# The ANALYST

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# THE ANALYST

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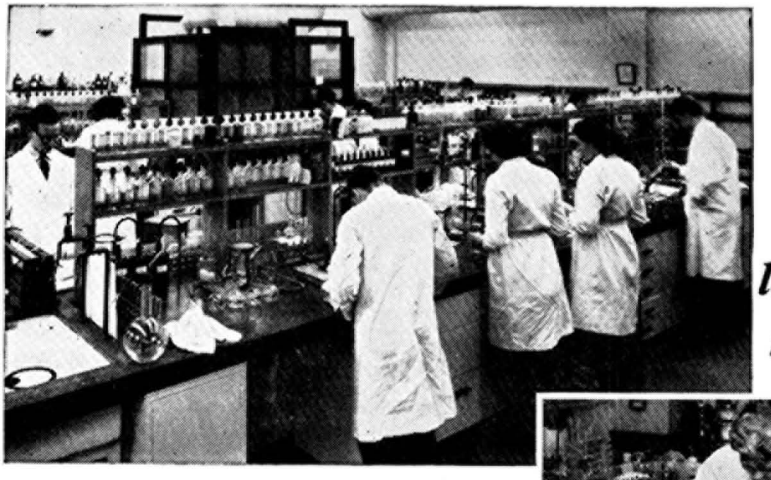
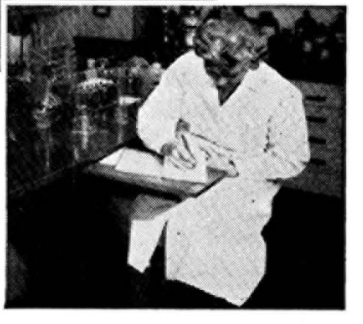
# Incidental information

No. 17

## *Items of interest from our laboratory notebooks*





### 9-(4-Dimethylaminophenyl)-2,3,7-trihydroxy-6-fluorone

A reagent for the spectrophotometric determination of **Ta** in the presence of **Zr, Nb** or **Ti.** (see V. A. Nazarenko and M. B. Shustova, *Zavodskaya Lab.* **2B,** 1283 (1957); C.A. **53,** 13874c (1959)). CODE 3862·3. Price 1g 9/9, 5g 40/-.

### 1,3-Diphenylpropan-1,3-dione (Dibenzoylmethane)

A reagent for the spectrophotometric determination of **U.** A procedure that includes ion-exchange separation from **Th** is described by H. J. Seim *et al. Anal. Chem.* **31,** 957 (1959). CODE 4004·45. Price 5g 7/6, 10g 13/6.

### 4-(2-Pyridylazo)-resorcinol, sodium salt (PAR)

An extremely sensitive reagent for the colorimetric determination of **Co, Pb** and **U.** (see F. H. Pollard *et al. Anal. Chim. Acta* **20,** 26 (1959)). CODE 7275·5. Price 1g 6/-, 5g 22/9, 10g 44/-.

### *o*-(Hydroxymercuri)-benzoic acid

A titrimetric reagent for $S^{2-}$, **thiourea, xanthates, mercaptans** and many other organic sulphur compounds. (see M. Wronski *Analyst* **83,** 314 (1958)). CODE 4691. Price 1g, 12/6, 5g 52/6.

### Phenyl 2-pyridyl-ketoxime

A colorimetric reagent for the determination of iron in strong alkalis and of **"oxidised" iron** in the presence of metallic iron. (see F. Trusell and H. Diehl *Anal. Chem.* **31,** 1978 (1959)). CODE 6711. Price 1g 30/-, 5g 135/-.

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# THE ANALYST

## PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

### ANNUAL GENERAL MEETING

THE eighty-eighth Annual General Meeting of the Society was held at 4.30 p.m. on Wednesday, March 7th, 1962, at the Midland Hotel, Peter Street, Manchester, 2. The Chair was occupied by the President, Dr. A. J. Amos, O.B.E., F.R.I.C. The Financial Statement for the year ending October 31st, 1961, was presented by the Honorary Treasurer and approved, and the Auditors for 1962 were appointed. The Report of the Council for the year ending March, 1962 (see pp. 324–333), was presented by the Honorary Secretary and adopted.

The Scrutineers, Messrs. J. B. Attrill and B. Hulme, reported that the following had been elected officers for the coming year—

*President*—A. J. Amos, O.B.E., Ph.D., B.Sc., F.R.I.C.

*Past Presidents serving on the Council*—R. C. Chirnside, J. H. Hamence, D. W. Kent-Jones and K. A. Williams.

*Vice-Presidents*—A. L. Bacharach, J. R. Edisbury and F. C. J. Poulton.

*Honorary Treasurer*—D. T. Lewis.

*Honorary Secretary*—R. E. Stuckey.

*Honorary Assistant Secretaries*—C. A. Johnson (Programmes) and S. A. Price.

*Other Members of Council*—The Scrutineers further reported that 535 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—A. A. Smales, 419; H. E. Brookes, 391; B. S. Cooper, 347; R. M. Pearson, 331; P. F. S. Cartwright, 304; J. F. Herringshaw, 293; D. I. Coomber, 260; R. J. Magee, 254; E. Cowley, 225.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—H. E. Brookes, P. F. S. Cartwright, B. S. Cooper, J. F. Herringshaw, R. M. Pearson and A. A. Smales.

S. G. Burgess, R. A. Chalmers, D. C. Garratt, S. H. Jenkins, C. A. Parker and D. W. Wilson, having been elected members of the Council in 1961, will, by the Society's Articles of Association, remain members of the Council for 1962.

J. Markland (Chairman of the North of England Section), A. F. Williams (Chairman of the Scottish Section), F. H. Pollard (Chairman of the Western Section), H. C. Smith (Chairman of the Midlands Section), C. Whalley (Chairman of the Microchemistry Group), W. Cule Davies (Chairman of the Physical Methods Group) and J. S. Simpson (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1962.

After the business outlined above had been completed, the meeting was opened to visitors, and Dr. D. W. Hill, D.Sc., Ph.D., F.R.I.C., F.T.I., delivered the Bernard Dyer Memorial Lecture (see pp. 324–341). At the close of the meeting the President presented Dr. Hill with the Bernard Dyer Memorial Medal.

## ORDINARY MEETING

An Ordinary Meeting of the Society was held at 2.45 p.m. on Wednesday, May 2nd, 1962, at the Wellcome Building, Euston Road, London, N.W.1.

The subject of the meeting was "The Determination of Sterols." At the afternoon session the Chair was taken by Professor R. A. Morton, F.R.S., and the following papers were presented and discussed: "Determination of Cholesterol for Clinical Purposes," by G. S. Boyd, Ph.D., A.H.-W.C., A.R.I.C.; "Determination of Cholesterol and its 7-dehydro Derivatives," by J. Glover, M.Sc., Ph.D., A.R.I.C.; "Determination of Vitamin D Secosterols," by E. Kodicek, M.D., Ph.D. The Chair at the evening session was taken by Dr. R. P. Cook and the following papers were presented and discussed: "Gas Chromatographic Examination of Sterols," by C. J. W. Brooks, Ph.D., A.R.I.C.; "The Determination of Animal Fat in Vegetable Fats by Gas Chromatographic Analysis," by K. R. Beerthuis, Dr.Chem.; "The Determination of Plant Sterols," by Professor T. W. Goodwin, D.Sc., F.R.I.C.; "Determination of Sterols of Wool Wax and Related Materials," by E. V. Truter, Ph.D., A.R.C.S., D.I.C.

## NEW MEMBERS

### Ordinary Members

Michael Roland Adams; Allan William Ashbrook; Harold Moritz Bee, B.Sc.(Lond.), A.R.I.C.; Robert William Bolland, B.Sc., Ph.D.(Lond.), A.R.I.C.; Kenneth John Carpenter, M.A., Ph.D.; Felicity Ann Cooper, B.A.(Cantab.); Kenneth Eley, M.P.S.; William John Fisher, A.C.T.(Birm.); Norman Henry Goddard, A.R.I.C.; Walter Harry Harper; Charles Henry Hughes, A.R.I.C.; Royston Arthur Jackson; Peter David Jones; Zuhair Matti Kassir, B.Sc. (Baghdad); Richard Hedley Moulson Keeble; Hubert Joost Kraaijeveld, B.Sc.(Glas.); Peter Longbottom, B.Sc.(Lond.); James Charles Manuel; George Victor Robert Mattock, B.Sc., Ph.D.(Lond.), A.R.I.C.; Derrick Moore; John C. Morrison, B.Sc., Ph.D.(Glas.), M.P.S., A.R.C.S.T.; Arthur Frederick Moyles, B.Sc.(Lond.); Dudley Mellor Peake, B.Sc.(Lond.), A.R.I.C.; Reginald Francis Phillips, M.A., B.Sc.(Oxon.), Ph.D.; Alyn Newton Roberts, A.R.I.C.; Thomas Hall Singleton; William John Stainsby, B.Sc., Ph.D.(Liv.), F.R.I.C.; James Morris Sturton, B.Sc.(Birm.), A.R.I.C.; Eric Thompson, A.R.I.C.; Christopher Henry Thorpe, B.Sc.(Lond.); Antony Inman Cecil Watts, A.R.I.C.

### Junior Members

Bryan John Alexander, B.A.(Cantab.); James Sabeston Caslaw; Paul Francis Knight, B.Sc. (Leic.); Brian Michael Lawrence; Ernest John Putman, B.Sc.(Leeds); Arthur McGruther Smith, B.Sc.(Glas.); Keith Martin Smith.

## SCOTTISH SECTION

An Ordinary Meeting of the Section was held at 7.15 p.m. on Friday, March 23rd, 1962, at the Royal College of Science and Technology, George Street, Glasgow, C.1. The Chair was taken by the Chairman of the Section, Mr. A. F. Williams, B.Sc., F.R.I.C.

The following paper was presented and discussed: "The History of Food Technology," by T. McLachlan, D.C.M., A.C.G.F.C., F.R.I.C., M.I.Biol.

## WESTERN SECTION AND PHYSICAL METHODS GROUP

A Joint Meeting of the Western Section and the Physical Methods Group with the South Wales Section of the Royal Institute of Chemistry was held at 6.30 p.m. on Friday, March 6th, 1962, in the Chemistry Department, University College, Singleton Park, Swansea. The Chair was taken by the Chairman of the Physical Methods Group, Dr. W. Cule Davies, F.R.I.C.

The subject of the meeting was "Fluorescence" and the following papers were presented and discussed: "Spectrofluorimetry," by C. A. Parker, B.Sc., Ph.D., F.R.I.C.; "X-ray Fluorescence Analysis," by R. J. Otter, B.Sc., Ph.D. (see summary below).

### X-Ray Fluorescence Analysis

Dr. R. J. Otter said that X-ray fluorescence analysis was the most powerful technique for elemental analysis that had been developed in recent years, and it had been applied in all types of industries. Its advantages were that over eighty elements could be determined both rapidly and accurately, and that it could be used for concentrations ranging from the parts per million level up to 70 per cent.

He briefly discussed the nature and origin of fluorescent X-ray spectra and the Philip's plane-crystal spectrometer used at Billingham was described.

Quantitative analysis was carried out by comparing samples with standards; these might be chemical or synthetic standards. The standards had to be as much like the samples as possible, both in their total compositions and their physical forms, otherwise matrix inter-element effects occurred owing to the different absorption properties of the matrix. Specific inter-element effects occurred if the radiation from one element was absorbed by another and therefore enhanced the radiation of the other. These inter-element effects were well understood and could be predicted and sometimes calculated.

The accuracy of X-ray fluoresence analysis depended on three main factors. These were counting errors, instrumental errors and sampling errors. Counting errors could always be calculated and instrumental errors could be minimised by the calibration techniques. The sample preparation had to be carefully controlled, so that all samples and standards had the same bulk density and surface finish. It was often possible to achieve a coefficient of variation of 1 per cent. or less.

Samples could be solid, including powders and pellets, or liquid and some special sample forms, such as deposits on thin sheets of paper, could also be examined. The analytical procedures were determined to a large extent by the sample form and some examples were discussed in detail in order to illustrate the methods of sample preparation and standardisation used, and to show how inter-element effects could be overcome. Values of the accuracy and the limits of detection were quoted in each case, together with the time required for the determination. The examples chosen included the determination of trace elements in liquids and solids, the determination of silica in cements, the analysis of metals and catalysts, the determination of silver on photographic film and of lead on filter-paper.

## MIDLANDS SECTION

The Seventh Annual General Meeting of the Section was held at 6.30 p.m. on Thursday, March 8th, 1962, at Regent House, St. Philip's Place, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. H. C. Smith, F.R.I.C., Dip.Ed. The following appointments were made for the ensuing year:—*Chairman*—Dr. H. C. Smith. *Vice-Chairman*—Mr. W. H. Stephenson. *Hon. Secretary*—Mr. G. W. Cherry, 48 George Frederick Road, Sutton Coldfield, Warwickshire. *Hon. Treasurer*—Mr. F. C. J. Poulton. *Hon. Assistant Secretary*—Mr. R. Adkins. *Members of Committee*—Mr. J. B. Aldred, Mr. B. E. Balfour, Dr. R. G. H. B. Boddy, Mr. H. J. C. Challis, Mr. W. T. Elwell, Mr. N. Nix, Mr. A. Turner and Mr. C. Whalley. Miss M. E. Tunnicliffe and Mr. J. Blenkin were re-appointed as Hon. Auditors.

An Ordinary Meeting of the Section was held at 7 p.m. on Thursday, March 29th, 1962, in the Nottingham and District Technical College, Burton Street, Nottingham. The Chair was taken by the Chairman of the Section, Dr. H. C. Smith, F.R.I.C., Dip.Ed.

The following paper was presented and discussed: "Applications of Radioisotopes in Analysis," by D. Gibbons, B.Sc., Ph.D., A.R.I.C.

## MICROCHEMISTRY GROUP

The thirty-fourth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, March 28th, 1962, at "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Vice-Chairman of the Group, Miss M. Corner, B.Sc., F.R.I.C.

The subject discussed was "Do-it-yourself Ideas in Microchemical Apparatus."

# Annual Report of the Council: March, 1962

THE last Annual Report of the Council—presented in March, 1961—recorded the increasing activities of the Society, the year being particularly notable for the fact that three major Symposia were held, two in London and one in Edinburgh. Such Symposia, although organised jointly with other Societies, require much time and effort, and it is not surprising that the meetings held during the past year have not been so ambitious. Nevertheless, the Programmes Committee is taking an increasing part in the Society's development and has continued to provide meetings of wide interest. One particularly successful meeting—a demonstration meeting of laboratory-built equipment—was held at the Chelsea College of Science and Technology in March. The Committee is continuing to cover the whole field of analysis and also to organise joint meetings with other bodies; a full programme has been planned for the 1962–63 Session. Dr. Haslam has resigned as Chairman of the Committee; his place has been taken by the immediate Past President, Mr. R. C. Chirnside; Mr. C. A. Johnson has replaced Mr. L. Brealey as Honorary Secretary.

The membership of the Society has again increased this year. For the first time in the Society's history the membership has exceeded 2000, the figure now being 2053, an increase of 55 over the membership last year. Although not spectacular, the steady and sustained increases in the number of members are particularly gratifying, there having been an increase of 395 from 1658 in 1954 to the present level.

For the second time in recent years the Society's Annual General Meeting is being held outside London. This time, at the invitation of the North of England Section, the Annual General Meeting and the Bernard Dyer Memorial Lecture are being held in Manchester, and it is hoped that this meeting and lecture will achieve the success of the meeting held in Birmingham in March, 1960.

The work of the Analytical Methods Committee is still increasing, and the appeal to Industrial and other organisations for funds has been successful, the total annual contributions for the coming year amounting to over £6000. Reports published during the current year included one by the Meat Products Sub-Committee—"Nitrogen Factors for Pork"—and another relating to the colorimetric determination of rotenone.

During the current year Council appointed a small Committee to consider the future development of *The Analyst*. The Society's finances are, to a large extent, linked with *The Analyst* and *Analytical Abstracts*, and both these journals continue to be successful financially. However, with the present increase in the volume and extent of publications in the analytical field, it was thought that the scope and the development of *The Analyst* ought to be reviewed periodically. With this in mind, opinions and comment have been sought from Society members working for official bodies, in universities and in industry. A report to Council is being prepared.

During 1956 the Society's headquarters and staff moved to the present offices at 14 Belgrave Square. The increase in the Society's work, in particular that of *Analytical Abstracts* and the Analytical Methods Committee, has meant that the available space is now fully occupied, and Council is giving some attention to the possibility of expansion.

The Council records with particular pleasure the award of the O.B.E. to the President, Dr. A. J. Amos. Council also records with pleasure the award of a Baronetcy to Sir Harry Jephcott, and the award of the O.B.E. to Dr. F. H. Banfield, Dr. E. Downing and Dr. H. J. T. Ellingham.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to Dr. R. T. Colgate, O.B.E., Dr. R. E. Essery, Mr. H. D. G. Holt, Mr. G. L. Hutchison, Mr. F. Major, Mr. T. McLachlan, D.C.M., and Mr. F. S. Shadbolt, who have completed 40 years of membership.

DEATHS—The Council regrets to have to record the deaths of the following members—

| | | |
|---|---|---|
| D. G. Allen | T. Cockburn | A. A. Henly |
| G. A. Bracewell | L. Eynon (Past President) | H. W. Hodgson |
| H. T. S. Britton | A. E. Fletcher | R. A. McNicol |
| E. P. Campbell | A. French | D. F. Phillips |
| C. L. L. Claremont | G. F. Hall | C. H. Wordsworth |

SOCIETY MEETINGS—Seven meetings of the Society were held during the year and the papers read and discussed were—

March, 1961, in London, Meeting for the Demonstration of Laboratory-made Equipment:

The pieces of apparatus shown at this meeting are listed in *The Analyst*, 1961, **86**, 277.

April, 1961, in London, Joint Meeting with the Oil and Colour Chemists Association:

"Some Problems in the Analysis of Surface Coating Materials," by C. Whalley, B.Sc., F.R.I.C.
"The Examination of Mixed Solvents Obtained from Plastic Adhesives, Lacquers and Surface Coating Preparations," by J. Haslam, D.Sc., F.R.I.C., A. R. Jeffs and H. A. Willis, B.Sc.
"The Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry," by D. R. Duncan, Ph.D., B.Sc.

May, 1961, in London:

"The Combustion of Organic Compounds by Ignition in Oxygen: the Determination of Carbon and Hydrogen," by G. Ingram, A.R.I.C.
"Use of Induction Heating in Carbon and Hydrogen Determinations," by Mrs. D. E. Butterworth.
"The Determination of Citronellol in Admixture with Geraniol: Further Studies of Formylation Reactions by Gas - Liquid Chromatography," by D. Holness, B.A.
"The Detection of 'Additional Elements' in Plastic Materials by the Oxygen Flask Combustion Method," by J. Haslam, D.Sc., F.R.I.C., J. B. Hamilton and D. C. M. Squirrell, B.Sc., F.R.I.C.

October, 1961, in London, two-day Meeting on Advances in Analytical Chemistry: Selected Topics Originating from Analytical Requirements in the Field of Nuclear Technology:

"Studies of the Boron - Curcumin Complex and its Use in Trace Boron Analysis," by M. R. Hayes, A.R.I.C., and J. Metcalfe, B.Sc.
"Applications of Micro-coulometry," by R. G. Monk, A.R.C.S., D.I.C., Ph.D., K. C. Steed and G. C. Goode, B.Sc., A.R.I.C.
"The Gravimetric Determination of Uranium as the Phosphate," by J. S. Wright, J. A. Ryan, A.R.I.C., and T. J. Hayes, A.R.I.C.
"A Study of the Determination of Oxgyen in Beryllium by Vacuum Fusion," by M. R. Everett and J. E. Thompson.
"The Application of the Conductimetric Method for the Determination of Carbon to Highly Alloyed Steels and the Less Common Metals," by J. E. Still, B.Sc., F.R.I.C., and I. R. Green, A.R.I.C.
"The Identification and Determination of Foreign Phases and Constituents in Metals, with Special Reference to Beryllium," by H. P. Rooksby, B.Sc., F.Inst.P., and I. R. Green, A.R.I.C.
"Developments in Emission Spectrography Arising from the Routine Determination of the Isotopic Abundance of Uranium," by R. Franklin and J. R. Hartley, B.Sc., A.R.I.C.
"Suspension Scintillation Counting of Carbon-14 Barium Carbonate," by H. J. Cluley, M.Sc., Ph.D., F.R.I.C.
"The Use of Isotope Dilution for the Determination of Hydrogen in Metals, with Particular Reference to Alkali Metals," by C. Evans, B.Sc., Dip.Chem.Eng., and J. Herrington, B.Sc.
"Reverse-phase Partition Chromatography," by T. J. Hayes, A.R.I.C., and A. Hamlin, B.Sc., F.R.I.C.
"Gas Chromatography in the Analysis of Inorganic Systems," by T. R. Phillips, Ph.D., B.Sc., and G. Iveson.
"The Analysis of Nuclear Reactor Carbon Dioxide for Gaseous Impurities," by R. M. S. Hall, M.A., A.R.I.C., A.Inst.P.

November, 1961, in London:

"Precipitation from Homogeneous Solution by Cation Release at Constant pH," by P. F. S. Cartwright, M.Sc., F.R.I.C.
"The Application of Atomic Absorption to the Rapid Determination of Magnesium in Electronic Nickel and Nickel Alloys," by T. R. Andrew, B.Sc., F.R.I.C., and P. N. R. Nichols.
"Rapid Identification and Determination of Residues of Chlorinated Pesticides in Crops by Gas - Liquid Chromatography," by E. S. Goodwin, A.R.I.C., R. Goulden, F.R.I.C., and J. G. Reynolds, F.R.I.C.

December, 1961, in London, Joint Meeting with the Infra Red Discussion Group on Applications of Infrared Spectroscopy to Quantitative Analysis:

Introductory Paper by W. R. Ward, M.A.
"The Analysis of Agricultural Chemicals by Infrared Spectroscopy," by P. G. Marshall, M.A.
"Quantitative Analysis of Milk and Other Emulsions by Infrared Absorption Spectroscopy," by J. D. S. Goulden, B.Sc., Ph.D.
"Quantitative Analysis of Phosphonitrilic Chloride Polymer Mixtures by Infrared Spectroscopy," by A. C. Chapman, B.Sc., Ph.D., A.Inst.P., R. T. Baggott, R. Harper and Miss I. Walker.
"Some Applications of Infrared Spectroscopy to Quantitative Analysis in the Pharmaceutical Industry," by H. D. C. Rapson, B.Sc., Ph.D., D.I.C., K. W. Austin and E. A. Cutmore, M.Sc.

February, 1962, in London, on New Analytical Reagents in Colorimetric Analysis:

"The Search for New Reagents for Absorptiometry: Some Theoretical Considerations," by Professor H. M. N. H. Irving, M.A., D.Phil., D.Sc., F.R.I.C., L.R.A.M.
"A Critical Examination of Some Chloranilates as Colorimetric Reagents," by J. T. Yardley, B.Sc., F.R.I.C.
"The Search for New Reagents for Absorptiometry: Some Practical Considerations," by T. S. West, B.Sc., Ph.D., A.R.I.C.
"Alizarin Complexan," by M. A. Leonard, B.Sc., Ph.D.
"Colorimetric Reagents for Iron," by E. J. Newman, B.Sc., A.R.I.C., and H. J. Cluley, M.Sc., Ph.D., F.R.I.C.

## Sections and Groups

The present membership of the Society and its Sections and Groups, as will be seen from the reports that follow, is—

| | |
|---|---|
| The Society | 2053 |
| North of England Section | 419 |
| Scottish Section | 123 |
| Western Section | 115 |
| Midlands Section | 357 |
| Microchemistry Group | 757 |
| Physical Methods Group | 844 |
| Biological Methods Group | 316 |

North of England section—The membership of the Section is 419, compared with 430 last year. During 1961, nine meetings were held including six Joint Meetings and the usual Summer Meeting. The papers read and discussed were—

Manchester, January, 1961, Annual General Meeting:

The Chairman's Address, by J. R. Edisbury, D.Sc., Ph.D.

Liverpool, March, 1961, jointly with the Physical Methods Group:

"X-ray Fluorescence in General Analysis," by D. E. Bromley, B.Sc., A.Inst.P.
"The Use of Radioactive Isotopes in Simple X-ray Fluorescent Analysis," by C. E. Mellish, B.A., D.Phil.
"Analysis by Nuclear Magnetic Resonance Techniques," by D. J. Ferrett, M.A., D.Phil.

Carlisle, April, 1961, jointly with the Scottish Section:

"The Determination of Nitrates and the Application of 'Dead-stop' Titrimetry," by A. F. Williams, B.Sc., F.R.I.C.
"Ion-exchange Resins as Analytical Tools," by T. R. E. Kressman, B.Sc., Ph.D., F.R.I.C.

Scarborough, June, 1961, Summer Meeting:

"Automation," by H. A. Thomas, D.Sc., M.Sc., M.I.E.E., S.M.I.R.E.

Liverpool, September, 1961:

"Some Analytical Problems in the Baking Industry," by R. A. Knight, B.Sc., F.R.I.C.

Sheffield, October, 1961, jointly with the Physical Methods Group and the Modern Methods of Analysis Group of the Sheffield Metallurgical Association:

"Application of Atomic-absorption Spectrophotometry to Metallurgical Analysis," by W. T. Elwell, F.R.I.C.
"Some Interferences in Flame Photometry," by M. S. W. Webb, B.Pharm., F.P.S., F.R.I.C., and P. C. Wildy, B.Sc.

Lancaster, October, 1961, jointly with the North Lancashire Section of the Royal Institute of Chemistry:

"The Analysis of Edible Oils Contaminated with Synthetic Ester Lubricants," by G. B. Crump, B.Sc., A.R.I.C.

Newcastle, November, 1961, jointly with the Newcastle upon Tyne and North-East Coast Section of the Royal Institute of Chemistry:

"Chemical Services on British Railways," by G. H. Wyatt, B.Sc., Ph.D., F.R.I.C.

Manchester, December, 1961, jointly with the Manchester and District Section of the Royal Institute of Chemistry:

"The Design and Construction of Laboratories," by R. R. Young, F.R.I.B.A., and P. J. Harrington.

SCOTTISH SECTION—Membership of the Section stands at 123 against last year's total of 127.

During 1961, eight meetings have been held by the Section, of which five were in Glasgow and one each in Edinburgh, Aberdeen and Carlisle. The last was a Joint Meeting with the North of England Section, as a follow-up to the similar venture of September, 1959, and it proved equally successful. The emphasis on Joint Meetings was maintained, two Glasgow meetings having been held jointly, one each with the local Sections of the Royal Institute of Chemistry and The Society of Chemical Industry, and another the annual "Conjoint" meeting sponsored by all four Chartered Bodies.

Continuing the policy of holding at least one meeting outside the main centres, Glasgow and Edinburgh, the Section met in Aberdeen University in October.

The Committee record their pleasure in the representation of the Society at the Ramsay Dinner by the President, who ably proposed the toast to "The City of Glasgow," to which the Lord Provost made reply.

The papers presented and discussed were—

Glasgow, January, 1961, Annual General Meeting:

"Chemical Research in the Electricity Supply Industry," by J. M. Ward, B.Sc., F.R.I.C.

Glasgow, February, 1961:

"Applications of Ion-exchange in Inorganic Analytical Chemistry," by R. A. Wells, B.Sc., F.R.I.C., M.I.M.M.
"Ion-exchange in the Electroplating Industry," by V. E. Gripp, B.Sc., A.R.C.S., A.R.I.C.

Glasgow, March, 1961:

"The Titration of Weak Acids in Non-aqueous Solvents," by G. R. Jamieson, B.Sc., F.R.I.C.
"High-frequency End-point Detection in Non-aqueous Titrimetry," by E. S. Lane, B.Sc., Ph.D., F.R.I.C.

Carlisle, April, 1961, jointly with the North of England Section:

Details of the papers read at this meeting are given in the report on the North of England Section.

Glasgow, October, 1961, jointly with the Glasgow Section of the Society of Chemical Industry, on Pentaerythritol:

"The Applications of Pentaerythritol," by A. W. E. Staddon, B.Sc.
"Analysis of Pentaerythritol," by A. F. Williams, B.Sc., F.R.I.C.

Aberdeen, October, 1961:

"Stannous Acetate as a Primary Standard," by W. Moser, B.Sc., A.R.I.C., and W. B. Simpson, B.Sc.
"Some Seldom-remembered Aspects of Analytical Technique," by R. A. Chalmers, B.Sc., Ph.D.
"The Analytical Chemistry of Technetium and Rhenium," by R. J. Magee, M.Sc., Ph.D., A.R.I.C.

Edinburgh, November, 1961:

"Recent Developments in Chromatography on Cellulose and Ion-exchange Cellulose," by N. F. Kember, A.R.P.S., A.R.I.C.

Glasgow, December, 1961, jointly with the Glasgow Sections of the Chemical Society and the Society of Chemical Industry and the Glasgow and West of Scotland Section of the Royal Institute of Chemistry:

"The Structure of Natural Products by Direct X-ray Analysis," by Professor J. Monteath Robertson, M.A., Ph.D., D.Sc., F.Inst.P., F.R.I.C., F.R.S.E., F.R.S.

WESTERN SECTION—The membership of the Section stands at 115, compared with a total of 102 last year.

Since the beginning of 1961 the Section has held eight meetings including the A.G.M. As is customary all of them have been joint meetings with the local sections of the Royal Institute of Chemistry or other bodies. The venue of the meetings has been rather more circumscribed than usual, and most have been held within 50 miles of Cardiff. Attendances have been quite good.

The papers presented and discussed were—

January, 1961, Bristol, Annual General Meeting, followed by joint meeting with the Bristol and District Section of the Royal Institute of Chemistry:

"The Analysis of Plastics," by J. Haslam, D.Sc., F.R.I.C.

March, 1961, Gloucester, jointly with the Bristol and District Section of the Royal Institute of Chemistry:

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

March, 1961, Swansea, jointly with the South Wales Section of the Royal Institute of Chemistry:

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

April, 1961, Cardiff, jointly with the Cardiff and District Section of the Royal Institute of Chemistry and the South Wales Section and the Food Group of the Society of Chemical Industry:

"Modern Legislation in Relation to Food Additives," by C. A. Adams, C.B.E., B.Sc., F.R.I.C., Barrister-at-Law.

May, 1961, Hereford, Summer Meeting jointly with the Midlands Section:

Film on "An Introduction to Ion Exchange."
"The Application of Ion-exchange Resins to Metallurgical Analysis," by J. R. Miller, M.A., F.R.I.C.

October, 1961, Salisbury, jointly with the Microchemistry Group and the Mid-Southern Counties Section of the Royal Institute of Chemistry on Trace Analysis in Archaeology:

"Analytical Techniques in Archaeology and the Arts," by E. T. Hall, M.A., D.Phil.
"The Applications of Spectroscopy to the Study of Roman and Medieval Glazed Pottery," by J. W. G. Musty, A.R.I.C.

November, 1961, Cheltenham, jointly with the Bristol and District Section of the Royal Institute of Chemistry:

Film on "Pembrokeshire, My County," from Esso Petroleum Co. Ltd.
Film on "The Twilight Forest," from Unilever Ltd.

December, 1961, Cardiff, jointly with the Cardiff and District Section of the Royal Institute of Chemistry:

"Analytical Research," by J. Haslam, D.Sc., F.R.I.C.

