulphur dioxide under these conditions is negligible, and 99·95 per cent. of the iron is extracted with negligible extraction of vanadium and chromium.

THE extraction of ferric iron from hydrochloric acid solutions by di-isopropyl ether has been widely used since its introduction in 1936 by Dodson, Forney and Swift.[1] The work described in this paper deals primarily with the recovery of vanadium after such an extraction.

The extraction of vanadium by di-isopropyl ether from concentrated hydrochloric acid has been studied by Dodson, Forney and Swift[1] and, more recently, by Lingane and Meites.[2] The latter workers found that vanadium^{V} is largely extracted; extraction from solutions of vanadium^{IV} is initially small, but increases with time as the vanadium is oxidised to vanadium^{V} by peroxides photolytically formed in the ether. Vanadium^{V} itself is slowly reduced by chloride until the two competing reactions produce a stationary state.

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Hence, to avoid extraction, the vanadium must be present entirely as vanadium$^{\text{IV}}$ and precautions must be taken to avoid the formation of peroxides. These precautions are inconvenient; further, we have found the usual procedure for reducing vanadium$^{\text{V}}$ to vanadium$^{\text{IV}}$ by evaporation with hydrochloric acid to be unsatisfactory. The procedure proposed here avoids both these difficulties.

EXTRACTION OF IRON

EFFECT OF HYDROCHLORIC ACID CONCENTRATION—

Portions (25 ml) of solutions of ferric chloride in various concentrations of hydrochloric acid were shaken by hand in 100-ml separating funnels with equal volumes of di-isopropyl ether for 3 minutes. The residual amounts of iron in the aqueous layers were determined absorptiometrically as the thiocyanate complex. For high concentrations of iron, the results obtained (see Table I) showed that the percentage of ferric iron extracted did not decrease at concentrations of acid greater than 8 M, as reported by Dodson, Forney and Swift,[1] but remained constant over the concentration range 8 to 9 M in acid; this confirms the work of Nachtrieb and Conway.[3]

TABLE I

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON EXTRACTION OF IRON

Each of our results is the mean of three determinations

Initial concentration of ferric iron, mg per ml	Ferric iron extracted when initial solution was— 6·0 M in acid, %	7·0 M in acid, %	7·5 M in acid, %	8·0 M in acid, %	8·5 M in acid, %	9·0 M in acid, %	10·0 M in acid, %
Our results; extraction at 20° to 25° C—							
54	99·2	99·90	99·92	99·95	99·95	99·95	—
Results of Nachtrieb et al.[3]*; extraction at 25° C—*							
47	98	99·6	99·8	99·89	99·91	99·93	99·85
Results of Dodson et al.[1]*; extraction at 25° C—*							
10	98·1	99·65	99·85	99·93	99·65	94·6	—

EFFECT OF IRON CONCENTRATION—

Nachtrieb and Fryxell[4] have shown that, owing to a "self-salting-out" effect, the completeness of extraction increases as the concentration of ferric iron is increased. We found that, in 8 M hydrochloric acid, the concentration of ferric iron can be increased to a very high level before any saturation of the organic phase is apparent; our results were—

Ferric iron initially present, mg per ml	10·8	48	54	60	108
Ferric iron extracted by equal volume of di-isopropyl ether, %	99·91	99·95	99·95	99·94	98·05

By comparison, extraction with isobutyl methyl ketone and pentyl acetate[5] (the superior method for small concentrations of ferric iron) fails for concentrations greater than 15 mg of ferric iron per ml if extraction is to be more than 99·90 per cent. complete.

EFFECT OF EXTRACTION TIME—

Extraction is complete after a very short time. The results below show the percentage of ferric iron extracted by an equal volume of di-isopropyl ether from 8 M hydrochloric acid containing 54 mg of ferric iron per ml.

Extraction time ..	5 seconds	15 seconds	30 seconds	1 minute	2 minutes	5 minutes	10 minutes
Ferric iron extracted, %	99·94	99·94	99·94	99·94	99·95	99·95	99·95

Some 1970 calories per mole are liberated when the iron is extracted[3]; with concentrated solutions, this produces an appreciable increase in temperature, which, in turn, produces a slight decrease in the equilibrium concentration of ferric iron in the organic phase. The slight increase in the percentage of iron extracted at times longer than 1 minute is attributed to gradual cooling.

EFFECT OF OTHER IONS—

The amount of ferric iron extracted from 8 M hydrochloric acid containing 54 mg of ferric iron per ml was found to be independent of the presence of hydrogen peroxide (0·2 N) and orthophosphoric acid (M) and was increased to 99·98 per cent. by the presence of 50 mg per ml of chromium$^{\text{III}}$.

EXTRACTION OF CHROMIUM

In confirmation of Dodson, Forney and Swift's work,[1] the extraction of chromium$^{\text{III}}$ from 0·8 M chromium$^{\text{III}}$ chloride in 8 to 9 M hydrochloric acid in the absence of iron was found to be less than 0·005 per cent. However, in the presence of high concentrations of iron the extraction of chromium$^{\text{III}}$ was enhanced; typical values are shown on p. 110.

EXTRACTION OF VANADIUM

REDUCTION OF VANADIUM$^{\text{V}}$ WITH HYDROCHLORIC ACID—

The absence of vanadium in the quinquivalent state is particularly important when large amounts of iron and chromium are present, because the "salting-out" effect of these ions greatly increases the amount of vanadium$^{\text{V}}$ extracted (to from 60 to 80 per cent. when the solution is M in iron). To ensure the absence of vanadium$^{\text{V}}$, Lingane and Meites[2] recommended evaporation with hydrochloric acid; in our hands this method gave incomplete reduction.

Five-millilitre portions of a solution 0·1915 M in vanadium (approximately 49 mg of vanadium, as vanadium$^{\text{IV}}$ and vanadium$^{\text{V}}$, in dilute hydrochloric acid) were evaporated to less than 1 ml and then almost to dryness with successive additions of 5- and 2-ml portions of 12 M hydrochloric acid. The residual vanadium$^{\text{V}}$ was titrated amperometrically ("dead-stop" method) with 0·01 N ferrous sulphate in the presence of N sulphuric acid and 0·5 M orthophosphoric acid. The results are shown in Table II and are similar to those observed by Kelley and Conant.[6] In contrast, chromium$^{\text{VI}}$ is rapidly and completely reduced to chromium$^{\text{III}}$ under these conditions; after the evaporation of 50 g of chromium trioxide with an excess of hydrochloric acid, amperometric titration with a solution of ferrous iron showed that less than 0·0002 per cent. of the chromium$^{\text{VI}}$ remained.

TABLE II

VANADIUM$^{\text{V}}$ CONTENTS OF SOLUTIONS AFTER EVAPORATION WITH HYDROCHLORIC ACID

Sample No.	Description of sample	V^{5+} content, as percentage of total V
1	Initial solution	23·2
2	Solution treated as described in text	11·8
3	As for sample No. 2, but in presence of 400 mg of iron, as $FeCl_3.6H_2O$	3·9
4	As for sample No. 2, but evaporations with hydrochloric acid repeated	6·8
5	As for sample No. 4, but in presence of 0·5 ml each of sulphuric and orthophosphoric acids	1·2

Moreover, evaporation of vanadium$^{\text{IV}}$ with hydrochloric acid in the presence of large amounts of chromium$^{\text{III}}$ was sometimes found to produce small but variable amounts (0 to 2 per cent.) of vanadium$^{\text{V}}$. Parallel experiments in the absence of vanadium gave a negligible blank; the reason is unknown. It is clear that procedures relying on evaporation with hydrochloric acid to reduce vanadium$^{\text{V}}$ are unsatisfactory.

EXTRACTION OF PEROXYVANADIUM—

Attempts to decrease the extraction of vanadium$^{\text{V}}$ by complexation with hydrogen peroxide were unsuccessful. Hydrochloric acid solutions 0·2 N in hydrogen peroxide and containing, as chlorides, 1·5 mg of vanadium and 48 mg of ferric iron per ml were extracted with equal volumes of di-isopropyl ether at 20° to 25° C for 3 minutes. The vanadium in the organic layer was back-extracted into water and determined absorptiometrically as the peroxy complex in the presence of orthophosphoric acid to decolorise ferric iron. The results were—

Initial concentration of hydrochloric acid, M	6·0	7·0	7·5	8·0	9·0
Vanadium extracted (iron present), %	0·2	0·45	—	2·5	6·5
Vanadium extracted (iron absent), %	0·02	0·08	0·11	0·17	0·24

REDUCTION OF VANADIUM^{V} WITH SULPHUR DIOXIDE—

It was observed that vanadium^{V} in 8 to 8·5 M hydrochloric acid could be reduced in the cold to vanadium^{IV} by sulphur dioxide. Tests were made at 24° C in the absence of iron and chromium and with an excess of sulphur dioxide (the normality of the sulphur dioxide was always greater than ten times that of the vanadium). Under such conditions, the kinetics of the reaction can be represented approximately by the equation—

$$\mathrm{Log}_{10}[V^{5+}]_t - \log_{10}[V^{5+}]_0 = -0{\cdot}38[SO_2].t$$

where t is the time in minutes and the quantities in brackets are the normalities of the species indicated at the times shown by the subscripts; the normality of the sulphur dioxide was assumed to be constant throughout. A rise in temperature of 10° C increased the value of the velocity constant by a factor of approximately 1·8.

The equation indicates that reduction of vanadium^{V} by sulphur dioxide is not rapid and requires a high concentration of sulphur dioxide if the reaction is to reach adequate completion in a reasonable time. For example, an initial concentration of vanadium of 0·1 N is reduced 1000-fold by 2 N sulphur dioxide in 4 minutes; the latter concentration corresponds approximately to that in the proposed procedure.

In 8 M hydrochloric acid, the reduction of ferric iron by sulphur dioxide is negligible, as shown by the results in Table III. Trial experiments showed that the presence of sulphur dioxide prevented the extraction of vanadium, and this approach was adopted.

TABLE III

REDUCTION OF FERRIC IRON BY SULPHUR DIOXIDE

	Ferric iron extracted by di-isopropyl ether—			
Ferric iron initially present, mg per ml	in absence of sulphur dioxide (A), %	after aqueous solution made 2·3 N in sulphur dioxide and set aside at 20° C for 12 hours (B), %	Ferric iron reduced by sulphur dioxide (A − B), %	Sulphur dioxide extracted, %
Nil	—	—	—	42
43	99·95	99·92	0·03	—
54	99·95	99·93	0·02	65

METHOD

REAGENTS—

Hydrochloric acid - sulphur dioxide reagent solution—Saturate 10 to 11 M hydrochloric acid with sulphur dioxide. An increase in volume occurs, which, for 10 M hydrochloric acid, reduces this concentration to 9·3 M. The concentration of sulphur dioxide at this stage is about 3 N. When this solution is added to iron and chromium as chlorides, further dilution occurs and the final concentration of hydrochloric acid is about 8·0 M. The final concentration of sulphur dioxide is always somewhat lower than that expected (2·6 N) because some loss by evaporation is unavoidable.

Di-isopropyl ether.

PROCEDURE—

Evaporate the sample containing iron, chromium and vanadium with hydrochloric acid until a scum just forms; do not overheat or subsequent solution will be slow. Dissolve the cold residue in hydrochloric acid - sulphur dioxide reagent solution, allowing 10 ml (or proportionately more if the sample contains more than 65 per cent. of iron) for every 1 g of sample. Cover the vessel, set aside for 5 minutes, and then shake with an equal volume of di-isopropyl ether for about 30 seconds (no precautions to avoid formation of peroxides need be taken). When the layers have been separated, wash the organic layer two or three times with half its volume of 8 to 9 M hydrochloric acid, and add these washings to the main aqueous layer.

RESULTS

The proposed procedure was carried out on a mixture of 1·08 g of iron^{III} (as $FeCl_3.6H_2O$), 1·0 g of chromium^{VI} (as CrO_3) and 0·2 g of vanadium^{V} (in chloride solution). The amount of iron remaining in the aqueous layer and the amounts of vanadium and chromium extracted by the di-isopropyl ether were determined as described below.

DETERMINATION OF RESIDUAL IRON IN AQUEOUS LAYER—

After the layers had been separated, the aqueous layer was treated with hydrogen peroxide at the boiling-point to oxidise any ferrous iron formed. The cold solution was again extracted with di-isopropyl ether, the organic layer was separated and back-extracted with water, and the iron in this aqueous extract was determined absorptiometrically as thiocyanate. Three such determinations gave results equivalent to 0·02 per cent. of the iron being in the initial aqueous phase. Hence the maximum amount of iron that can be left in the total aqueous phase is 0·02 *plus* (3 × 0·02/2) per cent., *i.e.*, 0·05 per cent.

DETERMINATION OF VANADIUM AND CHROMIUM IN ORGANIC LAYER—

After the initial separation of the layers, the organic layer was back-extracted with successive 10-ml portions of 8·0 M hydrochloric acid; each extract was evaporated to fumes with sulphuric acid, the vanadium was determined absorptiometrically as its peroxy complex, and the chromium was determined absorptiometrically as chromium^{III}. For the latter determination the vanadium was omitted; the results, each of which is the mean of the number of determinations shown in parenthesis, were—

Extract No.	1	2	3
Percentage of total vanadium in extract	0·063 (4)	0·021 (6)	<0·01 (5)
Percentage of total chromium in extract	0·45 (6)	<0·01 (2)	<0·01 (1)

No difference in these results was observed when the time of standing with sulphur dioxide was increased to 25 minutes; reduction is therefore adequate. The concentration of vanadium and chromium in the organic layer after the first extraction is appreciable, although the above figures indicate that it is negligible after washing with hydrochloric acid as specified under "Procedure." This was confirmed for vanadium as follows. The organic layer, after separation and washing twice with 10-ml portions of 8·0 M hydrochloric acid, as specified above, was evaporated to dryness. The residue was dissolved in water, and the solution was evaporated to fumes with an excess of sulphuric acid. The residue was dissolved in water and the iron removed by mercury-cathode electrolysis. The residual solution was evaporated to small volume, the sulphuric acid partly neutralised with sodium hydroxide, and the vanadium determined absorptiometrically as the peroxy complex. In three such determinations, the vanadium found in the washed di-isopropyl ether layer never exceeded 0·01 per cent. of that initially present. No loss of vanadium was detected in any other stage of the procedure.

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Elimination of Phosphate Interference in EDTA Determinations of Calcium and Magnesium in Plant Ash

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Precipitation of calcium and magnesium from ammoniacal solutions by phosphate can be suppressed with ammonium molybdate, so permitting interference from phosphate to be prevented in the determinations of calcium and magnesium with ethylenediaminetetra-acetic acid. The use of ammonium molybdate with sodium tungstate to separate calcium also permits direct determination with ethylenediaminetetra-acetic acid of magnesium in mixtures of calcium, magnesium and phosphate. Because this has a useful application to the analysis of plant ash, a rapid procedure for determining calcium and magnesium in the leaf ash of *Hevea brasiliensis* has been devised and found to compare favourably with independent methods. The precision of the proposed procedure is 0·76 per cent. for magnesium and 0·41 per cent. for calcium, and the accuracy for both elements is to within about 1 per cent.

Chemical analysis of plant ash in order to assess mineral-nutrient requirements is now well established practice. For tree crops, the leaf samples usually taken[1] always contain appreciable amounts of phosphate, which has been found to interfere in determinations of calcium and magnesium with ethylenediaminetetra-acetic acid (EDTA).[2] To prevent such interference, previous workers have either removed phosphate (by precipitation[3] or with ion-exchange resins[4]) or used dilute solutions for the EDTA titration, often with photometric determination of the end-point.[5] A rapid and simpler approach is described in this paper; it is based on masking the phosphate ion as the soluble molybdophosphate complex. Further, a procedure is described for determining calcium and magnesium in plant ash, magnesium being determined directly and calcium by difference. This is an improvement on existing procedures,[3,6] in which calcium is determined directly and magnesium by difference, because magnesium is normally present in much smaller amounts than is calcium; moreover, when the results are used to diagnose plant-nutrient requirements, magnesium is usually the more important element.[7]

Experimental

Precipitates of ammonium calcium phosphate and ammonium magnesium phosphate are formed when weakly acidic solutions of plant ash are made alkaline with ammonia before titration with EDTA. The cloudiness produced interferes visually with the estimation of the end-point, which is drawn-out and also premature,[2] because of the slow interaction between EDTA and the insoluble phosphates. Precipitation of calcium and magnesium from ammoniacal solutions containing phosphate is suppressed by adding ammonium molybdate. This is shown in Fig. 1, in which the amounts of ammonium molybdate solution needed to prevent precipitation (experimentally determined by a repeated process of trial and error) can be seen to be proportional to the concentrations of phosphate and of calcium *plus* magnesium in solution. The points plotted in Fig. 1 represent the minimum amounts of 20 per cent. w/v ammonium molybdate solution needed to prevent precipitation of calcium and magnesium phosphates for at least 1 hour after the addition of 20 ml of an ammonia - ammonium chloride buffer solution to 50-ml portions of solutions containing calcium, magnesium and phosphate. Curve B corresponds to the normal amounts of these constituents found in the leaf ash of *Hevea brasiliensis* and curve A to the maximum amounts likely to be found.

Solutions stabilised in this manner eventually produce precipitates, usually after about 1 hour, and when they are heated, calcium molybdate is partly deposited. More complete precipitation of calcium under such conditions is attained by using sodium tungstate, as suggested by Shapiro and Brannock.[8] The efficiency of molybdate and tungstate as precipitants of calcium from ammoniacal solutions containing calcium, magnesium and phosphate ions can be determined by titrating with standard EDTA solution the cations remaining after the precipitated calcium has been separated by filtration. When 100-ml portions of

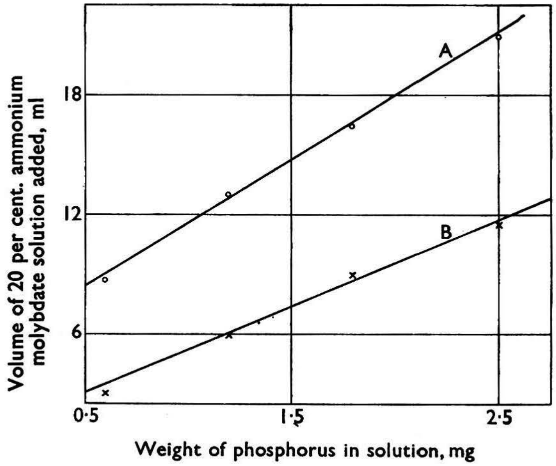

Fig. 1. Suppression by ammonium molybdate of precipitation of calcium and magnesium from ammoniacal solution by phosphate: curve A, solution containing 0·15 mg of calcium and 0·05 mg of magnesium per ml; curve B, solution containing 0·075 mg of calcium and 0·025 mg of magnesium per ml

hot ammoniacal solutions containing 7·5 mg of calcium, 2·5 mg of magnesium and 5 mg of phosphorus were treated with aqueous 20 per cent. w/v solutions of (*a*) ammonium molybdate and (*b*) sodium tungstate, the results were—

Volume of precipitant added, ml	10	20	30	40
Calcium precipitated by molybdate, %	75·9	85·7	94·4	95·0
Calcium precipitated by tungstate, %	113·0	119·9	110·3	106·1

Greater efficiency in precipitating calcium only can be attained by using ammonium molybdate and sodium tungstate together; results of experiments similar to those described above, but in which molybdate - tungstate mixtures were used as precipitant are shown in Table I and confirm this. The results above and in Table I were obtained from standard solutions of calcium chloride, magnesium sulphate and diammonium hydrogen orthophosphate, which were mixed to correspond to the average amounts of calcium and magnesium and the maximum amount of phosphorus found in leaf samples from rubber trees. The way in which these results can be used to frame a satisfactory procedure for determining calcium and magnesium is discussed later. The procedure described below was developed specifically for the analysis of leaf samples from *Hevea brasiliensis*, but should be applicable to other leaf samples of broadly similar composition.

TABLE I

PRECIPITATION OF CALCIUM BY MIXTURES OF MOLYBDATE AND TUNGSTATE

Composition of precipitant		
Ammonium molybdate solution, 20 per cent. w/v, ml	Sodium tungstate solution, 20 per cent. w/v, ml	Calcium precipitated, %
5	10	82·5
10	10	84·1
10	20	97·6
20	10	96·8
20	15	100·8
20	20	100·8
30	1	100·0
30	3	100·0
30	5	100·4
30	10	100·4
30	15	100·0
30	20	99·7
40	10	100·0

Method

Reagents—

All solutions should be prepared from analytical-reagent grade chemicals and distilled water.

Ammonium molybdate solution, 20 per cent. w/v.

Ammonium chloride - ammonium hydroxide solution—Dissolve 66 g of ammonium chloride and 600 ml of ammonia solution, sp.gr. 0·880, in 2·5 litres of water.

Hydroxylamine solution, 3 per cent. w/v.

Potassium cyanide solution, 2 per cent. w/v.

Eriochrome black T - potassium chloride mixture—Mix 0·2 g of Eriochrome black T with 50 g of potassium chloride until the indicator is evenly distributed.

EDTA solution, 0·01 M—Prepare from disodium ethylenediaminetetra-acetate dihydrate, and standardise against a solution of magnesium sulphate heptahydrate.

Sodium tungstate solution, 20 per cent. w/v—Prepare from the hydrated salt.

~~*Ammonia solution, 50 per cent. w/v.*~~ Ammonia solution, sp. gr. 0·880, dilute (1+1)

Procedure—

Titration of calcium plus magnesium—To a 25-ml aliquot containing about 4 mg of calcium and about 1·5 mg of magnesium add 20 ml of ammonium molybdate solution, mix thoroughly, and add 50 ml of ammonium chloride - ammonium hydroxide solution, 1 ml of hydroxylamine solution, 2 ml of potassium cyanide solution and 0·2 g of Eriochrome black T - potassium chloride mixture. Swirl thoroughly, and titrate with 0·01 M EDTA to the usual red to blue end-point.

Titration of magnesium—To a 50-ml aliquot of sample solution, *i.e.*, twice as much calcium and magnesium as in the previous titration, add 30 ml of ammonium molybdate solution and 10 ml of sodium tungstate solution. Swirl thoroughly, add 10 ml of 50 per cent. ammonia solution, and heat for 30 minutes at 80° to 90° C to precipitate calcium completely. Filter the solution immediately through a Whatman No. 2 filter-paper, and carefully wash the precipitate four times with 2 per cent. ammonia solution. Add the washings to the filtrate, then add 15 ml of 50 per cent. ammonia solution, 1 ml of hydroxylamine solution, 2 ml of potassium cyanide solution and 0·2 g of Eriochrome black T - potassium chloride mixture, and titrate as before with 0·01 M EDTA.

The second titre is a direct measure of the magnesium present in a 50-ml aliquot of the sample solution; the amount of calcium present is obtained from the difference between the second and twice the first titre.

Discussion of results

The curves in Fig. 1 show the conditions under which precipitation of calcium and magnesium from ammoniacal solutions containing phosphate may be prevented by adding ammonium molybdate to form a soluble molybdophosphate complex. In titrations with EDTA, interference from phosphate can be prevented in this way, but the amount of molybdate needed depends on the concentrations of calcium, magnesium and phosphate in solution. For example, when the proposed procedure is used, 20 ml of the ammonium molybdate solution may be interpolated from Fig. 1 as the amount needed for the maximum concentrations of calcium, magnesium and phosphate likely to be present in ash from the leaves of *Hevea brasiliensis.*

The ammonium molybdate solution, together with the ammonium chloride - ammonium hydroxide solution, buffers the solutions, which are titrated at a pH of about 9·5; this is lower than the value recommended by Schwarzenbach,[2] but has nevertheless been found to give satisfactory end-points. The recommended pH of 10 cannot be used, as, above pH 9·7, excessively large amounts of ammonium molybdate are needed to prevent precipitation of calcium phosphate.

Direct determination of magnesium—

The direct determination of magnesium in mixtures of calcium and magnesium depends on an initial quantitative removal of calcium. This is made difficult by the presence of phosphate, which forms precipitates with both calcium and magnesium in alkaline solutions. Precipitation of calcium as its oxalate from acid solution has been suggested, but the large excess of oxalate ion needed to avoid simultaneous precipitation of magnesium[9] interferes in the subsequent titration of magnesium with EDTA.[2] Ammonium molybdate will precipitate calcium from hot ammoniacal solutions; the results on p. 112 show that, in the presence of phosphate, precipitation is incomplete (between 75 and 95 per cent., depending on the amount of molybdate used). Cheng and Bray[6] used sodium tungstate to precipitate calcium from ammoniacal solutions in an EDTA procedure adapted for soil extracts. In the presence of appreciable amounts of phosphate, however, magnesium is also precipitated as its phosphate, and the results on p. 112 show that magnesium equivalent to more than 10 per cent. of the calcium present may be lost in this way from solutions containing phosphate.

The results in Table I show that suitable mixtures of ammonium molybdate and sodium tungstate solutions will effectively precipitate calcium from hot ammoniacal solutions also containing magnesium and phosphate. Calcium tungstate is deposited, but the large excess of molybdate forms a complex ion with phosphate and prevents simultaneous precipitation of magnesium phosphate. Extrapolation from curve B in Fig. 1 suggests that, for the titration of magnesium only by the proposed procedure in an aliquot containing 7·5 mg of calcium, 2·5 mg of magnesium and 5 mg of phosphorus, about 25 ml of 20 per cent. ammonium molybdate solution should be needed to prevent interference from phosphate. This is confirmed by the figures in Table I, which indicate that a mixture of 30 ml of the ammonium molybdate solution and 1 ml of the sodium tungstate solution is adequate to precipitate calcium without loss of magnesium from hot solutions. The precipitation of calcium by so small an amount of tungstate is slow, and in practice the excess provided by 10 ml of the sodium tungstate solution was found to be most suitable for leaf samples.

CATIONIC INTERFERENCE—

Cheng and Kurtz[10] have suggested the use of mixtures of potassium cyanide, triethanolamine and potassium ferrocyanide to prevent interference from heavy metals, iron, aluminium and manganese in EDTA titrations of magnesium and calcium in soil extracts. These metals are present in smaller amounts in leaf samples of *Hevea brasiliensis*, and it was found in practice that the slight interference from them could be overcome by using potassium cyanide only; this reagent has therefore been included in the proposed procedure.

COMPARISON WITH OTHER METHODS

A comparison was made between the proposed procedure and two standard methods used in these laboratories for routine analyses of leaf samples; these methods were Hunter's Titan yellow method for magnesium[11] and a flame-photometric method for calcium, which was applied after calcium had been precipitated as its oxalate in order to avoid interference from phosphate.[12] Solutions in dilute nitric acid of two dry ashes from each of five samples of leaves were analysed in duplicate by the three methods, and the results (see Table II) were expressed as percentages of oven-dry material.

TABLE II

CALCIUM AND MAGNESIUM FOUND IN LEAF SAMPLES FROM *Hevea brasiliensis*

Results are expressed as percentages of oven-dry material

		Magnesium found by—		Calcium found by—	
Leaf sample	Ash No.	proposed method, %	Titan yellow method, %	proposed method, %	flame-photometric method, %
A	1	0·279, 0·280	0·283, 0·283	0·472, 0·466	0·460, 0·463
	2	0·274, 0·276	0·289, 0·286	0·481, 0·479	0·470, 0·470
B	3	0·195, 0·191	0·187, 0·196	1·246, 1·250	1·275, 1·267
	4	0·190, 0·191	0·190, 0·196	1·256, 1·250	1·267, 1·267
C	5	0·193, 0·195	0·188, 0·188	0·769, 0·761	0·752, 0·755
	6	0·193, 0·195	0·188, 0·184	0·765, 0·757	0·758, 0·755
D	7	0·195, 0·198	0·188, 0·188	0·757, 0·757	0·765, 0·769
	8	0·198, 0·198	0·188, 0·188	0·757, 0·753	0·769, 0·765
E	9	0·201, 0·203	0·198, 0·198	1·428, 1·422	1.430, 1·447
	10	0·201, 0·204	0·201, 0·196	1·428, 1·424	1·438, 1·438
Mean ..	.. ..	0·212	0·210	0·934	0·939
Standard error..	..	±0·002	±0·002	±0·004	±0·004

A statistical examination of these results is summarised in Table III, from which the standard error of a single determination of magnesium by the proposed method can be calculated as ±0·00161 (coefficient of variation 0·76 per cent.); the corresponding values for the Titan yellow method are ±0·00289 and 1·37 per cent. For a single determination of calcium by the proposed method, the standard error is ±0·00380 (coefficient of variation 0·41 per cent.), and for the flame-photometric method the corresponding figures are ±0·00454 and 0·48 per cent. All these values are based on the variations between duplicate determinations on a given ash; differences in precision between the proposed and the other two methods are therefore not established, although a lower precision for the Titan yellow method is indicated at the 10 per cent. level of significance.

TABLE III

ANALYSIS OF VARIANCE OF RESULTS IN TABLE II

Source of variation	Degrees of freedom	Mean square × 10^8	
		Magnesium	Calcium
Methods	1	5523 (N.S.)	26,010 (N.S.)
Samples	4	1,233,798***	125,904,766***
Samples × methods	4	9360***	31,816***
Ashes within samples	5	83 (N.S.)	3865 (N.S.)
Ashes × methods within samples	5	1033 (N.S.)	1425 (N.S.)
Duplicates { proposed method	10 } 20	260 } 548	1440 } 1750
Duplicates { standard method	10	835	2060

*** Significant at the 0·1 per cent. level. N.S. = Not significant.

The analysis of the results also shows no significant difference between ashes on the same sample, whereas a highly significant interaction is shown between samples and methods. As a result, no significant differences between the means for the methods (see Table II) are established; this is because the standard errors for these means must be derived from the interaction mean square. These points can be confirmed by inspection of Table II, *e.g.*, it is evident that, for samples A and B, the Titan yellow method gave larger average values than did the proposed method, although for samples C, D and E the position was reversed.

ACCURACY—

The fact that the proposed method is sufficiently accurate for practical purposes is indicated by the good agreement with other methods. However, an independent check was made on prepared solutions containing calcium, magnesium and phosphate in combinations corresponding to the high and low amounts found in plant ash. The results are shown in Table IV, from which it can be seen that, on average, the recovery of magnesium is 1 per cent. low and that of calcium 1 per cent. high; the fact that the calcium figure depends upon the magnesium determination may explain this relationship. In general, the errors in recovery are acceptable since they are well within the error associated with preparing leaves for analysis.[13]

TABLE IV

RECOVERY OF CALCIUM AND MAGNESIUM FROM PREPARED SOLUTIONS BY PROPOSED METHOD

Composition of corresponding plant material			Recovery	
Calcium, %	Magnesium, %	Phosphorus, %	Magnesium, %	Calcium, %
1·0	0·5	0·4	98·2	101·7
1·0	0·5	0·1	98·6	101·3
0·3	0·5	0·4	99·6	102·9
0·3	0·5	0·1	99·7	102·4
1·0	0·1	0·4	99·5	99·9
1·0	0·1	0·1	99·1	99·7
0·3	0·1	0·4	99·1	100·9
0·3	0·1	0·1	99·1	100·9
		Average	99·1	101·2

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An Evaluation of the Formate Method for the Simultaneous Polarographic Determination of Copper and Lead in Steel

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The precise application of the well known formate method for the simultaneous polarographic determination of copper and lead in steel has been defined; a linear-sweep cathode-ray polarograph was used. Copper can be determined with a standard deviation of 0·006 per cent. at the 0·1 per cent. level in samples containing not more than 0·2 per cent. of molybdenum. By taking a smaller weight of sample the method can be extended to samples containing up to 2 per cent. of molybdenum, with some consequent loss in precision. By a slightly modified method, copper can be determined in pure iron down to a lower limit of 0·0001 per cent. after most of the iron has been separated by solvent extraction. Tin, arsenic, titanium and molybdenum are reduced at peak potentials coincident with the lead reduction, and the procedure is therefore suitable for determining lead in samples containing only residual amounts of tin, arsenic and titanium; interference from molybdenum is not serious, provided that the molybdenum content is not much in excess of the lead content. The method is particularly useful for the analysis of lead-bearing steels containing more than 0·05 per cent. of lead, and a standard deviation of 0·008 per cent. is claimed. The method has been applied to some thirty analysed samples ranging from high-purity iron to stainless steel, and confirmatory results are reported.

ONE of the few polarographic methods successfully used in the iron and steel industry is that for the simultaneous determination of copper and lead in a dilute hydrochloric acid solution buffered at pH 2 to 3 with sodium formate. Nickelson[1] first proposed the use of a formate solution for determining iron, copper, lead and zinc in aluminium alloys, and this was later applied to the determination of lead and copper in steel by incorporating reduction with hydrazine hydrochloride.[2,3] Westwood and Presser[4] also used this method for determining 0·004 to 0·03 per cent. of lead in nodular cast iron after removal of graphite by filtration; more recently, Ota[5] slightly modified the procedure in order to determine lead in free-cutting steel. The remarkable resolution of the square-wave polarograph permits the simultaneous determination of copper and lead in dilute hydrochloric acid solution without preliminary reduction of iron.[6] Although a much improved instrument compared with conventional polarographs, the Southern Instruments' cathode-ray polarograph used in this work will not resolve the copper wave in the presence of a large excess of ferric iron, and it is therefore essential to maintain the iron in the reduced state.

The original formate method was considerably simplified (personal communication from Mr. D. R. Curry) at the Bragg Laboratory, Naval Ordnance Inspection Establishment, to avoid taking aliquots and the use of a water bath. The sample is dissolved in 10 ml of diluted hydrochloric acid (1 + 1), and the solution is oxidised with potassium chlorate and boiled to expel chlorine. Five-millilitre portions of hydrazine hydrochloride solution (20 per cent. w/v) and a saturated solution of sodium formate and a 2-ml portion of starch solution (0·5 per cent. w/v) are then added. After being heated to reduce the iron, the solution is diluted to 25 ml, and the polarographic waves are recorded. Iron is converted to the ferrous state, thereby eliminating the current at zero potential due to ferric ions. Ferrous ions are reduced at the mercury electrode at −1·4 volts against the saturated-calomel electrode, and other metals having half-wave potentials more positive than this, such as copper (−0·25 volt) and lead (−0·45 volt), can be determined without interference from iron. Cupric copper present in the solution is reduced to the cuprous state by the treatment with hydrazine.