MIDLANDS SECTION—The membership of the Section is 357, consisting of 343 ordinary members and 14 junior members. This is a total increase of 14 members during the year. There are 9 Honorary Members of the Section.

Thirteen meetings were held during the year: 6 in Birmingham, 3 in Nottingham and 1 each in Wolverhampton, Coventry, Luton and Hereford. A joint meeting, at which a distinguished foreign lecturer was invited to speak, was again held with the Birmingham and Midlands Section of the Royal Institute of Chemistry. The lecturer this year was Professor L. Erdey of Budapest University.

*Elwell Award*, 1961—This annual award for the best paper on some aspect of analytical chemistry was won by Mr. M. L. Richardson, A.R.I.C., A.C.T., of John & E. Sturge Ltd., for his paper on "The Determination of Manganese in High-quality Calcium Carbonate by Means of Tetraphenylarsonium Chloride".

The papers presented and discussed were—

January, 1961, Wolverhampton:

"Polarography for Trace Analysis," by Mrs. B. Lamb, B.Sc.

February, 1961, Birmingham, jointly with the Association of Clinical Biochemists:

"The Use of Vapour-phase Chromatography in the Study of Human Lipid Metabolism," by H. G. Sammons, B.Sc., Ph.D.
"Some Recent Developments in Paper Chromatography," by C. S. Knight, M.Sc., Ph.D., A.R.I.C.

March, 1961, Luton:

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

March, 1961, Birmingham:

Annual General Meeting.

March, 1961, Nottingham:

"The Measurement of pH and Electrode Potential for Analytical Purposes," by G. Mattock, B.Sc., Ph.D., A.R.I.C.

April, 1961, Birmingham, jointly with the Physical Methods Group:

"Spectrofluorimetry," by C. A. Parker, B.Sc., Ph.D., F.R.I.C.
"Teslaluminescence Spectra," by R. J. Magee, M.Sc., Ph.D., F.R.I.C.

May, 1961, Nottingham, jointly with the Microchemistry Group, on Automation in the Analytical Laboratory:

"The Scope of Automation in the Laboratory," by G. Mattock, B.Sc., Ph.D., A.R.I.C.
"A Colorimetric-type Instrument for the Continuous and Automatic Analysis of Gases in the p.p.m. Range" and "An Automatic Titrimeter," by M. Akhtar, Ph.D., M.Sc., D.I.C.

May, 1961, Hereford, joint Summer Meeting with the Western Section:

Details of this meeting are given in the report on the Western Section.

September, 1961, Birmingham: presentation of papers for the Elwell Award, 1961:

"A Simple Chromatographic Gas-analysis Apparatus," by G. Blakemore.
"The Determination of Trace Amounts of Cobalt in Titanium," by J. S. Caslaw.
"The Determination of Manganese in High-quality Calcium Carbonate by Means of Tetraphenylarsonium Chloride," by M. L. Richardson, A.R.I.C., A.C.T.

October, 1961, Birmingham, jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry:

"Research Work in Analytical Chemistry at the Technical University of Budapest," by Professor L. Erdey.

October, 1961, Nottingham:

"Aquametry," by J. H. Thompson, B.Sc., Ph.D., A.R.I.C.

November, 1961, Coventry:

"The Analysis of Finishes on Yarns and Fabrics," by E. Mytum, M.A., F.R.I.C.

December, 1961, Birmingham:

"Fluorescent Indicators for the Determination of Metals," by W. I. Stephen, B.Sc., Ph.D., A.R.I.C.

MICROCHEMISTRY GROUP—The membership of the Group is now 757, an increase of 39 in the past year.

An address of greeting, on behalf of the Society, was presented to the Organising Committee of the International Symposium on Microchemical Techniques at Pennsylvania State University, U.S.A., in August, 1961, by Miss M. Corner, Vice-Chairman of the Group.

During 1961 three Ordinary Meetings of the Group were held: in London on February 24th (the Annual General Meeting of the Group followed by the retiring Chairman's address); in Nottingham on May 12th (jointly with the Midlands Section); in Salisbury on October 20th (jointly with the Western Section and the Mid-Southern Counties Section of the Royal Institute of Chemistry). The papers read were—

London:

"The Determination of Metals by Organic Reagents," by F. Holmes, B.Sc., A.R.I.C.

Nottingham:

Details of the papers read at this meeting are given in the report on the Midlands Section.

Salisbury:

Details of the papers read at this meeting are given in the report on the Western Section.

Five informal discussion meetings were held in London. The topics discussed and the speakers who introduced them were—

"Hydrogenation Methods in Microanalysis," introduced by R. A. D. Smith.
"The Separation and Determination of Traces of Iron," introduced by D. M. Peake and E. J. Newman, B.Sc., A.R.I.C.
"Quantitative Paper Chromatography—Inorganic," introduced by E. C. Hunt, B.Sc., and "Organic," introduced by D. Gross, Ph.D.
"Derivatography as a New Thermoanalytical Method," by Professor L. Erdey.
A Review of all Topics Discussed at these Meetings.

PHYSICAL METHODS GROUP—The number of Group Members is now 844. This is an increase of 62 since the last Annual General Meeting.

During the past year the Group has held six Ordinary Meetings; two were held in London and one each in Liverpool, Birmingham, Sheffield and Nottingham. The Liverpool Meeting was held jointly with the North of England Section, the Birmingham Meeting jointly with the Midlands Section and the Sheffield Meeting jointly with the North of England Section and the Modern Methods of Analysis Group of the Sheffield Metallurgical Association.

The papers read and discussed at the Ordinary Meetings of the Group were—

Atomic Absorption Spectroscopy—London, November, 1960:

"Some Factors Affecting Performance in Atomic-absorption Spectroscopy," by R. Lockyer, B.Sc., F.R.I.C.
"The Flame as a Source of Atoms," by C. A. Baker, M.A., D.Phil.
"The Application of Atomic-absorption Spectroscopy to Metallurgical Analysis," by W. T. Elwell, F.R.I.C., and J. A. F. Gidley, B.Sc., A.Inst.P.

Physical Methods in Medical Research—London, February, 1961:

"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 by Means of a Covered Platinum Electrode," by J. M. Bishop, M.D., M.R.C.P.
"Application of Infrared Spectroscopy to Some Problems of Medical Science," by A. E. Kellie, B.Sc., Ph.D., M.R.C.P.

Analysis of Intact Samples—Liverpool, March, 1961:

Details of the papers read at this meeting are given in the report on the North of England Section.

Birmingham, April, 1961:

Details of the papers read at this meeting are given in the report on the Midlands Section.

Sheffield, October, 1961:

Details of the papers read at this meeting are given in the report on the North of England Section.

Particle Size Analysis—Nottingham, October, 1961:

"Recent Investigations into Sedimentation Methods of Particle-size Analysis," by B. H. Kaye, M.Sc.
"Automatic Scanning Instruments for Counting and Sizing Microscopic Particles," by W. H. Walton, B.Sc., F.Inst.P.
"The Use of an Electrolytic Resistivity Method (Coulter Counter) for Particle-size Analysis," by I. C. Edmundson, B.Pharm., M.P.S.

BIOLOGICAL METHODS GROUP—During the year the membership of the Group has increased from 308 to 316.

In the year ending the Group has held, in addition to the Annual General Meeting, two ordinary meetings and two discussion meetings, and has made one laboratory visit. The papers read and discussed were—

December, 1960, London, Annual General Meeting:

Discussion on "Problems in the Control of Neomycin Quality," introduced by J. W. Lightbown, M.Sc., Dip.Bact.

February, 1961, London:

"The Use of Enzymes in Analysis," by C. J. Threlfall, B.Sc.

April, 1961, London:

Discussion on "The Principles Involved in Collaborative Studies," introduced by S. A. Price, B.Sc., F.R.I.C.

October, 1961, London:

"The Use of Bacteriophages in Epidemiology," by Miss E. M. Wilson, B.Sc.

ANALYTICAL METHODS COMMITTEE—Steady progress of work during the year is reported, despite some difficulties in maintaining an adequate secretariat staff. The total number of committees and panels remains the same (22) as last year. However, towards the end of the year three of these completed their programmes of work and, after approval of their reports for publication, they were disbanded: in return, three new projects for investigation have been proposed by the Joint Committee with the Pharmaceutical Society and as a result of preliminary exploratory work it is fully expected that three new Panels will be appointed early in 1962. In addition, two new Joint Panels of the Society (represented by the Analytical Methods Committee) with the Ministry of Agriculture, Fisheries and Food and the Association of British Manufacturers of Agricultural Chemicals, were appointed during the year on methods for (a) fluoracetamide residues and (b) 'Phosdrin' residues in foodstuffs: the secretariat of these Joint Panels is held by the M.A.F.F.

In addition to the Annual Report of the Committee, 4 Reports of Sub-Committees and Panels and a Report of special investigational work have been published in *The Analyst*. These are—

Reports of Sub-Committees and Panels:

"Nitrogen Factors for Pork," and "Nitrogen Content of Rusk Filler," } by the Meat Products Sub-Committee (*September*).

"The Colorimetric Determination of Rotenone," by the Joint Committee with the Pharmaceutical Society and the S.A.C. (*November*).

Report of Panel (set up jointly by the Scientific Sub-Committee of the Advisory Committee on Poisonous Substances Used in Agriculture and Food Storage, the Analytical Methods Committee of the Society, and the Association of British Manufacturers of Agricultural Chemicals):

"The Determination of Mercury Residues in Apples and Tomatoes" (*September*).

Report of Special Investigational Work:

"The Determination of Citronellol in Admixture with Geraniol," by D. Holness (*April*).

All but four committees have been actively at work during the year (two of these are in abeyance pending the outcome of investigations elsewhere). Special mention may be made of those committees that have completed all, or certain items, of their programmes of work and whose reports have been approved for publication. Two of the Panels of the Additives in Animal Feeding Stuffs Sub-Committee—on Antibiotics and on Synthetic Hormones—have prepared their reports and were disbanded in November: a third Panel, on prophylactics, has also prepared its report on nitrofurazone (a poultry coccidiostat), but it still has a long programme of work for the future: a fourth Panel, on water-soluble vitamins, has also completed its work on methods for Vitamin $B_{12}$, nicotinic acid and pantothenic acid, and the report on these is almost ready. Another Sub-Committee—on Trace Elements in Fertilisers and Feeding Stuffs—has also completed its work on some 20 methods, which are to be published collectively as a separate book. The Metallic Impurities in Organic Matter Sub-Committee has completed another item of its programme of work—on Copper—and it is hoped that the report will be published shortly.

The various Panels of the Joint Committee of the Society with the Pharmaceutical Society have been making progress. That on Lonchocarpus and Derris has recently been disbanded on completion of its programme, its second Report, on a colorimetric method for rotenone, having been published in November. The three new projects, mentioned earlier, now being investigated are on methods for thyroid, duboisia and vanilla.

The Society's second Research Scholar, Dr. J. H. Stevenson, completed his year's work at Rothamsted Experimental Station in October; he is now preparing a full report of his investigations on bio-assay methods for pesticide residues in foodstuffs.

Mr. S. C. Jolly, who was appointed as part-time Publications Secretary at the end of 1960, has made excellent progress on the revision of the Bibliography of Standard, Tentative

and Recommended or Recognised Methods of Analysis (originally published in 1951) and on the editing of all the recommended methods published since 1926 by the Analytical Methods Committee: the collected methods are to be published as the first part of a book that will include the revised and expanded Bibliography as its second part. Most of this book is now at the proof stage.

As in other years, a separate Report of the Analytical Methods Committee, giving full details of the work of all Sub-Committees and Panels, is being prepared and will be circulated to committee members and to all contributors to the Analytical Methods Trust Fund.

LIAISON WITH OTHER SCIENTIFIC ORGANISATIONS—During the year the appointments made were—

Joint Library Committee, Chemical Society:
Dr. J. G. A. Griffiths.
British Iron and Steel Research Association:
Mr. R. C. Chirnside represented the Society at the Fifteenth Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).
Parliamentary and Scientific Committee:
Dr. J. H. Hamence.
Royal Institute of Chemistry, Summer School Organising Committee:
Mr. A. N. Leather and Mr. C. Whalley.
International Congress XIX of Pure and Applied Chemistry, 1963, Scientific Committee:
Mr. C. Whalley.
B.S.I. Committee:
Mr. S. A. Price: Chemical Divisional Council.

The Council of the Society thanks all its representatives for the work they have carried out in the various Committees and at various meetings during the year.

HONORARY TREASURER'S REPORT—The Annual audit has been carried out by the Society's auditors, Messrs. Ridley, Heslop & Sainer, and the accounts and balance sheet for the year ended October 31st, 1961, have been circulated to all members. They show that the Society continues to prosper financially despite the increasing costs of administration and of publication.

Our printers, Messrs. W. Heffer & Sons Ltd., of Cambridge, informed the Society in August, 1961, that a new wages agreement with the Printing Trade Unions would result in the scales of charges for the production of *The Analyst* and *Analytical Abstracts* having to be increased by 10 per cent. In view of these increasing costs, Council has approved that the Society should make increases in its advertising rates. The new rates became operative as from September 1st, 1961, and are considered to be more nearly equivalent to those adopted by similar publications.

On the advice of the Society's brokers, Messrs. C. F. Chance & Co., of London, a further sum of £4819 5s. 8d. has been invested in various companies' shares, and the Society's Schedule of Investments shows the increased total.

Responsibility for the publication of approved Monographs has been accepted by the Society. Monograph No. 1, "Methods for the Analysis of Non-soapy Detergent (NSD) Products," by G. F. Longman and J. Hilton, of Unilever Research Laboratories, was published at the end of August, 1961, and has proved a great success. Because of the increased costs of publication, Council was in general agreement that some charge would have to be made to members of the Society who wished to be provided with copies of Monographs. Council approved that the price to members of any future Monographs be left to the discretion of the Finance Committee.

The revenue from the sales of *The Analyst* and *Analytical Abstracts* increased by nearly £1000. The total return from advertisements in both publications remained sensibly unchanged for the year, but revenue from this source should increase next year as the new rates become effective.

The outlook for 1962 is thus hopeful, but considerable attention will have to be paid to providing some addition to the Society's present office accommodation, which even now cannot provide adequately for the increasing needs of the permanent staff.

PROGRAMMES COMMITTEE—The Committee suffered a double loss at the beginning of the year in the simultaneous retirement of its former Chairman, Dr. J. Haslam, and its Secretary, Mr. L. Brealey. The policy of development referred to in last year's report has been maintained and highly successful joint meetings were held with the Oil and Colour Chemists Association (in April) and the Infra Red Discussion Group (in December). A very well attended Demonstration meeting was held at Chelsea College of Science and Technology in March. As in previous years, two evening meetings were devoted to the presentation of papers submitted for publication in *The Analyst*. Although attendance at these meetings is usually not so satisfactory as at other Society meetings, it is thought that they serve a useful function and it has been decided to retain meetings of this type during the coming session. In October a two-day meeting devoted to Advances in Analytical Chemistry arising from work in the field of Nuclear Technology was held in London, but the attendance was disappointing.

The possibility of holding at least one Society meeting each year in the provinces is being explored and it seems probable that this will become a regular feature in future years.

THE ANALYST—A survey made in August, a time of year when some 95 per cent. of of the year's subscriptions have been received, showed that *The Analyst* (and *Analytical Abstracts*) was being sent to 93 countries besides Great Britain and the Republic of Ireland. Nearly a half of the total circulation (including members of the Society as well as non-member subscribers) was to addresses in Great Britain and the Republic of Ireland, and about one-sixth to the United States of America; the remaining one-third was distributed over the rest of the world. The number of copies of each issue printed during 1961 was 6900; for 1962 this has been raised to 7000.

The 1961 volume of *The Analyst* contained 860 pages; this is slightly less than the previous year's record-breaking total, but is nevertheless greater than the average for 1959 and 1960 (842). Comparison with this average is legitimate, since the dispute in the printing trade in the autumn of 1959 led to some papers that would normally have been published in that year being held over for the 1960 volume. The numbers of papers and notes published bears this out: 102 papers and 59 notes in 1961, which would be compared with 118 and 66 for 1960, but with 103 and 59 if the average for 1959–60 is taken. Seven Review papers were published.

Summaries of 18 papers presented at meetings but not being published in full elsewhere were printed in the Proceedings of the Society, and 59 book reviews appeared.

Thirteen issues of the Bulletin were distributed with *The Analyst* during the year.

ANALYTICAL ABSTRACTS—No changes in the personnel of the Committee have been made in 1961.

The total number of abstracts published in Volume 8, 1961, was 5334 on 708 pages, compared with 5522 on 732 pages in 1960. This reduction is mainly due to the difficulty of maintaining an adequate staff; in spite of this, it has been possible, by being rather more selective, to reduce somewhat the average interval between the dates of publication of the original paper and its abstract.

The Index to 1960 was not published until May 23rd. This was entirely due to the printers being unable to complete by the scheduled date (April 27th).

Professor Saito, who has been our abstractor in Tokyo since we began publication, paid a visit to this country in September. As a result, it has been arranged that two additional abstractors will be appointed in Japan and Professor Saito will be responsible for the coverage of all Japanese journals and for the distribution of the work to these abstractors. This is a voluntary service on Professor Saito's part and should result in a more efficient and prompter service from Japan.

A. J. AMOS, *President.*

R. E. STUCKEY, *Honorary Secretary.*

# The Seventh Bernard Dyer Memorial Lecture
# Research and the National Economy

By D. W. HILL, D.Sc., Ph.D., F.R.I.C., F.T.I.

(*Delivered after the Annual General Meeting of the Society, March 7th,* 1962)

When you did me the honour of inviting me to deliver this, the seventh, Bernard Dyer Memorial Lecture, my intention, knowing Bernard Dyer's reputation as an analyst and consultant, was to speak on the role of the analyst in the textile industry. Unlike some of your earlier speakers in this series I never had the privilege of meeting Bernard Dyer, but as I read more about him and of his contributions to our science it was borne in upon me that he was much more than a technically able analyst. His professional skill was directed towards the improvement of what was then and still is the most basic of all our industries—agriculture—and in pursuit of this objective he carried out his own researches, was an assiduous student of the researches of others, and devoted himself to advising through personal contact and committee work any organisation, Governmental or other, that was committed to the improvement of the industry. It occurred to me, therefore, that Bernard Dyer was at least as much a man of affairs in his chosen field as he was a chemist and that, in consequence, he would welcome as a memorial to himself, a discussion not on a narrow technical field but on a broad canvas with the scientific and technical advance of industry as its background.

It cannot be denied that, in the modern world, scientists, whether they be analysts, research workers, teachers or industrialists, have a peculiar responsibility, deriving, as it did in Bernard Dyer's case, from particular knowledge and the conviction of its value. It cannot be denied that for many years past there has been an obvious malaise in the economy of the country. In the 1930's we had wholesale unemployment, cured only by a major war, and since the war we have had full employment accompanied by regularly recurrent financial crises. To overcome these crises we have tried every weapon in the economic armoury. To quote the *Financial Times* of November 28th, 1961: "We have tried cheap money and dear; physical controls and freedom, convertibility and inconvertibility, Budget deficits and Budget surpluses, reliance on high direct taxation and high indirect taxation, ample money supply and tight devaluation. . . . None of these things either singly or in combination one with the other, has succeeded except quite temporarily, over a period of sixteen years, in achieving our objectives."

What are these objectives? Undoubtedly to combine within the framework of a democratic society, solvency, growth and stability, and at least to maintain and preferably to expand our exports, by which alone we can support in these islands a population of some 50 million people. These objectives are material objectives that can be attained only by material advances and in consequence science and scientific research directed towards industrial development may be expected to have a great contribution to make to the development of the economy.

In attempting to define where we are going it is sometimes of advantage to look back over our shoulders at where we have come from, and we may derive some comfort from a brief study of the past, for it is not unreasonable to hope that what has been achieved may be a foretaste of what may be expected. It is trite to say that our present mode of living is conditioned by the advances of science, applied through industry to the needs of our age. This is the most important development of our time. Its impact may be imagined by trying to visualise a world devoid of its concrete results. Imagine, for example, a world without electricity—no electric light nor heat, no telephone, telegraph nor wireless, no electric power for industry, no motor cars, buses, aeroplanes nor submarines, no cinemas, no products of electro-technology, such as aluminium. Imagine a world without public health, antiseptics, anaesthetics, or all the manifold drugs from aspirin to antibiotics. Imagine a food situation without modern transport, without fertilisers and without refrigeration, in which every man was dependent for his survival literally on the efforts of his own hands.

Imagine, if you can, a world in which the abundant supply of controllable energy, to which we have become accustomed, was no longer available. When we travel by car, or train or aeroplane, we are not only using remarkable inventions produced by men's ingenuity, but we are employing 10, 20, 500 or 2000 horse-power placed at our disposal by science and used virtually without personal effort. It is the capital provided for us by energy converted to power that is the basic achievement upon which we live.

By its discoveries, science has transformed our world. Its inventions have made this civilisation possible and the skill of scientists and technologists keeps it going. Railways and road transport, shipping and aviation were born in the brains of scientists and technologists and are maintained by the application of their skill. The delicate network of communications spread over the face of the earth springs from humble beginnings in scientific laboratories. Vast new industries have been created by science and old ones have been revivified. Before the advent of the internal-combustion engine, natural oil was already an article of commerce, but it has now assumed a role in which it controls the destiny of nations. The demand for light, strong alloys has stimulated the production of new metals. Aluminium, which was exhibited at the Paris Exhibition in 1853 as a chemical curiosity is now produced at a rate of about 4½ million tons a year at a cost of about 1s. 7d. a lb.

The organic-chemical industries were founded on scientific investigations into coal tar, but in mineral oil and natural gas the organic chemist has found new raw materials to form the basis of a new chemical industry. It is within my lifetime that we began to understand the nature of polymers and now we have plastics available, not as substitutes for old materials, but as products most suited to their purpose. Nylon, Terylene and the acrylics are examples of the development of these ideas into the field of fibres.

We must expect new and great industries to arise from the application to industry of the results of scientific research. Our basic industries were built on technical supremacy and our new ones on the avid utilisation of the possibilities inherent in scientific research. Who can doubt, in the light of our past industrial history, that the future of our economy, based as it is upon industrial growth, lies in the acceptance and exploitation of the discoveries of science. The explanation of the financial columns of the newspapers is to be found increasingly in the reports from the research laboratories.

There is, of course, another side to this picture for scientific research has not only provided us with unparalleled advantages, it has also been responsible for some of our greatest problems. The most apparent of these to-day is the unlimited possibilities for destruction unleashed by the discoveries of science. The search for utilisable energy from 1769 when James Watt ushered in the industrial age, through 1831 when Faraday laid the foundations of the electrical industry and 1859 when Colonel Drake discovered oil in Pennsylvania to 1932 when Chadwick discovered the neutron and so cleared the path to the production of nuclear energy has culminated in an unbelievably destructive weapon in the hands of mankind. The control of this power is perhaps the greatest political problem of our time and its application to peaceful ends could be the greatest contribution of our generation to the nation's economy.

There are, however, more subtle ways in which scientific discovery has added to our economic problems. The raw materials upon which our earlier industrial supremacy was established are limited in number. At the beginning of the nineteenth century our growing pre-eminence was largely dependent upon illimitable supplies of easily won coal of high quality. As the then principal source of power, it placed the industrial world at our feet—but technological advance has made the coal fields of other nations comparable in importance to our own and has placed the principal sources of industrial power to-day outside our borders.

Scientific research has redistributed and evened out world resources of other raw materials too. Nitrogen from the Chile saltpetre beds upon which we were once dependent for munitions for war and fertilisers for agriculture has been replaced by the German chemist Haber from the inexhaustible supply of atmospheric nitrogen. Viscose rayon, discovered in Britain, can, as the Germans discovered during the last war, make nations independent of the American cotton belt; and nylon, discovered in America, can make us independent of the Japanese silk-worm.

The redistribution of the importance of raw materials has been accompanied in this century by the industrialisation of our former customers. Everywhere, science and technology has speeded up the rate at which they have been able to undertake for themselves the production of goods that we formerly supplied. The successful prosecution of scientific research implies that old plant, old methods and old products will become obsolete, ousted

from their entrenched positions by new plant, new methods and new products. Newcomers to the industrial scene have a manifest advantage. Great Britain is still to an alarming extent relying upon machinery, methods and products in which vast sums of money have been sunk in the past and which now constitute a millstone around the neck of the economy. Meanwhile, new products and new processes are being exploited by our competitors; and the power to do so has been given them by scientific research.

It is inevitable too, that new discoveries may sometimes produce social problems as well as economic advances. The disturbances that introduced the industrial age are common knowledge, but our national prosperity dated from that introduction. The provision of a desirable product more cheaply or more attractively by a new method may result in the virtual extinction of an industry. The replacement of wrought iron by steel, which could be produced at lower cost and possessed a greater strength-to-weight ratio, was not merely a scientific achievement. It was a force that brought social and economic factors of the first magnitude into play. The puddlers in the iron works, skilled men who had spent a lifetime in the service of wrought iron, became unemployed when puddling became obsolete.

The railway displaced the stage coach, and ostlers, innkeepers, coachmakers and many others saw the end of their employment in sight; but in return, the railways employed drivers, firemen, signalmen, platelayers, engineers, steel-workers and hosts of others. Steam displaced sail and steel displaced wood on the seaways, and craftsmen saw their livelihood slip away from them; but steam and steel made possible the great shipping and allied industries in which hundreds of thousands have since found employment. It may well be that we are now watching aircraft supersede ships; if so, we can be sure that the compensations of employment in the aircraft industry and all the facets of aircraft operation will be as great as those that preceded them. We have barely touched the fringe of the possibilities inherent in computers and automation, but they too will provide employment as well as disturb it. Social problems may indeed arise from scientific research, but the economic welfare of the nation depends now, as always, upon seizing the opportunities presented by new discoveries. Moreover, without the new discoveries we should have been faced by other equally disturbing problems—of poverty, hunger and disease, for example, in an expanding population.

Consideration of the employment provided by industries built upon or largely dependent upon research will give some idea of the economic impact of scientific discoveries. According to the Report on the Census of Production for 1958, the electrical, radio and electronics industries employed about 325,000 persons with a salary bill of £180m. The motor vehicle industry with 340,000 employees paid salaries and wages amounting to nearly £250m. The aircraft industry employed 275,000 persons and paid £190m. Chemicals, dyestuffs and drugs employed 197,000 and paid out £130m. Firms engaged in the production of man-made fibres employed 36,000 and paid out £24m. This list, which could be greatly extended, gives some idea of the material resources provided by industries using science and of the return they afford in the distribution of wealth. The benefits, of course, do not stop at direct employment and direct wages. Thousands more persons are indirectly employed by these industries to provide services and raw materials—coal, oil, iron and steel, paper and other commodities, as well as transport, banking and national and international postal and telegraph services.

It is not unreasonable to suggest from what scientific research has done in the past that we can depend upon it with some confidence for assistance in the future. But, since discovery is no respecter of people or places, the benefit that we can obtain will depend upon our own ability to make the best use of the opportunities offered to us. We, in this country, are not behind others in inventiveness or scientific achievement. Our past history testifies to the ability of our scientists and technicians. Television, radar, antibiotics and jet propulsion, to name only a few, were British discoveries.

No discovery, however, can have any impact upon the economy except through its application and exploitation, and in this we are reputed to lag behind others. In the words of the leading article in *Nature* for December 24th, 1960, we have no "tradition of using the results of scientific and technological advances." We must, therefore, devote ourselves to the twin tasks of discovery and application. Application can only be made of knowledge that is readily available. There must, in fact, be something to apply. This means that, not only must application and development be carried on under full pressure, but that an extensive programme of basic research must always be kept in operation. We are faced with a short term and a long term programme. The short term programme envisages the vigorous application of scientific results that have been obtained by long and arduous researches

in the past, and the long term programme requires that we prepare for the distant future by extensive fundamental research now.

Only by a recognition and acceptance of these twin tasks can we hope to solve the problems of our national economy. If we are to continue to live by our exports we must, as we did a century ago, supply products for which there is a demand and for which our foreign customers will willingly pay. Mr. S. P. Chambers, Chairman of I.C.I., writing in the *Financial Times* of January 4th, 1961, said "We can keep our balance of payments straight only by being among the world's leaders in the development of new products and new processes. Almost as important is the improvement of existing products and processes so that on prices and quality we can hold our own with the best of our competitors." Bearing in mind the limited range of our natural raw materials there can be only one answer to this challenge. New industries must be built upon our meagre resources and present industries must be able to produce with greater efficiency a wide range of new and desirable products.

To accomplish this in modern times requires a devotion to the application of scientific research. The developments that brought the great traditional industries of the country to the production levels and profitability they reached in the 19th century were the products of the inventive genius of individuals—men who turned to account the accumulated knowledge of the centuries. By the middle of the 19th century, this accumulated fund of available knowledge was beginning to run dry. The day of the inventor was passing; the day of the scientist, deliberately employed in a search for new industrial knowledge, was about to dawn. By the end of the century, industrial research laboratories had become a recognisable, if small, part of industrial organisation. How small may be judged from the fact that in 1900 the total annual expenditure on research and development in Great Britain was less than £1m. In 1958–59 we were spending at the rate of about £480m. a year. Within this period our industry has become increasingly technological and our economy more highly geared to the discoveries of research.

Not all of the £480m. spent on research, of course, is spent by industry. More than half of it (£266m.) was spent in industry, but of this, £154m. was provided by the Government, very largely for defence. Altogether, about two thirds (£320m.) of the total cost of the country's research efforts was met from Government funds and nearly three-quarters of this was for defence purposes. These figures emphasise first, the predominant influence of the Government in the total research effort of the country, and second, that even when the defence portion is removed the expenditure on civil research is now very high. It is a far cry from the £1m. of 1900 and there is little doubt that the cost of research will become higher yet. According to the F.B.I. Industrial Research Survey 1960, the number of qualified scientists and engineers engaged in research increased by about 1500 a year between 1956 and 1959, and it is reasonable to suppose that this rate of increase is being at least maintained. Not only is the amount of research increasing, but the cost is also increasing rapidly. It now costs twice as much to keep a research man working as it did 10 years ago. Expenditure on this scale obviously cannot be treated either haphazardly or lightly. The organisation of our research effort, its co-ordination and financing, especially perhaps the State contribution, are now matters of vital importance.

The great proportion of the nation's research is carried out in four major types of laboratories, namely, University laboratories, co-operative research associations, private industry and Government laboratories. Each of these, by virtue of its underlying philosophy and by its organisational structure, is peculiarly fitted to carry out particular types of research —fundamental research, applied research, development—though each may, and indeed does, overlap into other fields. In the interests of the economy it is essential to ensure that the different kinds of research are properly balanced.

It is probably true that there is no industrially usable research that has not been preceded at some time by fundamental research. The necessary fundamental research may have been carried out many years previously with no expectation of industrial usage and no recognition of its possible economic value, or it may have been an immediate precursor of a practical need where basic knowledge proved to be insufficient.

It is commonly accepted that the Universities are the natural home of fundamental research, to such an extent that fundamental research and academic research are sometimes mistakenly used as synonymous terms. The Universities are in fact by no means unique in carrying out fundamental research, but they probably remain the major source of completely unfettered advance into unknown fields. As Sir Edward Appleton said in an address

to the Parliamentary and Scientific Committee last year, "In a University we enjoy great freedom as regards choice of topics for research. We can concern ourselves with matters of interest rather than matters of practical use. Our task, as I see it, is to be continually saying the first word about things. Above all it is to leave the beaten track and dive into the woods." The tradition of freedom of the Universities that makes this possible is important. To interfere with it would be a disastrous loss both to the Universities and the economy.