As well as copper and lead, bismuth, molybdenum, antimony, titanium, tin and arsenic give polarographic waves in a formate base electrolyte in the region 0 to −0·6 volt. In two of the papers mentioned above, the effects of interfering elements on the measurement of the lead wave were examined. Westwood and Presser[4] stated that the method was not applicable to all types of pig iron, particularly if small amounts of copper were present; this caused a steep slope to the residual-current wave, which masked the lead step. For such samples, these workers separated lead from most of the iron and copper by solvent extraction. Ota[5] found that there was no interference from copper and molybdenum, provided that the concentrations of these elements did not exceed 0·4 and 0·1 per cent., respectively; he also stated that 0·1 per cent. of arsenic, 0·05 per cent. of tin and 2 per cent. of chromium did not interfere.

This paper describes an evaluation of the simplified method described in the personal communication referred to above; a linear-sweep cathode-ray polarograph was used. A study of interfering effects has been made, and the application of the method to the analysis of pure iron, mild steel and alloy steel has been considered.

DIRECT METHOD

I have made three modifications to the method described by Curry: (*a*) the volume of solvent acid has been increased to 12 ml to assist in the solution of alloy steel, (*b*) the final volume has been decreased to 20 ml to improve sensitivity and (*c*) the acid solution is evaporated to between 6 and 7 ml to achieve closer control over the acidity of the base electrolyte. With modification (*c*), the pH is between 2·4 and 2·8; at pH values above 3·0, basic iron salts are precipitated, with some consequent danger of loss of copper and lead by adsorption.

Well defined waves are produced for copper and lead, with peak potentials at −0·28 and −0·48 volt, respectively, against a mercury-pool anode. Calibration graphs are linear for both elements over the range examined (0·0005 to 0·30 per cent. in a 1-g sample).

For copper contents in the range 0·0005 to 0·005 per cent., the calibration points tend to be rather scattered about a straight line; poor reproducibility may therefore be expected. There is some degree of atmospheric oxidation if the reduced solution is set aside, and this results in the formation of ferric ions; this, in turn, gives rise to a standing current at zero potential, which cannot be fully backed-off, and it becomes difficult to measure the peak height. It is possible to minimise this effect somewhat by starting the potential sweep at the most negative value possible, but, in practice, concentrations of copper less than about 0·005 per cent. cannot be determined with any degree of precision in the presence of 1 g of iron.

During work on interfering elements, a sharply defined peak was observed at −0·16 to −0·20 volt when the instrument was used at high sensitivities. The occurrence of the wave is erratic and its peak height varies considerably; it has every appearance of a typical cathode-ray polarograph maximum wave, but it does not respond to the usual maximum suppressors, such as gelatin, starch, peptone and surface-active agents. The addition of starch to the base electrolyte, as recommended in the original method, has no effect on the wave, but the presence of starch serves to improve the definition of the copper wave and for this reason it is retained. Interference from this spurious wave is only noticeable at extremely low levels of copper content, and, in practice, it is possible accurately to measure peak heights down to the lower limit (0·005 per cent. of copper).

The preceding reduction of bivalent copper at —0·28 volt interferes with the determination of lead, so causing low results. The degree of interference varies considerably as a function of start potential and can be minimised, but not entirely overcome, by using the manufacturer's recommended technique[7] for measuring multiple waves. After measuring the copper wave, the start potential is re-set to bring the beginning of the lead wave on the zero point of the graticule on the oscilloscope screen, thus providing an almost horizontal base line for measuring the lead wave. This feature is demonstrated by the results in Table I, which show the effect of variation in start potential on peak current for solutions containing lead and lead *plus* copper. To minimise interference from copper, therefore, it is essential to start the potential sweep at the most negative value possible, and a value of —0·34 volt was selected for calibration. Ideally, all test solutions should be measured with this same start potential, but, if the wave has a sloping base line (owing to the presence of molybdenum), it may be necessary to start the sweep at a slightly more positive value; in practice, small variations (0·01 to 0·02 volt) have little effect on measurements of peak current.

TABLE I

EFFECT OF VARIATION IN START POTENTIAL ON INTERFERENCE FROM COPPER

Sample	Peak current with start potential of—			
	—0·25 volt, μA	—0·30 volt, μA	—0·32 volt, μA	—0·34 volt, μA
Matthey iron + 0·2 per cent. of lead	9·75	9·70	9·55	9·60
Matthey iron + 0·2 per cent. each of lead and copper	9·25	9·45	9·60	9·65

This method of overcoming interference from copper is completely effective only when the copper content does not exceed the lead content. If the copper-to-lead ratio is 3 to 1, results for lead will be about 4 per cent. low. At higher ratios, the degree of interference is approximately proportional, and with a copper-to-lead ratio of 10 to 1, results for lead at the 0·05 per cent. level will be about 15 per cent. low.

REAGENTS—

All reagents should be of the highest grade of purity obtainable.

Hydrochloric acid, diluted (1 + 1).

Starch solution, 0·5 per cent. w/v—Mix 0·5 g of soluble starch with 5 ml of water, and pour into 80 ml of boiling water. Boil gently for 5 minutes, cool, and dilute to 100 ml.

Standard copper solution A—Dissolve exactly 0·25 g of high-purity copper in a little nitric acid, evaporate to dryness, and dissolve the residue in 10 ml of hydrochloric acid. Cool, and dilute with water to 500 ml in a calibrated flask.

1 ml ≡ 0·5 mg of copper.

Standard copper solution B—Dilute 25 ml of standard copper solution A to 500 ml in a calibrated flask.

1 ml ≡ 25 μg of copper.

Standard lead solution[4]—Dissolve exactly 0·25 g of high-purity lead-metal grain in about 50 ml of diluted hydrochloric acid (1 + 1), adding potassium chlorate from time to time until solution is complete. Cool, add 50 ml of hydrochloric acid, and dilute to 500 ml in a calibrated flask.

1 ml ≡ 0·5 mg of lead.

PROCEDURE—

Transfer 1 g of sample to a 50-ml conical flask, add 12 ml of diluted hydrochloric acid (1 + 1), and heat gently until solution is complete. For samples containing more than 0·30 per cent. of copper and/or lead, take a smaller weight of sample, and add sufficient pure iron to give a total weight of 1 g. For the determination of copper in samples containing between 0·20 and 2·0 per cent. of molybdenum, take a smaller weight of sample, and dilute with pure iron to give a total weight of 1 g, such that the molybdenum content of the diluted sample does not exceed 2 mg.

Oxidise the solution by dropwise addition of a saturated solution of potassium chlorate to decompose carbides. Rinse the walls of the flask with a little water to dissolve any dried potassium chlorate, and concentrate the solution to between 6 and 7 ml by gentle boiling on a hot-plate. Remove the flask from the hot-plate, and add to the solution, from 10-ml dropping pipettes, 5 ml of a 20 per cent. w/v solution of hydrazine hydrochloride, 5 ml of a saturated solution of sodium formate and 2 ml of starch solution. Heat the solution on the hot-plate at about 90° C, with occasional swirling, until the iron appears to be completely reduced, and continue to heat for a further 10 minutes; do not allow the solution to boil. Cool, and dilute to 20 ml in a calibrated flask.

Transfer 2 to 3 ml of the solution to the cell of a cathode-ray polarograph (Southern Instruments Ltd.), remove oxygen by passing oxygen-free nitrogen for 5 to 10 minutes, and measure the peak heights of the waves for copper and lead. Suitable start potentials are —0·05 volt for copper contents in the range 0·025 to 0·25 per cent., —0·08 volt for copper contents in the range 0·005 to 0·025 per cent. and —0·34 volt for lead contents in the range 0·05 to 0·30 per cent.

With each batch of samples examine a reagent blank solution and a standard steel as a check on the calibration graphs. The standard lead steel should have a low content of copper. Express results in the range 0·005 to 0·05 per cent. to the nearest 0·0005 per cent., in the range 0·05 to 0·15 per cent to the nearest 0·002 per cent and in the range 0·15 to 0·30 per cent. to the nearest 0·005 per cent.

CALIBRATION—

For copper, prepare solutions each containing 1 g of copper-free iron dissolved in dilute hydrochloric acid. Oxidise these solutions, add to each amounts of standard copper solution suitable for the construction of calibration graphs to cover the ranges 0·005 to 0·05 per cent. and 0·05 to 0·30 per cent. of copper, and continue as described under "Procedure."

For lead, prepare a separate calibration graph to cover the range 0·05 to 0·30 per cent.; use lead-free iron as starting material.

INTERFERING ELEMENTS—

Bismuth—The sharply peaked wave for bismuth at —0·16 volt does not interfere with measurement of the copper wave, provided that the ratio of bismuth to copper does not exceed 2 to 1. Bismuth has not been detected in any of the irons and steels so far analysed by this method. Rooney,[8] however, has noted the presence of up to 0·0007 per cent. of bismuth in certain mild steels.

Molybdenum—Molybdenum gives a triple wave that constitutes the most serious source of interference in the determination of both copper and lead. In the absence of copper, 0·2 per cent. of molybdenum gives small waves at —0·28 and —0·47 volt; if copper is present, the first wave is masked by the coincident reduction of copper. If the concentration of molybdenum is increased to between 0·4 and 0·5 per cent., the first wave moves to a more negative potential (—0·34 volt) and a third wave appears at —0·15 volt. The peak potentials and peak currents of these waves are not reproducible; the peak potentials may vary within ±0·02 volt of the stated values. The tolerance level for molybdenum in the determination of copper is 0·20 per cent.; above this level, the molybdenum waves at —0·15 and —0·34 volt distort the copper wave, so producing low results. The effect of interference from molybdenum can be overcome by using a smaller weight of sample diluted with copper-free iron to an extent such that the weight of molybdenum in the diluted sample does not exceed 2 mg. Provided that decreased sensitivity and precision are acceptable, copper can be determined down to a lower limit of 0·05 per cent. in 100-mg samples of alloy steels containing up to 2 per cent. of molybdenum.

Interference from molybdenum in the determination of lead is more serious and is largely dependent on the ratio of the two elements. There is little or no interference when the molybdenum-to-lead ratio is 1 to 2, but when the ratio is increased to 1 to 1 results for lead are about 9 per cent. high. At higher ratios, a sloping base line and distortion of the lead wave make precise measurement difficult. However, interference from molybdenum can be overcome by double extraction with isobutyl acetate from a solution of the sample in aqua regia. Separation of molybdenum is not complete, but the content is sufficiently decreased to permit accurate measurement of the waves for copper and lead.

Antimony—Tervalent antimony gives a rather drawn-out wave with a rounded peak at −0·45 volt; this wave coincides with the lead wave and tends to merge with the copper wave when the antimony-to-copper ratio is about 1 to 1. Antimony has not been detected in any of the samples of steel so far analysed by this method, but past experience has shown that certain types of unrefined Swedish iron contain up to 0·02 to 0·03 per cent. of antimony. It is therefore necessary to separate antimony before determining copper in pure iron.

Titanium—The reduction of quadrivalent titanium to the tervalent state at −0·50 volt is comparatively insensitive. A concentration of 0·1 per cent. of the element gives a peak current equivalent to that for about 0·004 per cent. of lead, and at higher concentrations the degree of interference is difficult to measure, owing to partial hydrolysis of titanium. Provided that the titanium content does not exceed 0·1 per cent., there is no significant interference with the determination of 0·05 per cent. or more of lead.

Tin—Bivalent tin is reduced at −0·50 volt, but quadrivalent tin is not reduced in electrolytes containing formate. It should therefore be possible to remove interference from tin by oxidation to the higher valency with potassium chlorate. Unfortunately, there is some degree of reduction if the tin content is much above 0·05 per cent., and this results in enhancement of the coincident lead wave. There is, however, no interference from 0·05 per cent. of tin in the determination of lead at the 0·05 per cent. level; 0·05 per cent. is therefore the maximum tolerance for tin.

Arsenic—Tervalent arsenic is reduced at −0·50 volt, but the reaction is not highly sensitive and 0·05 per cent. of arsenic gives a peak current equivalent to that for about 0·005 per cent. of lead. Interference is not significant in the determination of above 0·05 per cent. of lead, provided that the level of soluble arsenic in the sample does not exceed 0·05 per cent.

EXTRACTION METHOD

At lower levels of copper content, the accuracy of the polarographic method can be improved if most of the iron is removed by extraction with isobutyl acetate.[9] Sensitivity is limited, however, by interference from the spurious wave mentioned earlier, which was eventually traced to an unidentified impurity in the sodium formate. Attention was given to alternative buffering agents, and it was found that the use of AnalaR sodium acetate was more satisfactory and caused no interfering waves. Solutions buffered with sodium acetate, however, are not suitable for the direct determination of copper and lead; the reduction of ferric iron by hydrazine is only partly complete, and some difficulties are experienced in the determination of lead in base electrolytes containing sodium acetate.

TABLE II

RECOVERY OF COPPER IN PRESENCE OF ANTIMONY AFTER SOLVENT EXTRACTION

The aliquot of solution used was equivalent to 2 g of sample

Sample	Copper found, %
AH iron	0·0016, 0·0014
AH iron + 0·05 per cent. of antimony	0·0016
AH iron + 0·10 per cent. of antimony	0·0015
Matthey iron	<0·0001
Matthey iron + 0·00025 per cent. of copper	0·0003, 0·0003
Matthey iron + 0·0025 per cent. of copper	0·0026, 0·0028
Matthey iron + 0·025 per cent. of copper	0·0248, 0·0256

After solvent extraction from an aqua regia solution the aqueous layer is heated to fumes with perchloric acid to remove organic matter, and the residue is dissolved in water. An aliquot of this solution is buffered at about pH 4 by adding sodium acetate solution. Hydrazine is added as before, and the solution is heated to reduce residual iron. Aliquots of the solution may also be used for determining other elements, such as nickel and cobalt,[10] which can conveniently be determined polarographically. Calibration graphs are linear over the range examined (0·0001 to 0·001 per cent. and 0·001 to 0·025 per cent. of copper in aliquots equivalent to 2 g of sample). In a base electrolyte containing sodium acetate the peak potential is −0·26 volt.

Solvent extraction removes antimony and so provides an effective means of overcoming interference from this element when present in pure iron. In a series of recovery experiments, different amounts of copper were added to 5-g samples of Matthey iron, and antimony was added to a sample of vacuum-melted pure iron known to contain 0·0015 per cent. of copper. The results are shown in Table II and indicate that recovery of copper was good at all levels. There was no wave for antimony, and the results for the AH iron confirm that removal of antimony was complete.

TABLE III

RESULTS FOR COPPER BY THE PROPOSED METHODS

Sample	B.C.S. No.	B.C.S. certificate value for copper, %	Direct method		Extraction method	
			No. of tests	Mean copper content, %	No. of tests	Mean copper content, %
Pure iron ..	149	<0·002	–	—	2	0·0005
	149/1	<0·001	–	—	4	0·0005
	260/1	0·005	2	0·0070	4	0·0045
AH iron ..	—	—	–	—	8	0·0016
Mild steel ..	271	0·010*	8	0·0065	2	0·0074
	272	0·015*	8	0·0130	2	0·0134
	273	0·160*	2	0·165	–	—
	274	0·040*	8	0·0385	–	—
	275	0·205*	2	0·210	–	—
	276	0·125*	2	0·130	–	—
	277	0·100*	8	0·098	–	—
Cast steel ..	230	0·085	2	0·084	–	—
Carbon steel ..	239/2	0·18	4	0·180	–	—
Magnet alloy ..	233	5·09	4	5·00†	–	—
	266	3·33	4	3·45†	–	—
Stainless steel..	235	~0·06	2	0·092	–	—

* Value quoted to the nearest 0·005 per cent.

† Decreased weight of sample used; result expressed to nearest 0·05 per cent.

Separation of elements interfering with the determination of lead is only partly complete; modifications incorporating solvent extraction are therefore not suitable for the determination of trace amounts of lead present in pure iron.

PROCEDURE—

Transfer 5 g of sample to a dry squat 600-ml beaker, and slowly add a mixture of 100 ml of hydrochloric acid, sp.gr. 1·18, and 15 ml of nitric acid, sp.gr. 1·42. Allow the sample to dissolve, without heating, cool the solution rapidly in a stream of running water, and transfer to a 500-ml separating funnel. Rinse the beaker with isobutyl acetate, add the rinsings to the contents of the separating funnel, and then add sufficient isobutyl acetate to give a total of 150 ml of solvent. Shake for 30 to 40 seconds, and allow the layers to separate; the extraction must be carried out under a fume hood.

Run the aqueous layer into the original beaker, add 10 ml of nitric acid, sp.gr. 1·42, and 5 ml of dilute perchloric acid (3 + 7), and evaporate to about 5 ml. Transfer the solution to a 50-ml conical flask, cover with a clock-glass, and continue evaporation to incipient fuming. Cool somewhat, rinse the walls of the flask with water, and again evaporate to incipient fuming. Extract the residue with water, cool, and dilute to 25 ml in a calibrated flask.

Transfer a 10-ml portion of the solution to a 50-ml conical flask, and add, from dropping pipettes, 1·0 ml of hydrochloric acid, sp.gr. 1·18, 2 ml of a 20 per cent. w/v solution of hydrazine hydrochloride, 5 ml of a saturated solution of sodium acetate and 1 ml of starch solution. Heat the solution to reduce the iron as before, dilute, and measure the polarographic wave for copper. Suitable start potentials are —0·03 volt for samples containing 0·001 to 0·025 per cent. of copper and —0·08 volt for samples containing less than 0·001 per cent.

Examine a reagent blank solution and a standard steel with each batch of samples. Express results in the range 0·0001 to 0·001 per cent. to the nearest 0·0001 per cent. and in the range 0·001 to 0·025 per cent. to the nearest 0·0002 per cent.

CALIBRATION—

Prepare solutions each containing 50 mg of copper-free iron dissolved in hydrochloric acid. (This assumes that extraction of iron from a 5-g sample is 99 per cent. complete.)

Oxidise the solutions with nitric acid, and add suitable amounts of standard copper solution for the construction of calibration graphs to cover the ranges 0·0001 to 0·001 per cent. and 0·001 to 0·025 per cent. To each solution add 5 ml of dilute perchloric acid (3 + 7), evaporate to fuming, dilute to 25 ml, and take a 10-ml aliquot as described above.

APPLICATION TO THE ANALYSIS OF STEEL AND PURE IRON

COPPER—

The direct method has been applied to standard samples of mild steel, stainless steel and magnet alloy, and the results are compared with British Chemical Standard certificate values in Table III. The standard deviation for copper, calculated from the results for B.C.S. Nos. 271 and 277, is 0·001 per cent. at the 0·01 per cent. level and 0·006 per cent. at the 0·1 per cent. level. Table III also includes results for copper found in pure iron and mild steel after solvent extraction. The standard deviation calculated from the results for the sample of AH iron is 0·0002 per cent. at the 0·002 per cent. level.

TABLE IV

COPPER FOUND BY DIRECT METHOD IN STEELS CONTAINING MOLYBDENUM

Sample	B.C.S. No.	B.C.S. certificate value for— copper, %	B.C.S. certificate value for— molybdenum, %	Weight of sample, g	Copper found, %
Mn - Mo steel	214	0·24	0·26	0·5	0·25, 0·26
Ni - Cr - Mo steel ..	219	0·15	0·61	0·2	0·15, 0·16
High-speed steel ..	241/1	~0·10	0·52	0·2	0·10, 0·10
Low-alloy steel	251/1	0·55	1·51	0·1	0·53, 0·53
	254	0·11	1·29	0·1	0·10, 0·12
	254/1	0·34	0·23	0·5	0·35, 0·35
	256	0·23	0·53	0·2	0·25, 0·25
	257	0·31	0·32	0·2	0·29, 0·32
	258	0·19	0·43	0·2	0·16, 0·18

Results for eight standard samples of low-alloy steel and one high-speed steel, which contain up to 1·5 per cent. of molybdenum, are shown in Table IV. Decreased weights of sample were used, and the standard deviation for copper is between 0·01 and 0·02 per cent.; this value compares favourably with the reproducibility claimed for the British Standard procedure,[11] in which 2,2′-biquinolyl is used.

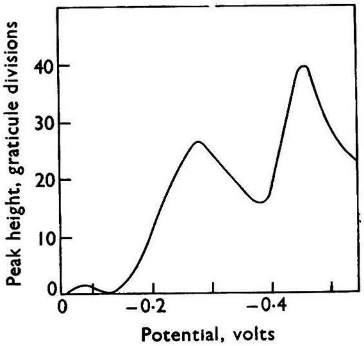

Fig. 1. Typical polarogram for copper and lead in a lead-bearing steel. Sample MGS 274 containing 0·19 per cent. of lead and 0·19 per cent. of copper (sensitivity setting, 2·5; volume of solution, 20 ml)

LEAD—

Interference from elements giving waves coincident with the lead wave restricts the application of the method to steels containing more than 0·05 per cent. of lead. The copper-to-lead ratio in such steels rarely exceeds 3 to 1, and for practical purposes interference from copper can therefore be disregarded. The method is particularly suitable for lead-bearing steels, provided that the molybdenum content is not much in excess of the lead content.

The direct method has been used for the simultaneous determination of lead and copper in a series of six lead-bearing steels that had previously been analysed for lead by the B.I.S.R.A. Methods of Analysis Committee,[12] who used their gravimetric method involving precipitation by hydrogen sulphide; the results found by both methods for copper and lead are shown in Table V. The lead content of each sample was determined six times by the proposed method, and the maximum standard deviation was 0·008 per cent. of lead. Each result for copper is the mean of two determinations. A typical polarogram for one of these samples is shown in Fig. 1. The somewhat high result for lead in sample MGS 360 is due to interference from the molybdenum in the sample (0·21 per cent.). With this exception, the results are in good agreement with those found previously.[12] When a modified procedure incorporating solvent extraction before polarographic measurement in a solution buffered with sodium formate was used, lead contents of 0·175 and 0·180 per cent. were found for sample MGS 360.

TABLE V

SIMULTANEOUS DETERMINATION OF COPPER AND LEAD BY DIRECT METHOD

Each result for lead by the proposed method is the mean of six determinations and each result for copper the mean of two

Sample	Sample No.	Lead found by Methods of Analysis Committee,* %	Lead found by proposed method, %	Standard deviation, %	Copper found by proposed method, %
Lead steel (B.C.S. No. 212)	MGS 163	0·280	0·280	0·007	0·115
Free-cutting steel ..	MGS 196A	0·175	0·175	0·004	0·195
	MGS 257A	0·076	0·080	0·008	0·175
	MGS 272	0·115	0·114	0·006	0·265
Carbon steel	MGS 274	0·185	0·185	0·002	0·190
Ni - Cr - Mo steel ..	MGS 360	0·175	0·190	0·006	0·220

* Except for sample MGS 257A, these results are expressed to the nearest 0·005 per cent.

CONCLUSIONS

It has been shown that the well known polarographic method for the simultaneous determination of copper and lead in steel can give precise results within certain limits of application. The modified method is extremely simple and rapid in operation, involving only three basic steps—dissolution, reduction and polarographic measurement. When used in conjunction with a cathode-ray polarograph, the method is particularly suitable for the routine batch analysis of large numbers of samples by relatively unskilled staff.

TABLE VI

INTERFERENCE WITH POLAROGRAPHIC DETERMINATION OF LEAD IN LEAD-BEARING STEELS

Element	Ratio of element to lead	Remarks
Arsenic	—	Maximum permissible level 0·05 per cent.
Titanium	—	Maximum permissible level 0·10 per cent.
Tin	—	Maximum permissible level 0·05 per cent.
Molybdenum	1 to 2	No interference
	1 to 1	Results about 9 per cent. high
Copper	1 to 1	No significant interference
	3 to 1	Results about 4 per cent. low
	10 to 1	Results about 15 per cent. low at 0·05 per cent. level

Only two elements interfere with the determination of copper: antimony when present in a ratio with copper greater than 1 to 1, and molybdenum when present in amounts greater than 0·2 per cent. The method is free of interference from all other elements normally used in the manufacture of steel and should be capable of application to steels having a wide range of compositions. The standard deviation for copper is 0·006 per cent. at the 0·1 per cent. level. Interference from up to 2 per cent. of molybdenum can be overcome by using a smaller weight of sample, with some consequent loss in precision; in such determinations the standard deviation is about 0·01 to 0·02 per cent. of copper for a 100-mg sample.

Results for lead are less satisfactory, principally owing to molybdenum, which gives a coincident reduction wave; interference is serious if the molybdenum-to-lead ratio exceeds 1 to 1. Molybdenum and iron can be removed by extraction with isobutyl acetate, but this involves some complication of an otherwise simple procedure. Titanium, arsenic and tin interfere if present in more than residual amounts, and there is some interference from the preceding reduction of copper. With certain restrictions, summarised in Table VI, the polarographic method can give accurate results for steels containing more than 0·05 per cent. of lead; this makes it particularly suitable for analysing lead-bearing steels.

For the determination of copper in pure iron, the limit of sensitivity and the precision of the method at low levels of copper content can be considerably improved if most of the iron is removed by extraction with isobutyl acetate. Further, the composition of the base electrolyte is modified by substituting sodium acetate for sodium formate. Impurities present in the latter reagent make it unsuitable for the determination of small amounts of copper. After solvent extraction, the lower limit of detection is 0·0001 per cent. and the standard deviation is 0·0002 per cent. of copper at the 0·002 per cent. level.

Separation of elements that interfere with the determination of lead is only partly complete after solvent extraction; the method for determining copper in pure iron is therefore not suitable for the simultaneous determination of lead present in trace amounts. A more thorough separation of interfering elements is essential, and Rooney's method,[8] which incorporates selective extraction of the lead - dithizone complex, is eminently suitable.

Since this work was completed, Rooney[13] has reported on the effects of several elements that interfere with the determination of trace amounts of lead in cast iron by the formate buffer method. Rooney added 0·01 per cent. of each element to a vacuum-melted grey iron containing 0·005 per cent. of lead. He found that the peak current for tin decreased rapidly as the pH was increased from 1·0 to 2·5 and was negligible at pH values above 2·8. Similarly, the peak height for arsenic decreased with increasing pH; it diminished rapidly above pH 2·6 and was negligible above pH 3·0, when arsenic apparently ceased to be reducible. On the other hand, interference from molybdenum increased with increasing pH and was maximal at about pH 3. The reduction potentials of arsenic and molybdenum were also critically dependent on pH. The interference from antimony and bismuth in the determination of copper noted in this paper was confirmed. Rooney's work demonstrates the need for close control of the pH of the base electrolyte so that interference effects are consistent.

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Rapid Determination of Beryllium

A Paper-chromatographic Method

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A simple, rapid and sensitive paper-chromatographic method has been developed for determining beryllium in beryllium-containing ores and allied materials. Eriochrome cyanine R is used as colour-forming reagent, and interference is overcome by impregnating the paper with ethylenediaminetetra-acetic acid. As little as 0·002 μg of beryllium can be detected.

During ore-dressing experiments for the beneficiation of beryllium-containing pegmatites, the need arose for a rapid method of determining a wide range of concentrations of beryllium in the various fractions. The extreme toxicity of beryllium compounds, even in contact with the skin,[1] led us to seek a method involving few manipulations, even at the expense of accuracy, so that health hazards would be minimal.

Since beryllium accompanies aluminium in conventional analytical schemes, time-consuming separations cannot be avoided if the determination is made gravimetrically,[2] especially with complex samples. More recent instrumental methods are based on spectrophotometry[3 to 8] or fluorimetry,[8 to 13] but the dyes used in these methods are not specific and some common metals interfere. Partial separation of beryllium is therefore necessary, and methods involving extraction, electrolysis and ion exchange have been introduced; these methods are lengthy. Hill[6] described a method for the direct determination of beryllium in alloys without chemical separation and recommended its application to ores; he used ethylenediaminetetra-acetic acid (EDTA) and cyanide as masking agents and Eriochrome cyanine R as colour-forming reagent. However, this method is time-consuming and involves removal of silica, fusion of the residue with potassium hydrogen sulphate, dissolution and filtration. Spectrographic methods[14,15] require expensive equipment, which many laboratories may not be able to afford.

We have devised a rapid and simple paper-chromatographic method, in which manipulations are few and the amount of beryllium involved need be only a fraction of a microgram. The chromatogram is developed on paper impregnated with an aqueous solution of EDTA (disodium salt); ethyl methyl ketone - hydrochloric acid - water or ethanol - hydrochloric acid - water is used as developing solvent and Eriochrome cyanine R as colour-forming reagent. The blue-violet beryllium - dye complex is compared with standard chromatograms for quantitative determinations, and amounts as small as 0·002 μg of beryllium can easily be detected visually.

EXPERIMENTAL

Whatman No. 1 chromatography paper (type CRL/1) was used throughout this work, and chromatograms were developed as described by Hunt, North and Wells.[16]

EXAMINATION OF SOLVENT MIXTURES—

Times of development and R_F values were investigated; an ascending-solvent technique was used, with three solvent mixtures—

A. Ethyl methyl ketone (7·5 ml), concentrated hydrochloric acid (1·5 ml) and water (1 ml).

B. Ethanol (9 ml) and 5 N hydrochloric acid (1 ml).[17,18]

C. n-Butyl alcohol (8 ml) and concentrated hydrochloric acid (2 ml).[17,18]

Portions (0·01 ml) of beryllium sulphate solution containing 0·5 μg of beryllium were placed on 9-cm strips of paper, development was allowed to take place, the chromatograms were dried in air, and the spots of beryllium were detected with a 0·5 per cent. solution of 8-hydroxyquinoline in 60 per cent. ethanol. The results were—

Solvent mixture	A	B	C
Time of development	40 minutes	30 minutes	5 hours
R_F value	0·7	0·7	0·15

Aluminium is one of the elements causing serious interference in the determination of beryllium, and this is important because of its high concentration in relation to beryllium in natural samples and the similarity in colour between the complexes of aluminium and beryllium with Eriochrome cyanine R. When solvent mixture A or B was used, it was found that the bands produced by 0·1 μg of beryllium and 2 μg of aluminium were distinctly separate, but those produced by 10 and 20 μg of aluminium overlapped the beryllium band. This difficulty was overcome as described under "Removal of Interference." With regard to speed, solvent mixtures A and B were equally suitable.

CHOICE OF COLOUR-FORMING REAGENT—

Solutions of quinalizarin, 8-hydroxyquinoline, morin and Eriochrome cyanine R were examined. Portions (0·01 ml) of standard solutions of beryllium sulphate containing from 0·002 to 0·5 μg of beryllium per 0·01 ml were chromatographed with solvent mixture B. The chromatograms were dried in air, exposed to ammonia vapour and then treated with a solution of the colour-forming reagent.

With a 0·05 per cent. solution of quinalizarin in 0·1 N sodium hydroxide, the beryllium formed a pale pink complex; the limit of detection was 0·5 μg of beryllium.

With a 0·5 per cent. solution of 8-hydroxyquinoline in 60 per cent. ethanol, 0·5 μg of beryllium could be detected in ultra-violet light after a short exposure to ammonia vapour. Prolonged exposure (about 30 minutes) permitted the detection of 0·1 μg of beryllium. However, fading of the fluorescence, apparently caused by evaporation of ammonia, was observed.

With a 0·02 per cent. solution of morin in acetone, 0·002 μg of beryllium could be detected in ultra-violet light, but fading of fluorescence was again observed.

When a 0·075 per cent. solution of Eriochrome cyanine R in water was used, however, the colour of the blue-violet beryllium complex remained stable and 0·002 μg of beryllium could easily be detected. Because of its high sensitivity and stability, this reagent was the most suitable of those tested; the best results by visual comparison with standards were obtained in the range 0·005 to 0·3 μg of beryllium.

REMOVAL OF INTERFERENCE—

Eriochrome cyanine R forms dark red to red-violet complexes with a number of elements,[19] some of which occur naturally with beryllium; others have R_F values similar to that of beryllium. It was thought that interference from these elements could be overcome by impregnating the chromatography paper with EDTA. Accordingly, 0·01-ml portions of a solution containing 0·1 μg of beryllium, 10 μg of ferric iron and 20 μg of aluminium were placed on separate strips of paper that had been dipped in 2·5, 5 and 10 per cent. aqueous solutions of EDTA and then dried in air. The sample spots were dried under uniform conditions by placing the treated strips of paper in a beaker floating on boiling water.[16]

When chromatograms were developed with solvent mixture A or B and Eriochrome cyanine R was used as colour-forming reagent, only beryllium was visible on paper impregnated with the 10 per cent. solution of EDTA, but the crystals of EDTA visible on the paper caused uneven flow of solvent. Impregnation of the paper with the 2·5 per cent. solution of EDTA did not entirely mask the 20 μg of aluminium present, and this interfered with the detection of beryllium. Paper impregnated with the 5 per cent. solution of EDTA was satisfactory, up to 50 μg of aluminium and up to 500 μg of ferric iron causing no interference, but the beryllium band was somewhat diffuse and trailing.

It was thought that, if iron and aluminium remained masked, compact bands of beryllium would be obtained if the beryllium were allowed to migrate only a short distance from the point of application. Solvent was therefore permitted to ascend only part of the strip, and compact well defined bands of beryllium were obtained when the solvent front had travelled 3·5 to 4 cm. Next, a 0·01-ml portion of solution containing 20 μg of aluminium and 10 μg each of copper, cobalt, nickel, lead, ferric iron, vanadium^{V} and the ion UO_2^{2+} was chromatographed under these conditions on paper impregnated with the 5 per cent. solution of EDTA. None of these elements, the amounts of which were considered to be in excess of those likely to occur with up to 0·3 μg of beryllium from natural sources, was detectable with Eriochrome cyanine R.