In addition to its fundamental character University research possesses certain other features. It is peculiarly suitable for training young men in the methods of research; they receive the stimulus of contact with a fertile and disciplined mind together with actual demands upon themselves that are within their capabilities and that can be brought within the academic time limits for higher degrees. It is characteristic too of University research that it is openly published in scientific journals where it can be subjected to the critical appreciation of other scientists.

In 1958–59 the Universities were spending some £23m. on research. The greater part of this (about £19m.) came from Government sources, mainly through the University Grants Committee but also through the Research Councils, notably the Department of Scientific and Industrial Research.

Once the fundamental research has been completed it must for the sake of industry be converted from general knowledge to usable information. This step may be, and usually is, longer and more difficult than the original basic research. It may also require a different personal approach. If it is to produce any economic benefit research must not only be initiated and communicated, which is the University function, but it must also be harnessed. Academic research, like art, is an aesthetic activity. Industrial research, on the other hand, though it may have an aesthetic content, must in the long run pay off. Academic and applied research are thus complementary.

Additionally, the development of basic knowledge to usable information may require a different organisational approach. Where research is aimed at investigating phenomena without necessarily doing anything about them, the organisation may be based upon an academically homogeneous group; this is the normal pattern for a University. Where, however, research is aimed at solving a problem that may have arisen elsewhere, *e.g.*, in industry, organisation by project is often preferable so that sufficient scientific disciplines can be brought to bear; this is a standard pattern for industry and for Research Associations.

There are now fifty-two Research Associations covering some 60 per cent. of the productive industry of the country. They are characterised particularly perhaps by the outlook engendered by an industry-wide responsibility. Identified with industry, in fact an integral part of it, they retain the inestimable advantage of a central position free from immediate commercial and profit pressures, but with a research policy directed clearly and plainly to the advancement of industry. As professional research workers, they lack the freedom of the University approach, but in return they are ideally suited for the arduous, time-consuming task of converting fundamental knowledge to useful information for the benefit of industry. Because of their broad industrial view they are able to look beyond the confines of immediate needs to the more distant future, and in so doing they must often seek solutions for which knowledge is either absent or insufficient. In consequence, they share with Universities a responsibility for carrying out fundamental research, though it may often be more clearly directed to a useful objective.

Like Universities too they have an educational function. Because of their close contact with and understanding of industry they play an important role in the education of industry at the technical level, and particularly, in encouraging the adoption of new ideas. They have, therefore, introduced a scientific approach, especially into traditional industries like steel, textiles, leather and food. They have induced individual firms to start research laboratories of their own, have trained personnel in scientific and technical fields for industry and have contributed significantly to formal education in association with technical colleges and Universities.

They have a further responsibility deriving from their research work, namely, the provision of an unrivalled information service for industry. They maintain libraries and liaison activities and provide a trouble-shooting service for industry. This latter service is dependent upon past researches and in eliminating waste, faults and errors is invaluable for the steady increase in industrial efficiency it produces.

The Research Associations are supported jointly by industry and Government. They started just over 40 years ago and in that time the industrial contribution has risen from £100,000 a year to £6·1m. In the same period the Government contribution has gone from £70,000 to £1·7m. For this I have calculated, from information supplied to me by Directors, that they make an annual return to industry in the form of direct and measurable benefits of something in excess of £100m. On a present expenditure of some £8m. a year this is a good return.

Private industrial laboratories range all the way from small laboratories concentrating on the day-to-day problems of their respective firms to great and world-famous organisations supported by very big concerns. In the nature of things these big organisations are able to take a wide view and plan on a long term so that they, like Universities and Research Associations, indulge in a proportion of fundamental research designed to provide the basic knowledge necessary for future technological advances. Their first responsibility, of course, must always be the profitability now and in the future of their own organisation. To this extent, they are more limited in their approach than the Research Associations and much more than the Universities, but within this limitation they are immensely effective.

If the function of the Universities in this field is mainly fundamental research, that of the Research Associations applied or conversion research, then the function of industrial laboratories may be described as exploitation research. It is their job to bring research results to the ultimate end of industrial production without which there can be no benefit to the economy. To some extent all exploitation is a gamble, and if this is a desirable gamble, then the likelihood of winning must be increased by every available means. It is here that the industrial laboratory must play a major role; to do this it needs considerable resources so that the distribution of risks can be sufficient to avert disaster.

Discounting defence research, private industry was spending in 1958–59 about £124m. on civil research, of which some £12m. came from Government sources. A further £142m. was provided from Government sources for defence research in private industry, and some part of this, of course, might be expected to benefit civil developments.

Finally, we come to Government laboratories. These are the responsibility of various Government Departments, such as the Post Office and the Ministry of Transport and of the Research Councils—the Department of Scientific and Industrial Research, the Agricultural Research Council, the Medical Research Council and the Nature Conservancy. Their functions cover all the fields of fundamental research, applied research and exploitation research, with perhaps a special responsibility for research leading to the establishment and maintenance of standards. Generally speaking, their interests are defined by national needs that cannot be met conveniently in other ways. Road and transport research, for example, are of national importance beyond the scope of industrial concerns, and agriculture and public health are obvious fields for direct Government support. In 1958–59 Government expenditure on civil research in its own laboratories amounted to £46·5m.

We have therefore a picture of four main sources of civil research directed to the benefit of the economy spending in 1958–59 a total of rather more than £200m. distributed as to £23m. by Universities mainly for fundamental research; £8m. by Research Associations for a mixture of fundamental and applied research and technical services to industry; £124m. by private industry for a mixture of fundamental and applied research and development mostly restricted to the firms in question; and £46·5m. by Government research stations for a wide range of research and other activities of general importance to the economy. The Government's contribution to this expenditure totalled £80m. divided as to £20m. to Universities, £1·7m. to Research Associations, £12m. to private industry, usually through research contracts, and £46·5m. in its own establishments. In greater or lesser degree, all this research is essential to the community. Our main problems are to see that we are investing enough of our national resources in research and that these are properly allocated to achieve the greatest benefit.

It would probably be agreed by everybody that we are spending too much on defence research for the good of the economy. Unfortunately, it would also probably be widely accepted that in present world conditions we have little choice in the matter. The most that one can hope for is that the very big resources being devoted to this object are being wisely and economically used. The Government is aware of the dangers and set up in 1958 a Committee on the Management and Control of Research and Development. Its Report was published in January last.

In the civil field, it has been suggested by some people that our apparent deficiency in exploiting new discoveries should be offset by concentrating on applied research and development for a period of years and, if necessary, reducing the resources devoted to fundamental research. This would, I believe, be a grave error, for fundamental research provides the scientific capital on which future technological advance will be based. On the other hand, there is good reason for suggesting that the resources devoted to technological research should be considerably increased and that expenditure on fundamental research should be more critically examined than it now is. As I have pointed out earlier, applied research and development are usually vastly more expensive than fundamental research. Examples may perhaps speak louder than words.

Out of something like 100,000 known organic chemicals, at the beginning of this century only three had a fibrous structure, cellulose, keratin and fibroin, all natural products, and nobody knew why these differed from all others. Elementary analysis of sugar and cellulose gave the same result, but the difference between a crystal of sugar and a cellulose fibre was inexplicable. The ability to make synthetic fibres depended upon the discoveries that all polymers consist of simple molecules, monomers, linked together by normal chemical bonds and that in fibres these polymers had a chain-like structure—so-called linear polymers. This was fundamental research with which the names of Staudinger, Meyer, Mark, Haworth, Hirst, Clibbens and Pierce were associated. Once this foundation had been laid the way was open for Caruthers and the Du Pont laboratories to discover nylon and for Du Pont subsequently to develop it to a commercial product, which, with rayon, Terylene and the acrylic fibres has revolutionised social standards of dress.

Transistors, now a growing industrial field, depended in the first place upon the discovery and development of the quantum theory and its application by A. H. Wilson to understanding the behaviour of semi-conductors. With this background Shockley at the Bell Telephone Laboratories was able to propose the possibility of controlling the "movable" electrons in a semi-conductor so that first, point-contact transistors and later, junction transistors, could be produced.

The fundamental steps leading to the release of nuclear energy are too well known to need repetition, but the industrial application of nuclear energy and of isotopes required, after the initial academic success, a Harwell, a Calder Hall and a Seascale to bring it to fruition.

These examples illustrate several points. First, they show the time lag between original discovery and industrial exploitation. In all the above instances the fundamental work preceded the first industrial steps by about 30 years. With the rapid increase in technological research this time lag seems to be decreasing and will no doubt decrease further. Nevertheless, the support of fundamental research remains essentially an investment in the next generation.

Second, they demonstrate the interdependence of all kinds of research. Each of them was preceded by fundamental research, in all three instances carried out without expectation of industrial application, followed by orientated basic research in which an industrial aim had become apparent, and concluded by an industrial development. As the recent Report of the Advisory Council for Scientific Policy pointed out, "Both fundamental and applied research are vital to the scientific effort as a whole; they are interdependent, and each would suffer from deficiencies in the other."

Third, they illustrate vividly the relative costs of fundamental and other kinds of research.

With a total expenditure on research of all kinds approaching 2·5 per cent. of the Gross National Product it is important to ensure that the distribution over the different kinds is properly balanced. Over the various agencies for research discussed earlier it may be assumed that in 1958–59 the Universities were spending the whole of their £23m. on fundamental research; the Research Associations about £2 to £3m.; private industry about £12m.; and Government research stations about £16m.; in all a total of rather more than £50m. This leaves something less than £200m. for all other forms of research and development, including technical services. This can hardly be considered sufficient to take advantage of the expenditure on fundamental research and is certainly less than is being spent for this purpose in the United States and probably Russia.

If we are not to accept a reduction in expenditure on fundamental research the balance can only be put right by increasing the expenditure on applied research and development. Such increase must come either from industry or from Government. Industry is already

spending, as I have pointed out earlier, about £124m. in its own laboratories and it is unlikely to spend more unless particular incentives are provided. This opens up a tremendous field of discussion on the possibilities of providing incentives through taxation policy, allowable obsolescence and plant replacement reliefs, tariffs and import quotas and credit facilities for export. I do not propose to enter into this except to say that assistance to industry to carry out civil research should be more obviously fitted into a broader policy than it now appears to be.

Direct Government assistance, on the other hand, could with relative ease be adjusted more satisfactorily to the present needs. In the analysis of expenditure given earlier one feature that stands out is the relatively small amount contributed from Government sources to the Research Associations, and especially the steady decrease in the proportion of the Government support—from 70 per cent. of the industrial contribution in the early years to 28 per cent. in 1958–59—at a time when all other forms of Government supported research have been growing at a tremendous rate. Spread over the forty-six Research Associations operating in 1958–59, their total average income was £174,000. The picture is, in fact, worse than this, since eight Associations accounted for more than half the total expenditure, whereas nine had incomes below £50,000 and a further fifteen below £100,000 a year. An increased State investment in Research Associations could undoubtedly result in a valuable return to the economy.

On the face of it support for Research Associations seems to be the weak link in our organisation for civil research. Perhaps what is needed is a fresh examination of the position along the lines advocated by Professor C. F. Carter in a lecture to the Manchester Literary and Philosophical Society in October 1959 when he stated: "Lord Hailsham, I think, ought to encourage joint technical and economic appraisal of the opportunities for State-encouraged scientific developments."

This year is National Productivity Year and all that I have tried to say in this address is perhaps best summed up in the message from H.R.H. the Duke of Edinburgh to mark the inauguration of the new effort. "No amount of economic juggling," he said, "can alter the fact that in the long run our solvency depends upon the efficiency of our industries and upon our national productivity. In order to maintain, let alone improve, our standard of living we have got to export our manufactured goods in the face of very tough competition from other highly industrialised and industrious countries. We can only compete with success if we can maintain a high standard of efficiency in productivity. The only alternative is lower wages and salaries and none in their senses wants that.

"Efficiency can only be maintained by a continuous process of improvement and innovation. Therefore, the great value of the National Productivity Year will lie in the atmosphere which it generates, the contacts which it helps to make and the need for a continuing effort which it manages to stimulate. The whole nation stands to gain from the success of this venture, particularly if it can inspire a spirit of co-operation and joint endeavour which alone can help this country to overcome the challenge of the future."

I can only add that the "efficiency of our industries" and "a continuous process of improvement and innovation" can only come about by sustained scientific and technological effort. It seems to me that Bernard Dyer's work for agriculture was characterised by devotion to precisely those ideals, which I believe are now essential to the well-being of industry as a whole. I am sure that he would have endorsed these ideals and it is therefore to his memory that I dedicate this essay, which, as I explained at the outset, was inspired by his example.

# Square-wave Polarography with Special Reference to the Analysis of Zirconium and Hafnium*

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Experiments to assess the application of a Mervyn - Harwell square-wave polarograph, particularly to the direct determination of impurities and alloying constituents in zirconium, are described. These tests have shown that copper, lead, molybdenum, tungsten and zinc can be determined in certain zirconium-based materials by direct polarographic methods; copper can be determined simultaneously with molybdenum. A direct polarographic determination of any one of these metals (or two when simultaneous determinations are possible) takes about 45 minutes, whereas determinations by alternative chemical procedures take much longer.

Tests have also shown that copper, tungsten and cadmium can be determined in hafnium after simple solution of the sample.

Detailed explanations of the principles of polarography appear in various publications,[1,2,3] and continued progress in this important field of analytical chemistry has led to the development of instruments, such as cathode-ray and square-wave polarographs, which incorporate novel devices for improving sensitivity and resolution. Of these instruments commercially available to date, the Mervyn - Harwell square-wave polarograph is one of the most sensitive; a comparative study of recently developed instruments[4] supports this view and indicates that the square-wave polarograph also gives favourable resolution.

Experiments with a Mervyn - Harwell square-wave polarograph were carried out to assess in particular the possibility of providing direct polarographic methods for determining certain metals in zirconium and its alloys.

## Experimental

### Polarographic characteristics of metal ions—

Preliminary tests were made to establish the sensitivity for about fifteen different metal ions in various supporting electrolytes; the ions chosen corresponded to metals normally present in zirconium and its alloys. The behaviour of each ion at the concentration of 5 $\mu$g per ml was studied separately in a range of de-oxygenated supporting electrolytes, polarograms being recorded over the range 0 to about $-1{\cdot}0$ volt. The polarographic characteristics of the ions studied are listed in Table I and correspond to metals at the concentration of 500 p.p.m., based on 0·1 g of sample in 10·0 ml of supporting electrolyte. A typical polarogram showing the reduction waves produced by copper, lead, cadmium and zinc (each at the concentration of 5 $\mu$g per 10 ml) is reproduced in Fig. 1.

### Application of square-wave polarography to analysis of zirconium and its alloys—

Tables II and III are based on the general specification for the composition of reactor-grade zirconium. From these and the results in Table I, it appeared that the square-wave polarograph could provide sensitivity adequate for the direct determination of several metals (with use of selected supporting electrolytes) in zirconium and Zircaloys. Further tests were therefore made at concentrations near to the specified limits for these particular metals. In tests with added zirconium or Zircaloy, the metal (0·1 g) was dissolved in fluoroboric acid, either alone or mixed with the particular supporting electrolyte being examined; the solution was then oxidised, usually with nitric acid. The results of these tests are briefly summarised below.

*With* 10 *ml of* M *hydrochloric acid as supporting electrolyte*—Tests were made with added cadmium, copper, lead, tin and zinc. When zirconium 10 was present, results for cadmium and tin were low and erratic, probably owing to the presence of fluoride.[5] Because of the

* Presented at the meeting of the Society on Wednesday, April 4th, 1962.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF METAL IONS IN VARIOUS SUPPORTING ELECTROLYTES

Each ion was tested at the concentration of 5 $\mu$g per ml

| Supporting electrolyte | Ion tested | Sensitivity setting (maximum = 1) | Half-wave potential, volts (against mercury-pool anode) | Height of wave, mm | Ions for which no reduction wave was observed |
|---|---|---|---|---|---|
| Hydrochloric acid, M .. .. | $Cd^{2+}$ | 1/256 | −0·64 | 55 | $Al^{3+}$, $Ca^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Mo^{6+}$ and $V^{4+}$ |
| | $Cu^{2+}$ | 1/128 | −0·25 | 105 | |
| | $Pb^{2+}$ | 1/64 | −0·44 | 110 | |
| | $Sn^{4+}$ | 1/8 | −0·47 | 110 | |
| | $Ti^{4+}$ | 1/4 | −0·89 | 50 | |
| | $W^{6+}$ | 1/2 | −0·77 | 55 | |
| | $U^{6+}$ | 1/8 | −0·28 | 120 | |
| | $Zn^{2+}$ | 1/64 | −1·02 | 125 | |
| Sulphuric acid, 0·75 M .. | $Cd^{2+}$ | 1/128 | −0·96 | 110 | $Al^{3+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Sn^{4+}$, $Ti^{4+}$, $W^{6+}$ and $V^{4+}$ |
| | $Cr^{3+}$ | 1/64 | −1·28 | 100 | |
| | $Cu^{2+}$ | 1/128 | −0·35 | 160 | |
| | $Pb^{2+}$ | 1/64 | −0·75 | 110 | |
| | $U^{6+}$ | 1/8 | −0·59 | 90 | |
| | $Zn^{2+}$ | 1/8 | −1·39 | 130 | |
| Hydrochloric acid, 0·5 M - ammonium citrate, 0·5 M | $Cd^{2+}$ | 1/128 | −0·65 | 90 | $Co^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Mn^{2+}$, $Ni^{2+}$, $Sn^{4+}$, $W^{6+}$, $V^{4+}$ and $Zn^{2+}$ |
| | $Cu^{2+}$ | 1/64 | −0·23 | 175 | |
| | $Pb^{2+}$ | 1/64 | −0·48 | 95 | |
| | $Ti^{4+}$ | 1/8 | −0·92 | 75 | |
| Hydrochloric acid, 5 M .. | $Cd^{2+}$ | 1/128 | −0·62 | 100 | $Al^{3+}$, $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Mo^{6+}$, $Ni^{2+}$, $Ti^{4+}$, $V^{4+}$ and $Zn^{2+}$ |
| | $Cu^{2+}$ | 1/128 | −0·23 | 85 | |
| | $Pb^{2+}$ | 1/64 | −0·44 | 115 | |
| | $Sn^{4+}$ | 1/128 | −0·47 | 140 | |
| | $W^{6+}$ | 1/32 | −0·58 | 70 | |
| Perchloric acid, M .. .. | $Cd^{2+}$ | 1/128 | −0·92 | 110 | $Al^{3+}$, $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Ni^{2+}$, $Sn^{4+}$, $W^{6+}$ and $Zn^{2+}$ |
| | $Cu^{2+}$ | 1/16 | −0·28 | 110 | |
| | $Pb^{2+}$ | 1/32 | −0·72 | 200 | |
| | $Mo^{6+}$ | 1/32 | −0·48 | 185 | |
| Sulphuric acid, 0·75 M - ammonium citrate, 0·2 M | $Cd^{2+}$ | 1/16 | −0·96 | 200 | $Al^{3+}$, $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Ni^{2+}$, $Sn^{4+}$, $Ti^{4+}$, $V^{4+}$ and $Zn^{2+}$ |
| | $Cu^{2+}$ | 1/128 | −0·35 | 110 | |
| | $Pb^{2+}$ | 1/32 | −0·76 | 160 | |
| | $W^{6+}$ | 1/128 | −1·32 | 90 | |
| Nitric acid, 0·25 M .. .. | $Cd^{2+}$ | 1/128 | −0·97 | 125 | $Cr^{3+}$, $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Sn^{4+}$, $Ti^{4+}$, $V^{4+}$ and $Zn^{2+}$ |
| | $Cu^{2+}$ | 1/128 | −0·42 | 175 | |
| | $Pb^{2+}$ | 1/64 | −0·73 | 110 | |
| | $Mo^{6+}$ | 1/64 | −0·56 | 155 | |
| | $U^{6+}$ | 1/32 | −0·49 | 50 | |
| Ammonium hydroxide, M - ammonium citrate, 0·2 M - ammonium chloride, 0·5 M | $Cd^{2+}$ | 1/128 | −0·67 | 100 | $Cr^{3+}$, $Co^{2+}$, $Mn^{2+}$, $Mo^{6+}$, $Sn^{4+}$, $Ti^{4+}$ and $V^{4+}$ |
| | $Cu^{2+}$ | 1/64 | −0·36 | 80 | |
| | $Fe^{3+}$ | 1/8 | −0·38 | 135 | |
| | $Pb^{2+}$ | 1/64 | −0·45 | 100 | |
| | $Ni^{2+}$ | 1/8 | −1·11 | 65 | |
| | $Zn^{2+}$ | 1/64 | −1·21 | 30 | |
| Sodium hydroxide, M - sodium citrate, 0·2 M | $Cd^{2+}$ | 1/128 | −0·60 | 75 | $Cr^{3+}$, $Mn^{2+}$, $Mo^{6+}$, $Ni^{2+}$, $Sn^{4+}$, $Ti^{4+}$, $W^{6+}$, $U^{6+}$ and $V^{4+}$ |
| | $Cu^{2+}$ | 1/64 | −0·27 | 95 | |
| | $Co^{2+}$ | 1/8 | −1·36 | 65 | |
| | $Fe^{3+}$ | 1/64 | −0·74 and −1·40 | 55 and 30 | |
| | $Pb^{2+}$ | 1/64 | −0·56 | 60 | |
| | $Zn^{2+}$ | 1/8 | −1·34 | 170 | |

erratic behaviour of tin and the fact that the waves for tin and lead coalesce in this medium, the direct determination of either metal was impracticable. Results for copper were satisfactory in the presence of zirconiums 10, 20 and 30. The wave for zinc coalesced with that produced by reduction of hydrogen ions, but, provided that the concentration of hydrochloric

acid was decreased to less than 0·5 M and the solution was oxidised with bromine instead of nitric acid, zinc could be determined (simultaneously with copper) in zirconiums 10 and 30. In the presence of zirconium 20, a wave at −1·1 volts (probably produced by the alloying amount of nickel) caused distortion of the wave for zinc.

*With* 25 *ml of* 0·75 M *sulphuric acid as supporting electrolyte*—Tests were made with added cadmium, chromium, copper, lead and zinc. The waves for cadmium, chromium and zinc were obscured by a large wave produced by reduction of hydrogen ions, but results for the simultaneous determination of copper and lead in zirconiums 10 and 20 were satisfactory. Results for copper in zirconium 30 were also satisfactory, but the wave for lead was obscured by a large wave at about −0·6 volt produced by reduction of molybdenum. Tests to assess

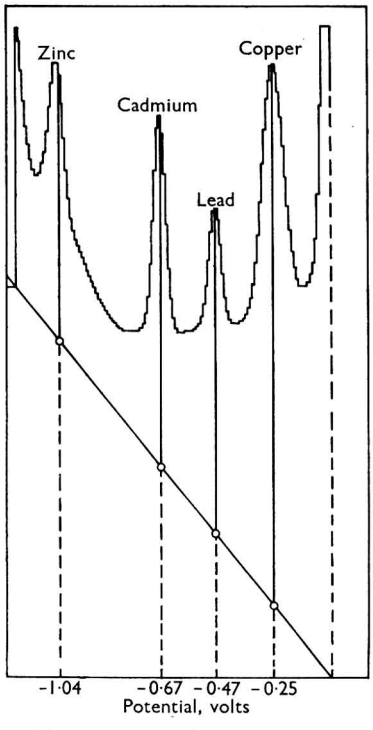


Fig. 1. Typical square-wave polarogram for 5 μg each of zinc, cadmium, lead and copper in 10 ml of 0·5 M hydrochloric acid (sensitivity, 1/16; scan-rate switch set at 3)

the possibility of determining molybdenum were made, but, owing to incomplete and variable reduction, the heights of the waves obtained were erratic.

*With* 10 *ml of* 0·5 M *hydrochloric acid* - 0·5 M *ammonium citrate as supporting electrolyte*—Tests were made with added cadmium, lead and titanium. In presence of zirconium, recoveries of cadmium were low and variable. Recovery of lead in presence of zirconiums 10 and 20 was quantitative, but in presence of zirconium 30 the wave for lead was obscured by that for copper. Quadrivalent titanium gave a well defined wave at −0·92 volt in absence of zirconium, but, in tests with added zirconium, the wave did not appear, because of the formation of a titanium - fluoride complex (fluoroboric acid was present).

*With* 10 *ml of* 5 M *hydrochloric acid as supporting electrolyte*—Tungstate ions produce well defined waves in solutions greater than 4 M in hydrochloric acid,[6] and this electrolyte was selected primarily to assess its application to the determination of tungsten in zirconium-based materials. Tests were also made in the presence of added cadmium, lead and tin. The wave for cadmium coalesced with that produced by the reduction of hydrogen ions, and the waves for lead and tin coalesced.

In presence of zirconium the wave for tungsten at —0·58 volt was not obtained. This was attributed to reduction of tungstate ions by nascent hydrogen produced during solution of the sample and the inability of nitric acid, under the test conditions, to effect its re-oxidation. Tests showed that re-oxidation could be achieved by boiling the sample solution with ammonium persulphate; in this way, satisfactory results were obtained in presence of zirconiums 10 and 30. In tests with zirconium 20 the wave for tungsten was obscured by that for tin.

*With nitric acid as supporting electrolyte*—Tests were made with added cadmium, copper and molybdenum in 0·25 M nitric acid. The wave for cadmium was obscured by that produced by reduction of hydrogen ions.

Tests in presence of zirconium showed that the simultaneous determination of copper and molybdenum in zirconiums 10, 20 and 30 was possible in nitric acid (1 to 1·6 M), provided

TABLE II

ALLOYING ELEMENTS PRESENT IN REACTOR-GRADE ZIRCONIUM

| Sample | Element present | Range of concentrations, % |
|---|---|---|
| Zirconium 10 | None; unalloyed zirconium | — |
| Zirconium 20 | Tin | 1·20 to 1·70 |
| | Iron | 0·07 to 0·20 |
| | Chromium | 0·05 to 0·15 |
| | Nickel | 0·03 to 0·08 |
| Zirconium 30 | Copper | 0·46 to 0·66 |
| | Molybdenum | 0·5 to 0·6 |

TABLE III

LIMITS OF IMPURITIES (UNLESS PRESENT AS ALLOYING ELEMENTS) IN REACTOR-GRADE ZIRCONIUM

Limits specified for elements not studied in this work are not included

| Impurity | Maximum concentration present, p.p.m. | Impurity | Maximum concentration present, p.p.m. |
|---|---|---|---|
| Aluminium | 75 | Nickel | 70 |
| Cadmium | 0·5 | Tin | 200 |
| Chromium | 200 | Titanium | 50 |
| Cobalt | 20 | Tungsten | 100 |
| Copper | 50 | Uranium | 3 |
| Iron | 1500 | Vanadium | 50 |
| Lead | 100 | Zinc | 100 |
| Molybdenum | 50 | | |

that the sample solution was boiled with ammonium persulphate to ensure the presence of sexavalent molybdenum.

*With other supporting electrolytes*—Further tests indicated that no direct methods for determining metals in zirconium-based materials were possible when the other supporting electrolytes mentioned in Table I, *viz.*, M perchloric acid and the ammoniacal and alkaline media, were used. However, these electrolytes could be used provided that zirconium was first isolated.

APPLICATION OF SQUARE-WAVE POLAROGRAPHY TO ANALYSIS OF HAFNIUM—

The direct polarographic methods suitable for determining copper and tungsten in zirconium were shown to be equally applicable for determining these metals (with specified limits of 50 and 100 p.p.m., respectively) in hafnium. Further tests with 0·5 M hydrochloric acid as supporting electrolyte and 0·1-g samples of hafnium showed that cadmium could be satisfactorily determined over the range 2 to 10 p.p.m.

METHODS

A reagent blank and a "control" must be included with the examination of each batch of samples. Prepare the control by adding a convenient amount of the appropriate standard metal solution to a duplicate of one of the samples. Always calculate the metal content of the sample by reference to the height of the wave for the control solution.

### Determination of Lead in Zirconiums 10 and 20

REAGENTS—

*Fluoroboric acid*—To 280 ml of transistor-grade hydrofluoric acid maintained at 10° C add, in small portions, 130 g of boric acid. Store in a polythene bottle.

*Sulphuric acid, sp.gr.* 1·84—Use the lead-free grade.

*Nitric acid, sp.gr.* 1·42—Transistor grade.

*Standard lead solution*—Dissolve 0·1 g of high-purity lead in 50 ml of transistor-grade nitric acid diluted (1 + 1), and dilute to 1 litre; dilute 50 ml of this solution to 1 litre.

1 ml ≡ 5 μg of lead.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5·0 ml of dilute sulphuric acid (1 + 4) and 0·3 to 0·4 ml of fluoroboric acid; heat to about 70° C to assist solution. Oxidise with 0·2 ml of nitric acid, and boil gently for about 1 minute to remove nitrous fumes. Cool, and dilute to 25 ml in a calibrated flask. Transfer the solution to a polarographic cell, allow argon to bubble through for about 2 minutes, and record a polarogram at 25° C under the following conditions—

| | |
|---|---|
| *Start potential*— | −0·65 volt. |
| *Scan rate*— | 3. |
| *Sensitivity*— | 1/16 or 1/8. |

The half-wave potential of lead occurs at about −0·78 volt.

### Determination of Tungsten in Zirconiums 10 and 30 and Hafnium

REAGENTS—

*Hydrochloric acid, sp.gr.* 1·18—Micro-analytical reagent (M.A.R.) grade.

*Ammonium persulphate solution, 25 per cent.*—Dissolve 25 g of ammonium persulphate in about 75 ml of water, and dilute to 100 ml. This reagent must be prepared daily.

*Standard tungsten solution*—Dissolve 0·1794 g of sodium tungstate, $Na_2WO_4.2H_2O$, in water, and dilute to 1 litre.

1 ml ≡ 0·1 mg of tungsten.

Dilute 50 ml of this solution to 1 litre.

1 ml ≡ 5 μg of tungsten.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5·0 ml of hydrochloric acid, sp.gr. 1·18, 2·0 ml of water and 0·25 ml of fluoroboric acid; heat to about 70° C to assist solution. Oxidise with 0·5 ml of ammonium persulphate solution, and allow to simmer gently for about 5 minutes. Cool, dilute to 10·0 ml, and record a polarogram under the following conditions—

| | |
|---|---|
| *Start potential*— | −0·45 volt. |
| *Scan rate*— | 3 or 4. |
| *Sensitivity*— | 1/8 or 1/4. |

The half-wave potential of tungsten occurs at about −0·57 volt.

### Determination of Copper and Molybdenum in Zirconium 30

REAGENTS—

*Standard copper solution*—Dissolve 0·2 g of high-purity copper in 10 ml of transistor-grade nitric acid diluted (1 + 1), and dilute to 1 litre.

1 ml ≡ 0·2 mg of copper.

*Standard molybdenum solution*—Dissolve 0·3684 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in water, and dilute to 1 litre.

1 ml ≡ 0·2 mg of molybdenum.