Zirconium forms a pink complex with Eriochrome cyanine R, but only under acid conditions; when exposed to ammonia vapour, the zirconium complex is colourless. This behaviour suggests a possible method for determining zirconium in the presence of beryllium, and it is hoped to develop such a method.

METHOD

REAGENTS—

Hydrofluoric acid, 40 per cent.

Hydrochloric acid, sp.gr. 1·18—Analytical-reagent grade.

EDTA solution, 5 per cent., aqueous—Prepare from disodium ethylenediaminetetraacetate dihydrate.

Solvent mixtures—Add 10 ml of water and 15 ml of hydrochloric acid, sp.gr. 1·18, to 75 ml of ethyl methyl ketone (solvent mixture A) or add 10 ml of 5 N hydrochloric acid to 90 ml of ethanol (solvent mixture B). These mixtures should be prepared from analytical-reagent grade materials.

Ammonia solution, sp.gr. 0·880.

Eriochrome cyanine R solution, 0·075 *per cent., aqueous.*

Standard beryllium solutions—Dissolve 0·1964 g of beryllium sulphate tetrahydrate in 50 ml of hydrochloric acid, sp.gr. 1·18, and dilute to 500 ml with water; this solution contains 20 μg of beryllium per ml. Dilute portions of this solution with approximately 1 M hydrochloric acid to prepare solutions containing 0·002, 0·005, 0·01, 0·03, 0·06, 0·1, 0·15, 0·20, 0·25 and 0·3 μg of beryllium per 0·01 ml.

PROCEDURE—

Weigh 20 to 100 mg of finely pulverised sample into a small platinum dish, digest with 5 ml of 40 per cent. hydrofluoric acid, evaporate to dryness on a water bath, and repeat the evaporation with a further 5 ml of hydrofluoric acid. To the residue add 5 ml of diluted hydrochloric acid (1 + 1), and set the dish aside on the water bath until solution is complete. When cool, transfer the solution to a 25-ml calibrated flask, and dilute to the mark with water. (For samples containing only a few parts per million of beryllium, use weights up to 1 g and a proportional amount of hydrofluoric acid.) Impregnate a sheet of Whatman No. 1 chromatography paper (type CRL/1) by immersing it in the 5 per cent. solution of EDTA, remove the excess of EDTA solution by wiping with filter-paper, and allow to dry suspended in the horizontal position. With a micropipette, apply 0·01 ml of sample solution (corresponding to 0·002 to 0·3 μg of beryllium) to the treated paper. Dry the sample spots by clipping the ends of the sheet together to form a cylinder and placing it in a beaker floating on boiling water. After 2 minutes, remove the paper, place it in a 600-ml beaker containing 10 to 15 ml of solvent mixture A or B, and cover the beaker with a clock-glass. Allow the solvent front to travel about 4 cm up the paper, then remove the paper, and allow it to dry in the air or, preferably, on the water bath as before. Expose the dried sheet to ammonia vapour by placing it in a covered 600-ml beaker containing a 50-ml beaker filled with ammonia solution, sp.gr. 0·880. When the paper smells of ammonia (after a few minutes), lift it from the beaker, and spray it on both sides with Eriochrome cyanine R solution. Determine the beryllium content of the sample by comparing the band produced with those produced by 0·01-ml portions of the standard beryllium solutions chromatographed on the same sheet.

RESULTS

The proposed method was tested with a sample known to contain 99·7 per cent. of beryllium oxide. The sample was dissolved in hydrofluoric acid to simulate the conditions used to decompose rocks, and the solution was evaporated with concentrated sulphuric acid until fumes were evolved. The residue was dissolved in approximately 1 M hydrochloric acid, and aliquots of this solution were chromatographed; the amounts of beryllium found corresponded to between 92 and 100 per cent. of beryllium oxide in the sample. When the hydrofluoric acid was not removed by evaporation with sulphuric acid and beryllium was chromatographed as fluoride, neither the intensity of the coloured complex nor the widths of the bands differed from those obtained when the beryllium was present as sulphate.

The reproducibility of the method was found by analysing beryl (theoretically, pure beryl contains 5·4 per cent. of beryllium). Three independent samples, to one of which was added an amount of beryllium sulphate tetrahydrate corresponding to about 5 per cent. of beryllium, were decomposed with hydrofluoric acid, and the solutions were treated by the proposed procedure. The results were 4·8, 5·0 (after allowance for added beryllium) and 5·0 per cent. of beryllium.

Visual comparison with standard chromatograms is satisfactory for determining 0·002 to 0·3 μg of beryllium, and it was thought that this would permit the determination of beryllium over a wide range of concentrations in rock samples.

The proposed method was therefore applied to various fractions of beryllium-containing pegmatite obtained in beneficiation experiments; the sum of the results for the fractions corresponded to 91 per cent. of the beryllium present in the sample. In further experiments reproducibility tests were made on beneficiation samples having lower concentrations of beryllium, known amounts of beryllium being added to two samples in each series of determinations. The results are summarised in Table I.

TABLE I

BERYLLIUM FOUND IN BENEFICIATION SAMPLES

Fraction	Sample No.	Number of determinations	Mean beryllium content found, %	Maximum deviation from mean, %
Head sample	1	6	0·79	±0·03
	2	11	0·10	±0·03
Concentrate	3	6	6·02	±0·41
	4	2	1·33	±0·03
	5	4	0·49	±0·06
	6	3	0·37	±0·05
Tailings	7	2	0·30	0·00
	8	2	0·01	±0·001
	9	5	0·022	±0·003
	10	5	0·005	±0·001

Since samples containing beryllium in the range 1 to 20 p.p.m. were not available, two such samples were prepared and then analysed by the proposed method; the results are shown in Table II. The beryllium bands obtained for mixture No. 2 were compared with standard chromatograms prepared from solutions containing 0·002 to 0·04 μg of beryllium.

TABLE II

BERYLLIUM FOUND IN PREPARED MIXTURES

Mixture No.	Constituents	Expected beryllium content, p.p.m.	Beryllium content found, p.p.m.
1	Tailings* (10% w/w) *plus* beryllium-free pegmatite (90% w/w)	20 to 25	20 to 22, 20 to 25
2	Mixture No. 1 (5% w/w) *plus* beryllium-free quartz (95% w/w)	1	1 to 2, 1 to 2,† 1 to 2

* Sample No. 10 in Table I.

† Result corrected for known amount of beryllium added to mixture before decomposition.

In all experiments, samples of pegmatite were decomposed with hydrofluoric acid; no other method of extracting beryllium from ores was examined.

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Notes

A SIMPLIFIED SPECTROPHOTOMETRIC ASSAY OF GRISEOFULVIN IN FERMENTATION SAMPLES

For the spectrophotometric determination of griseofulvin in fermentation samples, it is necessary to take into account irrelevant ultra-violet absorption due to materials other than griseofulvin. Ashton and Tootill[1] have outlined a method of assay in which optical densities are measured at seven equally spaced wavelengths. The necessary computations must be made with a calculating machine and even then are time-consuming. The method described in this Note involves only a simple calculation and has the advantage of allowing standards to be set up at the same time as samples.

METHOD

At seven wavelengths, which must be equally spaced, *e.g.*, 288, 290, 292, ... 300 mμ, the optical densities of a standard solution of pure griseofulvin in butyl acetate and of a butyl acetate solution of the sample being tested (which need not be a fermentation sample) are ascertained for all but the middle wavelength; the latter solution containing material giving rise to irrelevant absorption. For convenience in what follows, the seven wavelengths (x_i) are written as −3, −2, −1, 0, 1, 2 and 3, but use of the wavelengths themselves would give the same results, although rather more arithmetic would be involved. The results can then be tabulated as shown in Table I

TABLE I

SUGGESTED FORM FOR TABULATING RESULTS

Wavelength (x_i)	Absorption of standard (y_i)	Absorption of sample (Y_i)	Irrelevant absorption (y'_i)
−3	y_1	Y_1	y'_1
−2	y_2	Y_2	y'_2
−1	y_3	Y_3	y'_3
0	y_4	Y_4	y'_4
1	y_5	Y_5	y'_5
2	y_6	Y_6	y'_6
3	y_7	Y_7	y'_7

Let p be the proportion of pure griseolfulvin in the sample. Then we postulate that—

$$Y_i = py_i + y'_i$$

where i has the values 1, 2, . . . 7.

We intend to show that p can be calculated from the equation—

$$p = \frac{(Y_2 + Y_3 + Y_7) - (Y_1 + Y_5 + Y_6)}{(y_2 + y_3 + y_7) - (y_1 + y_5 + y_6)} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

the only assumption being that the irrelevant absorption follows a quadratic curve and the absorption of pure griseofulvin a cubic curve over the range of wavelengths used.

Let the absorption of the standard be expressed by the equation—

$$y_i = \mathrm{a} + \mathrm{b}x_i + \mathrm{c}x_i^2 + \mathrm{d}x_i^3$$

and the irrelevant absorption by the equation—

$$y'_i = \mathrm{A} + \mathrm{B}x_i + \mathrm{C}x_i^2.$$

Then the absorption of the sample, which is given by

$$Y_i = py_i + y'_i$$

can be expressed as

$$Y_i = (p\mathrm{a} + \mathrm{A}) + x_i(p\mathrm{b} + \mathrm{B}) + x_i^2(p\mathrm{c} + \mathrm{C}) + x_i^3(p\mathrm{d})$$

and therefore

$$\begin{aligned} Y_1 &= (p\mathrm{a} + \mathrm{A}) - 3(p\mathrm{b} + \mathrm{B}) + 9(p\mathrm{c} + \mathrm{C}) - 27(p\mathrm{d}) \\ Y_2 &= (p\mathrm{a} + \mathrm{A}) - 2(p\mathrm{b} + \mathrm{B}) + 4(p\mathrm{c} + \mathrm{C}) - 8(p\mathrm{d}) \\ &\vdots \\ Y_7 &= (p\mathrm{a} + \mathrm{A}) + 3(p\mathrm{b} + \mathrm{B}) + 9(p\mathrm{c} + \mathrm{C}) + 27(p\mathrm{d}) \end{aligned}$$

It follows, therefore, that

$$(Y_2 + Y_3 + Y_7) - (Y_1 + Y_5 + Y_6) = 36p\mathrm{d}.$$

Similarly, we can write

$$\begin{aligned} y_1 &= \mathrm{a} - 3\mathrm{b} + 9\mathrm{c} - 27\mathrm{d} \\ y_2 &= \mathrm{a} - 2\mathrm{b} + 4\mathrm{c} - 8\mathrm{d} \\ &\vdots \\ y_7 &= \mathrm{a} + 3\mathrm{b} + 9\mathrm{c} + 27\mathrm{d} \end{aligned}$$

from which it follows that

$$(y_2 + y_3 + y_7) - (y_1 + y_5 + y_6) = 36\mathrm{d}.$$

Equation (1) is seen to follow.

EXAMPLE

The calculation given by Ashton and Brown[2] in the paper to which Ashton and Tootill's is an appendix can be carried out by using equation (1). The relevant experimental results obtained by Ashton and Brown are shown in Table II.

Substitution of these values in equation (1) gives—

$$p = \frac{(0{\cdot}568 + 0{\cdot}494 + 0{\cdot}134) - (0{\cdot}562 + 0{\cdot}253 + 0{\cdot}176)}{(2{\cdot}015 + 1{\cdot}762 + 0{\cdot}476) - (1{\cdot}996 + 0{\cdot}900 + 0{\cdot}622)}$$

$$= \frac{0{\cdot}205}{0{\cdot}735} = 0{\cdot}2789.$$

Hence the concentration of the sample is 0·2789 × 29·922 = 8·35 µg per ml, where 29·922 µg per ml is the sum of the three standard concentrations involved. This is for practical purposes the same as the value of 8·36 µg per ml calculated by Ashton and Brown.

TABLE II

EXPERIMENTAL RESULTS USED IN CALCULATION

Wavelength, mµ	Absorption of standard*	Absorption of sample
288	1·996	0·562
290	2·015	0·568
292	1·762	0·494
294	—	—
296	0·900	0·253
298	0·622	0·176
300	0·476	0·134

* Each value is the sum of three sets of readings.

DISCUSSION OF THE METHOD

Dilution factors are allowed for in the usual way; thus, if the sample is a dilution of 1 in 100 and the standard contains 9 µg of griseofulvin per ml, the concentration of the sample is 9 × 100 × p µg per ml.

It is easy to make full use of a standard set up at the same time as a sample. This has the advantage of minimising errors, such as those possibly introduced by the use of different batches of solvent from day to day.

Only six wavelengths are used in equation (1), and care must be taken to ensure that the middle one is the one left out. It would be wrong, for example, to study six consecutive wavelengths and then to use equation (1).

The effect of errors of measurement is likely to be minimised if the wavelength omitted corresponds to an absorption about half-way down the steep part of the slope, as indicated in Fig. 1; we have found that the best wavelengths to use are 288, 290, 292, 296, 298 and 300 mμ. A suitable concentration for both standard and sample is about 10 μg per ml.

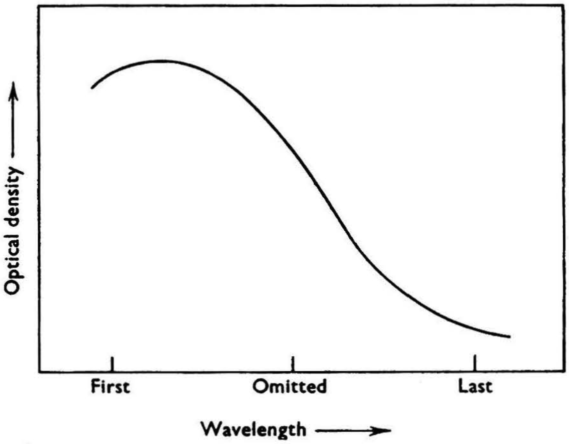

Fig. 1. Diagram showing best position of omitted wavelength for minimising measurement error effect

The results obtained can be applied to products other than griseofulvin when it has been established that the irrelevant absorptions lie on a quadratic curve or straight line and the pure-material absorptions on a cubic curve over the range of wavelengths used.

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THE DETERMINATION OF GLYCOGEN IN OYSTERS

METHODS described for determining glycogen in meat and fish products are time-consuming; the procedure described below permitted the glycogen content of a number of samples of oyster meat to be determined on a routine basis.

METHOD

It has been found that glycogen, like starch, can be dispersed in a calcium chloride solution of sp.gr. 1·30 and pH 2·3 and that the amount present in the solution can be determined by polarimetry. The procedure for determining glycogen is identical with those described previously for determining starch in wheat flour[1] and sausage meat[2] except that (*a*) the weight of sample used is 10 g and (*b*) soluble protein is precipitated by using 5-ml portions of Carrez's solutions I and II instead of 2-ml portions.

The specific rotatory power of oyster glycogen was determined in calcium chloride solution and found to be 203°. Therefore, if P is the optical rotation of the calcium chloride dispersion when measured at 20° C in a 20-cm tube with a polarimeter, the glycogen content is given by—

$$\text{Glycogen present, \%} = \frac{P \times 10^4}{406 \times \text{Weight of sample, g}}.$$

If a saccharimeter is used to measure the optical rotation, the result calculated from this formula should be multiplied by 0·3462.

A check on the result can be made as described below.

Add 3 ml of concentrated hydrochloric acid to 50 ml of the filtered calcium chloride dispersion contained in a suitable flask, and heat under reflux for 1 hour. Cool, dilute to 100 ml with calcium chloride solution, and determine the optical rotation, R, in a 20-cm tube at 20° C. Then—

$$\text{Glycogen present, \%} = \frac{(P - 2R) \times 10^4}{300 \times \text{Weight of sample, g}}$$

Again, if a saccharimeter is used, the result calculated from this formula should be multiplied by 0·3462.

Alternatively, an aliquot of the hydrolysed glycogen dispersion may be de-calcified by treatment with potassium oxalate or by passage through an ion-exchange resin, *e.g.*, Amberlite IR-120 in the sodium form, and the reducing matter determined, as glucose, by the micro Somogyi technique.

$$\text{Glycogen present, \%} = \text{Glucose, \%} \times 0{\cdot}9.$$

DISCUSSION OF THE METHOD

The samples of oyster meat should be finely comminuted, otherwise extraction of the glycogen may be incomplete. If any length of time is to elapse between sampling and analysis, the samples should be preserved in formaldehyde to prevent hydrolytic degradation of the glycogen. In practice, about 80 ml of a 10 per cent. solution of formaldehyde to each 200 ml of meat has proved effective. Oysters so far examined have shown no decrease in glycogen content over 4 weeks, nor has decomposition of the meat itself become apparent.

Discrepancies may occasionally occur between the amounts of glycogen found by the optical-rotation and reducing-value methods, such discrepancies being due to the presence of glucose in the original sample. Chromatography has confirmed the presence of traces of glucose in these instances. With such samples, it is best to determine the amount of glycogen present by means of the difference in rotation before and after hydrolysis.

When the samples have been preserved in formaldehyde, the amount of glycogen is more conveniently expressed as a percentage of the total solids. The total solids are determined by mixing the sample with sand in a metal dish and heating to constant weight at 100° C in the manner recommended for determining moisture in meat and meat products.

The glycogen contents of samples examined in this laboratory by the proposed method have varied between 12 and 25 per cent. of the total solids. These results are similar to those obtained by Humphrey's method,[3] which involves alkaline extraction, precipitation of the extracted glycogen by ethanol, hydrolysis to glucose and determination of the sugar produced by Shaffer and Somogyi's method.[4] This indicates that the calcium chloride solution is effective in removing glycogen from oyster tissues.

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CHROMATOGRAPHIC REAGENTS FOR SOME ORGANIC SUBSTANCES

DURING work on carbohydrate chemistry we have studied three chromatographic reagents, one for certain nitrogenated substances and the other two for carbohydrates and their esters.

REAGENT FOR NITROGENATED SUBSTANCES

The reagent is prepared by mixing equal volumes of a 10 per cent. aqueous solution of sodium metaperiodate and a 3·5 per cent. aqueous solution of picric acid. (The latter solution is maintained at 100° C during preparation of the reagent to ensure that the picric acid remains dissolved.) The chromatogram is sprayed with the reagent mixture until it is thoroughly wet and is then allowed to dry completely at room temperature; it is then heated in an oven at 110° C for 5 to 15 minutes. The colour usually develops 10 or 15 minutes after heating.

The substances listed in Table I give a pink colour on a yellow background. Some other substances, *e.g.*, arginine, alanine and asparagine, also produce a colour with this reagent, but only when present in larger amount (50 μg) and only after prolonged heating and a subsequent lengthy period at room temperature. Some non-nitrogenated carbohydrates produce a colour, but again only when present in larger amount, *e.g.*, 100 μg of cellobiose and 40 μg of glucose (both after being heated for 10 minutes).

TABLE I

SUBSTANCES FORMING COLOURS WITH PERIODATE - PICRIC ACID REAGENT

Substance	Amount present, μg	Heating time, minutes
Amino acids and related substances—		
L-Cysteine	10	3 to 5
Tryptophan	5 to 10	3 to 5
Tryptamine hydrochloride	5	Colour formed in cold
Serotonin	2 to 4	Colour formed in cold
Creatinine	No colour with 100 μg	—
Glutathione	15 to 20	10
β-Indolepropionic acid	10	5
Glycine	20	15
Nitrogenated carbohydrates—		
D-Glucosamine	10 to 20	10
N-Acetyl-D-glucosamine	10	5
N-Benzoyl-D-glucosamine	40	20 to 30
Glucosaminic acid oxime	10 to 20	5
NN′-Diacetylcellobiosylidenediamine*	10 to 20	10
NN′-Diacetyl-lactosylidenediamine*	20	10
Streptomycin	50	10†
Heterocyclic compounds—		
Indole	5 to 10	5
Barbituric acid	10	5
Thiobarbituric acid	10	5
Parabanic acid	20	10
Thiohydantoin	10	Colour formed in cold
Penicillin	30 to 50	5 to 10†

* This substance will be described elsewhere.

† Colour developed after subsequent standing for 2 hours at room temperature.

The use of this reagent could obviously be extended to the assay of other substances, such as alkaloids having indolic nucleii, but we have not attempted this.

REAGENTS FOR CARBOHYDRATES AND THEIR ESTERS

The first reagent is a mixture of (*a*) 2 volumes of a 2 per cent. solution of picric acid in methanol and (*b*) 1 volume of a 10 per cent. solution of sodium in methanol; the mixture is prepared shortly before use. The chromatogram is sprayed, allowed to dry at room temperature and then heated in an oven at 110° C for 5 to 15 minutes. Pink spots on a yellow background appear in presence of reducing sugars or their acetyl or benzoyl esters.

The second reagent is a modification of the well known alkaline silver nitrate reagent. Three solutions are prepared and stored separately: (*a*) a 0·3 per cent. solution of silver nitrate in methanol, (*b*) methanol saturated with ammonia and (*c*) a 7 per cent. solution of sodium in methanol. The reagent is prepared by mixing these solutions in the ratio 5 : 1 : 2, respectively, and colour is developed by dipping the chromatogram in the mixture. After being set aside at room temperature for a few minutes, reducing and non-reducing carbohydrates and their acetyl and benzoyl esters produce brown, yellowish or greenish spots on a beige background.

These two reagents could be useful in the reversed-phase paper chromatography of carbohydrate esters. Some of the substances assayed with these reagents are listed in Table II; the assays were made in order to ascertain the range of sensitivity of the reagents and were generally carried out by placing spots of a 1 per cent. solution of the substance on rectangular pieces of Whatman No. 1 chromatography paper. The amounts of the compounds listed in Table II are approximate. The acetyl and benzoyl esters of sugars were assayed on non-treated paper.

TABLE II

CARBOHYDRATE DERIVATIVES ASSAYED WITH THE PICRIC ACID AND SILVER NITRATE REAGENTS

Substance	Amount assayed with— silver nitrate reagent, µg	Amount assayed with— picric acid reagent, µg
Galaheptonic lactone	10	—
NN′-Diacetyl-lactosylidenediamine*	10	—
D-Glucosaminic acid nitrile penta-acetate	10	10
Penta-acetyl-D-glucose	10	10
Pentabenzoyl-D-glucose	20	20

* This substance will be described elsewhere.

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THE CO-PRECIPITATION OF PHOSPHATE WITH LEAD MOLYBDATE IN THE BRITISH STANDARD METHOD FOR DETERMINING PHOSPHORUS IN STEEL

THE precipitation of phosphorus as ammonium molybdophosphate was investigated in detail by Stockdale,[1] who also studied the British Standard method,[2] in which this reaction is used for determining the phosphorus content of steel. He estimated that co-precipitation of phosphate with the lead molybdate caused the final result to be high by about 1 in 200, but did not give experimental details. A radiochemical study has shown that the amount of co-precipitation is somewhat less than this estimate, even for steels having fairly high contents of phosphorus. As Stockdale commented, the determination is affected to only a trifling extent by co-precipitated phosphate.

EXPERIMENTAL

A 2-g sample of the steel was dissolved in a mixture of nitric and hydrochloric acids, perchloric acid was added, and the solution was evaporated until fumes were evolved. The solution was cooled, and hydrochloric acid and then hot water were added. The solution was then boiled and filtered, any residue being re-treated and added to the filtrate. After the combined filtrates had been heated to fumes with hydrobromic acid, the residue was dissolved in water, ammonium nitrate was added, together with about 2 µc of phosphorus-32, as orthophosphate, and the phosphorus was precipitated at 80° C as ammonium molybdophosphate. The precipitate was collected, washed free from iron salts and dissolved in a 50 per cent. aqueous solution of ammonia, and molybdenum was re-precipitated as lead molybdate by adding lead acetate solution. The procedure recommended in the British Standard was carefully followed, particular attention being paid to the correct volume of solution at the various stages. The precipitate was collected and washed with hot water, the combined filtrate and washings were diluted to 500 ml, and a 10-ml portion of this solution was counted in a Mullard MX124 liquid counter with an Ecko scaler, type N530F. The precipitate was dissolved in a dilute aqueous solution of sodium hydroxide, and this solution, after dilution to 10 ml, was counted with the same equipment.

DISCUSSION OF RESULTS

Determinations were made on steels having different contents of phosphorus under the conditions stipulated in the British Standard. The percentage of total phosphate carried down with the precipitate was calculated from the corrected count rates for the filtrate and the re-dissolved lead molybdate; the results are shown in Table I.

Although these results range rather widely, as is usual in co-precipitation studies, there is a clear tendency towards greater precipitation of phosphate as the phosphorus content of the steel increases. However, the highest value recorded in a single experiment corresponds to an increase of only 0·32 per cent. in the weight of the lead molybdate; the mean value for a medium phosphorus steel is about 0·16 per cent., *i.e.*, approximately one-third of Stockdale's estimate.

Ammonium molybdophosphate was also prepared by Thistlethwaite's method[3]; 3·5 times the stoicheiometric amount of an acid solution of ammonium molybdate was added to a solution of potassium dihydrogen orthophosphate containing, as radioactive tracer, about 2 μc of phosphorus-32, as orthophosphate. The precipitate so obtained was treated in the same way as the molybdophosphate precipitates from the steels. The results for phosphate co-precipitated with lead molybdate in this experiment ranged from 1·48 to 1·89 per cent., the mean value for four determinations being 1·68 per cent. The amount of phosphate used was equivalent to that in a 2-g sample of a steel containing 0·048 per cent. of phosphorus.

TABLE I

PHOSPHATE CO-PRECIPITATED WITH LEAD MOLYBDATE

Phosphorus content of steel, %	Number of determinations	Phosphate co-precipitated, %
0·010	8	1·08 to 1·98 (mean 1·40)
0·020	6	1·26 to 2·33 (mean 1·77)
0·047	5	1·70 to 3·20 (mean 2·14)
0·062	6	1·99 to 3·44 (mean 2·50)

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APPARENT LOSS OF IRON DURING FUSION OF SILICATE MATERIALS WITH SODIUM HYDROXIDE IN NICKEL CRUCIBLES

DURING an investigation into rapid methods for analysing aluminosilicates and materials of high silica content it was observed that iron was apparently retained by the nickel crucibles in which the sample was decomposed. Although it has been appreciated for some time that reduction of iron oxide during fusion can cause retention in platinum crucibles, to the best of our knowledge no such loss has been reported for nickel crucibles.

This apparent loss of iron was observed when samples were decomposed by fusion with sodium hydroxide in nickel crucibles. The melt was subsequently decomposed with hot water, and solution was completed in nitric acid. After dilution to a definite volume, the iron was determined spectrophotometrically by means of *o*-phenanthroline. All the results were low, and there was a definite indication that the loss was proportional to the amount of iron present (see Table I).

TABLE I

COMPARISON OF RESULTS FOUND BY ACID DECOMPOSITION AND FUSION WITH SODIUM HYDROXIDE

Sample	Accepted iron content, as Fe_2O_3, %	Iron content found, as Fe_2O_3, by—	
		acid decomposition, %	fusion with sodium hydroxide, %
Silica brick	0·66	0·66	0·64
	0·79	0·80	0·71
	0·84	0·83	0·74
Clay	0·98	0·93	0·93
	2·05	2·09	1·94
Firebrick	2·17	2·07	1·92
	2·81	2·75	2·51
	3·30	3·25	3·02

Portions of the same samples were also decomposed by volatilising the silica with hydrofluoric acid in platinum dishes, fluoride being removed by subsequent evaporation to dryness with sulphuric acid. The residue was dissolved in hydrochloric acid and the determination completed spectrophotometrically as before. Results by this technique were in fair agreement with accepted values and, when plotted on the calibration graph obtained for prepared solutions, were reasonably close to the line (see Fig. 1, curve A).

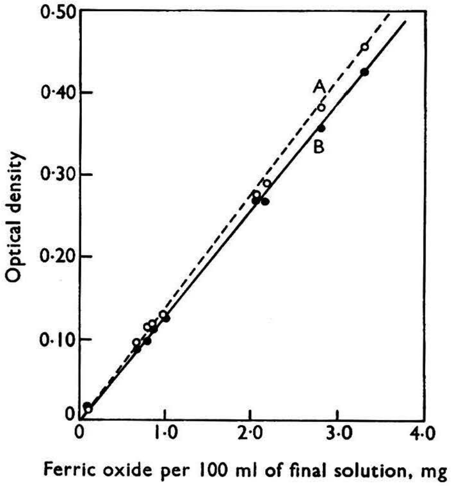

Fig. 1. Calibration graphs for iron content: curve A, prepared solution (hydrofluoric - sulphuric acid treatment); curve B, two standard samples (fusion with sodium hydroxide)

Results obtained by fusion with sodium hydroxide were also on a straight line (see Fig. 1, curve B), which was substantially identical with an empirical calibration obtained by decomposing standard samples in the same manner. This suggests that the effect can be obviated by a calibration based on fusions of standard samples (see Table II).

Table II

Iron contents found by using calibration graph based on fusions of standard samples

Sample	Accepted iron content, as Fe_2O_3, %	Iron content found, as Fe_2O_3, %
Silica brick	0·79	0·76
	0·84	0·80
Clay	0·98	0·99
	2·05	2·07
Firebrick	2·17	2·11
	2·81	2·74

It was at first thought that these errors arose from interference by nickel, but a calibration with prepared solutions to which aliquots from a blank fusion had been added was identical with that from pure solutions alone. It appears, therefore, that some of the iron in the sample is retained by the nickel crucible in a form such that it is not removed even by thoroughly rinsing the crucible with acid after the fusion. This loss of iron could be accounted for by assuming that some of it is reduced and then forms an alloy with the nickel of the crucible. The peculiarity of this phenomenon lies in the apparent constancy of the ratio of the loss to the total iron content of the sample.

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DETERMINATION OF SAMARIUM AND OTHER RARE EARTHS

ACCURATE methods for determining rare-earth metals at high and low concentrations are becoming increasingly important, owing to the increased use of these metals in alloys and the high thermal-neutron absorption characteristics exhibited by some of them, even at low concentrations. With the exception of samarium, reliable methods are available for determining these metals when present in major amounts. At low concentrations also, samarium is the most difficult to determine of those elements having high thermal-neutron absorption.

Table I summarises methods that have been investigated for determining samarium, together with the reasons for their almost complete failure. However, despite the partial failure of emission-spectroscopic procedures, such an approach seemed to be the most promising for determining samarium, particularly when it is considered that other rare earths can readily be determined in this way. Application of a spectrographic method to this determination presented two problems: (*a*) the choice of a suitable interference-free line for samarium in the determination of alloying amounts of samarium and (*b*) the development of a suitable procedure for concentration when the metal is present as impurity.

The procedure for isolating samarium must be tailored to suit the sample. For example, in the presence of elements not precipitated in ammoniacal solution, *e.g.*, magnesium and calcium, initial separation can be made by precipitating samarium, as hydroxide, in the presence of hydrogen peroxide. When an element such as iron or zirconium is present, samarium can be concentrated by a method based on precipitation of rare earths as their oxalates, with or without initial precipitation as hydroxide. These separations, however, do not remove cerium or thorium, and attempts to concentrate rare earths by first precipitating undesirable elements may result in loss of samarium, *e.g.*, separation of aluminium or thorium as benzoate or iodate results in partial precipitation (and loss) of samarium as hydroxide.

TABLE I

METHODS INVESTIGATED FOR DETERMINING SAMARIUM

Method	Limitations
Absorption spectrophotometry at 401 to 402 mμ of an aqueous solution of chloride or perchlorate	Lower limit for reliable measurement is above 1 g of samarium per litre
Solution of sample in hydrochloric acid under an atmosphere of hydrogen, addition of a ferric salt and titration of ferrous ions with dichromate solution	Low results caused by loss of samarous ion in the reaction $Sm^{2+} + H^+ \rightarrow Sm^{3+} + \frac{1}{2}H_2$
Precipitation of samarous sulphate from ethanolic solution in presence of a reductant, *e.g.*, sodium amalgam	Precipitation incomplete
Precipitation as oxide or fluoride on a cerium, yttrium or aluminium carrier and spectrographic determination with the carrier as internal standard[1 to 6]	Lack of spectral lines free from overlapping lines of other rare earths. At low concentrations, there is a dearth of sufficiently sensitive lines, especially in the ultra-violet region
Polarography	Half-wave potentials of rare earths are close together

The most satisfactory method for separating cerium from samarium is by precipitation of basic ceric nitrate,[7] but, in presence of magnesium, preliminary precipitation of cerium and samarium, as hydroxide, is essential to avoid the formation of soluble ceric magnesium nitrate. Thorium is best separated from samarium by extraction, as thorium nitrate, into tri-n-butyl phosphate and subsequent volatilisation of residual thorium as tetrachloride.[8] To achieve complete recovery and separation of rare earths from the traces of unextracted thorium, the chlorination conditions must be modified to suit the type of furnace used. The anhydrous rare-earth chlorides present after removal of thorium tend to hydrolyse, but this can be avoided and the recovery of rare earths made quantitative if the residue is fused with pyrosulphate.

A combination of the methods outlined above is the basis of the procedure used for determining samarium in typical alloys.

Samarium lines in the region 2000 to 4350 A and several in the visible region are listed in Table II, with observations as to suitability. A d.c. arc source and an aluminium carrier were used in the determination of alloying amounts of samarium; measurements were made with an ARL spectrograph (wavelength range 2160 to 4330 A) and the lines used were those for samarium at 4280·8 A and aluminium at 3050·1 A.

When it is necessary to determine small amounts of samarium, it has been found possible to use lanthanum, which has a relatively simple spectrum, as internal standard. Lanthanum was chosen because it occurs naturally with samarium and has similar chemical characteristics in the tervalent state; we had previously used lanthanum as internal standard in the spectrographic determination of other elements.[9] Further, lanthanum can be accurately determined by similar spectrographic methods and gives satisfactory working curves for the logarithms of the intensity ratios of the samarium lines at 3230·5, 3239·6 and 3254·4 A to the lanthanum line at 2855·9 A when a d.c. arc source is used. The curves for the samarium lines at 3230·5 and 3239·6 A are identical; the line at 3254·4 A is more subject to interference, but is the most sensitive. The lower limit of detection for all three line pairs is a samarium-to-lanthanum ratio of approximately 0·002 to 1.