Standardise this solution before use.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5 ml of water and 0·5 ml of fluoroboric acid; heat to about 70° C to assist solution. Add 10·0 ml of transistor-grade nitric acid and 0·5 ml of 25 per cent. ammonium persulphate solution, and allow to simmer gently for 5 minutes. Cool, dilute to 100 ml, and record a polarogram under the following conditions—

*Start potential*— —0·20 volt.
*Scan rate*— 3 or 4.
*Sensitivity*— 1/128.

The half-wave potentials of copper and molybdenum occur at about —0·35 and —0·50 volt, respectively.

## Determination of Copper and Molybdenum in Zirconiums 10 and 20 and of Copper in Hafnium

REAGENTS—

*Standard copper solution*—Dilute 25 ml of the standard solution containing 0·2 mg of copper per ml to 1 litre.

1 ml ≡ 5 μg of copper.

*Standard molybdenum solution*—Dilute 25 ml of the standard solution containing 0·2 mg of molybdenum per ml to 1 litre.

1 ml ≡ 5 μg of molybdenum.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5·0 ml of water and 0·5 ml of fluoroboric acid; heat to about 70° C to assist solution. Add 2·0 ml of transistor-grade nitric acid and 0·5 ml of 25 per cent. ammonium persulphate solution (see Note), and allow to simmer gently for 5 minutes. Cool, dilute to 25 ml, and record a polarogram under the following conditions—

*Start potential*— —0·20 volt.
*Scan rate*— 3 or 4.
*Sensitivity*— 1/4 or 1/8.

The half-wave potentials of copper and molybdenum occur at about —0·38 and —0·50 volt, respectively.

NOTE—Addition of persulphate solution is unnecessary when determining copper in hafnium.

## Determination of Zinc in Zirconiums 10 and 30

REAGENTS—

*Hydrochloric acid*, 1 M—Dilute 83 ml of M.A.R. hydrochloric acid, sp.gr. 1·18, to 1 litre.

*Standard zinc solution*—Dissolve 0·1 g of high-purity zinc in 5 ml of hydrochloric acid, sp.gr. 1·18, and dilute to 1 litre; dilute 25 ml of this solution to 500 ml.

1 ml ≡ 5·0 μg of zinc.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5 ml of water and 0·5 ml of fluoroboric acid; heat to about 70° C to assist solution. Oxidise with about 0·1 ml of bromine (added to the cold solution), and warm gently until the bromine has volatilised. Cool, add 1·0 ml of 1 M hydrochloric acid, dilute to 10 ml, and record a polarogram under the following conditions—

*Start potential*— —0·80 volt.
*Scan rate*— 3 or 4.
*Sensitivity*— 1/8 or 1/16.

The half-wave potential of zinc occurs at about —1·06 volts.

### Determination of 2 to 10 p.p.m. of Cadmium in Hafnium

REAGENTS—

*Standard cadmium solution*—Dissolve 0·1 g of high-purity cadmium in 10 ml of M.A.R. hydrochloric acid, sp.gr. 1·18, and dilute to 1 litre; dilute 5 ml of this solution to 1 litre.

1 ml ≡ 0·5 μg of cadmium.

PROCEDURE—

Dissolve 0·1 g of sample in a mixture of 5·0 ml of 1 M hydrochloric acid and 0·3 to 0·4 ml of fluoroboric acid; heat to about 70° C to assist solution. Oxidise with 0·2 ml of concentrated nitric acid, and allow to simmer gently to remove nitrous fumes. Cool, dilute to 10 ml, and record a polarogram under the following conditions—

| | |
|---|---|
| *Start potential*— | −0·50 volt. |
| *Scan rate*— | 3 or 4. |
| *Sensitivity*— | Full or 1/2. |

The half-wave potential of cadmium occurs at about −0·67 volt.

## CONCLUSIONS

Tests with a square-wave polarograph have shown that the direct polarographic determination of copper, lead, molybdenum, tungsten and zinc can be carried out independently in certain zirconium-based materials and that copper and molybdenum can be determined simultaneously. Copper, tungsten and cadmium can also be determined directly in solutions of hafnium. The methods described have been satisfactorily applied in the determination of these metals in the control analysis of zirconium, Zircaloys and hafnium and have effected a considerable saving in time and manpower. For example, the determination of tungsten in zirconium 30 by the earlier chemical procedure is difficult and tedious because it involves separation of trace concentrations (less than 100 p.p.m.) of tungsten from relatively large amounts (0·5 per cent.) of molybdenum.

The constant interest and encouragement of Mr. W. T. Elwell, Division Chief Analyst, is acknowledged.

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# The Determination of Gold by Extractive Titration*

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An extractive-titration technique is described for determining gold in solutions 0·5 N in sulphuric acid. The reagent, a solution of dithizone in chloroform, is standardised against a gold solution of known concentration. The method is free from interference by most other metals, with the notable exceptions of mercury and, to a much lesser extent, platinum. Interference from mercury can be overcome by volatilisation, and that from platinum by reducing the gold to metal and removing it by filtration. Results are high in presence of appreciable amounts of hydrochloric and nitric acids, but these can be removed by evaporation until fumes of sulphur trioxide are evolved. Close adherence to the specified technique leads to results within $\pm 1$ per cent. of the gold content. A method for assaying gold ore with extractive titration as the final stage is described in detail.

GOLD can be determined by a wide variety of methods. In pure solution, precipitation as the metal is effected by many reducing agents, *e.g.*, sulphur dioxide, sodium oxalate and ferrous iron, and the gold can then be separated on a fine filter-paper, ignited and weighed. Titrimetrically, auric gold can be determined by reduction to the metal with standard sodium oxalate solution and then titration of the excess of oxalate with potassium permanganate solution; alternatively, ammonium ferrous sulphate and potassium dichromate solutions can be used.[1,2] Gold may also be determined iodimetrically,[1,2] and an indirect determination involves use of ethylenediaminetetra-acetic acid.[3] The fact that gold can be easily reduced to the metallic state is the basis of its separation from most elements, if necessary, mercury, lead or tellurium being used as a collector for small amounts. The gold content can then be determined gravimetrically by strong ignition of the precipitate, cupellation and weighing the resulting gold bead.[4,5]

For the determination of gold in trace amounts, several colorimetric reagents can be used, *e.g.*, *p*-dimethylaminobenzylidenerhodanine, rhodamine B and dithizone. Other methods are based on oxidation of certain organic compounds by auric gold to give highly coloured products. These methods have been well reviewed by Sandell.[6]

In this laboratory, however, a method was required that would be sufficiently sensitive for determining gold at about the milligram level and would also be fairly rapid and suitable for routine analysis. I have used the colorimetric determination of gold with dithizone[7,8] with fairly satisfactory results. In this method, auric gold in 0·5 N sulphuric acid solution is allowed to react with a 0·001 per cent. w/v solution of dithizone in carbon tetrachloride to give a yellow-brown solution of gold dithizonate, and the excess of dithizone is removed by washing with dilute ammonia solution. The method is relatively free from interference by other metals, except copper, but the dithizone reagent must be free from diphenylthiocarbodiazone (the oxidation product of dithizone). This compound dissolves in carbon tetrachloride to give a yellow-brown solution and has an absorption curve closely resembling that of gold dithizonate.[8] It is therefore necessary, when this procedure is used, to remove diphenylthiocarbodiazone from the dithizone as described by Sandell.[9] Moreover, the determination is applicable only to small amounts of gold (about 40 $\mu$g being the upper limit), and, as the amounts of gold involved in this work were greater than this, undesirably large dilutions were necessary. The method was therefore considered to be unsatisfactory for routine use.

However, it has advantages, in principle at least, over other methods in the freedom from interference and convenience of extraction as against filtration, and it was decided to try the extractive-titration technique with use of a 0·01 per cent. w/v solution of dithizone. It was hoped that, by working at this higher concentration and by standardising the dithizone solution against a pure gold solution of known concentration, purification of the dithizone would be unnecessary. This proved to be so, and the procedure finally developed was satisfactory.

* Presented at the meeting of the Society on Wednesday, April 4th, 1962.

## Experimental

Experiments were carried out with a 0·01 per cent. w/v solution of dithizone in carbon tetrachloride prepared without purification of the dithizone. A stock solution of gold was prepared by dissolving chloroauric acid, $HAuCl_4.xH_2O$ (containing approximately 51 per cent. of gold), in water to give a solution containing about 1 mg of gold per ml. This solution was assayed gravimetrically. A standard solution containing 0·1 mg of gold per ml was prepared for experimental purposes by placing 10 ml of the stock solution (by pipette) in a 100-ml calibrated flask, adding 10 ml of 5 N sulphuric acid and diluting to the mark. Aliquots of this solution (10 ml, equivalent to 1 mg of gold) were placed by pipette in 100-ml separating funnels and extractively titrated with the dithizone solution. It was found that the dithizone solution was most satisfactorily delivered from a dry burette having an ungreased tap secured in position with an elastic band; no leakage from the burette occurred under these conditions. (The burette was dried by rinsing it with acetone and then drawing a current of air through it by suction from a vacuum line.) The initial titration to determine the approximate end-point was carried out by adding 5-ml portions of dithizone solution, shaking the funnel vigorously for 20 seconds and allowing the layers 40 seconds in which to separate. The organic layers, which were run off after each addition of reagent, were coloured golden brown by the gold dithizonate until excess of dithizone had been added, when the carbon tetrachloride layer was either tinged with or coloured green, depending on the amount of the excess. A second titration, covering the last 5 ml in 1-ml additions, determined the end-point to within 1 ml, and a third titration, with additions of 0·2 ml of dithizone solution *plus* 5 ml of pure carbon tetrachloride, determined the end-point to 0·2 ml. The burette reading for the end-point was taken as the reading before the appearance of a clear green colour in the organic layer. For this final titration, dithizone solution to within 1 ml of the total volume necessary was added initially, the funnel was shaken vigorously, and the organic phase was removed after the layers had been allowed to separate for 40 seconds; the titration was then completed by adding 0·2-ml portions of titrant. (During extractions with carbon tetrachloride, it is not necessary to release pressure from the separating funnel by opening the tap, and this was avoided to prevent slight amounts of the aqueous phase from being lost by spraying out.)

The titrations were found to be reproducible to within 0·2 ml on volumes of about 30 ml for 1 mg of gold, but separation of the organic and aqueous phases was rather obscured by the precipitation of gold dithizonate. Also, the dithizone itself did not dissolve as readily as expected in the carbon tetrachloride (solubility at room temperature is approximately 0·05 g per 100 ml); even after being warmed on a steam-bath for some time, several small particles of dithizone remained undissolved.

Dithizonates in general are much more soluble in chloroform—as is dithizone itself (2·0 g per 100 ml at room temperature)—and it was decided to try this solvent. The dithizone was found to dissolve readily and completely after being warmed for a few minutes on a steam-bath, and the gold dithizonate was completely soluble in the organic layer, permitting clean separation of the two phases. An unexpected discovery was that the titres of 0·01 per cent. w/v solutions of dithizone in chloroform were about half of those for corresponding solutions in carbon tetrachloride, *i.e.*, 15 to 16 ml per mg of gold.

An attempt to ascertain the molar ratios involved in the reaction was rather unsatisfactory. A weighed sample of the dithizone in use was dissolved in carbon tetrachloride, and the solution was shaken with dilute ammonia solution; dithizone was extracted into the aqueous phase, and the main impurity, diphenylthiocarbodiazone, was retained in the carbon tetrachloride. This was run off, and the dithizone was recovered by acidifying the aqueous phase and then extracting it with carbon tetrachloride. The solution was washed and evaporated to dryness, and the residue was weighed; a purity of not better than 85 per cent. was indicated. An assessment of the amounts involved in the reaction showed that the ratio of gold to dithizone for the reaction in chloroform seemed to be approximately 1 to 1, whereas in carbon tetrachloride it was 1 to 2, *i.e.*, the straightforward formation of auric dithizonate, $Au(HDz)_3$, earlier reported[7,8] was not confirmed.

The main disadvantage of chloroform as opposed to carbon tetrachloride as solvent was its greater volatility, but this was countered by standardising the solution against 10 ml of gold solution (1 ml $\equiv$ 0·1 mg of gold) just before it was required and then at 3-hourly intervals. The solution was stored in a dark-glass bottle having a tightly fitting stopper and showed only a slight increase in concentration (about 0·5 per cent.) throughout the day.

The final titration was carried out by an initial extraction to within 0·5 ml of the end-point, the last 0·5 ml being covered in 0·1-ml additions of the dithizone solution *plus* 2 ml of chloroform.

Two aspects of the titration were next investigated, namely, the influence of acid concentration and the recovery of gold at various concentrations.

INFLUENCE OF ACID CONCENTRATION—

Solutions containing 0·1 mg of gold per ml were prepared from the stock solution in different concentrations of sulphuric acid. A 10-ml portion of each solution was titrated, and recovery was found to be essentially the same for all solutions tested; the results were—

| | | | | |
|---|---|---|---|---|
| Concentration of sulphuric acid, N .. .. .. .. | 0·3 | 0·5 | 0·7 | 1·0 |
| Titre of 0·01 per cent. w/v dithizone solution, ml .. .. | 15·7 | 15·7 | 15·7 | 15·6 |

*i.e.*, the concentration of sulphuric acid was not critical.

It was found, however, that the presence of hydrochloric acid caused high results, with modification of the colour changes of the titration. Just before the end-point, the organic phase assumed a bright cerise colour (instead of yellow-brown), and a blue-grey colour instead of green indicated the slight excess of dithizone. For solutions 0·3 N in sulphuric acid and 0·1 or 0·3 N in hydrochloric acid, the titres found were, respectively, 16·9 and 17·2 ml of 0·01 per cent. dithizone solution. This effect was less pronounced with nitric acid, the colours of the organic layer remaining unaffected, but recoveries were slightly high, as shown by the results below.

| | | | |
|---|---|---|---|
| Acidity in sulphuric acid, N .. .. .. .. .. | 0·7 | 0·7 | 0·3 |
| Acidity in nitric acid, N .. .. .. .. .. .. | 0·1 | 0·3 | 0·3 |
| Titre of 0·01 per cent. w/v dithizone solution, ml .. .. | 16·0 | 16·3 | 16·3 |

These experiments showed that the concentrations of hydrochloric and nitric acids required some measure of control, and it was found to be satisfactory to add sulphuric acid to solutions containing excess of hydrochloric or nitric acids (or both) and to boil until fumes were evolved. The solution was then allowed to cool and was diluted with water. The precipitated gold was dissolved by adding 6 drops of hydrochloric acid and 2 drops of nitric acid and evaporating to small volume (almost to the stage when fumes were evolved). Excess of acid was removed by diluting and re-evaporating, and the volume was then adjusted to make the solution 0·5 N in sulphuric acid.

RECOVERY OF GOLD AT DIFFERENT LEVELS—

Various aliquots of pure gold solutions 0·5 N in sulphuric acid were titrated, with the results shown in Table I; 10 ml of the solution containing 0·1 mg of gold per ml were used as standard. Recovery in all these determinations was satisfactory, but the most accurate results were obtained when a 10-ml aliquot of the gold solution was taken.

The method finally adopted is described below.

## METHOD

REAGENTS—

*Dithizone solution, 0·01 per cent. w/v, in chloroform*—Weigh 0·025 g of analytical-reagent grade diphenylthiocarbazone, transfer to a clean dry 500-ml conical flask, add 250 ml of chloroform, and warm gently on a steam-bath for about 5 minutes. Cool, and transfer to a dark-glass bottle having a well fitting stopper.

*Stock gold solution, about 1 mg per ml*—Dissolve 2 g of chloroauric acid, $HAuCl_4.xH_2O$ (containing about 51 per cent. of gold), in water, filter, if necessary, and adjust the volume to 1 litre. Assay this solution gravimetrically.

*Standard gold solution*—This solution should contain about 0·1 mg of gold (accurately known) per ml. By pipette, place 10 ml of stock gold solution in a 100-ml calibrated flask, add 50 ml of water and 1·5 ml of sulphuric acid, and swirl the flask. Cool, dilute to the mark, and mix thoroughly.

STANDARDISATION OF DITHIZONE SOLUTION—

By pipette, place 10 ml of standard gold solution in a 100-ml separating funnel, and add 5 ml of dithizone solution from a burette. Shake the funnel vigorously for 30 seconds, and allow the layers to separate for a further 30 seconds. Carefully run off the organic layer,

and add further 5-ml portions of dithizone solution until the organic layer is green. Repeat with a further 10 ml of standard gold solution, adding in one portion all but the last 5 ml of the volume of dithizone solution previously used. Shake the funnel vigorously for 30 seconds, and allow the layers to separate for 30 seconds as before. Carry out the last stage of the titration in 1-ml additions of dithizone solution until the organic layer is green. Finally, repeat the titration, initially adding dithizone solution to within 0·5 ml of the end-point, and carry out the last stage by making 0·1 ml additions *plus* 2 ml of chloroform. Take the end-point as the burette reading before the appearance of the pure-green colour in the organic layer. (The two rough titrations can be omitted if the approximate volume of dithizone solution required is known from experience.)

PROCEDURE FOR DETERMINING GOLD—

By pipette, place an aliquot of sample solution (preferably 10 to 25 ml) containing 0·2 to 1·5 mg of gold in 0·5 N sulphuric acid in a 100-ml separating funnel, and continue as described above. If hydrochloric or nitric acid is known or suspected to be present, evaporate until fumes of sulphur trioxide are evolved, as previously described. Calculate the gold content of the aliquot of sample solution from the equation—

$$\text{Gold present in sample aliquot, mg} = \frac{cv}{v'}$$

in which c is the amount of gold (in milligrams) present in 10 ml of the standard solution and $v$ and $v'$ are the volumes (in millilitres) of dithizone solution used for standardisation and determination, respectively.

TABLE I

RECOVERIES OF VARIOUS LEVELS OF GOLD

| Gold content present, mg per ml | Aliquot taken, ml | Titre of dithizone solution, ml | Gold found, mg | Recovery, % |
|---|---|---|---|---|
| 0·10 | 10 | 15·6 | 1·00 | 100·0 |
| 0·02 | 10 | 3·1 | 0·199 | 99·5 |
| | 20 | 6·3 | 0·404 | 101·0 |
| | 30 | 9·6 | 0·615 | 102·6 |
| 0·05 | 10 | 7·8 | 0·500 | 100·0 |
| | 20 | 15·7 | 1·007 | 100·7 |
| | 25 | 19·7 | 1·263 | 101·0 |
| 0·15 | 10 | 23·5 | 1·506 | 100·4 |
| | | 23·6 | 1·513 | 100·9 |

DISCUSSION OF THE METHOD

The time taken for a determination, including standardisation, is 30 minutes, and results are reproducible to within ±1·0 per cent. of the weight of gold present at the 0·2- to 1·5-mg level.

The sensitivity of the extractive titration can be increased by using a 0·005 per cent. w/v solution of dithizone in chloroform and standardising with 10 ml of a solution containing 0·025 mg of gold per ml.

Experiments were next carried out to test the applicability of this extractive-titration technique to the determination of gold in samples containing organic matter and other metals.

RECOVERY AFTER WET OXIDATION—

The samples to be analysed contained a certain amount of organic material, and it was necessary to ensure good recovery of the gold after wet oxidation. Aliquots of stock gold solution were placed, by pipette, in 100-ml Kjeldahl flasks, and 0·5 g of sucrose was added to each. The mixtures were oxidised by adding 5 ml of nitric acid, boiling until the initial vigorous evolution of brown fumes ceased, adding 1·5 ml of sulphuric acid and then boiling gently, with the dropwise addition of nitric acid, until no further charring occurred. Each digest was then allowed to cool and was diluted with about 10 ml of water. Some gold separated during wet oxidation, and more was precipitated at the dilution stage. This gold was dissolved by adding 6 drops of hydrochloric acid and 2 drops of nitric acid and evaporating the solution to small volume (about 3 ml) but not to fuming. Sometimes close examination

of the solution showed small particles of gold that had not dissolved, and the addition of 2 drops of hydrochloric acid, 1 drop of nitric acid and 10 ml of water, with further boiling, was generally sufficient to dissolve these last traces. Each solution was again diluted and evaporated to remove excess of acid and was finally diluted to 100 ml. Application of the proposed method to 10-ml aliquots of these solutions led to theoretical recoveries of gold; the results were—

| | | | | |
|---|---|---|---|---|
| Gold present, mg | 0·25 | 0·70 | 0·90 | 1·20 |
| Gold found, mg | 0·25 | 0·699 | 0·90 | 1·20 |
| Recovery, % | 100 | 99·8 | 100 | 100 |

INTERFERENCE BY OTHER METALS—

Although many metals form dithizonates under suitable conditions, the only possible sources of interference under the conditions of the proposed method are copper, mercury, palladium, platinum, silver and tellurium. Gold can be separated by reduction with various reducing agents, *e.g.*, Metol, *p*-phenylenediamine and hydroquinone, in hot (1 + 9) hydrochloric acid solution,[10,11] and ferrous sulphate and oxalic acid in dilute acid solution. Stannous chloride cannot be used, as palladium, platinum, mercury and silver are also precipitated. However, it was decided to test the interference of some of these metals without separation.

*Copper*—A solution was prepared to contain, in 0·5 N sulphuric acid, 10 mg of gold and 50 mg of copper per 100 ml; 10-ml aliquots were extractively titrated, and theoretical recovery was obtained, with no interference from the copper.

A solution containing 50 mg of copper per 100 ml, in 0·5 N sulphuric acid, was prepared, and a 20-ml aliquot was shaken for 30 seconds with 0·1 ml of a 0·01 per cent. solution of dithizone in chloroform *plus* 3 ml of chloroform. The organic layer remained green and showed only a blue-violet colour after being shaken for a further 1 minute, *i.e.*, there was no interference from copper. This may be explained by the slow rate of extraction of copper dithizonate from mineral acid solution. The rate would be even slower with chloroform as solvent than with carbon tetrachloride, owing to the lower equilibrium concentration of dithizone in the aqueous phase. Another factor may be the presence in the chloroform used of an impurity inhibiting extraction of copper, as has been reported for some grades of carbon tetrachloride.[12]

*Mercury*—A solution was prepared to contain, in 0·5 N sulphuric acid, 10 mg of gold and 50 mg of mercury per 100 ml, and a 10-ml aliquot was titrated. As expected, heavy positive interference was obtained, the organic layers being coloured by the bright orange of mercury dithizonate. This interference was overcome by transferring a 50-ml aliquot of the solution to a wide-necked 100-ml conical flask, adding a few millilitres of hydrochloric acid and evaporating to dryness; the flask was then heated around its base, sides and neck to volatilise the mercury. The residual gold was dissolved in 6 ml of hydrochloric acid *plus* 1 ml of nitric acid, and the solution was washed into a 100-ml Kjeldahl flask. A 1·0-ml portion of sulphuric acid was added, and the solution was evaporated until fumes were evolved. When the solution was cool, 10 ml of water, 6 drops of hydrochloric acid and 1 drop of nitric acid were added. The gold was dissolved by evaporating the solution to small volume, and excess of acid was removed by dilution and re-evaporation. The solution was then diluted to 50 ml in a calibrated flask, and 10-ml aliquots were titrated. The experiment was repeated with a solution containing 5 mg of gold and 50 mg of mercury. Good results were obtained, the colours of the organic layers showing the presence of gold only; the results were—

| | | |
|---|---|---|
| Gold present, mg | 10·0 | 5·0 |
| Gold found, mg | 10·0 | 4·98 |
| Recovery, % | 100 | 99·6 |

*Silver*—A 10-ml portion of silver nitrate solution, containing 100 mg of silver, and 10 ml of stock gold solution, containing 10 mg of gold, were placed by pipette in a 100-ml Kjeldahl flask, 1·5 ml of sulphuric acid were added, and the mixture was evaporated until fumes were evolved. After the solution had been cooled and diluted, hydrochloric acid was added in excess, *plus* 2 drops of nitric acid, and the mixture was boiled and diluted to 100 ml in a calibrated flask; 10-ml aliquots were titrated. However, the physical bulk of the silver chloride precipitate prevented evaporation to small volume to remove excess of acid, and results were slightly high. In further experiments, therefore, the solution was separated from most of the silver chloride by decantation, and a 50-ml aliquot of solution was evaporated to small volume. This solution was made up to 50 ml in a calibrated flask, and 10-ml aliquots

were titrated, with good results. At lower concentrations of silver, when the bulk of the silver chloride was considerably less, no separation was needed. Typical results for solutions containing 10 mg of gold were—

| | | | |
|---|---|---|---|
| Silver present, mg .. | 100 | 30 | 100 |
| Gold found, mg .. .. | 10·35* | 10·00* | 10·00† |
| Recovery, % .. .. | 103·5 | 100 | 100 |

* Silver chloride not separated. † Silver chloride separated.

*Platinum*—Solutions containing gold and platinum as the chlorides in 100 ml of 0·5 N sulphuric acid were prepared, and 10-ml aliquots were titrated. High recoveries were obtained, as shown by the results below.

| | | | |
|---|---|---|---|
| Gold present, mg .. .. .. | 10·0 | 5·0 | 10·0 |
| Gold found, mg .. .. .. | 10·2* | 5·1* | 11·2† |
| Recovery, % .. .. .. | 102 | 102 | 112 |

* 5 mg of platinum present. † 100 mg of platinum present.

Sulphur dioxide solution was added to a solution containing 5·00 mg of gold and 50 mg of platinum, and the mixture was warmed on a steam-bath for 30 minutes. The precipitated gold was separated on a Whatman No. 42 filter-paper, and the paper *plus* precipitate was transferred to a 100-ml Kjeldahl flask and oxidised by heating with 2 ml of sulphuric acid and small additions of nitric acid. The gold was brought into solution by the usual method, and the solution was diluted to 100 ml in a calibrated flask. The titration of 10-ml aliquots of this solution gave a result of 4·98 mg of gold, *i.e.*, recovery was 99·6 per cent.

*Other metals*—A mixture was prepared to contain 10·00 mg of gold and 100 mg each of cobalt, copper, nickel, manganese, iron, tin, zinc, lead and cadmium. Sulphuric acid (1·5 ml) was added, and the mixture was heated to fumes in a Kjeldahl flask. The solution was cooled and diluted, and the gold was dissolved by treatment with hydrochloric and nitric acids as before, the solution then being diluted to 100 ml. The solution was filtered to remove lead sulphate, and 10-ml aliquots were titrated; results were rather high, recoveries from triplicate experiments being 103·3, 102·6 and 104·0 per cent.

Obviously, from the preceding results, the most accurate determinations of gold in the presence of large amounts of foreign ions are effected by first separating gold as the metal, but for many purposes this may not be considered necessary.

## Applications of the method

### Therapeutical preparations containing gold—

Such preparations, used mainly in the treatment of rheumatoid arthritis, are generally solutions of organo-gold compounds, in which the gold is linked via a sulphur atom. The determination of gold content is straightforward and merely entails wet oxidation of a suitable portion of sample containing about 2 to 12 mg of gold, dilution to 50 or 100 ml and titration of 10-ml aliquots.

### Gold ores—

It was thought that the extractive titration might be suitable for the final stage in assaying gold ore, and three samples of ore were acquired for experimental purposes. These samples were ground to 200 mesh and are briefly described below.

*Ore No.* 1—Crown gold ore, from the Rand, South Africa; this ore contained about 20 pennyweights (dwt) of gold per long ton, iron being the main metallic impurity.

*Ore No.* 2—Crown gold ore *plus* granite, in a (1 + 1) mixture; the gold content of the mixture was about 10 dwt per long ton.

*Ore No.* 3—An ore containing about 25 dwt of gold per long ton and also containing silver (7 oz per long ton) and some copper, arsenic, antimony and zinc.

The preliminary treatment of the ores was as described by Jankovský,[13] and the determination was carried out as follows.

> Weigh accurately (to 0·1 g) about 30 to 35 g of ore, and transfer to a 1-litre beaker. Add 150 ml of sulphuric acid, cover with a clock-glass, boil for 3 hours, and allow to cool thoroughly. Carefully, with stirring and cooling, dilute to about 800 ml with water, heat to boiling-point to dissolve salts, and set aside to cool and to allow most of the

undissolved material to settle. Filter, with suction, through a 7·0-cm Whatman No. 42 filter-paper supported on a Buchner funnel (a Hartley three-piece funnel is recommended), and thoroughly wash the residue with hot water; discard the filtrate. Apply suction to the residue until it is dry, transfer to a silica dish, and ignite at approximately 550° C for about 30 minutes.

Allow the ignited material to cool, and transfer it to a 250-ml beaker. Extract with about 50 ml of aqua regia for 15 minutes, warming gently on a steam-bath in a fume cupboard, and then dilute with about 50 ml of water. Filter, with suction, through a sintered-glass crucible (porosity No. 3), and wash the residue, by decantation, with diluted hydrochloric acid (1 + 3). Pour the filtrate and washings into a 250-ml beaker, and evaporate to about 25 ml. Transfer to a 100-ml Kjeldahl flask, add 1 ml of sulphuric acid, and evaporate over a low flame until fumes of sulphur trioxide are evolved. Allow to cool, dilute with about 10 ml of water, add 6 drops of hydrochloric acid and 2 drops of nitric acid, and boil to dissolve the gold as described previously. (This small volume is insufficient to dissolve all the salts that separate, but the gold is completely taken up.)

Dilute, and again evaporate to about 3 or 4 ml, dilute to 25 ml, and filter through an 11-cm Whatman No. 42 filter-paper, collecting the filtrate in a 50-ml calibrated flask. Thoroughly wash the residues in the Kjeldahl flask and on the filter-paper with water, add the washings to the contents of the calibrated flask, and dilute to the mark. Mix thoroughly, and titrate 10-ml aliquots with a 0·005 per cent. w/v solution of dithizone in chloroform. (Standardise the dithizone solution with 10 ml of a solution containing 0·025 mg of gold per ml in 0·5 N sulphuric acid.)

The results found by this method for the ore samples were—

| Ore No. | 1 | 2 | 3 |
|---|---|---|---|
| Gold content, dwt per long ton | ~20 | ~10 | ~25 |
| Gold found, dwt per long ton | 20·7, 20·0, 20·7 | 10·2, 9·9, 10·5 | 24·9, 25·7, 24·7 |

The extractive titration should also be applicable to the determination of gold, after preliminary destruction of the cyanide, in the cyanide leaching liquor used in extracting gold ore.

## Conclusions

The proposed extractive-titration technique is capable of giving satisfactory results, provided that the conditions described, particularly as to the volumes of titrant and sample solution, are complied with. The sharp contrast between the yellow-brown colour of gold dithizonate and the green colour of free dithizone makes the end of the titration particularly easy to see, and the method has been used successfully for the routine analysis of samples containing gold over a wide range of concentrations.

I thank the Royal School of Mines, South Kensington, for kindly supplying the samples of gold ore, together with the relevant information about their compositions, and I am grateful to the Directors of Benger Laboratories Ltd. for permission to publish this paper.

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# An Automatic Coulometric-titration Assembly*

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An assembly is described for carrying out coulometric titration at approximately constant current; an electronic unit is used to integrate the amount of current supplied from a simple battery-operated resistor network. Potentiometric end-point indication permits the use of a conventional titrator-controller to decrease the current in the vicinity of the end-point and terminate the generating current at the pre-set end-point potential. The output from the integrator is fed to a potentiometric recorder, which displays the result in a bar presentation. The assembly includes a second potentiometric recorder to record the titration curve.

Determinations of chromium with electro-generated ferrous ions and of chloride with electro-generated silver ions are described to indicate the application of the assembly. Typical results show a mean error in the determination of chromium of +0·03 per cent. for 2 mg, with a standard deviation of ±0·18 per cent., and for 0·02 mg a mean error of −3·2 per cent., with a standard deviation of ±1·27 per cent. In the determination of chloride the mean error for 3·6 mg was +0·07 per cent., with a standard deviation of ±0·17 per cent., and for 0·2 mg a mean error of +1·6 per cent. and a standard deviation of ±4·65 per cent.

Coulometric titration is the term used to describe the determination of substances in solution with reagents generated electrolytically. Provided that the electrolytic processes take place without side-reactions and that the substance being determined reacts stoicheiometrically with the generated reagent, the amount of electricity that passes is a direct measure of the amount of substance present. The principles of coulometric analysis and descriptions of a wide range of apparatus and applications have been given by Lingane[1] and Delahay,[2] and regular reviews on electro-analysis and coulometric analysis have appeared.[3,4,5] Lewis[6] has recently surveyed coulometric methods in analysis and has paid some attention to the instrumentation required.

Three basic methods are used for measuring the amount of current passed during electrolysis: (*i*) by means of a chemical coulometer, (*ii*) accurate measurement of the time for which a controlled constant current flows and (*iii*) electro-mechanical or electronic integration. Chemical coulometers, although capable of extremely high accuracy, are less suitable for routine use because they are necessarily time-consuming and may require elaborate additional apparatus. With the second method, high accuracy can only be achieved by using a closely controlled current supply, together with an electrical or electronic timing unit. The third method is attractive, since it provides a direct measure of the amount of current, as does a chemical coulometer, without the need for additional chemical operations.

Many workers[7,8,9,10] have studied the use of low-inertia integrating motors, for which the speed of shaft rotation is a linear function of the applied voltage. Accuracy of integration and reproducibility of 0·1 to 0·2 per cent. have been claimed, although Lingane[11] has pointed out that calibration factors may vary by as much as 0·4 per cent. from day to day. Electronic methods for integrating current with respect to time are based on the charging of an electrical capacitor. Ramsay, Brown and Croghan[12] used the simplest possible arrangement in the micro-determination of chloride with a capacitor connected in series with the electrolysis cell. Booman[13] used a more elegant arrangement in which the changing current in controlled-potential electrolysis was fed to a capacitor-amplifier integrating system. Recently, W. G. Pye & Co. Ltd. have introduced a commercial integrating amplifier suitable for current-time integration in the range required for coulometric analysis, although it has so far been used mainly for integrating the signals from gas-chromatographic detectors.

## Description of apparatus

### Integrating amplifier—

The integrating amplifier operates by building up a charge on a capacitor connected across an amplifier; the arrangement of the circuit is shown schematically in Fig. 1. An

* Presented at the meeting of the Society on Wednesday, April 4th, 1962.

input-voltage signal causes a current to flow through resistor R, and an amplifier of infinite gain would maintain point A at constant potential, the capacitor C charging up at a rate proportional to the applied signal. The charge at any time is proportional to the total signal, and this produces an output potential at point B. In practice, the amplifier will have a finite gain, $g$, and point A will therefore change by a voltage $V/g$, where V is the voltage at B. The effect of this is best seen when the input is zero and there is a charge on the capacitor, for example, at the end of a determination. There will be a small reverse current through resistor R, owing to discharge of capacitor C, but this current, by the action of the amplifier, will be decreased to $(V/g) \div R$, so that the integrating capacitor will tend to discharge much more slowly. Compensation for this slow discharge can be made by a manually pre-set control in the amplifier, so that the charge on the capacitor is maintained constant, producing temporarily the effect of a perfect leak-free capacitor.

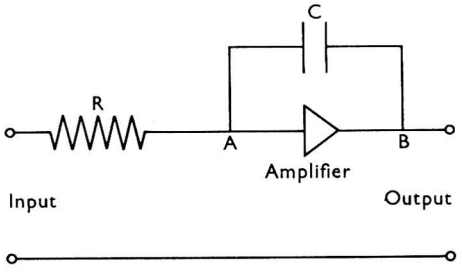


Fig. 1. Schematic diagram of integrating amplifier

The amplifier has a voltage output of up to 10 mV. The three range settings of $\times 1$, $\times 3$ and $\times 10$ and sensitivity selection ranges of $\times 0{\cdot}1$(A), $\times 1$(N) and $\times 10$(B) give nine ranges of 0 to 3 up to 0 to 3000 volt - seconds. A means is provided for discharging the capacitor when required by operating a built-in or external switch.

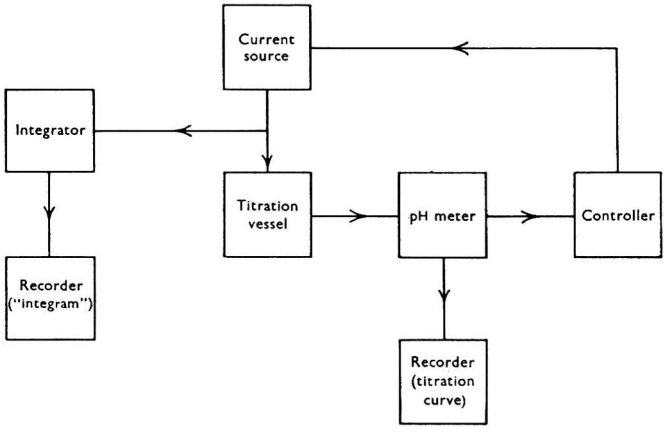


Fig. 2. Diagram of automatic coulometric-titration assembly

In the normal method of presentation, the output from the integrating amplifier is fed to a potentiometric recorder (full-scale deflection 10 mV). The recorder pen moves across the chart at a rate dependent on the rate of charging of the capacitor, and the distance moved across the chart is a measure of the charge on the capacitor. In order to effect expansion of the scale, a micro-switch on the recorder discharges the integrating capacitor just short of full-scale deflection, returning the recorder pen towards the electrical zero. Immediately after the capacitor has been discharged, charge builds up and the recorder pen again moves across the chart. When the input to the integrating amplifier is zero the recorder pen remains stationary; it can be returned to zero by discharging the capacitor. A typical "integram" is shown in Fig. 5 (p. 359).

APPARATUS FOR AUTOMATIC COULOMETRIC ANALYSIS—

As pointed out by Smythe,[9] coulometric analysis is of great importance in the field of automatic analysis. After the introduction of the sample, mixed with a suitable electrolyte, into the reaction vessel, all subsequent operations can be carried out simply by electrical switching. The block diagram in Fig. 2 shows how a number of commonly used laboratory instruments can be linked with an integrating amplifier and a simple current source to give automatic coulometric titrations with a permanent record of the progress of and current passed during the reaction.

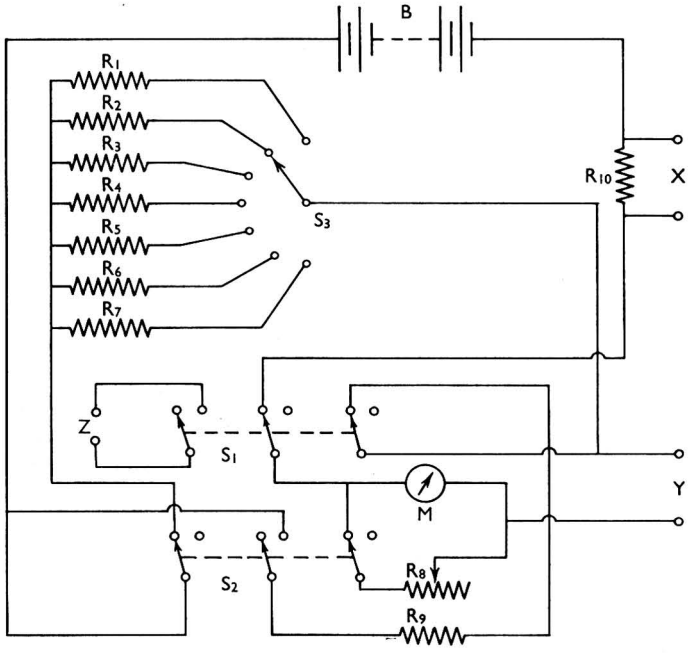


Fig. 3. Circuit of current source (for values of components, see Appendix, p. 361)

The current source is a simple battery-operated resistor network (see Fig. 3) having a number of switched current ranges. Current is derived from a 100-volt battery, B, feeding into the resistor network, $R_1$ to $R_7$, a suitable range being selected by switch $S_3$. In series with the generator electrodes, Y, is a standard resistor, $R_{10}$, across which the integrating amplifier is connected at X. The output from the integrating amplifier feeds into a potentiometric recorder. For reactions to which a potentiometric end-point is appropriate, *e.g.*, acid - base, redox, etc., suitable electrodes in the reaction vessel supply a voltage to a pH meter, the output from which feeds a recorder and a titrator - controller. At a pre-set voltage in the vicinity of the end-point, the titrator - controller operates a relay, $S_2$ (shown in Fig. 3 in the normal current "ON" position), which switches the battery feed from the main current-range resistor selected by $S_3$ to a fixed resistor, $R_9$, thereby decreasing the generating current to a low level. At the same time, the shunt, $R_8$, on the current-indicating meter, M, is removed, suitably increasing the sensitivity of the meter. At the detector-electrode voltage corresponding to the end-point, the titrator - controller operates relay $S_1$ (shown in the "ON" position), switching off the current. An additional set of contacts, connected at Z to the "RESET" terminals on the integrating amplifier, discharge the integrating capacitor, indicating completion of the titration on the integral record.

The values chosen for resistors $R_1$ to $R_7$ allow currents in the range 0·2 to 50 mA to be selected, although in fact the lowest current used was 0·66 mA. For the purpose of this work, it was considered sufficient to provide only one level of "low-current" supply near the

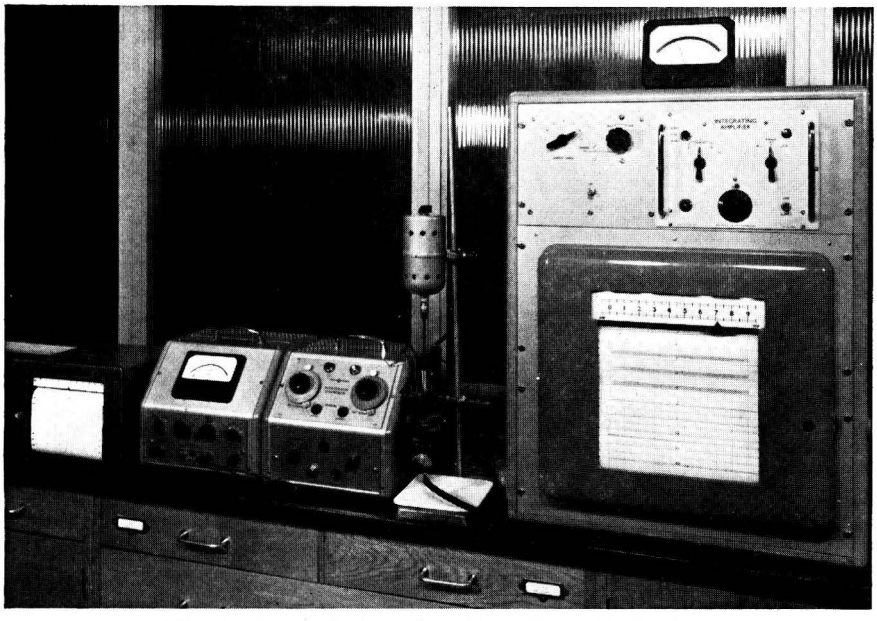

Fig. 4. Assembly for automatic coulometric titration

[To face page 358

end-point, and this, as shown above, is determined by $R_9$ giving 0·4 mA. A more sophisticated arrangement would be to select with $S_3$ a suitable "low-current" resistor to decrease the initial current by a constant fraction for each range. The complete assembly is shown in Fig. 4, and a typical titration curve and "integram" are given in Fig. 5.

## Use of the assembly

### Calibration of integrating system—

The integrating amplifier was calibrated by integrating for a given time the flow of current from a battery through a standard resistor. Since all subsequent work was carried out on the 0 to 300, 0 to 90 and 0 to 9 volt - second ranges, only these three were calibrated. For the 0 to 300 and 0 to 90 volt - second ranges, a current of 9 mA was maintained for 360 seconds through a high-stability resistor (100 ohms $\pm$ 0·02 per cent.), the potential drop across the resistor being measured at intervals with a Precision Potentiometer and the time with a stop-watch calibrated in fifths of a second. The first range produced a deflection across the chart of approximately 9 inches, and the second one of approximately 30 inches.

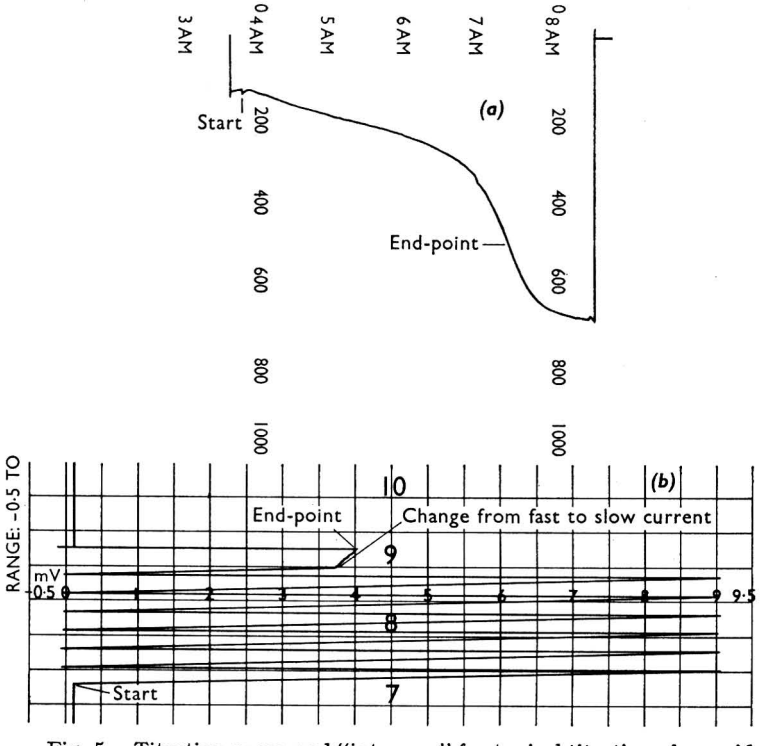


Fig. 5. Titration curve and "integram" for typical titration of an acid with electro-generated hydroxyl ions. (Although shown in full here, the titration curve would normally be terminated at the end-point)

For the smallest range, a current of 0·9 mA was used for a similar time, producing a deflection of approximately 30 inches. During a calibration, the current as shown by the measured potential drop across the standard resistor changed linearly by about 0·1 per cent., permitting an accurate mean value to be calculated. The results of the calibration are shown in Table I.

The electrical method of calibration was checked 6 months later by titrating analytical-reagent grade potassium hydrogen phthalate with hydroxyl ions, an external-generation cell based on the design of DeFord, Pitts and Johns[14] being used; in four determinations of 0·055 milli-equivalent, the mean error was +0·06 per cent.

DETERMINATION OF CHROMIUM—

The procedure used was that of Cooke and Furman,[15] as modified by Smythe.[9] With a weight pipette, standard potassium dichromate solution was placed in the titration vessel, which contained sulphuric acid and ammonium ferric sulphate solution. The generating

TABLE I

CALIBRATION OF INTEGRATING AMPLIFIER

| Integrator range setting | Nominal range, volt - seconds full scale | Actual range, volt - seconds full scale | Mean, volt - seconds full scale |
|---|---|---|---|
| A; ×1 | 300 | 279·7<br>280·9<br>280·2<br>280·5<br>280·1<br>279·2 | 280·1 ± 0·6 |
| N; ×3 | 90 | 86·98<br>87·18<br>87·44<br>87·20<br>87·08<br>87·10 | 87·16 ± 0·16 |
| B; ×3* | 9 | 8·923<br>8·921<br>8·937<br>8·927<br>8·947 | 8·93 ± 0·01 |

* The calibration procedure was repeated on this range 3 and 6 months after the initial work; calibration figures of 8·88 ± 0·01 and 8·90 ± 0·01 volt - seconds full scale, respectively, were obtained.

current used was varied for different concentrations of chromium, and platinum and calomel electrodes were used to follow the course of the reaction. When the indicated potential reached 600 mV, the titrator - controller unit switched the generating current to a lower value and at 510 mV switched it off. A blank titration was carried out on the supporting electrolyte before the potassium dichromate solution was added. The results for various concentrations of chromium are shown in Table II.

TABLE II

RESULTS FOR DETERMINATION OF CHROMIUM

| Chromium present, mg | Integrator range | Generating current, mA | Number of determinations | Mean error, % | Standard deviation of mean error, % |
|---|---|---|---|---|---|
| 0·023 | B; ×3 | 2 | 6 | −3·21 | ±1·27 |
| 0·053 | B; ×3 | 2 | 8 | −1·31 | ±0·68 |
| 0·488 | N; ×3 | 22 | 9 | −0·48 | ±0·32 |
| 0·980 | N; ×3 | 21 | 11 | −0·30 | ±0·31 |
| 1·970 | A; ×1 | 36 | 8 | +0·03 | ±0·18 |

DETERMINATION OF CHLORIDE—

The procedure used was that described by Lingane.[16] The supporting electrolyte contained 50 per cent. of ethanol to depress the solubility of the silver chloride formed, and the standard solution of sodium chloride was added from a weight pipette. A saturated-calomel electrode (connected with the solution by a salt bridge) and a silver indicator electrode were used to detect the end-point of the reaction. The results found for various concentrations of chloride are shown in Table III.

DISCUSSION OF RESULTS AND APPARATUS

The results obtained in both determinations carried out with the assembly compare well with those given in the literature. Cooke and Furman[15] reported average errors of ±0·1 per cent. for 1 to 9 mg of chromium and 1 per cent. for 0·17 mg. Smythe[9] found relative

mean errors ranging from +5 per cent. for 0·017 mg of chromium to −0·2 per cent. for 17·34 mg. Lingane[16] found an average error of −0·004 mg in determining 0·2 to 8 mg of chloride, with an average deviation of ±0·005 mg.

TABLE III

RESULTS FOR DETERMINATION OF CHLORIDE

The integrator range used was N × 3

| Chloride present, mg | Generating current, mA | Number of determinations | Mean error, % | Standard deviation of mean error, % |
|---|---|---|---|---|
| 0·18 | 0·66 | 14 | +1·58 | ±4·65 |
| 0·60 | 12 | 34 | −1·16 | ±1·41 |
| 2·13 | 12 | 8 | +0·204 | ±0·17 |
| 3·60 | 23 | 9 | +0·067 | ±0·17 |

It is clear that the apparatus described gives good accuracy. It is often desirable to have a permanent record of the results in routine analysis, and for research purposes useful data can accrue from recording the titration curve. Further development of the apparatus is contemplated with a view to automation of the sample and electrolyte additions. In this form, the unit would be suitable for use in plant monitoring and control.

We acknowledge with thanks the helpful suggestions and advice of Mr. R. S. Evans and Mr. R. B. G. Benson and the technical assistance of Mr. D. Harbidge.

## Appendix

LIST OF COMPONENTS USED IN CONSTRUCTION OF CURRENT SOURCE

B = Battery; 100-volt high-tension tapping (Ever Ready Portable 40).
$S_1$, $S_2$ = Electromagnetic relay, 230 volts a.c., 3-pole, 2-position (Besson and Robinson (Harlow) Relays, Harlow, Essex; type D52).
$S_3$ = Single-pole 8-position selector switch.
$R_1$ = 510,000-ohm 0·5-watt carbon resistor, tolerance ±5 per cent.
$R_2$ = 200,000-ohm 0·5-watt carbon resistor, tolerance ±5 per cent.
$R_3$ = 95,000-ohm 0·5-watt carbon resistor, tolerance ±5 per cent.
$R_4$ = 56,000-ohm 0·5-watt carbon resistor, tolerance ±5 per cent.
$R_5$ = 5000-ohm 5-watt wire-wound resistor, tolerance ±5 per cent.
$R_6$ = 2700-ohm 5-watt wire-wound resistor, tolerance ±5 per cent.
$R_7$ = 2200-ohm 5-watt wire-wound resistor, tolerance ±5 per cent.
$R_8$ = 100-ohm wire-wound variable resistor (Colvern Ltd., Romford, Essex).
$R_9$ = 250,000-ohm 0·5-watt carbon resistor, tolerance ±5 per cent.
$R_{10}$ = 100-ohm ±0·02 per cent. resistor (W. G. Pye & Co. Ltd., Cambridge; catalogue No. 7502).

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# The Detection and Determination of 5-Nitro-2-furfuraldazine in Nitrofurazone

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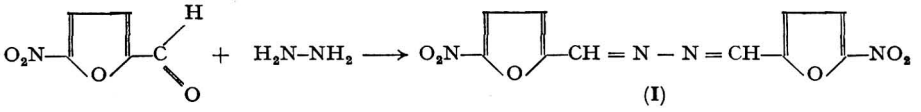
Methods for detecting 5-nitrofurfuraldazine in nitrofurazone have been investigated, and a convenient method for determining the compound has been developed. The procedure is based on the solubility of 5-nitrofurfuraldazine in chloroform, its separation by chromatography on a column of alumina and subsequent measurement with an ultraviolet spectrophotometer.

Since the reports by Dodd and Stillman[1] and Dodd[2] that nitrofurazone (5-nitro-2-furfurylidene semicarbazone) was a potentially active antibacterial compound, the drug has been applied to the treatment of many human and animal infections. Its use in avian coccidiosis has been recognised by the inclusion of a monograph for nitrofurazone in the British Veterinary Codex.[3]

The manufacture of nitrofurazone by allowing 5-nitrofurfuryl diacetate to react with semicarbazide hydrochloride is well established.[4] The purification of semicarbazide hydrochloride adds to the cost of the final product, and some manufacturers have recently used impure semicarbazide and semicarbazone intermediates. When such intermediates contain hydrazine, this will react with hydrolysed 5-nitrofurfuryl diacetate to give 5-nitrofurfuraldazine (I).




(I)

We have recently examined samples of nitrofurazone from some European and Middle Eastern sources. Although the New and Non-official Remedies (N.N.R.) grade of the drug complied with the qualitative requirements,[5] it was found that a 0·5 per cent. solution of the compound in polyethylene glycol yielded a precipitate when diluted with water. Infrared-spectrophotometric examination of this precipitate indicated that it might be 5-nitrofurfuraldazine.

Among the tests routinely applied by us to nitrofurazone in the assessment of purity is one in which the compound is dissolved in dimethylformamide and the solution is subsequently diluted to a standard volume with water. Good pharmaceutical grades of nitrofurazone remain in solution during this test, but some of the imported samples yielded a precipitate. When no precipitate is formed, or after removal of the precipitate, the absorption is measured at 375 m$\mu$, the maximum for nitrofurazone. The work reported here describes the methods developed to detect and determine 5-nitrofurfuraldazine in the presence of nitrofurazone.

## Experimental

### Preparation of 5-nitrofurfuraldazine—

5-Nitrofurfuraldazine was prepared by allowing 2 equivalents of 5-nitrofurfural to react with 1 equivalent of hydrazine hydrate in ethanol. The brownish yellow solid that separated was removed by filtration and then recrystallised from dimethylformamide; this yielded orange-yellow crystals melting at 249° C (with decomposition). Elemental analysis showed that the crystals contained 43·1 per cent. of carbon, 2·46 per cent. of hydrogen and 20·1 per cent. of nitrogen; the theoretical contents are 43·1, 2·17 and 20·1 per cent., respectively.

The infrared spectrum of the crystallised material was determined with a Hilger H800 spectrophotometer, the potassium bromide disc technique described by Cross, Stevens and Watts[6] being used. The spectrum showed peaks arising from the 5-nitrofuran and the C=N groups.

### Properties of 5-nitrofurfuraldazine—

*Solubility*—The solubility of the azine in water is about 0·2 mg per litre at 20° C; in chloroform, this figure is 900 mg per litre, and in 95 per cent. ethanol it is 18 mg.

*Absorption characteristics*—The ultraviolet-absorption curve of the azine exhibits a maximum in chloroform at 378 mμ ($E^{1\%}_{1cm} = 1359$); in a 0·2 per cent. aqueous solution of dimethylformamide, the maximum is again at 378 mμ ($E^{1\%}_{1cm} = 1200$). Beer's law was obeyed within the range 0·8 to 6 mg of the azine per litre, which was adequate for the amounts present in the samples of nitrofurazones.

*Photosensitivity*—5-Nitrofurfuraldazine, in common with other nitrofurans, is photosensitive, and solutions containing it should not be exposed to daylight for long periods. Exposure for short periods to fluorescent or incandescent lighting appears to have no serious effects.

DETECTION OF 5-NITROFURFURALDAZINE—

In an attempt to utilise the observation that 5-nitrofurfuraldazine was relatively insoluble in aqueous dimethylformamide, 100-mg amounts of N.N.R.-grade nitrofurazone containing known added amounts of 5-nitrofurfuraldazine were dissolved in separate 10-ml portions of dimethylformamide, and each solution was diluted to 100 ml with distilled water; the results are shown in Table I.

TABLE I

DETECTION OF 5-NITROFURFURALDAZINE IN AQUEOUS DIMETHYLFORMAMIDE

| Nitrofurazone taken, mg | 5-Nitrofurfuraldazine added, mg | Observation |
|---|---|---|
| 100 | Nil | No precipitate |
| 100 | 0·25 | |
| 100 | 0·50 | |
| 100 | 1·00 | |
| 100 | 1·50 | Precipitate after 10 minutes |
| 100 | 2·00 | Immediate precipitate |

Infrared-spectrophotometric examination of the separated precipitate showed that it was a mixture of 5-nitrofurfuraldazine and nitrofurazone.

This method, of possible value when relatively large amounts of 5-nitrofurfuraldazine are present, was considered to be insufficiently sensitive and specific for routine application to samples of nitrofurazone.

Separation of nitrofurazone from 5-nitrofurfuraldazine was then attempted by passing a solution of the compounds in dimethylformamide through a column of alumina. Nitrofurazone was retained on the column, and the less strongly adsorbed 5-nitrofurfuraldazine was collected in the first eluate. Nitrofurazone is itself fairly readily soluble in dimethylformamide, and separation by this technique necessitated the use of long columns; alternative techniques for separation were therefore investigated.

Further work showed that nitrofurazone was only slightly soluble in chloroform (92 mg per litre at 20° C) compared with the much greater solubility of 5-nitrofurfuraldazine (900 mg per litre at 20° C). Chloroform could therefore be used to dissolve the small amounts of nitrofurfuraldazine present in the nitrofurazone. The two compounds were further separated by passage of a chloroform solution containing them through a column of neutral alumina. Nitrofurazone was retained as a narrow orange band at the head of the column, whereas the 5-nitrofurfuraldazine was rapidly eluted.

During the initial examination of the suspect samples of nitrofurazone the chloroform eluate containing the nitrofurfuraldazine was evaporated carefully to dryness while protected from daylight. The dry yellow residue was weighed and then examined by infrared spectroscopy and thin-layer chromatography. Pure nitrofurazone treated in this manner left no residue when the solvent was evaporated.

INFRARED EXAMINATION OF RESIDUE—

The infrared spectrum of the residue was obtained as described previously.[6] All spectra suggested that 5-nitrofurfuraldazine was present, although some spectra were modified by the presence of a further impurity. This second impurity, present in much smaller amount, has not yet been fully identified; it is characterised by the existence of an intense peak in the 1750-$cm^{-1}$ region, which probably arises from a C=O stretching mode.

A sample of pure 5-nitrofurfuraldazine was dissolved in chloroform, and the solution was passed through a column of alumina. Evaporation of the solvent yielded a yellow residue,

the infrared spectrum of which was identical with that of the original nitrofurfuraldazine (see Fig. 1).

THIN-LAYER CHROMATOGRAPHY—

A study of the residue was made by thin-layer chromatography on glass plates (200 mm square) coated with modified silica gel support as described by Stahl.[7,8] A mixture of 3 volumes of benzene and 2 volumes of acetone was used as the mobile phase. The weighed residue obtained from the eluate from the column was dissolved in sufficient dimethylformamide to give a 1 per cent. solution, and a 5-$\mu$l portion was spotted on to the plate. Similar amounts of pure nitrofurfuraldazine and nitrofurazone were also placed on the plate.

The chromatograms were allowed to develop at 20° to 25° C until the solvent front had travelled 10 cm from the origin. The plate was dried and then sprayed with a 0·5 M solution of potassium hydroxide in ethanol, which produced a transient blue-green colour in the nitrofurfuraldazine zone and a dull red-brown with the nitrofurazone. 5-Nitrofurfuraldazine travelled with the solvent front, whereas nitrofurazone had an $R_F$ value of 0·23.

Reference has been made above to the occasional presence of a second impurity. Thin-layer chromatography revealed that this material had an $R_F$ value of 0·65 and that it developed a dull red-brown colour when sprayed with the ethanolic solution of potassium hydroxide.

In all instances when a chloroform-soluble residue was obtained during the examination of samples of nitrofurazone, this has been confirmed as nitrofurfuraldazine; on no occasion was nitrofurazone detected, thereby confirming its complete retention during the chromatographic separation.

The foregoing method provided a qualitative check on the purity of the samples of nitrofurazone examined, but a spectrophotometric determination was considered to be preferable. Since 5-nitrofurfuraldazine in chloroform solution exhibited a maximum absorption at 378 m$\mu$, with an $E^{1\%}_{1cm}$ value of 1359, this suggested a possible method for the quantitative determination of this impurity once it had been separated from the nitrofurazone.

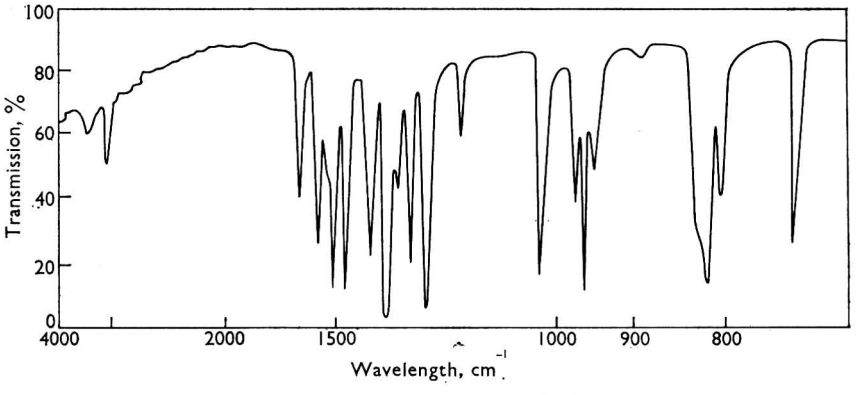



Fig. 1. Infrared spectrum of 5-nitrofurfuraldazine

## METHOD

APPARATUS—

A glass chromatographic tube, 35 cm long and 1 cm internal diameter, with the terminal restricted end joined to a short length of 1-mm capillary tubing.

REAGENTS—

*Neutral aluminium oxide*—Brockmann activity I.
*Chloroform*—Analytical-reagent grade.

PREPARATION OF COLUMN—

Insert a small plug of cotton-wool in the restricted end of the chromatographic tube, add sufficient alumina to give a column between 5 and 6 cm in depth, and consolidate it by tapping. Rinse the column with 20 ml of chloroform, and allow the excess of solvent to drain away; ensure that the surface of the alumina remains covered.