TABLE II

EVALUATION OF SAMARIUM LINES FOR ANALYTICAL USE AFTER REMOVAL OF CERIUM

Wavelength, A	Remarks
Below 3200	No visible lines separate from other rare-earth lines
3211·8	Not reliable
3218·6	Not detectable
3230·5	Iron must be absent or removed; high concentrations of cerium interfere, owing to broadening of cerium line at 3231·2 A
3236·6	Overlapped by neodymium line at 3236·5 A
3239·6	Reading must be made carefully (praseodymium line at 3240·0 A)
3254·4	Only usable if neodymium is absent or present in low concentrations (neodymium line at 3254·1 A); iron must be absent or removed (iron line at 3254·1 A)
3306·4	Overlapped by neodymium line at 3306·4 A
3321·2	Faint; overlapped by neodymium line at 3321·4 A (if present in quantity)
3382·4	Overlapped by neodymium line at 3382·8 A (if present in quantity)
3445·6	Very faint for oxide samples; slight interference from neodymium line at 3445·9 A
3634·3	Overlapped by neodymium line at 3634·3 A
3649·5	Overlapped by lanthanum line at 3649·5 A
3661·3	Overlapped by neodymium line at 3661·3 A
3670·8	Overlapped by lines for praseodymium and europium (3670·8 A) and neodymium (3670·9 A)
3694·0 to 3854·2	Overlapped by cyanogen bands; line at 3854·2 A is clear of other rare-earth lines
3933·6	Affected by broadening of lanthanum line at 3936·2 A
3983·1	Overlapped by lines for gadolinium (3983·0 A) and neodymium (3983·2 and 3983·4 A)
4106·6	Overlapped by cyanogen band and a neodymium line
4220·7	Not detectable
4244·7	Overlapped by neodymium line at 4244·6 A
4251·8	Overlapped by lines for praseodymium (4251·5 A), gadolinium (4251·7 A) and cerium (4251·9 A)
4256·4	Overlapped by lanthanum and neodymium lines at 4256·5 A
4262·7	Overlapped by lines for lanthanum (4262·3 A) and praseodymium (4262·8 A)
4279·7	Overlapped by lines for europium (4279·7 A), praseodymium (4280·1 A) and lanthanum (4280·3 A)
4280·8	Overlapped by neodymium line at 4280·7 A
4285·5	Overlapped by praseodymium line at 4285·5 A and broadening of lanthanum line at 4287·0 A
4286·6	Affected by broadening of lanthanum line at 4287·0 A
4292·2	Affected by broadening of lanthanum line at 4296·0 A. Line has been used with a 5-μ slit, background correction and special densitometer for determining high concentrations of samarium, even in presence of cerium
4296·7	Affected by broadening of lanthanum line at 4296·0 A
4304·9	Overlapped by lines for lanthanum (4304·1 A), neodymium (4304·4 A) and gadolinium (4304·9 A)
4309·0	Overlapped by praseodymium line at 4308·9 A
4318·9	Overlapped by lines for praseodymium (4319·0 A) and neodymium (4319·3 A)
4323·3	Overlapped by neodymium line at 4323·3 A
4329·0	Overlapped by praseodymium line at 4328·9 A and lines for praseodymium and europium at 4329·4 A
4334·1	On extreme limit of instrument used; overlapped by praseodymium line at 4333·9 A
4467·3	Beyond limit of instrument used, but evaluated with direct-reading equipment; subject to complex interference from cerium
4745·7 6861·1	Beyond range of instrument used; appear to be free from interference by overlapping lines

RESULTS

The separations and procedures outlined for determining major amounts of samarium were applied to mixtures containing known amounts of rare earths, together with thorium, zirconium calcium and magnesium. Rare-earth oxalate precipitates and filtrates were converted to oxide and weighed; all precipitates and evaporated filtrates were then examined spectrographically, the choice of spectrographic lines being made by examination of similar mixtures of known composition precipitated from solution as hydroxides and subsequently ignited to oxides. To confirm interferences from overlapping lines, three exposures were made adjacent to each other on the film with (*i*) pure samarium oxide, (*ii*) a typical rare-earth sample and (*iii*) the pure oxide of the suspected interfering element. Working curves were prepared in the same way from solutions containing 50 mg of the carrier - internal standard (lanthanum or aluminium), as chloride, and different amounts of samarium, etc.; these solutions contained no interfering metals and were not subjected to any initial separation procedure. Finally, the entire separation procedure was applied to typical solutions; the results, which indicate that recovery of samarium was satisfactory, were—

Samarium added, mg per 50 mg of lanthanum ..	0·30	0·80	2·0
Samarium found, mg per 50 mg of lanthanum ..	0·26	0·80	1·8

In addition to this work, the determination of other rare-earth metals was investigated, aluminium being used as carrier - internal standard, so permitting these additional elements (and lanthanum) to be simultaneously determined; the procedure used was the same as that for samarium. Full working curves were drawn for those metals so far detected in commercial alloys, including lanthanum, cerium, praseodymium and neodymium, and partial curves for europium and gadolinium at impurity levels (about 0·01 per cent. of total rare earths). For the other rare earths, limits of detection were established by examining high-purity calcium and magnesium-containing samples, hydroxide precipitation only being used; the results are summarised in Table III.

TABLE III

DETERMINATION OF RARE EARTHS WITH ALUMINIUM AS CARRIER - INTERNAL STANDARD

The aluminium line at 3050·1 A was used as reference

Element	Line used, A	Lower limit* for 10 g of sample with 50 g of aluminium, p.p.m.	Elements causing interference
Lanthanum ..	3988·5	1	—
Cerium	4012·4 4186·6†	10	—
Preseodymium ..	4225·3	1	High concentrations of samarium, dysprosium and gadolinium
Neodymium ..	3382·8	∼0·5	—
	4303·5	0·5	Praseodymium, if present in similar concentration
Samarium	4280·8	10	All other rare earths in low concentrations
Europium	3972·0	0·5	High concentrations of cerium and praseodymium
Gadolinium ..	3362·2	0·5	Cerium and high concentrations of lanthanum, neodymium, thulium, ytterbium and yttrium
Terbium	3324·4	1	Cerium and praseodymium
Dysprosium ..	4000·5	1	Cerium
Holmium	3456·0	0·1	
Erbium	3906·3	0·1	
Thulium	3131·3	1	
Ytterbium	3289·5	0·1	
Lutecium	2911·6	∼0·1	—
	3472·5	0·1	Cerium and high concentrations of most other rare earths
Yttrium	3242·3	0·1	Cerium and samarium
Scandium	4023·7	1	Cerium, lanthanum and high concentrations of neodymium

* The lower limit was taken as being twice the concentration at which the line faded into the background. These limits are for trace determinations only; if one rare earth, or more, is present in high concentration, it will act as a diluent and will decrease the amount of both carrier and impurity in the electrode, thereby increasing the lower limit by decreasing the total amount of light emitted by the element being determined.

† Wavelength used only for high alloy ranges.

All spectrographic analyses were made with an ARL 1·5-metre instrument, with a complete burn and d.c. arc exposure. Samples were mixed with an equal weight of graphite and packed in United Carbon cup electrodes (type 101L); the counter-electrode was of ¼-inch diameter graphite, spherically ended and conical (60°) at the tip. Interference could be reduced by using a narrow entrance slit (5 to 20 μ), but this decreased the intensity of light reaching the film, lowered the sensitivity and increased the limit of detection. A 40-μ slit was found to be the best compromise.

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STATUTORY INSTRUMENTS*

1960—No. 2261. The Arsenic in Food (Amendment) Regulations, 1960. Price 3d.

These Regulations, which came into operation on December 14th, 1960, amend The Arsenic in Food Regulations, 1959 (S.I. 1959, No. 831, mentioned in Analyst, 1959, **84**, 397), *by increasing from 2 to 5 parts per million the maximum amount of arsenic permitted in brewers' yeast intended for use by manufacturers in the manufacture of yeast products.*

1960—No. 2331. The Skimmed Milk with Non-Milk Fat Regulations, 1960. Price 6d.

These regulations, which will come into operation on September 19th, 1961, (a) *impose requirements as to the labelling and advertising of certain "specified foods" that have the appearance of milk, condensed milk or dried milk and that contain skimmed milk and non-milk fat;* (b) *prohibit the labelling or advertising of the specified foods in a manner suggestive of milk or anything connected with the dairy interest; and* (c) *provide that the Condensed Milk Regulations, 1959 (S.I. 1959, No. 1098, mentioned in* Analyst, 1959, **84**, 523), *and the Public Health (Dried Milk) Regulations, 1923 to 1948, shall not apply to any specified food.*

FOOD STANDARDS COMMITTEE

Report on Bread and Flour

THE Ministry of Agriculture, Fisheries and Food, the Ministry of Health, the Department of Health for Scotland and the Home Office have announced the publication of a report by the Food Standards Committee making recommendations for control over the composition, description and labelling and advertising of bread and flour.

The main recommendations on bread are that there should be a statutory permitted list of the ingredients that may be used in bread; that descriptions of "protein" breads should be controlled; that slimming claims in connection with bread should be controlled; and that exaggerated claims for enrichment of bread or for energy-producing qualities should be prohibited.

The Committee recommends that the present regulations requiring all flour to contain certain nutrients should be continued unchanged for the present and that only certain bleaching and improving agents should be allowed for the treatment of flour.

Before deciding whether and to what extent the recommendations should be implemented, the Ministers will give full consideration to any representations made by interests concerned. Copies of the Report may be obtained from H.M. Stationery Office, price 4s. 6d. (plus 4d. postage).

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* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

Book Reviews

JOURNAL OF THE FORENSIC SCIENCE SOCIETY. Volume I, Number 1, September, 1960. Editor: S. S. KIND, B.Sc., F.L.S., M.I.Biol. Pp. 68. Harrogate, Yorkshire: The Forensic Science Society. Annual Subscription (two parts per year) 40s.; Single numbers 20s.

The recent formation of the Forensic Science Society calls for some comment, since most of its practising members will be analysts. The issuing of the first number of its Journal, which is to appear twice yearly, is an appropriate occasion for this to be done.

The 19th century saw the development of forensic medicine, and, since an important aspect of such work dealt with poisoning, the foundations of toxicology were laid. For the detection and determination of poisons, expert chemical knowledge and expertise are required, and by the beginning of the present century the most eminent toxicologists were qualified in both medicine and chemistry.

During and after the development of forensic medicine, chemists in other fields were called upon for legal purposes. For example, when the first old-age pension scheme was introduced over 50 years ago, evidence of date of birth was required. Many applicants had no birth certificates, and entries in family bibles or other documents were submitted as evidence. Frequently, alterations or emendations had been made, and expert evidence was required regarding authenticity. This involved the chemical composition of inks, their rates of fading, the order in which changes had been made and an application of chemistry, photography and microscopy. Certain chemists specialised in such fields and gave great assistance to the courts.

As science advanced, more and more use was made of it for legal purposes, in which public analysts, government departments and consultants all took part. *The Analyst* contained many papers in this field; mention may be made of the contributions of Dr. Roche Lynch, former President of the Society, and of Dr. Mitchell, for many years Editor of *The Analyst*.

In 1938 the Home Office set up regional laboratories to assist the police in criminal investigations. The record of these laboratories during more than 20 years shows that they are interested solely in presenting the whole of the ascertainable facts to a court and are not for or against anyone who may be charged.

Forensic science to-day requires knowledge of all branches of science. It further requires the ability to make proper deductions from ascertained facts. It is a specialised field, and for this reason it justifies a new Society in which personal contact and circulation of ideas are particularly important. The Journal is needed to circulate the specialised information useful to the members, which other societies might consider inappropriate for their publications. This does not mean isolation from the main body of science, but a channeling of relevant parts from each branch.

The first issue of this Journal contains the Chairman's Address at the Inaugural meeting, accounts of lectures and papers given at a symposium, correspondence, case notes, reviews, abstracts and a contributed paper.

Forensic scientists will frequently be required to give evidence as expert witnesses. The attitude that such a witness should adopt is admirably expressed in the following quotation from the opening address of the Chairman, Dr. Patterson, at the Inaugural meeting, when stating the objects of most investigations in forensic science. "Stated as an abstraction it is to attempt to answer this question: Are cause A and effect B directly related? The Courts, and through them society at large, would like an unequivocal Yes or No. It is often impossible to give such an answer. We cannot say, for instance, that this blood came from that individual or that this object caused that damage. The only valid scientific conclusion is that cause A and effect B *could have been* related, which is a very different thing from saying that they *were* related. No amount of clever cross-examination should ever budge an expert witness from this position in such instances, or indeed from a position of certainty, if this has been established. He has the whole weight of science behind him, provided that the methods by which his conclusion has been reached are fully exposed to the criticism of scientific opinion." J. R. NICHOLLS

TEXTBOOK OF PHARMACOGNOSY. By T. E. WALLIS, D.Sc., F.R.I.C., F.P.S., M.I.Biol., F.L.S. Fourth Edition. Pp. xii + 640. London: J. & A. Churchill Ltd. 1960. Price 50s.

That another edition of this book has been called for within 5 years is eloquent testimony of its worth. The description given in the review of the third edition (*Analyst*, 1956, **81**, **247**) may equally be applied to the fourth, but the whole of the text has been revised to bring it in line with modern developments, particularly in relation to the constituents of drugs, an aspect that has been the focus of much research in recent years. Further, the value of the text is now enhanced by the addition of two new chapters, the one giving detailed schemes for describing the morphological characters of drugs and the other comprising general instructions for systematic study of powdered drugs, with a series of Tables arranged so as to provide a comparative view of histological characters.

After studying this book with its fine illustrations (247 of them) one is impressed by the wealth of information in it of value to analysts, and this feature alone recommends it as an important work of reference.

NOEL L. ALLPORT

Publications Received

DIE FLAMMENSPEKTRALANALYSE: GRUNDLAGEN UND VERFAHREN VON FLAMMENPHOTOMETRIE UND FLAMMENSPEKTROGRAPHIE. By Prof. Dr. WOLFGANG SCHUHKNECHT. Pp. xii + 258. Stuttgart: Ferdinand Enke Verlag. 1960. Price (paper) DM 65.50; (cloth boards) DM 69.

X-RAY MICROSCOPY. By V. E. COSSLETT, M.A., Ph.D., and W. C. NIXON, M.A., Ph.D. Pp. xiv + 406. London: Cambridge University Press. 1960. Price 80s.

THE DETERMINATION OF GASES IN METALS. Pp. viii + 308. London: The Iron and Steel Institute. 1960. Price 63s.
Report of a symposium organised by The Society for Analytical Chemistry in conjunction with The Iron and Steel Institute and The Institute of Metals.

LABORATORY AND WORKSHOP NOTES 1956–58. Compiled and edited by RUTH LANG, Ph.D., A.Inst.P., for The Institute of Physics. Pp. xii + 218. London: Edward Arnold (Publishers) Ltd. 1960. Price 40s.
A fifth selection reprinted from the Journal of Scientific Instruments.

THE COMPOSITION OF FOODS. By R. A. MCCANCE, C.B.E., M.D., Ph.D., F.R.C.P., F.R.S., and E. M. WIDDOWSON, D.Sc. Pp. viii + 252. London: Her Majesty's Stationery Office. 1960. Price 30s.
Medical Research Council Special Report Series No. 297.

MISES AU POINT DE CHIMIE ANALYTIQUE PURE ET APPLIQUÉE ET D'ANALYSE BROMATOLOGIQUE. Edited by J.-A. GAUTIER. Huitième Série. Pp. ii + 148. Paris: Masson et Cie. 1960. Price 26 NF.

PHYSIKO-CHEMISCHE GRUNDLAGEN UND TABELLEN ZUR QUALITATIVEN ANALYSE (MIT AUSNAHME DER GASANALYSE) (W. D. TREADWELL). Edited by Prof. Dr. O. GÜBELI and Dr. W. PRODINGER. Pp. xii + 236. Vienna: Verlag Franz Deuticke. 1960. Price 168 Austrian schillings.

HANDBOOK OF MICROBIOLOGY. By MORRIS B. JACOBS, Ph.D., and MAURICE J. GERSTEIN, B.S.. M.S. Pp. x + 322. Princeton, New York, Toronto and London: D. Van Nostrand Co, Inc. 1960. Price $8.50; 64s.

SPOT TESTS IN ORGANIC ANALYSIS. By FRITZ FEIGL, Eng., D.Sc. Translated by RALPH E. OESPER, Ph.D. Sixth English Edition. Pp. xx + 675. Amsterdam, London, New York and Princeton: Elsevier Publishing Co.; London: D. Van Nostrand Co. Ltd. 1960. Price 65s.