PROCEDURE—

Accurately weigh 100 ± 10 mg of nitrofurazone into a 50-ml beaker, add 20 ml of chloroform, and warm on a steam-bath, with stirring, for 5 minutes. Cool, transfer the solution and as much solid as possible to the column, allow the column to drain under gravity, and collect the solvent in a 100-ml calibrated flask. Rinse the beaker with 10 ml of chloroform, and pour the rinsings on to the column when the surface of the alumina is almost exposed; repeat the rinsing with two further 10-ml portions of chloroform. Dilute the combined eluates in the flask to 100 ml with chloroform at 20° C. When necessary, dilute further with chloroform at 20° C to provide a solution suitable for spectrophotometric measurement. (For samples of nitrofurazone containing about 3 per cent. of 5-nitrofurfuraldazine, a suitable dilution factor is 5 ml further diluted to 50 ml.)

Measure the absorption of the final dilution at 378 mμ in a stoppered 1-cm silica cell; use a matched cell containing chloroform as blank, and keep all solutions protected from daylight. Calculate the percentage of 5-nitrofurfuraldazine in the sample by using the value of 1359 for $E^{1\%}_{1cm}$.

## RESULTS

Solutions of known amounts of 5-nitrofurfuraldazine in chloroform were examined by the proposed method. The results, which confirm that satisfactory recovery of nitrofurfuraldazine is possible, were—

| | | | | | | |
|---|---|---|---|---|---|---|
| Azine present, mg .. .. | 0·39 | 0·98 | 1·97 | 2·95 | 3·93 | 4·91 |
| Azine recovered, mg .. .. | 0·39 | 0·97 | 1·93 | 2·93 | 3·85 | 4·82 |

The method was then applied to mixtures of pure nitrofurazone and 5-nitrofurfuraldazine; the results were——

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Azine present, % w/w .. | Nil | 0·51 | 0·95 | 2·05 | 3·12 | 4·19 | 4·97 |
| Azine found, % w/w .. | Nil | 0·48 | 0·93 | 2·03 | 3·13 | 4·21 | 4·97 |

Finally, eight suspect samples of nitrofurazone were analysed; the "apparent nitrofurazone" content of each sample was also determined in an aqueous dimethylformamide solution by the usual ultraviolet method, an $E^{1\%}_{1cm}$ value of 810 at 375 mμ being used. The results are shown in Table II. For those samples of nitrofurazone containing more than 1·5 per cent. of nitrofurfuraldazine, the dimethylformamide solution to be used in the ultraviolet assay yielded a precipitate when diluted with water. This precipitate was removed by filtration before the ultraviolet-absorption measurements were made.

TABLE II

RESULTS FOR SUSPECT SAMPLES OF NITROFURAZONE

| Sample No. | 5-Nitrofurfuraldazine found, % | "Apparent nitrofurazone" content on dry basis, % w/w |
|---|---|---|
| 1 | 0·66 | 99·8 |
| 2 | 5·3 | 99·8 |
| 3 | 3·4 | 98·2 |
| 4 | 4·7 | 98·7 |
| 5 | 3·1 | 98·9 |
| 6 | 2·8 | 99·6 |
| 7 | 0·04 | 99·7 |
| 8 | 0·95 | 100·2 |

We thank the Directors of Smith Kline and French Laboratories Ltd., in whose laboratories this investigation was carried out, for permission to publish and also those colleagues who rendered useful assistance in the work.

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# The Characterisation of Amides by the Formation of Diphenylmethyl Derivatives

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It is shown that amides of carboxylic and sulphonic acids can be conveniently characterised by treatment with diphenylmethanol to form diphenylmethyl derivatives. A simple general procedure is described, and the melting-points for the derivatives of twenty amides are recorded.

Although amides are usually characterised by hydrolysis and subsequent identification of the liberated acid, it is often desirable to form a derivative of the original compound. The most widely used procedure[1,2] is to form the xanthydryl derivative, but, owing to disproportionation of the reagent and other reasons, this method is not always satisfactory. Formation of mercury derivatives[3] and reaction with phthaloyl chloride to give *N*-acylphthalimides[4] have been proposed, but these procedures have not come into general use.

The reaction of diphenylmethanol (benzhydrol) with amides in the presence of toluene-*p*-sulphonic acid has now been shown to be widely applicable and yields satisfactory derivatives with an extensive range of amides derived from carboxylic and sulphonic acids.

## Method

Reagents—

*Diphenylmethanol.*

*Toluene-*p*-sulphonic acid.*

*Acetic acid, glacial.*

Procedure—

A mixture of the amide (1·0 g), diphenylmethanol (1·0 g), toluene-*p*-sulphonic acid (1·0 g) and glacial acetic acid (10 ml) is boiled under reflux for 30 minutes (as the mixture is heated a transient blue colour is produced). The hot mixture is poured into 10 volumes of water, the crude derivative then being precipitated. Generally, one crystallisation of this material gives the pure derivative.

## Discussion of results

All the primary carboxyamides and sulphonamides examined, including urea and urethane, gave satisfactory derivatives having melting-points distributed over a wide range of temperatures (see Table I).

Under the standard conditions, malonamide gave the bisdiphenylmethyl derivative and succinamide gave the mono-substituted compound. Attempts to form a derivative with phthalamide were unsuccessful, phthalimide being the major product. Urea gave the bis(*N*-diphenylmethyl) derivative, the yield being improved by using double amounts of diphenylmethanol and toluene-*p*-sulphonic acid. The mother liquor from the crystallisation of the bis(*N*-diphenylmethyl)urea yielded a small amount of the mono-substituted compound,

This method of characterisation is generally only suitable for compounds containing $-CONH_2$ and $-SO_2NH_2$ groups, and attempts to form derivatives with phthalimide and succinimide were unsuccessful. *N*-Methylacetamide failed to form a derivative, and the principal product from acetanilide was *p*-(diphenylmethyl)acetanilide, previously obtained by a number of methods including a similar reaction in the presence of concentrated sulphuric acid.[11]

## TABLE I

### MELTING-POINTS OF DIPHENYLMETHYL DERIVATIVES OF AMIDES

| Amide | Solvent used for crystallisation | Melting-point found, °C | Melting-point reported in literature, °C | Reference* | Elemental analysis: Theoretical carbon content, % | Elemental analysis: Theoretical hydrogen content, % | Elemental analysis: Carbon found, % | Elemental analysis: Hydrogen found, % |
|---|---|---|---|---|---|---|---|---|
| Acetamide | Benzene | 148·5 to 149·5 | 145 to 147 | 5 | — | — | — | — |
| Acetanilide | Nitromethane | 166 to 168 | 166 to 167 | 6 | — | — | — | — |
| Benzamide | Ethanol, 96 per cent. | 175 to 176 | 174 to 176 | 5 | — | — | — | — |
| Benzenesulphonamide | Ethanol, 96 per cent. | 185 to 186 | 183 to 184 | 5 | — | — | — | — |
| n-Butyramide | Mixture (1 + 1) of carbon tetrachloride and light petroleum, boiling range 60° to 80° C | 121·5 to 123 | — | — | 80·6 | 7·6 | 80·4 | 8·0 |
| Isobutyramide | Benzene | 146·5 to 147·5 | — | — | 80·6 | 7·6 | 80·8 | 7·5 |
| Chloroacetamide | Light petroleum, boiling range 80° to 100° C | 131 to 132 | 138 to 139; 128 | 7; 8 | — | — | — | — |
| Formamide | Light petroleum, boiling range 80° to 100° C | 132 to 134 | 132 to 134 | 5 | — | — | — | — |
| Malonamide | Ethanol, 96 per cent. | 234 to 235 | — | — | 80·2† | 6·0† | 80·6 | 5·9 |
| *p*-Methoxybenzamide | Ethanol, 96 per cent. | 198 to 199 | — | — | 79·4 | 6·0 | 79·3‡ | 6·1‡ |
| *p*-Nitrobenzamide | Ethanol, 96 per cent. | 223 to 224 | — | — | 72·3 | 4·85 | 72·45 | 4·9 |
| Phenylacetamide | Ethanol, absolute | 164 to 165 | — | — | 83·7 | 6·35 | 84·1 | 6·7 |
| Propionamide | Light petroleum, boiling range 100° to 120° C | 143 to 144 | 144·5 | 9 | — | — | — | — |
| Salicylamide | Benzene | 159·5 to 160 | — | — | 79·2 | 5·65 | 78·9‡ | 5·9‡ |
| Succinamide | Ethanol, 96 per cent. | 221 to 222 | — | — | 72·3§ | 6·4§ | 72·5 | 6·4 |
| *o*-Toluamide | Ethanol, 96 per cent. | 181 to 182 | — | — | 83·7 | 6·35 | 83·9 | 6·4 |
| *p*-Toluamide | Ethanol, 96 per cent. | 177·5 to 178 | — | — | 83·7 | 6·35 | 83·4 | 6·35 |
| Toluene-*p*-sulphonamide | Ethanol, 96 per cent. | 155 to 156 | 155 to 156 | 5 | — | — | — | — |
| Urea | Ethanol, 96 per cent. | 271 to 272† | 271 to 272† | 5 | — | — | — | — |
| Urea | Benzene | 146 to 147§ | 143§ | 10 | — | — | — | — |
| Urethane | Light petroleum, boiling range 100° to 120° C | 128 to 129 | 128 to 129 | 5 | — | — | — | — |

* See reference list, p. 368.
† Value for bisdiphenylmethyl derivative.
‡ This compound also gave a satisfactory result for nitrogen content.
§ Value for mono(diphenymethyl) derivative.

As expected,[5,12] this procedure gave *N*-(diphenylmethyl)amides with most compounds. The structural aspects of this work are being further investigated.

We thank Mr. A. Sarsfield for technical assistance.

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# The Determination of Zinc by Neutron Activation

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Several samples widely different in composition have been analysed for zinc by neutron activation. The method devised for separating zinc in a radiochemically pure form included the use of a column of dithizone retained with an organic solvent on cellulose acetate; this separation was completed sufficiently rapidly to permit convenient measurement of the activity of the 52-minute $^{69}$Zn nuclide if an increase in sensitivity over that provided by measuring the activity of the 13·8-hour $^{69m}$Zn nuclide was required.

The application of neutron-activation techniques to analytical problems has permitted methods to be devised for determining extremely small amounts of many elements having suitable nuclear characteristics. Schemes have been reported for the determination of zinc by neutron activation,[1,2] but these have been of rather specialised application and have required measurement of the gamma-active 13·8-hour $^{69m}$Zn nuclide. The lower levels for the determination of zinc by neutron activation and other methods have been considered elsewhere[2,3,4] and will not be reconsidered here, but the sensitivity attained by measuring the radioactivity of the $^{69m}$Zn nuclide after the sample has been irradiated in a flux of $1{\cdot}5 \times 10^{12}$ neutrons per sq. cm per second for 12 hours is little better than that achieved by conventional colorimetric methods; consequently, although a procedure that permits calculation of mass loss and tolerates the presence of traces of impurities in reagents is preferable to one that does not, relatively little use has been made of the method. An increase in the period of irradiation of the samples or irradiation at a higher neutron flux would improve the potential sensitivity of the method, but these procedures are of limited application, since long periods of irradiation are likely to prove inconvenient, and, even if a flux in excess of $1{\cdot}5 \times 10^{12}$ neutrons per sq. cm per second were available, the activity induced in the matrix material could be sufficiently high to require special handling techniques, so significantly complicating the procedure. There is, however, another method whereby a 10-fold increase in the saturation specific activity of the zinc can be achieved; this is by measuring the beta-activity of the 52-minute $^{69}$Zn nuclide, if facilities are available for processing the sample soon after its removal from the reactor and before radioactive decay offsets the increased sensitivity that is to be gained from assaying the shorter-lived nuclide. The method described below was found to be suitable for determining zinc in a variety of samples after neutron activation, the final measurements being carried out by assaying the activity of the 52-minute or the 13·8-hour nuclide.

## Practical considerations—

When the sample has been irradiated, the zinc must be isolated from all other elements that might contribute to the final measured activity, and, in view of the short half-life of the $^{69}$Zn isotope, any method used to effect this separation should be rapidly completed. A column of dithizone retained on cellulose acetate, as used previously in the separation of indium,[5] will extract zinc quantitatively from an acetate medium of pH 5, and, since the element can be recovered completely by elution with hydrochloric acid, the possibility of using this procedure as a basis for rapidly freeing the zinc from contamination was investigated. The widely different acidities used for extraction and elution of the zinc do not yield the element in a chemically pure form, and a number of metals that might cause radiochemical interference, *e.g.*, indium, cadmium, gallium$^{III}$,[6] tin$^{II}$ and cobalt$^{II}$, will appear in the eluate together with the zinc. The separation may be considerably improved by using solutions more closely similar in acidity for extraction and elution, but a slower rate of flow is needed for satisfactory separation under these conditions, and this is inconvenient if the activity of the nuclide having the short half-life is to be measured. Consequently, an iron scavenge and precipitation by quinaldic acid were used in conjunction with the simple separation on dithizone to provide radiochemically pure zinc, rather than employing a slower chromatographic procedure. A further advantage of this technique is that the small amount of precipitated zinc quinaldate can be rapidly heated to fumes with nitric - perchloric acid

mixture to precipitate any traces of silica that may have been carried through to this stage of the procedure and which, if not removed before the sample solution is placed on the column, might separate during operation of the column and seriously decrease the rate of liquid flow.

## Experimental

### Preparation of dithizone columns—

The columns of dithizone used for separating zinc were similar to those previously used for separating indium[5] and consisted of a solid support of cellulose acetate retaining dithizone and a (1 + 1) mixture of chloroform and carbon tetrachloride.

The column material was prepared by placing the 44- to 85-mesh fraction of a sample of cellulose acetate (obtained from British Celanese Ltd.) in a beaker and stirring into it a concentrated solution of purified dithizone[7] dissolved in carbon tetrachloride - chloroform mixture (1 + 1) until free liquid was visible at the bottom of the beaker. The organic solvent was then slowly evaporated in a current of air, and the dry powder was stored in a bottle in the dark until required. Before use, chloroform - carbon tetrachloride mixture was added to the dithizone - cellulose acetate powder (1·0 ml per g) and was distributed evenly throughout the solid phase by stirring. Sodium acetate - hydrochloric acid buffer solution of pH approximately 5 was added, and the slurry was made up into a column in the usual way. Finally, a plug of glass-wool was pressed down on top of the column to hold the cellulose acetate in position. The columns used for separating zinc from activated samples were approximately 2 cm in diameter and 25 cm long; rates of flow were from 15 to 25 ml per minute.

### Irradiation—

Portions (about 100 mg) of the sample to be analysed were accurately weighed and sealed into thin-walled silica tubing (4 mm bore). Standards of zinc nitrate solution prepared from Specpure zinc rod were also sealed into 4-mm silica tubing, and samples and standards were irradiated together for periods varying from 20 minutes to several hours (depending on the zinc content of the sample and the half-life of the isotope to be measured) in a flux of approximately $1{\cdot}5 \times 10^{12}$ neutrons per sq. cm per second.

### Solution of samples—

Samples were dissolved after being sintered at 480° ± 20° C with sodium peroxide in a nickel crucible for 10 minutes or by boiling with a mixture of either hydrofluoric and perchloric or hydrochloric and nitric acids. When acid attack was used, the irradiated sample was emptied directly out of the silica tube into the acid mixture, to which had been added 10 mg each of iron (as ferric chloride) and zinc carrier. The sodium peroxide sinter was transferred, after heating, to an aqueous phase containing 10 mg each of iron and zinc carrier, prepared by adding 1 ml of iron solution and 2 ml of zinc carrier solution (see "Reagents") to a few millilitres of distilled water. The hydroxides so precipitated were dissolved by acidifying the solution with the minimum amount of hydrochloric acid.

## Method

### Reagents—

*Zinc carrier solution*—Prepare a solution containing 5 mg of zinc per ml by dissolving zinc rod in dilute nitric acid.

*Iron solution*—Prepare a solution containing 10 mg of iron per ml by dissolving ferric chloride in water.

*Hydrofluoric acid, 40 per cent.*

*Perchloric acid, 72 per cent., sp.gr.* 1·70.

*Nitric acid, sp.gr.* 1·42.

*Hydrochloric acid, sp.gr.* 1·18.

*Sodium peroxide*—Powdered and containing not less than 85 per cent. of $Na_2O_2$.

*Sodium hydroxide solution, concentrated, aqueous.*

*Ammonia solution, sp.gr.* 0·880.

*Indicator*—B.D.H. "4·5" indicator (obtained from the British Drug Houses Ltd.).

*Quinaldic acid solution*—Prepare a 2 per cent. aqueous solution, and neutralise with sodium hydroxide.

*Tartaric acid, crystalline.*

*Buffer solution*—Adjust the pH of 2 N sodium acetate to approximately 5 with hydrochloric acid, and set aside over a solution of dithizone in the organic solvent mixture.

*Dilute perchloric acid*—Allow 0·002 N perchloric acid to stand over a solution of dithizone in the organic-solvent mixture.

*Dilute hydrochloric acid*—Allow N hydrochloric acid to stand over a solution of dithizone in the organic-solvent mixture.

*Organic-solvent mixture*—Mix equal volumes of chloroform and carbon tetrachloride.

*Ethanol, absolute.*

PROCEDURE—

To an acid solution of the sample containing 10 mg each of iron and zinc carrier add excess of sodium hydroxide or ammonia solution, boil to coagulate the precipitated hydroxides, and filter. Acidify the filtrate by adding hydrochloric acid dropwise, add 1 ml of iron solution, and repeat the iron scavenge by adding alkali, boiling and filtering. After the second precipitation of iron hydroxide, dissolve 1 to 2 g of tartaric acid in the filtrate, add 4 drops of indicator, and adjust the pH to about 4·5 with hydrochloric acid or ammonia solution.

Precipitate the zinc by adding 10 to 20 ml of quinaldic acid solution, and separate the zinc quinaldate from the supernatant liquid by centrifugation; discard the aqueous phase. Warm the precipitate with 10 ml of nitric acid to oxidise as much of the organic matter as possible, add 5 ml each of nitric and perchloric acids, and heat until fumes of perchloric acid are evolved to destroy the organic complex. Adjust the pH of the residual solution to about 5 with sodium acetate - hydrochloric acid buffer solution, and filter through glass-wool to remove any silica that might have been precipitated. Shake the filtrate with the organic-solvent mixture to saturate the aqueous phase with solvent, and separate the lower non-aqueous phase. Allow the aqueous phase to run through a dithizone - cellulose acetate column, wash the column with 50 ml of buffer solution and 100 ml of dilute perchloric acid, and finally elute the zinc with dilute hydrochloric acid; collect 75 ml of eluate as soon as the hydrochloric acid begins to leave the column. Dissolve 1 to 2 g of tartaric acid in the eluate, add 4 drops of indicator, and adjust the pH to about 4·5 with hydrochloric acid or ammonia solution. Precipitate the zinc by adding 10 to 20 ml of quinaldic acid solution, and separate the zinc quinaldate from the supernatant layer by centrifugation; discard the aqueous phase. Wash the precipitate with water, spin in a centrifuge, discard the aqueous phase, and make the precipitate into a slurry with a little ethanol. Transfer the slurry to a weighed counting tray, evaporate to dryness under an infrared lamp, weigh to determine the chemical yield, and measure the activity of the sample.

When convenient, transfer each zinc standard from its silica ampoule to a beaker containing 2 ml of zinc carrier solution, wash the ampoule once with nitric acid and twice with distilled water, and add the washings to the contents of the beaker. If there is no likelihood of any impurities being present in the irradiated zinc or being eluted from the silica ampoule, precipitate the zinc as quinaldate, wash, and transfer to a counting tray as described above. When there is a possibility of contamination of the standard with activities likely to interfere with the final radiochemical assay, the standard should be treated in the same way as the sample to achieve satisfactory results.

## MEASUREMENT OF RADIOACTIVITY

The counting trays containing the precipitated zinc quinaldate were placed on an automatic beta-counter and moved in turn beneath an end-window Geiger - Müller tube for beta-assay. Each completed count was recorded by a print-out to permit the decay of samples and standards to be conveniently compared over a period of several half-lives. A separate series of experiments indicated that no self-absorption occurred.

Gamma-assay was by means of a gamma-scintillation assembly associated with a 99-channel pulse analyser. The zinc contents of the samples were calculated from the total gamma-counts and also from the counts within the 0·44-MeV peak. The two series of results were always found to agree within the limits of experimental error.

## PROCEDURE FOR SAMPLES OF HIGH ZINC CONTENT

One of the advantages of neutron activation over many other analytical techniques is the ease with which correction may be made for chemical yield, thereby avoiding the necessity for quantitative recovery at each step of a multi-stage separation procedure.

Correction for mass loss during processing is usually applied, assuming that the amount of metal isolated from the sample or irradiated as standard is negligible by comparison with the amount of carrier used. When this is not so, and if the use of smaller samples or increased amounts of carrier is undesirable, allowance must be made for the additional metal present in the system. Consequently, when samples of high zinc content were analysed, sample and standard solutions were made up as shown below from components containing zinc—

| Sample solution | Standard solution |
|---|---|
| $x$ mg of sample* | $x$ mg of sample |
| $y$ ml of standard zinc solution | $y$ ml of standard zinc solution* |
| $z$ ml of carrier solution | $z$ ml of carrier solution |

the asterisk denoting the component of each solution that was irradiated. As the total-zinc contents of both solutions were similar, the usual yield correction could be applied.

## Discussion of the method and results

Although the method described above was designed primarily for determining zinc by assay of the 52-minute $^{69}$Zn nuclide, it was considered desirable for the same procedure to be equally applicable to measurement of the activity of the 13·8-hour $^{69m}$Zn nuclide. In view of the difference between the half-lives of these two isotopes, control of irradiation and decay times could not be extensively used to limit possible radiochemical interference; consequently, isolation of zinc in radiochemically pure form was dependent largely on the development of an efficient means of chemical separation. Several elements are likely to be extracted together with zinc by a column of dithizone from an acetate phase prepared by dissolving the fumed quinaldic acid residue in sodium acetate buffer solution, and some of these will be eluted by N hydrochloric acid. In spite of the extensive application of solutions of dithizone to the separation and determination of metals,[8] the reactions of several elements with dithizone are either in doubt or have not been well characterised.[9] Nevertheless, it is likely that elements following zinc in the eluate from the column will be those forming complexes with dithizone that are of rather limited stability to acid; of these elements, indium and, to a lesser extent, cadmium are likely to cause radiochemical interference if present in appreciable amounts in the sample. Further interference may arise from elements forming dithizonates only slightly stable in a liquid - liquid system, but which are extracted more readily when the complexing agent is retained on a column of cellulose acetate. Thus, gallium$^{III}$, which is appreciably extracted from an aqueous phase by a solution of dithizone in carbon tetrachloride only when the aqueous phase is weakly acidic and when the concentration of free ligand acid is high,[10] will appear with zinc in the eluate from the column and must be removed before the final assay. It was therefore considered necessary to include in the procedure a scavenge with hydroxide and a precipitation by quinaldic acid to prevent such interferences; hydroxide was precipitated by adding either sodium hydroxide or ammonia solution, but the former was always used when there was a possibility of the zinc being contaminated with cadmium.

In all experiments, the gamma-ray spectra indicated that the zinc isolated for the determination was radiochemically pure (a typical example is shown in Fig. 1), and counting was begun less than 100 minutes after the start of processing. Yields were usually better than 70 per cent. Some results are shown in Table I.

### Table I

Zinc contents found by proposed method

The limits shown are the standard deviations of several determinations

| Sample | Beta-assay | | Gamma-assay | |
|---|---|---|---|---|
| | Time of irradiation | Zinc content found | Time of irradiation | Zinc content found |
| Granite G-1 .. .. | 1 hour | 45·1 ± 2·1 p.p.m. | 14 hours | 43·9 ± 0·1 p.p.m. |
| Diabase W-1 .. .. | 1 hour | 86·1 ± 6·1 p.p.m. | 14 hours | 84·7 ± 2·3 p.p.m. |
| Alloy No. 85a .. .. | 30 minutes | 210 ± 5·0 p.p.m. | 1 hour | 202 ± 6·0 p.p.m. |
| Alloy No. 87 .. .. | 20 minutes | 788 ± 25 p.p.m. | 30 minutes | 771 ± 30 p.p.m. |
| Alloy No. 86c .. .. | 20 minutes | 1·42 ± 0·13 per cent. | 20 minutes | 1·49 ± 0·15 per cent. |

The values found for the zinc contents of the rocks W-1 and G-1 agree well with the preferred values of 83 and approximately 40 p.p.m.[11] and are similar to those found colorimetrically, but slightly higher than the polarographic results reported recently.[12] Previous analyses of the National Bureau of Standards aluminium alloy (wrought) No. 85a and silicon - aluminium alloy No. 87 gave zinc contents ranging from 150 to 230 p.p.m. for No. 85a and from 650 to 900 p.p.m. for No. 87, the average values being 190 and 770 p.p.m., respectively.

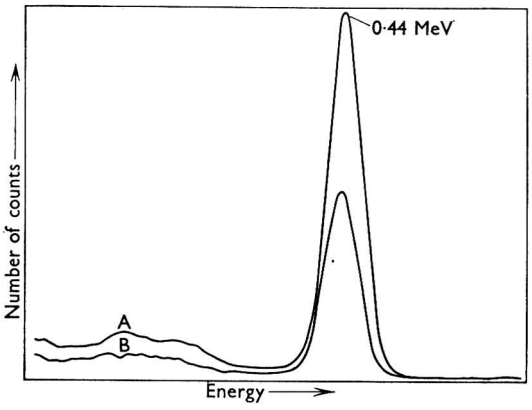


Fig. 1. Typical gamma-ray spectra of zinc isolated from: curve A, standard; curve B, granite G-1

The aluminium alloy (casting) No. 86c could have been conveniently analysed by techniques having lower sensitivities than neutron activation because of its relatively high zinc content, but the results found by activation are in substantial agreement with the quoted value of 1·50 $\pm$ 0·01 per cent., although the spread of the determinations is greater. For the results in Table I, about 100 mg of sample were taken, but the higher sensitivity of the neutron-activation technique could prove useful for the analysis of samples having high zinc contents if only limited amounts were available. However, in this event, considerable care would be necessary to ensure that the analyses were representative of the sample.

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# The Rapid Determination of Nitrate in Fresh and Saline Waters

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The method described by Hartley and Asai for determining nitrate has been modified to eliminate the need for prior removal of chloride. The reaction between 2,6-xylenol and nitrate takes place in a sulphuric acid medium in the presence of ammonium chloride, and the concentration of the product is determined by optical-density measurements at 304 mμ with a spectrophotometer. The range of the method has been extended to 55 p.p.m. of nitrate-N, and the need for evaporating some of the less concentrated samples has been removed by the use of 4-cm cells. The sensitivity of the modified method, which is applicable to river and estuary waters and sewage effluents, is 0·13 p.p.m. of nitrate-N at 95 per cent. confidence limits. Coefficients of variation of 1·8 and 0·7 per cent. have been obtained for 10 and 40 p.p.m. of nitrate-N, respectively. Interference from nitrite, ferrous iron and sulphamic acid is overcome. A single determination takes 45 minutes, and many determinations can be made simultaneously.

In a method involving use of Devarda's alloy, the slow absorption by the alloy of nitrogen from the atmosphere has been shown to affect the blank value.

The phenoldisulphonic acid method, widely used for determining nitrate in water, is tedious and subject to several interferences; the fact that ammonium salts can interfere was apparently not noticed until 1960.[1] Other methods in common use include (*a*) determination of the ammonia formed after reduction with various metallic reducing agents and (*b*) the brucine method. Recent workers[2,3] have improved the reliability of the brucine method, although rigorously controlled conditions and simultaneous determinations of standards are still necessary. The need for a rapid and reliable method for determining nitrates led to the work described below. Several recent methods were tested before that of Hartley and Asai[4] was selected for detailed examination.

## Experimental

Because of the ease with which nitrite can be determined, much attention has been given to the establishment of conditions for reproducible conversion of nitrate into nitrite. Strict attention to experimental detail is always necessary, and Meerman[5] considers that quantitative conversion is impracticable. In our experiments, destruction of the nitrite formed in Procházková's method[6] (hydrazine as reducing agent) proceeded rather more rapidly than was claimed. Several workers have described techniques in which reduction is carried out by zinc dust in the presence of ammonium hydroxide, and high yields of nitrite were claimed.[7,8,9,10] However, the use of ammonium hydroxide is best avoided in laboratories where small amounts of ammonia are determined, and experiments in which the ammonium hydroxide was replaced by a solution of disodium ethylenediaminetetra-acetate adjusted to a pH of 10·2 to 11·2 with sodium hydroxide were unsuccessful. Attempts to use other metallic reducing agents (lead, tin, antimony, iron and cadmium) and hydroxylamine were also unsuccessful. The method described by Hill, Pivnick, Engelhard and Bogard,[11] in which nitrate is reduced to nitrite by a culture of *Pseudomonas oleovorans*, was more satisfactory, but reproducibility was not good, and the technique was considered to be too exacting for routine use. A colorimetric method depending on the oxidation of 3,3′-dimethylnaphthidine[12] was not sufficiently accurate for our purposes.

### Nitration of 2,6-xylenol—

Good results were obtained by using Hartley and Asai's tentative method,[4] in which the product of the reaction between nitrate and 2,6-xylenol in highly acid medium is determined colorimetrically (Asai[13] gave reasons for regarding the 2,6-isomer as the most suitable of the six xylenols). The investigations described below had two aims: (*i*) to eliminate the need for removing chloride and (*ii*) to study the scope and limitations of the method.

REACTION MEDIUM—

Hartley and Asai described two alternative procedures, the acid mixture used being either 75 per cent. v/v sulphuric acid or a mixture of equal volumes of sulphuric and orthophosphoric acids. In a preliminary test, samples of sewage effluent were mixed with suitable amounts of acetic acid and the two acid mixtures. The smaller increment in optical density was obtained with the 75 per cent. acid, indicating less interference from organic matter, and this mixture was used exclusively in subsequent experiments.

Portions (8 ml) of sulphuric acid were dispensed with an automatic piston pipette (type PP3) obtained from W. G. Flaig & Sons Ltd.

EFFECT OF CHLORIDE—

In the presence of chloride results are high; Hartley and Asai recommend removal of chloride by addition of silver sulphate and then filtration. We found that chloride causes a large increase in optical density, which becomes constant when the concentration of chloride in the reaction mixture exceeds 0·7 per cent. The shift in maximum wavelength from 322 to the region of 304 m$\mu$ supports Asai's suggestion[13] that the effect of chloride is to reduce the nitrate to a nitrosating species, which then reacts to give 4-nitroso-2,6-xylenol. The optical density attained is consistent with a yield of 80 to 90 per cent. of the theoretical amount of 4-nitroso-2,6-xylenol ($\epsilon = 20{,}400$). A further effect of increase in concentration of chloride is to prevent interference from bromide also present in saline samples. A similar increase in sensitivity in the presence of chloride was found by West and Lyles with their chromotropic acid method.[14]

The stability of the product is greatly enhanced by dilution with water; this procedure has the further advantage of giving a more useful working range. The optical density remains constant for 2 hours at room temperature or 2 days in the dark at 5° C.

EFFECT OF TEMPERATURE—

The absorption was increased when cooled reagents were used. The technique finally adopted was to cool the sulphuric acid in a refrigerator before adding the sample and xylenol reagent solution (the order of addition stated by Hartley and Asai is important). Results are substantially constant when the initial temperature of the acid is between 0° and 10° C, but the best agreement between replicates is near the middle of this range.

PURITY OF REAGENTS—

Results were erratic when reagents of purity less than the best available were used. All water used in this work was redistilled from alkaline permanganate.

INTERFERENCES—

The substances listed in Table I were tested for interference at the levels shown.

Nitrite reacts similarly to nitrate, although to a slightly lesser extent. For pure solutions of nitrite Beer's law is obeyed up to at least 60 p.p.m. of nitrite-N, and the absorption corresponds to a 79 per cent. yield of 4-nitroso-2,6-xylenol. In the proposed method, as in the original procedure, nitrite is destroyed by sulphamic acid. Since large amounts of sulphamic acid interfere, a small and approximately constant amount is added as described below. In the presence of sulphamic acid the upper limit of accuracy of the method is 40 p.p.m. of nitrate-N.

A value for total oxidised nitrogen can be obtained after oxidising the nitrite to nitrate. Since soluble oxidising agents will interfere with the subsequent determination unless removed, the oxidation is most conveniently effected by shaking the sample, acidified with a few drops of concentrated sulphuric acid, with solid sodium bismuthate; excess of bismuthate is removed by filtration. This procedure gives rather high blank values and is not recommended for accurate work.

Ferrous iron is occasionally present in surface waters and trade effluents, but its concentration may be decreased to an insignificant level by dilution. Alternatively, ferrous salts may be removed by shaking the sample (20 ml) vigorously with 10 g of a sulphonic acid type of cation-exchange resin in the sodium form. Sulphamic acid is also removed by the resin, so that nitrate can be directly determined in the range 40 to 55 p.p.m. after destruction of nitrite. The resin must be thoroughly washed with distilled water and stored and used in a slightly moist condition.

TABLE I

EFFECTS OF VARIOUS SUBSTANCES ON DETERMINATION OF 10 p.p.m. OF NITRATE-N BY PROPOSED METHOD

| Substance added | Concentration in sample, p.p.m. | Effect |
|---|---|---|
| $Ca^{2+}$ | 200 | None |
| $Mg^{2+}$ | 50 | None |
| $Mn^{2+}$ | 20 | None |
| $Fe^{2+}$ | 5 | Insignificant |
| $Fe^{2+}$ | 10 | Recovery of nitrate 4 per cent. high; blank value slightly increased |
| $Fe^{3+}$ | 20 | No direct interference; optical densities (1-cm cells) of blank and test solutions increased by 0·04 unit |
| $Cl^-$ | $2 \times 10^4$ | None |
| $Br^-$ | 65 | None ($2 \times 10^4$ p.p.m. of $Cl^-$ also present) |
| $I^-$ | 1 | None |
| $IO_3^-$ | 1 (as I) | None |
| $CrO_4^{2-}$ | 10 | Insignificant |
| $H_3BO_3$ | 500 | None |
| $H_3PO_4$ | 10 | None |
| Phenol | 10 | None |
| Sulphamic acid | Various | Negative interference, especially at high concentrations of nitrate-N |
| Hypochlorite | 1 (as "residual chlorine") | None |
| $H_2O_2$ | Various | Much interference |
| $IO_4^-$ | Various | Much interference |
| $S_2O_8^{2-}$ | Various | Much interference |

## METHOD

### REAGENTS—

*Sulphuric acid, 80·5 to 83·3 per cent. w/w, sp.gr. 1·733 to 1·762 at 20° C*—Mix 455 ml of M.A.R. sulphuric acid (98 to 100 per cent.) with 171 ml of nitrate-free water.

*Ammonium chloride solution, 24 per cent. w/v.*

*2,6-Xylenol reagent solution*—Dissolve 0·122 g of 2,6-xylenol in 50 ml of analytical-reagent grade acetic acid, and add the solution to 50 ml of 24 per cent. ammonium chloride solution. Shake the vessel, and warm to dissolve any precipitated ammonium chloride.

*Sulphamic acid papers*—Cut a disc of 5·5-cm Whatman No. 5 filter-paper into sixteen equal segments, and soak the pieces in a warm solution of 5 g of sulphamic acid (of the grade intended for an organic analytical standard) in 10 ml of water. Allow the segments to dry on a watch-glass, and store in a stoppered bottle.

### PRE-TREATMENT OF SAMPLE—

Dilute the sample, if necessary, until it contains less than 55 p.p.m. of nitrate-N and less than 5 p.p.m. of ferrous iron. If a significant amount of nitrite is present, dilute further to decrease the concentration of nitrate-N to less than 40 p.p.m., then add a sulphamic acid paper, stir, and set aside for 5 minutes (one paper contains sufficient sulphamic acid to destroy 2 mg of nitrite-N in 20 to 100 ml; if the volume is less than 20 ml, use a smaller paper).

### DETERMINATION OF NITRATE—

Cool 8 ml of the sulphuric acid to between 0° and 10° C in a 50-ml Erlenmeyer flask, and, without delay, add the sample (1 ml) and 2,6-xylenol reagent solution (1 ml); make these additions by pipette directly into the bulk of the solution. Mix by gentle swirling, set aside for 5 minutes, add 15 ml of water, and set aside for 15 minutes. With an ultraviolet spectrophotometer, measure the optical density at 304 mμ in silica cells against a reagent blank solution. Concentrations of nitrate-N in excess of 30 p.p.m. give an inconveniently high optical density in 0·5-cm cells; for such concentrations, dilute test and blank solutions with a further 25 ml of water before making the reading. The optical density remains constant for 2 hours at room temperature or for 2 days in a refrigerator.

If the sample contains much organic matter or more than 5 p.p.m. of ferric iron, determine the necessary correction by adding 0·5 ml each of acetic acid and ammonium chloride solution instead of the 2,6-xylenol reagent. Measure the optical density at 304 mμ against a blank solution prepared similarly, with water instead of the sample and with use of the same cells and dilutions as in the test; subtract the optical density from that found in the test.

Ascertain the concentration of nitrate from a calibration graph plotted from the results obtained for standard solutions of potassium nitrate (1-ml portions of separate potassium nitrate solutions must be used for obtaining different points on the graph).

## Results

The proposed method has been used successfully for determining nitrate in river water, estuary water and sewage effluents. The standard deviation of eight determinations of the blank value in 4-cm cells was 0·011 optical-density unit; the sensitivity of the method at 95 per cent. confidence limits is therefore 0·13 p.p.m. of nitrate-N, corresponding to an optical density of 0·022. The method as described above is insufficiently sensitive for determining the small amounts of nitrate present in the open sea.

### Table II

Comparison of results by proposed and official methods

| Sample | Nitrate added (as N), p.p.m. | Total nitrate (as N) found by— official method, p.p.m.* | Total nitrate (as N) found by— proposed method, p.p.m. | Added nitrate (as N) found by— official method, p.p.m. | Added nitrate (as N) found by— proposed method, p.p.m. |
|---|---|---|---|---|---|
| Sewage effluent | — | 20·6 | 21·6 | — | — |
| | — | 33·7 | 35·3 | — | — |
| | — | 0·6 | 2·1 | — | — |
| | — | 39·8 | 41·0 | — | — |
| Storm sewage | — | 0·0 | 0·1 | — | — |
| Domestic sewage | 0·0 | 0·5 | 0·0 | — | — |
| | 4·95 | 6·0 | 5·0 | 5·5 | 5·0 |
| | 9·9 | 10·2 | 9·8 | 9·7 | 9·8 |
| | 14·85 | 14·7 | 14·45 | 14·2 | 14·45 |
| Thames water from Purfleet (salinity 18·8 parts per thousand) | 0·0 | 1·25 | 0·85 | — | — |
| | 4·95 | 5·75 | 5·6 | 4·5 | 4·75 |
| | 9·9 | 10·0 | 10·6 | 8·75 | 9·75 |
| | 14·85 | 15·5 | 16·0 | 14·25 | 15·15 |
| Thames water from Southend (salinity 31·2 parts per thousand) | 0·0 | 0·0 | 0·5 | — | — |
| | 4·95 | 3·75 | 5·3 | 3·75 | 4·8 |
| | 9·9 | 8·75 | 9·95 | 8·75 | 9·45 |
| | 14·85 | 14·5 | 15·25 | 14·5 | 14·75 |
| Thames water from Kingston | 0·0 | 4·0 | 5·2 | — | — |
| | 4·95 | 9·75 | 10·2 | 5·75 | 5·0 |
| | 9·9 | 14·75 | 15·3 | 10·75 | 10·1 |
| | 14·85 | 19·25 | 20·2 | 15·25 | 15·0 |
| Effluent from bacon factory | 0·0 | 0·0 | 0·0 | — | — |
| | 4·95 | 5·5 | 4·9 | 5·5 | 4·9 |
| | 9·9 | 9·25 | 9·9 | 9·25 | 9·9 |
| | 14·85 | 14·25 | 14·3 | 14·25 | 14·3 |

* Corrected for nitrite content (determined separately).

From 0 to 50 p.p.m. of nitrate-N, deviations from Beer's law are small, although it is necessary to use a calibration graph. Above 50 p.p.m., the sensitivity begins to diminish, but the reproducibility remains satisfactory to 55 p.p.m. in the absence of sulphamic acid. The coefficients of variation found for nitrate standards in pure water were 1·8 per cent. for 10 p.p.m. of nitrate-N and 0·7 per cent. for 40 p.p.m.

Results by the proposed method for a number of samples are shown in Table II; comparative figures obtained by a standard method involving use of Devarda's alloy[15] are included. When possible the methods were tested for bias by adding known amounts of nitrate to the samples and determining the amounts recovered. These results show fair agreement between

the two methods except at very low concentrations. The erratic recoveries of added nitrate by the standard method are probably connected with the uncertainty of the blank value, which largely arises from nitrogen present in the Devarda's alloy. Although alloy having a very low nitrogen content is available commercially, the amount of nitrogen increases on standing, and a sample was shown to absorb 5 $\mu$g of nitrogen per g per month when freely exposed to the atmosphere; this contamination was not removed by washing with 0·001 N hydrochloric acid. The standard method is also reputed to be unreliable when much nitrogenous organic matter is present; however, interference from organic matter in the proposed method, which is usually negligible, is easily allowed for by the procedure described above.

A single determination by the proposed method takes approximately 45 minutes and twenty determinations may be completed in 90 minutes. Comparable figures for the standard method are 75 minutes and 2 hours, and separate determinations of nitrite are necessary if a figure for nitrate (as opposed to total oxidised nitrogen) is required.

Other advantages of the proposed method are that no distillation apparatus is necessary and that the volume of sample required is much smaller.

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# The Determination of Constituents of Rocks and Minerals by Gas Chromatography

## Part I. The Determination of Carbon Dioxide

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A method is described for determining carbon dioxide in rocks and minerals. Orthophosphoric acid is used to decompose the sample contained in a reaction vessel attached to a gas chromatograph. The liberated carbon dioxide is eluted with hydrogen, separated from other gases by passage through a column containing silica gel and finally detected by means of a thermal-conductivity cell.

The separation of carbon dioxide on columns of silica gel has been described by several workers[1,2,3,4] primarily concerned with the separation and determination of this gas in gaseous mixtures. Recent experience with a column of silica gel and a thermal-conductivity cell[5] for the analysis of residual or outlet gases from catalytic-conversion processes has suggested that it is feasible to use such a system for determining carbon dioxide in rocks and minerals.

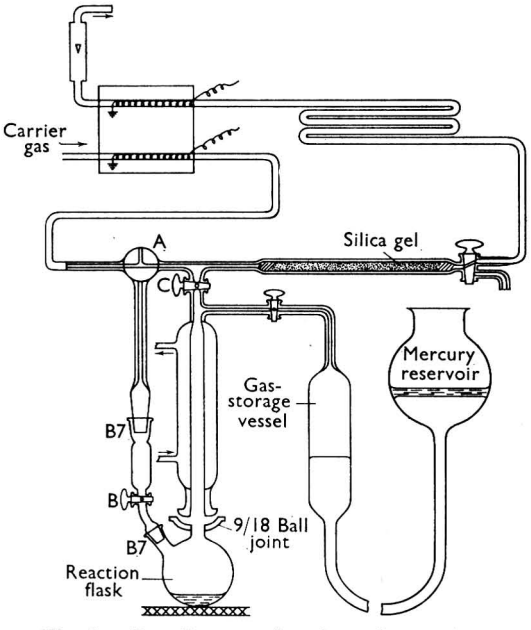


Fig. 1. Reaction vessel and gas-flow system

To accomplish this it is necessary to transfer the carbon dioxide from the mineral to the gas chromatograph in a small finite volume. As all carbonate minerals are not decomposed at the same rate, it was decided to complete the decomposition of the sample in a reaction vessel attached to the chromatograph before admitting any of the gaseous products to the column. Provision was also made for drying the gases from the reaction vessel to prevent the rapid deterioration of the column that would otherwise ensue.

### Description of apparatus

The reaction vessel and gas-flow system used are shown in Fig. 1.

The reaction vessel consists of a small round-bottomed flask of capacity about 12 ml, a reflux condenser and a tap funnel of capacity about 2 ml. A reservoir is provided for the storage of gas before its elution with hydrogen carrier gas. In earlier experiments it had been found that the column of silica gel deteriorated rapidly unless provision was made for drying the gas from the reaction flask. A convenient way of doing this was by including a glass tube approximately 4 inches long and packed with a coarse grade of self-indicating silica gel. This drying tube was regenerated when necessary by heating (in practice, once a day); a heating tape was convenient for this purpose, although care was required to avoid overheating. The reaction vessel is completed by a series of taps permitting hydrogen to pass from the reference arm of the thermal-conductivity cell to the column of silica gel either directly or via the reaction flask. The conical ground-glass joints of the reaction vessel are fitted with polytetrafluoroethylene sleeves and are heavily spring-loaded; the ball-joint, size 9/18, is also spring-loaded and is carefully lubricated with Apiezon T grease.

The completed gas-flow system is of the conventional type, consisting of a thermal-conductivity cell, chromatographic column and gas-flow meter (Rotameter). In the initial experiments, a "home-made" thermal-conductivity cell was used, but, while this work was in progress, a Griffin and George cell (mark II) became available; this cell was more sensitive than the "home-made" one, and was used subsequently. If required, an increased response can be obtained by using an even more sensitive detector, such as a Gow - Mac thermal-conductivity cell (type TE-II).

The column used for the separation consists of a 6-foot length of copper tubing ($\frac{3}{16}$-inch outside diameter) packed with silica gel that has previously been ground, sifted to 40- to 60-mesh size and dried in an oven at 105° C for 2 hours. The column was packed straight and then coiled on a 4-inch diameter former.

No provision was made for controlling the temperature of the column or the cell, as the unit is housed in an even-temperatured room. The small fluctuations in temperature that did occur were found not to affect calibration with carbon dioxide. The reaction vessel and Rotameter are mounted on standard laboratory scaffolding; the column and the cell, which is embedded in a sand-bath, lie on the bench. All connections are made with $\frac{1}{8}$-inch internal diameter pressure tubing. The pressure of the hydrogen carrier gas in the system is monitored and regulated at the cylinder head, no other adjustments being necessary.

The electrical circuit is of the conventional Wheatstone-bridge type, the out-of-balance potential being fed to a potentiometric recorder. For most rocks and minerals examined the recorder was set to a full-scale deflection of 5 mV.

## Method

The weight of sample used will depend upon its carbon dioxide content. For limestones and other rocks consisting largely of carbonate minerals (magnesite, dolomite, siderite, etc.), use about 5 mg of sample; if material is limited, as little as 0·5 mg can be used, although the accuracy of the determination, which depends on the ability to interpret the chromatogram, will then be much decreased.

For rocks and other samples containing only small amounts of carbonate minerals, use up to 1 g of sample. In order to determine carbon dioxide contents in the parts per million range, it may also be necessary to use a recorder with a full-scale deflection of 1 mV.

### Calibration—

In order to obtain a good peak response to carbon dioxide it is necessary to use the maximum katharometer current. Adjustments to the rate of flow of carrier gas were difficult to make at flows less than about 100 ml per minute. (For this reason the results in Table I were found with the carrier gas flowing at this rate.)

By operating the instrument in an even-temperatured room, effects attributable to changes in temperature were avoided. Slow but steady deterioration of the column was noted, however, and it is necessary to check the calibration of the instrument with each set of determinations.

As both the height and the area of the peak vary linearly with the concentration of carbon dioxide, a single standard is sufficient to identify the calibration. Pure calcium carbonate was used for this purpose.

PROCEDURE—

Remove the reaction flask, clean it carefully, and weigh into it a suitable amount of sample. Re-assemble the apparatus, greasing the ball-joint and B7 sockets with Apiezon T, and place 1 to 2 ml of diluted orthophosphoric acid (1 + 1) in the tap funnel.

With hydrogen gas passing directly from the reference arm of the thermal-conductivity cell to the chromatographic column, adjust the inlet-gas pressure at the cylinder head to give a steady reading on the Rotameter equivalent to 100 ml per minute. Open tap A to the reaction vessel, then open tap B; close both these taps immediately the orthophosphoric acid has entered the flask. Lower the mercury reservoir to accommodate gas from the reaction flask in the storage vessel.

With use of a microburner, gently boil the contents of the flask for 2 to 3 minutes, or longer if a large sample has been used. Cool the flask by immersion in a beaker of cold water, and transfer the gas from the storage vessel to the flask by raising the mercury reservoir. Turn tap C to the position in which gas from the reaction vessel passes to the column, and open taps A and B to complete the circuit via the reaction flask. The recorder traces first a peak arising from the air in the reaction vessel and then, separated from it, a second peak, the area of which corresponds to the liberated carbon dioxide.

Calibrate the apparatus by carrying out a determination as described above on a sample of pure calcium carbonate.

TABLE I

CARBON DIOXIDE CONTENTS OF SOME ROCKS AND MINERALS

| Sample No.* | Rock material | Carbon dioxide found by— gas chromatography, % | traditional procedure, % |
|---|---|---|---|
| M173 | Magnesite, Anaphi, Greece | 49·7 | 50·9 |
| R128 | Limestone, Cannington Park, Somerset | 43·8 | 43·9 |
| R131 | Limestone, Beer, Devon | 43·6 | 43·7 |
| R38 | Calcite, Sukulu Hills, Uganda | 43·2 | 42·9 |
| R73 | Carbonatite, Napak, Uganda | 40·4 | 40·4 |
| R129 | Limestone, Lyme Regis, Dorset | 38·7 | 38·8 |
| R93 | Carbonatite, Kangankunde, Nyasaland | 32·2 | 32·1 |
| 1163 | Barytocalcite, Blagill Mine, Cumberland | 30·5 | 30·5 |
| 1149 | Witherite, Farneycleugh Mine, Northumberland | 20·7 | 20·7 |
| 1155 | Witherite, Longcleuch Mine, Northumberland | 19·0 | 19·0 |
| 1479 | Albite-diabase, Kelham, Nottinghamshire | 14·6 | 14·4 |
| M174 | Scapolite rock, unknown locality | 1·34 | 3·4† |
| 1009 | Quartz-diorite, Close Quarry, Embleton, Cockermouth, Cumberland | 0·61 | 0·57 |
| 1629 | Lamprophyre, Rudha na Cloiche, Loch Sunnart, Argyllshire | 0·26 | 0·23 |
| G-1 | Granite, Westerly, Rhode Island, U.S.A. | 0·06 | 0·08(9) |
| W-1 | Diabase, Centerville, Virginia, U.S.A. | 0·044 | 0·06(9) |
| R78 | Granite, Kloof Nek, Cape Town, South Africa | 0·029 | None reported |
| 1626 | Lamprophyre, Port na h-Uamha, Loch Sunnart, Argyllshire | 0·011 | |
| 1644 | Tonalite, Allt Glas Dhoire Mòr, Loch Lochy, Inverness-shire | 0·0096 | |
| R117 | Granite, Burn of Roerwater, Shetland | 0·0065 | |
| 1651 | Trondhjemite-porphyry, Allt an Fhaing, Callop, Loch Shiel, Argyllshire | 0·0050 | |

* Numbers prefixed by M and R are for samples from the collection of one of us; those without letter prefixes are for samples from the Collection of Analysed Rocks and Minerals, Geological Survey and Museum, London, S.W.7.

† The difficulties of decomposing scapolite with mineral acids are well known; the value of 3·4 per cent. was obtained only after prolonged boiling.

## RESULTS

The results of several determinations of carbon dioxide by the proposed method are shown in Table I, where they are compared with those obtained by the traditional procedure involving absorption by soda asbestos and subsequent weighing.[6,7,8]

## CONCLUSIONS

The feasibility of gas-chromatographic methods for determining carbon dioxide in rocks and minerals has been demonstrated; the results agree well with those obtained by a traditional method. The determination is rapid and requires only small samples (0·5 to 5·0 mg)

of carbonate rocks and minerals. The sensitivity to carbon dioxide is high; when a 1-g sample and a 1-mV recorder are used, as little as 5 p.p.m. can be detected. Hydrogen sulphide, liberated from some rocks and minerals by the action of orthophosphoric acid, does not interfere. There is no reagent blank value, and a permanent record of the determination is obtained.

Disadvantages include the dependence of the method on an external standard, *i.e.*, calcium carbonate, and the need for the calibration to be checked with each batch of samples.

The work described in this paper forms part of the programme of Warren Spring Laboratory, D.S.I.R., and is published by permission of the Director. We thank Mr. G. A. Sergeant for the gift of analysed specimens.

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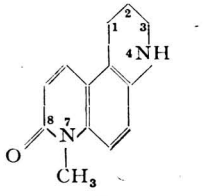
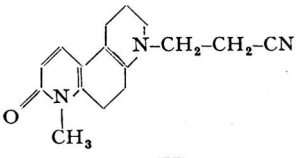
# Notes

## A REAGENT FOR THE SMALL-SCALE DETECTION OF ACRYLONITRILE

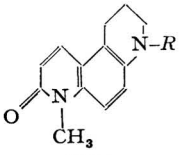
THE more specific of the chemical methods for detecting or determining acrylonitrile depend on its additive reactivity towards, for example, secondary amines such as piperidine[1,2] and morpholine[3]; in the method described here, 1,2,3,4,7,8-hexahydro-7-methyl-8-oxo-4,7-phenanthroline (**I**) is similarly used. The distinctive feature of this method is that the tertiary-amine product of the reaction, 4-(2-cyanoethyl)-1,2,3,4,7,8-hexahydro-7-methyl-8-oxo-4,7-phenanthroline (**II**), can be directly detected by delicate tests not effective for the cyanoethylation products of piperidine and morpholine.




(**I**)




(**II**)




(**III**)

These tests are so sensitive that, although the amounts of **II** isolated are only small proportions of the theoretical yields, acrylonitrile can be detected in a few microlitres of solution at a concentration (depending on the solvent) of about 0·1 per cent. The method therefore has the advantage over that described by Brockway[1] of being effective on a much smaller scale. Further, although its sensitivity at best only approaches that claimed by Štěpánek and Černá,[4] this test is more convenient in operation than is theirs and allows a wider choice of solvent for the acrylonitrile.

Separation of **II** from unreacted **I** is effected in a few minutes by chromatography on phosphorylated cellulose paper. The separated spot of **II** is detected by means of (*a*) its intense yellow colour and intense fluorescence in ultraviolet light (both properties dependent on pH in aqueous solution, but not appreciably so for **II** adsorbed on cellulose phosphate paper) and (*b*) a highly sensitive colour reaction with nitrous acid.

With nitrous acid, a red colour is generally formed by tertiary amines (**III**; $R$ = alkyl), but not by **I**, which is converted[5] into the expected 4-nitroso-derivative. The colour rapidly fades if nitrous acid is present in too high a concentration.

Substances mixed with acrylonitrile and which react with **I** to yield alkylated products (**III**) do not necessarily interfere with the test, as such products are usually separated from **II** at the chromatographic stage.

### METHOD

REAGENTS—

*Solvent for acrylonitrile*—Useful solvents include glacial acetic acid (used for most of the work described), water (within the limit of about 7 per cent. w/v imposed by solubility), methanol and isopropyl alcohol; the last two are of particular interest in that they have been used[6,7] for the azeotropic concentration of acrylonitrile from dilute solutions. Any organic solvent miscible with glacial acetic acid can be routinely used if preliminary examination confirms its general suitability and (particularly for concentrations of acrylonitrile less than 0·5 per cent.) its favourable influence on sensitivity. Moderate concentrations of alkalis in the solution do not interfere, being overborne by the glacial acetic acid in the reagent solution.

*Acetic acid*—The glacial acetic acid used as solvent for acrylonitrile and for **I** need not be purer than laboratory-reagent grade. The developing solvent is prepared by diluting this acid to approximately 30 per cent. v/v.

*Reagent solution*—A 10 per cent. w/v solution of **I**, a stable yellow solid,[5] in glacial acetic acid. This solution gradually darkens, but remains useful during 1 or 2 days; eventually, accumulated impurities interfere with the chromatography.

*Cuprous chloride catalyst*—This need not be freshly prepared. Batches prepared as described by Vogel,[8] but on a smaller scale, remain catalytically active after several weeks of storage in stoppered tubes.

*Cellulose phosphate paper*—Whatman P20 paper is suitable when prepared in the hydrogen form by immersing it briefly in cold dilute hydrochloric acid (*e.g.*, 60 ml of 0·5 N acid per 400 sq. cm of paper), washing with successive portions of distilled water until the acid reaction disappears and then drying in a current of warm air. If protected from exposure to fumes, paper so treated retains its character for weeks. The paper is used dry and without any preliminary equilibration with the solvent.

*Nitrous reagent for spraying*—Two drops of an approximately 10 per cent. solution of sodium nitrite mixed with 25 ml of N hydrochloric acid; this solution is useful during 1 day.

PROCEDURE—

Mix approximately equal volumes, *e.g.*, 0·1 ml, of the reagent and acrylonitrile solutions, together with cuprous chloride (approximately 2 mg; the amount is not critical) in a glass tube of internal diameter 3 to 4 mm and about 10 cm long with one sealed end. Draw out and seal the other end of the tube, and heat in a boiling-water bath for 30 minutes. Cool the tube, and transfer 2 to 3 μl of its contents to a strip of cellulose phosphate paper. With 30 per cent. acetic acid as solvent (ascending), allow a chromatogram to develop until the solvent front has moved about 5 cm beyond the original spot. When present in amounts greater than about 5 μg, compound **II** is directly visible as a yellow spot of $R_F$ about 0·4.

Dry the strip in a current of warm air, and inspect it by ultraviolet light. Its typical appearance is of a blue-green spot little extended from the origin, together with a bluish white area at the solvent front and, if **II** is present, a distinct intermediate yellow spot. Compound **I** remains at the origin, but fluorescence there mainly arises from decomposition products of **I** and possibly also of **II**, whereas material at the solvent front corresponds in position and fluorescence to the 4-acetyl derivative of **I** (**III**; $R = COCH_3$).

Lightly spray the dried strip with nitrous reagent; the spot of **II** becomes a red or pink colour that fades gradually. (The various fluorescences are not destroyed by this treatment.) No prominent colour is normally produced in any other area of the chromatogram, but a faint pink cusp to the original spot may occasionally be discerned and apparently arises from the fluorescent material there; other possible contributors of "red-reacting" material are discussed below.

The initial scale of the test can, if desired, be reduced to a few microlitres by using as reaction vessel a capillary tube previously dusted internally with cuprous chloride.

## SENSITIVITY

With many organic solvents, including glacial acetic acid, methanol and isopropyl alcohol, the minimum useful fluorescent spot is obtained when the test is applied to acrylonitrile at a concentration, depending on the solvent, of about 0·2 per cent. (Minimal fluorescence is obtained when 0·5 to 1 μg of **II**, mixed with **I**, is subjected to chromatography.) In aqueous solution, as little as 0·02 per cent. of acrylonitrile can be detected. When carefully regulated volumes were used in tests on (1 + 1) serial solutions of acrylonitrile in acetic acid, the degree of fluorescence was approximately proportional to the concentration of acrylonitrile over the range about 0·2 to 2 per cent. The colour reaction is marginally less sensitive than the fluorescence.

Over a wide range, the ratio of liquid volume to air space in the reaction tube has no perceptible effect on the sensitivity of the test when the acrylonitrile is dissolved in acetic acid.

When acrylonitrile is to be detected in relatively high concentration, the time of heating in the water bath can conveniently be decreased, *e.g.*, 1 minute is adequate for the recognition of undiluted acrylonitrile.

## SPECIFICITY

The principal classes of compound that might react with **I** to convert it into a tertiary amine are α,β-unsaturated carbonyl compounds, alkyl halides and epoxides; epoxides would be expected to react alternatively with glacial acetic acid.

Some members of the first two groups were subjected to the proposed procedure, each as a 5 per cent. solution in glacial acetic acid. Of six α,β-unsaturated carbonyl compounds (acrylamide, ethyl acrylate, ethyl cinnamate, ethyl crotonate, diethyl maleate and methyl methacrylate) and five halides (chloroacetamide, β-chloropropionitrile, ethyl bromide, ethyl bromoacetate and ethyl β-chloropropionate), only diethyl maleate and ethyl bromoacetate gave spots that moved considerably from the origin.

Some of the other compounds, *e.g*, ethyl acrylate, gave positive responses to the nitrous spray reagent in areas adjacent to or within the original spots. β-Chloropropionitrile in particular did

not react appreciably, for it would have given rise to a detectable amount of **II**. The spot from the maleate was not completely separated from the original spot and was atypical in giving no red colour with the spray reagent. The spot from the bromoacetate travelled adjacent to the solvent front. Bromoacetate seriously hindered the detection of 1 per cent. of acrylonitrile in acetic acid when present with it at the concentration of 10 per cent., but not at 1 per cent., whereas the presence of maleate was not detrimental at the higher level.

These findings suggest that only exceptionally will interference with the detection of acrylonitrile arise from a reactive substance mixed with it and that, even in such circumstances, the interference might be resolved by further chromatography.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## THE DETERMINATION OF STIBINE

DURING a study of the rate of evolution of the toxic gas stibine from lead - acid accumulators, a method for its determination was developed. This method, which has since been used extensively, lacks the sensitivity of methods based on the photometric determination of quinquivalent antimony as its complex with rhodamine B[1] or methyl violet,[2] but gives greater accuracy and involves less manipulation.

Haring and Compton,[3] when engaged in a similar investigation, showed that a solution of iodine was an excellent absorbent for stibine and determined the stibine content of gases evolved during the charging of accumulators by measuring the time required to decolorise a known volume of 0·0001 N iodine and assuming the reaction to be—

$$SbH_3 + 3I_2 \longrightarrow SbI_3 + 3HI.$$

Alternatively, the excess of iodine could be titrated. Disadvantages of this method are that the iodine may volatilise and there is a possibility that the hydrogen iodide formed may be oxidised.

Direct colorimetric determination of antimony in the absorbent solution is clearly preferable. Several methods have been described for determining tervalent antimony in acidified solutions of potassium iodide as the yellow iodo-antimonite ion[4] or as a complex with pyridine[5] or thiourea.[6] Formation of free iodine by atmospheric oxidation may be suppressed by reducing agents such as sulphur dioxide,[5] ascorbic acid[7] or sodium hypophosphite.[8] McChesney[7] showed that the best conditions for determining the iodo-antimonite ion occur in a solution containing approximately 8 per cent. by weight of potassium iodide and 8 per cent. by volume of concentrated sulphuric acid. A solution of iodine in this medium is therefore not only an excellent absorbent for stibine, but is also suitable for subsequent determination of the collected antimony once the excess of iodine has been removed. Ascorbic acid, as used by McChesney to suppress formation of iodine, is inadequate for removing the excess of free iodine in the absorbent solution, but sodium hypophosphite is more effective, its action being catalysed by acid.