REPRINTS OF "ANALYTICAL CHEMISTRY OF BERYLLIUM" BY L. E. SMYTHE AND R. N. WHITTEM

REPRINTS of the Review Paper, "Analytical Chemistry of Beryllium" by L. E. Smythe and R. N. Whittem, published in this issue of *The Analyst* (pp. 83–94), will be available shortly from the Assistant Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, at 5s. per copy, post free. A remittance for the correct amount, made out to The Society for Analytical Chemistry, MUST accompany the order; these reprints are not available through Trade Agents.

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Conciseness of expression should be aimed at: clearness is increased by adopting a logical order of presentation, with suitable paragraph or section headings.

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(*c*) Description of method. Working details of proposed methods are most concise and clear when given in the imperative mood, and should normally be given in this form, *e.g.*, "Dissolve 1 g of sample in 10 ml of water, and add. . . ." Well known procedures must not be described in detail.

(*d*) Presentation of results.

(*e*) Scope and validity of results.

(*f*) Conclusions and, if required, a short summary of the principal results.

Tables, diagrams, etc.—The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns may often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables must be supplied with titles and be so set out as to be understandable without reference to the text.

Tables or graphs may be used, but not both for the same set of results, unless important additional information is given by so doing.

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1. Dunn, J. T., and Bloxam, H. C. L., *J. Soc. Chem. Ind.*, 1933, **52**, 189T.
2. Mitchell, C. A., *Editor*, "Allen's Commercial Organic Analysis," Fifth Edition, J. & A. Churchill Ltd., London, 1932, Volume 9, p. 149.

For books, the edition (if not the first), the publisher and the place and date of publication should be given, followed by the volume or page number, or both if required.

The entry of "personal communications" in the reference list is not justified; full acknowledgment of such unpublished sources should be made in the text or in the acknowledgments at the end of the paper.

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S. Tapper-Jones,
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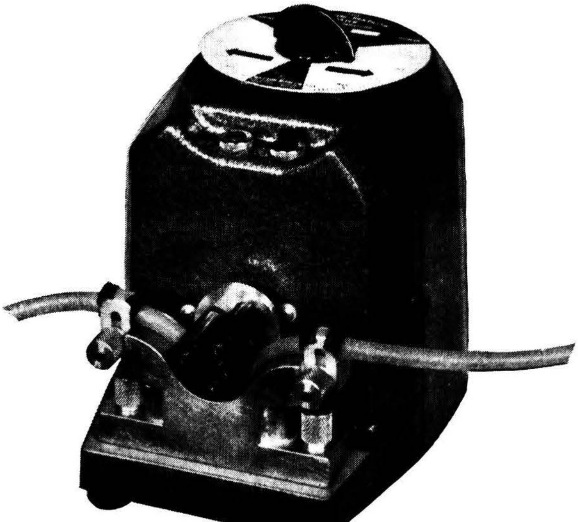

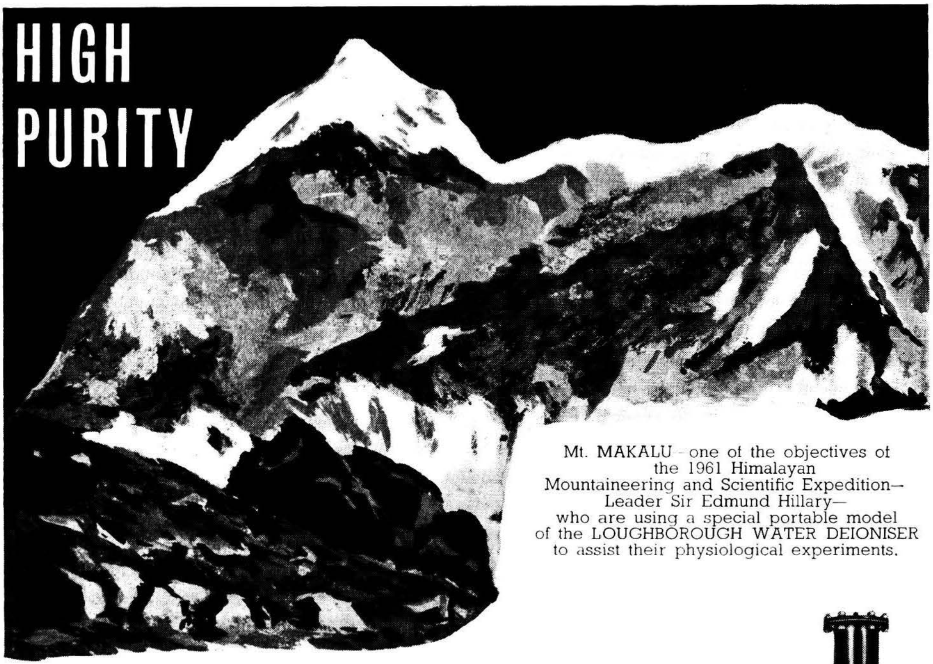
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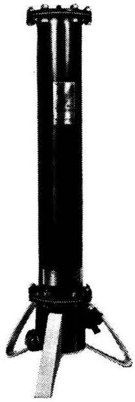

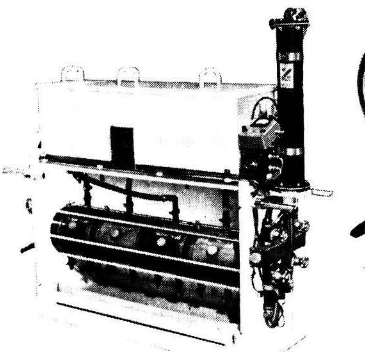

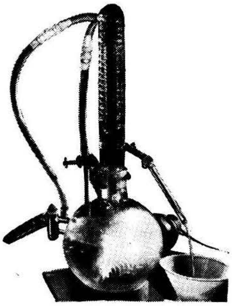

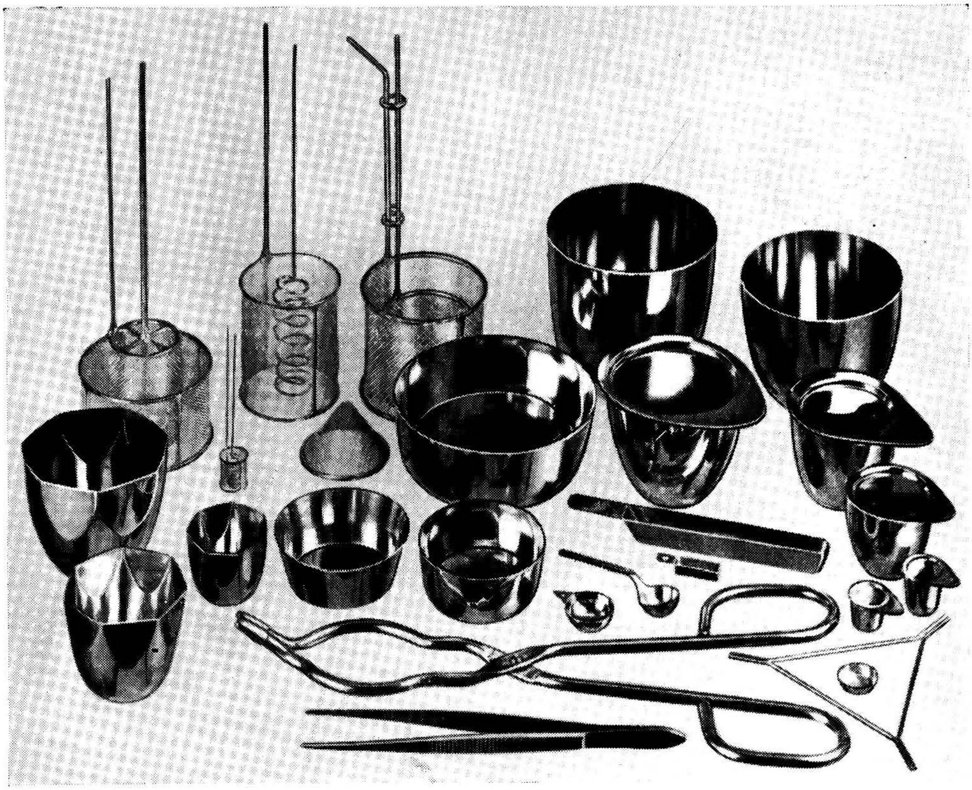

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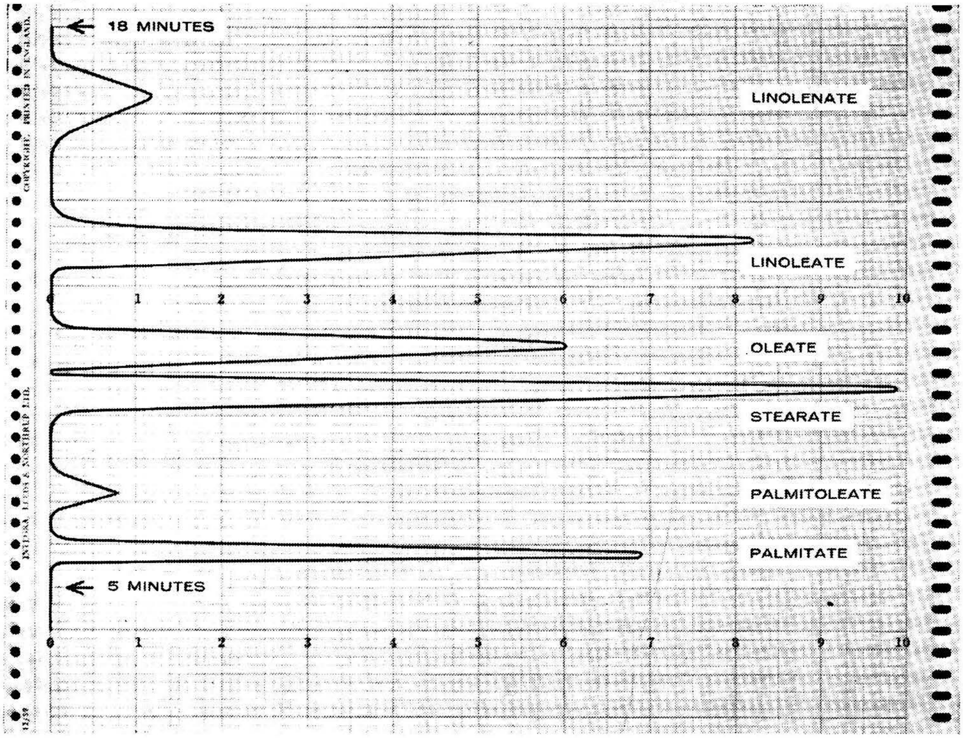

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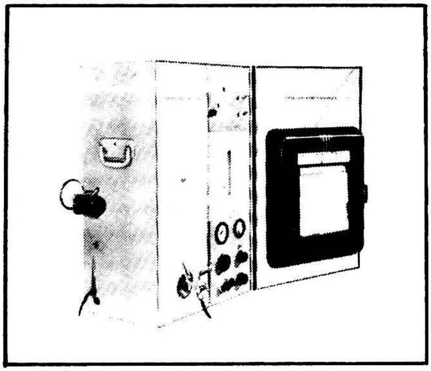

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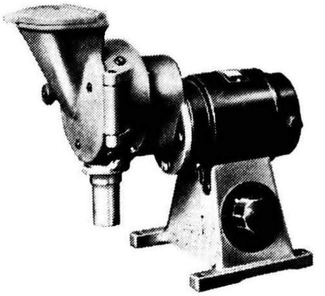

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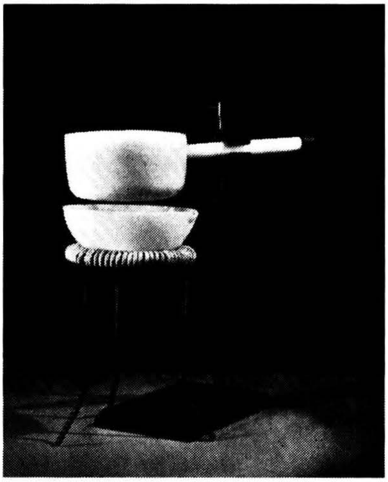

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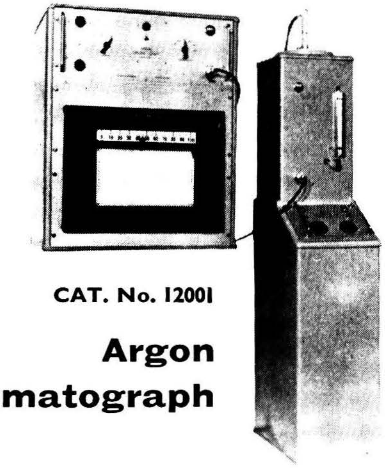

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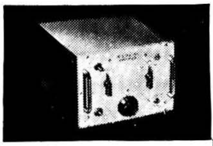

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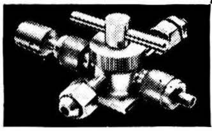

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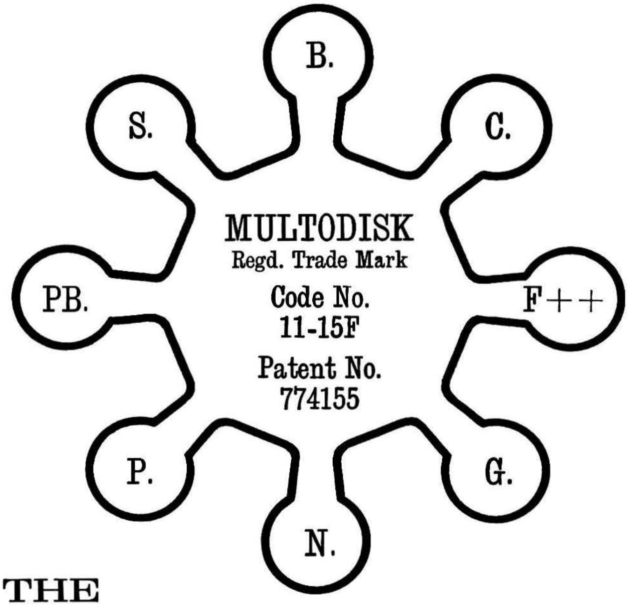
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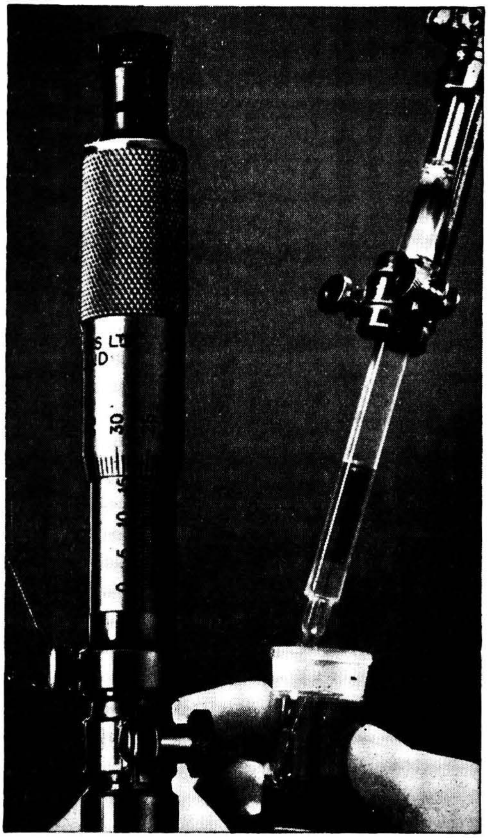

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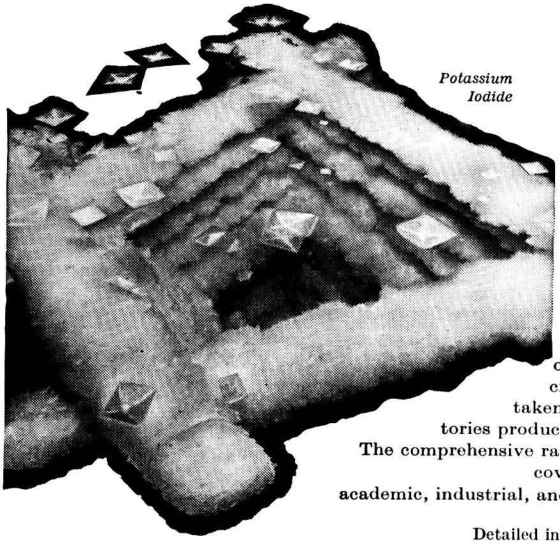
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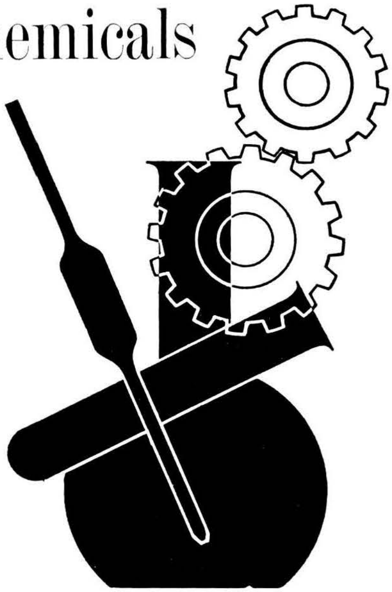

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THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

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