### METHOD

REAGENTS—

All reagents must be of recognised analytical grade.

*Absorbent solution*—Prepare to contain 10 g of iodine, 80 g of potassium iodide and 80 ml of sulphuric acid, sp.gr. 1·84, per litre.

*Sodium hypophosphite.*

*Standard antimony solution*—Dissolve 0·2665 g of anhydrous antimony potassium tartrate, 80 g of potassium iodide, 80 ml of sulphuric acid and 5 g of sodium hypophosphite in water, and dilute to 1 litre.

1 ml ≡ 0·10 mg of antimony.

PROCEDURE—

Allow the stream of gas to bubble through a known volume, usually 10 or 50 ml, of the absorbent solution for a measured time. Transfer the solution to a stoppered bottle containing approximately 1 g of sodium hypophosphite, and set aside for about 20 minutes to reduce the excess of iodine. Measure the optical density at 425 m$\mu$ against water, and ascertain the amount of antimony present by comparison with a calibration graph.

If 1-cm cells are used, measurements can be made over the range 1 to 70 mg of stibine per litre with a standard deviation of 0·5 mg per litre, *i.e.*, 0·01 to 0·7 mg of stibine when 10 ml of absorbent are used or 0·05 to 3·5 mg with 50 ml of absorbent.

CALIBRATION—

Dilute measured portions of standard antimony solution to 10 or 50 ml with absorbent solution. Transfer the solutions to stoppered bottles each containing about 1 g of sodium hypophosphite, and, after the iodine has been reduced, measure the optical densities at 425 m$\mu$. Plot a graph relating optical density to weight of antimony present.

## DISCUSSION OF THE METHOD

The sensitivity of the method may be increased 6-fold by measuring the optical density at 330 m$\mu$, but this does not appear to give any greater accuracy.

A direct check on the validity of the method by converting a known amount of antimony to stibine cannot be readily achieved, but comparison with an independent method of determining stibine via the antimony - rhodamine B complex showed that the proposed procedure was satisfactory. Charge gas from a small accumulator was blown in a stream of air for 5 to 10 minutes through a bubbler containing 10 ml of the absorbent solution. The stream was then switched for the same time to another bubbler containing 10 ml of a 6 per cent. solution of mercuric chloride in 6 N hydrochloric acid. The latter solution was then diluted to 100 ml with 6 N hydrochloric acid, and the antimony content of a 10-ml aliquot was determined by Ward and Lakin's method,[9] *viz.*, oxidation to the quinquivalent state by ceric sulphate, extraction into 10 ml of di-isopropyl ether and then addition of 2 ml of a 0·02 per cent. solution of rhodamine B in N hydrochloric acid; optical-density measurements were made at 550 m$\mu$. For purposes of calibration, measured volumes of a solution containing 0·2665 g of anhydrous antimony potassium tartrate in 1 litre of 6 N hydrochloric acid (*i.e.*, 0·1 mg of antimony per ml) were added to 10-ml portions of the mercuric chloride absorbent solution, and each mixture was diluted to 100 ml with 6 N hydrochloric acid. A calibration graph was prepared by plotting the optical densities of the di-isopropyl ether solutions of the rhodamine B complex derived from 10-ml aliquots as described above. The results of a series of such comparisons are shown in Table I.

TABLE I

COMPARISON OF RESULTS BY PROPOSED AND RHODAMINE B METHODS

| Sample No. | Proposed method | | Rhodamine B method | |
|---|---|---|---|---|
| | Optical density at 425 m$\mu$ | Stibine found, mg | Optical density at 550 m$\mu$ | Stibine found, mg |
| 1 | 0·11 | 0·028 | 0·24 | 0·027 |
| 2 | 0·10* | 0·025* | 0·45 | 0·053 |
| 3 | 0·42 | 0·113 | 0·92 | 0·115 |
| 4 | 0·42 | 0·113 | 0·95 | 0·120 |
| 5 | 0·64 | 0·171 | 1·37 | 0·176 |

* Gas allowed to bubble through absorbent solution for only half the time used in the rhodamine B method.

The only common gas that interferes with the proposed method is hydrogen sulphide, which causes precipitation of sulphur; arsine, frequently present together with stibine, does not interfere.

The optical density of the iodo-antimonite complex was unchanged after the solutions had been kept in stoppered bottles for over 18 months; however, it is temperature-dependent, decreasing by approximately 0·5 per cent. for an increase of 1° C in temperature.

Dixon and Kiff[10] showed that stibine is readily oxidised in air to form a suspension of antimony oxides, and one advantage of the proposed method is that such oxides, being soluble in the absorbent, are included in the determination of stibine. To decrease the possible decomposition of stibine to a minimum, the length of tubing between source and absorber should be as short as possible, and use of rubber tubing should be avoided.

I thank the Admiralty for permission to publish this Note.

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## THE DETERMINATION OF TRACES OF LEAD IN DRINKING WATER

The methods currently recommended[1,2] for determining lead in drinking water involve colorimetric measurement either visually as the sulphide or spectrophotometrically as the dithizonate. The sulphide method is not applicable to water containing organic matter and iron and has a low precision. The methods involving extraction of lead dithizonate with chloroform are of more general application, but are lengthy and tedious to perform, especially if zinc is present. The American method[2] claims a lower detection limit of 5 $\mu$g of lead and that results are within $\pm 6\,\mu$g of the true value in the range 10 to 50 $\mu$g.

The work of Snyder[3] has shown that, at pH 11·5, lead dithizonate is completely extracted into chloroform, the excess of dithizone remaining in the aqueous phase. Johnson and Polhill[4] made use of this observation in preparing their method for determining lead in food. They also introduced the use of sodium hexametaphosphate to prevent or delay the precipitation of alkaline-earth phosphates during the extraction of lead dithizonate.

Extraction of the dithizonate at pH 11·5 coupled with the use of sodium hexametaphosphate was thought to offer prospects of a rapid single-extraction mono-colour method for determining lead in drinking water. For this mono-colour technique it is preferable to use dilute aqueous dithizone. The Society for Analytical Chemistry's Lead Panel Report[5] describes a convenient way of preparing this reagent in a purified form.

Johnson and Polhill used sodium hexametaphosphate in their preliminary extraction of the lead and not in the determination stage. We have found that, at the concentration used, this material has no effect on the recovery of lead and is effective in preventing any precipitation occurring during the analysis of hard waters.

Ferric iron interfered, with resultant low recoveries of lead. By adding 1 ml of 1 per cent. hydroxylamine hydrochloride solution, up to 0·5 mg of iron per litre can be tolerated in the sample. The use of larger amounts of hydroxylamine hydrochloride solution gave increased blank values. The presence of large amounts of iron together with lead appears to be unlikely, since of twenty-one samples of drinking water containing lead, only one contained more than 0·2 mg of iron per litre.

The proposed method is thought to offer a rapid yet precise procedure for determining the lead content of drinking water and is suitable for routine use. The average time taken for each determination is 10 minutes. Down to 1 $\mu$g of lead can be detected with confidence, and over the range 0 to 25 $\mu$g the method has a precision well within $\pm 1$ $\mu$g.

## Method

Reagents—

All reagents should be of recognised analytical quality. Solutions should be prepared with distilled or ion-free water.

*Alkaline cyanide solution*—Mix 340 ml of ammonium hydroxide, sp.gr. 0·880, 75 ml of 2 per cent. w/v sodium sulphite ($Na_2SO_3$) solution, 30 ml of 10 per cent. w/v potassium cyanide solution and 605 ml of water.

*Sodium hexametaphosphate solution, 10 per cent. w/v*—Render the solution low in lead by adjusting to pH 9 with ammonium hydroxide and washing with a solution of dithizone in chloroform. Make just acid, and extract the residual dithizone with chloroform. Adjust to pH 9·5 for maximum stability during storage.

*Hydroxylamine hydrochloride solution, 1 per cent. w/v.*

*Ammonium hydroxide*, 0·5 N.

*Chloroform*—Analytical-reagent grade chloroform has been found suitable for use without further purification.

*Dithizone, stock solution, 0·1 per cent. w/v, in chloroform*—Store in a refrigerator.

*Dithizone, working solution*—Shake 6 ml of dithizone stock solution with 10 ml of 0·5 N ammonium hydroxide. Allow to separate, reject the lower layer, and pass the aqueous phase through filter-paper that has been wetted with water.

*Standard lead solution*—(*a*) Dissolve 1·60 g of lead nitrate in water, add 10 ml of concentrated nitric acid, and dilute to 1 litre. (*b*) Dilute 1 volume of (*a*) to 100 volumes with water; prepare freshly as required.

1 ml of (*b*) ≡ 10 μg of lead.

Procedure—

Into a 100-ml separating funnel, the tap and stem of which are dry, measure 50 ml of the sample of drinking water or such smaller volume diluted to 50 ml as shall contain not more than 25 μg of lead. Add 1·0 ml of sodium hexametaphosphate solution and 1·0 ml of hydroxylamine hydrochloride solution, and swirl to mix. Add 30 ml of alkaline cyanide solution, and again mix. Add 0·5 ml of dithizone working solution (this may conveniently be added by means of a burette graduated to 0·02 ml) and 10·0 ml of chloroform. Shake the funnel vigorously for 1 minute, and allow the phases to separate. Insert a small plug of dry cotton-wool into the stem of the funnel, and, after running the first 1 to 2 ml to waste, fill a 1-cm cell with the chloroform extract of the lead dithizonate. Measure, with a suitable spectrophotometer, the optical density of this extract against chloroform at the absorption maximum at about 520 mμ.

Carry out a blank determination on 50 ml of distilled water in an identical manner. Determine the amount of lead in the volume of sample taken corresponding to the net optical density obtained by reference to a standard curve prepared as described below.

Table I

Recovery of lead added to various waters

| Sample | Hardness of water (as $CaCO_3$), mg per litre | Lead present, mg per litre | Lead added, mg per litre | Lead found, mg per litre |
|---|---|---|---|---|
| 1 | 20 | Nil | 0·20 | 0·19 |
| 2 | 130 | Nil | 0·20 | 0·20 |
| 3 | 150 | Nil | 0·20 | 0·20 |
| 4 | 270 | Nil | 0·20 | 0·21 |
| 5 | 270 | Nil | 0·40 | 0·42 |
| 6 | 270 | 0·09 | 0·20 | 0·29 |
| 7* | 270 | Nil | 0·20 | 0·19 |
| 8 | 350 | Nil | 0·20 | 0·20 |

* Also contained 0·5 mg of iron per litre.

Preparation of standard curve—

To 50 ml of distilled water contained in a 100-ml separating funnel add suitable amounts of the standard lead solution to cover the range 0 to 25 μg of lead, extract as described above, and measure the corresponding optical densities. The curve relating optical density to amount of lead should be linear over this range.

Note—The method is extremely sensitive, and precautions should be taken to prevent extraneous contamination of reagents and apparatus.

## Results

Recovery of added lead—

The recoveries of lead added to several waters of various degrees of hardness have been determined and the results are shown in Table I. The lead was added as 1 or 2 ml of the standard lead solution.

Reproducibility—

The lead contents of two drinking waters have been determined several times by the proposed method. The results obtained, expressed as mg of lead per litre were: (1) 0·088, 0·085, 0·090, 0·089, 0·089 and 0·090; (2) 0·46, 0·47, 0·47, 0·46 and 0·46.

Permission to publish this Note has been given by the Government Chemist, Department of Scientific and Industrial Research.

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# THE DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS

Numerous semi-micro methods are available for determining sulphur, and many variants of gravimetric, volumetric and colorimetric finishes are described in the literature.[1] Zimmermann's method,[2] which, in my experience, has been capable of giving satisfactory results, was occasionally found to give inconsistent and low values, and this led to investigations of various aspects of the rather complicated and special apparatus used. As a result of these investigations an alternative procedure was examined. Complete oxidation of the sample in an oxygen-filled flask ensured fixation of sulphur, which was not always certain in the fusion procedure of Zimmermann's method. Other elements present, such as halogens and phosphorus, could also be determined simultaneously by taking suitable aliquots.

A method for the quantitative reduction of sulphate to sulphide from a reducing acid solution[3] was next examined and adapted to the semi-micro scale; tests on inorganic sulphate standards showed that hydrogen sulphide could be quantitatively recovered. Further, the relatively simple distillation apparatus required little attention during the determination, and, when two sets of apparatus were used, a determination could be completed in less than 45 minutes.

## Method

Apparatus—

*Combustion flask*—A 400-ml conical flask fitted with a B24 socket and cone; the cone has a 6-inch length of platinum wire (0·04-inch diameter) sealed into its base and shaped into a conical spiral.

*Distillation and absorption assembly*—This is shown in Fig. 1.

Reagents—

*Reducing mixture*—Heat a mixture of 200 ml each of hydriodic acid, sp.gr. 1·70, and hydrochloric acid, sp.gr. 1·18, and 50 ml of hypophosphorous acid (50 per cent. w/w) under reflux for one hour. Store the colourless solution in a stoppered dark-glass bottle. If the reagent is stored for more than a week, repeat the heating under reflux before use.

*Absorption solution*—Add 5 ml of 100-volume hydrogen peroxide to 95 ml of approximately 0·1 N sodium hydroxide.

*Sodium hydroxide*, 5 N—Dissolve 200 g of sodium hydroxide in distilled water, and dilute to 1 litre.

*Orthophosphoric acid*, 10 M—Dilute 684 ml of orthophosphoric acid, sp.gr. 1·74, to 1 litre.

*Sodium thiosulphate*, 0·02 N—Dilute 50 ml of previously standardised 0·1 N sodium thiosulphate to 250 ml in a calibrated flask; prepare this solution freshly each day.

*Iodine, approximately* 0·02 N—Dissolve 40 g of potassium iodide in 60 ml of distilled water, then dissolve 2·5 g of iodine in this solution, and dilute to 1 litre.

*Starch solution*—Mix 50 ml each of glycerol and distilled water, bring to the boil, add 1 g of starch suspended in 2 to 3 ml of distilled water, and boil for 3 minutes, with stirring. Cool, and store in a stoppered bottle.

*Nitrogen*—Pure ("white spot").

*Oxygen.*

PROCEDURE—

Accurately weigh between 5 and 15 mg of sample, depending on the sulphur content, into a tared ashless filter-paper (or filter-paper - cellulose-tape wrapper if it is a volatile liquid). Place 10 ml of absorption solution in the 400-ml conical flask, and flush well with a rapid flow of oxygen. Place the wrapped sample, fuse uppermost, in the previously ignited platinum spiral, ignite the fuse, and immediately insert the stopper in the neck of the flask. Incline the flask, and slowly rotate it until combustion ceases.

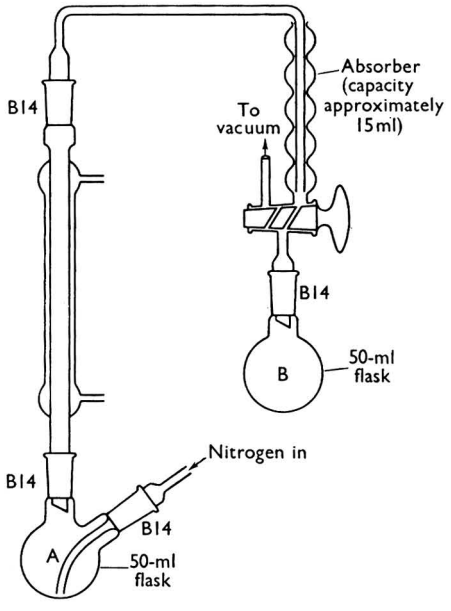


Fig. 1. Distillation and absorption assembly

Shake the flask until all the misty vapours have been absorbed (usually 5 to 10 minutes), remove the stopper, and wash it with a little distilled water. Transfer the solution and washings quantitatively to the two-necked 50-ml flask (A in Fig. 1), and evaporate almost to dryness. Place 10 ml of 10 M orthophosphoric acid in the round-bottomed 50-ml flask (B in Fig. 1), and connect it to the absorption assembly; the joint should be greased. Connect a vacuum line to the side-tube, evacuate the flask, close the tap, and place 10 ml of 5 N sodium hydroxide in the absorber. Dry the inside of the condenser and bubbler tube, and attach to the absorber. Place 10 ml of reducing mixture in flask A, connect the nitrogen-inlet tube, and flush with nitrogen until the solution is colourless. Connect flask A to the condenser, adjust the rate of flow of nitrogen to about 1 bubble per second, and heat the mixture under reflux for 30 minutes. Increase the rate of flow of nitrogen to approximately 3 bubbles per second, and continue to heat under reflux for a further 10 minutes.

Lower the absorber assembly, disconnect the bubbler tube, wash it through with distilled water, and add the washings to the sodium hydroxide solution. Carefully open the tap, and allow this solution to run into the evacuated flask B. When only sufficient liquid to maintain the seal remains, close the tap, and place 10 ml of the iodine solution, by pipette, in the absorber; allow this to run slowly into flask B, and again maintain the liquid seal. Rinse the absorber two or three times with distilled water, and allow the rinsings to run into flask B as already described. Shake the flask and attached absorber for one minute, and cool in a water bath. Open the tap to atmosphere, disconnect flask B, and wash any adhering solution from the joint into the flask. Titrate the contents of the flask with 0·02 N sodium thiosulphate to a pale-straw colour, add approximately 0·5 ml of starch solution, and continue the titration to the disappearance of the blue colour.

Carry out a blank determination with 10 ml of 5 N sodium hydroxide and 10 ml of 10 M orthophosphoric acid. Cool, dilute to approximately 30 ml, add 10 ml of the iodine solution from a pipette, and titrate as before.

## Conclusion

The general over-all simplification of the procedure avoided the need for fusion processes and expensive apparatus, and results by the proposed method for various types of standard and research compounds were considered to be satisfactory. A few results are shown in Table I.

Table I

Sulphur found in standard and research compounds

| Sample | Theoretical sulphur content, % | Sulphur content found, % |
|---|---|---|
| Sulphamic acid .. .. .. .. | 33·03 | 33·10, 32·85 |
| Triphenyl phosphorotetrathionate .. | 32·90 | 32·90, 32·75 |
| *S*-Benzylthiuronium chloride .. .. | 15·82 | 15·65, 15·60 |
| Sulphonal .. .. .. .. .. | 28·09 | 28·25 |
| Dimethyl hydrogen phosphorodithioate .. | 40·54 | 40·55 |
| 4-Chlorobut-2-yn-1-yl-*N*-(4-chlorobenzenesulphonyl) carbamate .. .. .. | 9·99 | 10·05 |

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# THE DETECTION OF SUNSET YELLOW FCF AND ORANGE GGN IN TABLE JELLIES

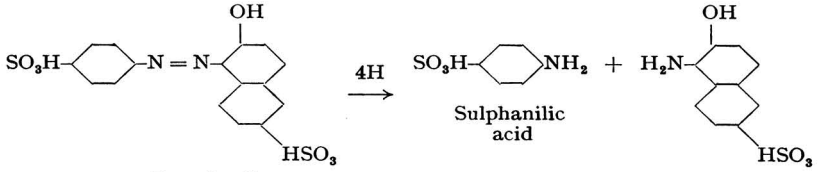
The Colouring Matter in Food Regulations, 1957,[1] permit the use of Sunset yellow FCF (1-*p*-sulphophenylazo-2-naphthol-6-sulphonic acid) in foods offered for sale in the United Kingdom, but not the use of the isomeric orange GGN (1-*m*-sulphophenylazo-2-naphthol-6-sulphonic acid). Orange GGN, however, is permitted as a food colour in Western Germany, and it is therefore possible that foods coloured with orange GGN, either alone or mixed with Sunset yellow FCF, may be offered for sale in the United Kingdom. The particular problem of detecting orange GGN in table jellies has been studied, but the method evolved should be applicable to other situations.

## Experimental

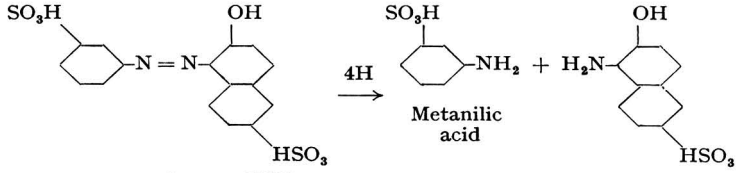
Preliminary work indicated that unambiguous differentiation between Sunset yellow FCF and orange GGN by absorptiometric measurements in the visible or ultraviolet region of the spectrum was not possible, owing to the great similarity between the absorption curves of the

two dyes. Infrared examination of the two dyes as potassium bromide discs showed that, although their spectra differ, the differences are not sufficient for detecting small amounts of orange GGN in Sunset yellow FCF.

Several chromatographic techniques were tried in attempts to separate the dyes. Various types of chromatography paper were used, with both aqueous and organic solvents, and cellulose columns were also tried without success. However, differentiation between Sunset yellow FCF and orange GGN was achieved by reducing the dyes with tin and hydrochloric acid, thereby producing sulphanilic acid from Sunset yellow and metanilic acid from orange GGN (see equations below).




Sunset yellow




Orange GGN

The sulphanilic and metanilic acids were then separated by chromatography on filter-paper, a mixture of n-butyl alcohol, ethanol and water being used as developing solvent, and the separated acids were revealed by spraying the paper with a solution of *p*-dimethylaminobenzaldehyde, with which they condense to form a yellow colour. In this way it was possible to detect with certainty 2·5 per cent. of orange GGN in Sunset yellow.

Recovery of the colouring matter from commercial table jelly in a state of purity sufficient to permit effective chromatographic separation proved to be difficult. The wool-dyeing method described by the Association of Public Analysts[2] was a valuable first step by which most of the gelatin could be removed, but, in recovering the dye from the well washed wool by stripping with ammonia solution, some degradation of the wool was unavoidable, and the degradation products interfered with chromatographic separation of the sulphanilic and metanilic acids. To overcome this difficulty, the dyes were extracted from acid solution with n-pentyl alcohol. Even then, separation was less perfect than that obtained with the dyes themselves, and the smallest amount of orange GGN detectable in Sunset yellow recovered from table jelly was about 5 per cent.

## Method

### Apparatus—

*Chromatography tank*—Suitable for the downward elution of paper chromatograms approximately 18 cm wide and 40 cm long.

*Chromatography papers*—Prepare strips of Whatman No. 4 filter-paper approximately 18 cm wide and 40 cm long; draw on each strip a line parallel to and 7 cm from one of the 18-cm ends to define the origin from which chromatograms are run.

### Reagents—

*Extracted wool*—Treat 16 g of white de-greased wool fabric by bringing to the boil in a mixture of 8 ml of ammonia solution, sp.gr. 0·880, and 400 ml of water. Wash well with hot and cold water, and store in cold water until required.

*n-Pentyl alcohol*—Distil n-pentyl alcohol (mixed isomers), and collect the fraction boiling between 120° and 130° C.

*Granulated tin*—Analytical-reagent grade.

*Sulphanilic acid containing 2 per cent. of metanilic acid*—Dissolve 0·98 g of sulphanilic acid and 0·02 g of metanilic acid in 75 ml water, add 15 ml of 1·0 M hydrochloric acid, dilute to 100 ml with water, and mix well.

*Eluting solvent*—Mix 3 volumes of n-butyl alcohol, 1 volume of water and 1 volume of industrial absolute ethanol.

p-*Dimethylaminobenzaldehyde spray reagent*—Dissolve 1 g of *p*-dimethylaminobenzaldehyde in 100 ml of ethanol, and add 5 ml of concentrated hydrochloric acid; this reagent should be freshly prepared as required.

EXTRACTION OF DYES ON TO WOOL AND RECOVERY THEREFROM—

To a jelly weighing about 125 g add 250 ml of water, and warm to dissolve. Add sufficient concentrated hydrochloric acid to make the solution definitely acid to Congo red paper (about 3 ml are usually needed). Add about 8 g (dry weight) of extracted wool to the acidified solution, bring to the boil, with stirring, and allow the wool to remain in the hot liquid for 5 minutes. Remove the coloured wool, replace it by a fresh 8-g portion of extracted wool, and repeat the dyeing procedure. Wash all the coloured wool vigorously with cold water until it is *absolutely free from gelatin*; squeeze the wool in a 2-litre beaker of cold water that is continuously renewed until no trace of turbidity can be seen in the vicinity of the wool. Place the wool in a beaker containing 200 ml of water and 4 ml of ammonia solution, sp.gr. 0·880, and bring to the boil; remove the wool, place it in another portion of the ammonia - water mixture, and again bring to the boil. Filter the extracts through a Whatman No. 1 filter-paper into an 800-ml beaker, and evaporate to about 50 ml. Filter this solution through a Whatman No. 1 filter-paper into an evaporating basin, and evaporate to dryness on a steam-bath. Treat the residue with 2·0 ml of cold 3·0 M hydrochloric acid, and filter the solution through a small sintered-glass funnel (porosity No. 4). Dilute the filtrate to 10 ml with 1·0 M hydrochloric acid, extract with two 10-ml portions of n-pentyl alcohol, and evaporate the combined extracts to dryness on a steam-bath. Dissolve the residue in 2·0 ml of 3·0 M hydrochloric acid, and again filter through a small sintered-glass funnel.

REDUCTION, CHROMATOGRAPHY AND DETECTION—

To the filtered solution of the dyes in 3·0 M hydrochloric acid contained in a hard-glass test-tube add a piece of granulated tin weighing 0·5 to 1·0 g, and boil gently until all dye has been reduced and the solution is almost colourless. Place 7 $\mu$l of the reduced solution as a spot on the origin line of a chromatographic strip. Place a similar spot of standard sulphanilic acid - metanilic acid mixture on the line in a position not less than 4 cm from the spot of reduced solution and not less than 3 cm from the edge of the paper. Allow the spots to dry in air, and develop the chromatogram by downward elution with the eluting solvent. (The atmosphere in the chromatographic tank must be saturated with solvent vapour before the chromatogram is placed therein; the paper must be supported so that it is vertical for about 3 cm above the spots, and solvent is fed to the paper from a trough at a point 3 cm before this line of support.) Allow development to proceed for 18 hours at about 24° C in a position free from draughts and not exposed to sunlight. Remove the strip, allow it partly to dry in air, and then spray with the freshly prepared solution of *p*-dimethylaminobenzaldehyde.

A yellow stain due to sulphanilic acid (from Sunset yellow FCF) will be seen centred at about 16 cm below the line of origin. A yellow stain centred at about 2 cm below the lower edge of the sulphanilic acid stain will be seen if metanilic acid (from orange GGN) is present.

## DISCUSSION OF THE METHOD

The proposed procedure is based on the assumption that a 4-oz jelly is coloured with about 50 mg of dye; the sulphanilic acid - metanilic acid standard gives a comparison at the correct concentration for the reduction products of this weight of dye.

The method was applied to commercial orange jellies having the composition: citric acid, 1 g; gelatin, 15 g; sugar, 55 g; glucose syrup, 38 g; water, 22 g; Sunset yellow FCF, 50 mg; orange flavouring. It was then applied to the same jellies after the addition of 10- or 5-mg portions of orange GGN. The resulting chromatograms clearly indicated the absence or presence of orange GGN.

On the chromatograms of the reduced dyes, small pink and yellow stains were observed above the stain due to sulphanilic acid; these were absent from the standard. The stains presumably arise from products of the other portion of the dye molecule and seem to vary from one reduction to another. This anomaly has not been investigated because it does not affect the main issue, but a possible explanation is that the amine group tends to be removed from the 1-amino-2-naphthol-6-sulphonic acid either during or after scission.

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# Apparatus

## A BUBBLE-PISTON FLOW INDICATOR WITH CONSTANT-RATE BURETTE

FOR several applications a simple gravity-feed burette permitting constant rate of flow of fluid as well as the determination of volume delivered would be desirable. The conventional gravity-feed burette does not provide these features, but can readily be modified to do so. The modification is accomplished as described below.

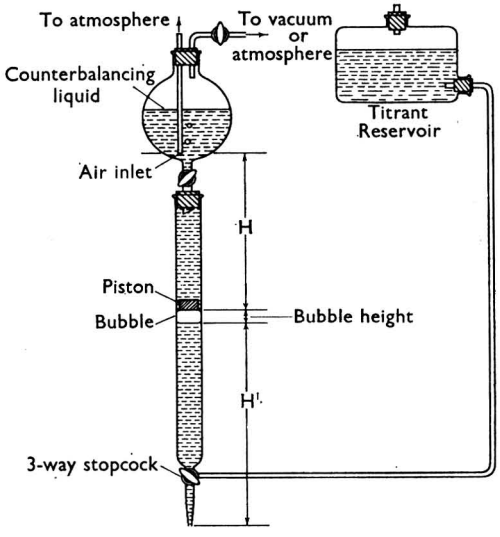


Fig. 1. Gravity-feed burette fitted with bubble piston flow-indicator. Hydrostatic head = H + H'

For the purpose of indicating volume withdrawn, the burette is equipped with a fairly close fitting but freely movable piston held in a fixed relation to the column of liquid in the burette by resting on a bubble of gas. If the piston is properly floated, substantially no liquid flows in either direction past the piston or bubble, even though the column of liquid rises or falls in the burette. The piston's buoyancy should be such that it will sink slowly when no gas bubble is beneath it. (It is possible to use a material less dense than is the liquid if a dependent part is hanging in the gas bubble and is therefore unsupported by the liquid.) When the bubble is in position below the piston, gas is prevented from leaking upward from the bubble and through the annular space around the piston by the surface tension of the liquid in the burette. If the piston is insufficiently buoyed, the gas pressure will overcome the surface tension of the liquid and the gas will escape past the piston. Liquid is prevented from flowing down the annular space because of the gas pressure beneath and the surface tension. Pistons are conveniently short cylinders, and have been made from glass, Teflon, polythene and rubber.

For the purpose of achieving constant flow, a constant hydrostatic head is maintained on the burette. This may be achieved in several ways. Use of a Mariotte bottle for the purpose has been discussed by Taylor and Escudero-Molins.[1]

Described below is a version of the Mariotte bottle involving extremely simple equipment for maintaining the constant hydrostatic head and for providing a means of filling the burette without having to inject a new bubble with each filling. This consists merely of a raised reservoir for titrant, a 3-way stopcock at the burette exit to provide for filling and a separating funnel, with appropriate tubing connections to atmosphere, fitted into the top opening of the burette.

Fig. 1 shows the burette fitted with the bubble-piston flow-indicator and this version of the Mariotte bottle for maintaining a constant head.

The burette is operated as described below. The titrant reservoir is filled and raised to a position above the separating funnel, and the 3-way stopcock is turned to admit titrant to the burette. The stopcock on the tubing leading from the separating funnel to atmosphere or the vacuum line is also opened. Liquid then fills the system running upward through the annular space around the piston into the separating funnel. When the titrant has covered the end of the lower tubing that admits air into the separating funnel, a bubble can be blown into position under the piston by attaching a hose to the burette tip and forcing air through the tip while the 3-way stopcock is turned to the exit position. This stopcock is thereafter turned back to admit more titrant, and, with the bubble in position, the bubble-piston assembly will then rise to the upper portion of the burette. At the same time, the counterbalancing titrant above the bubble-piston assembly flows into the separating funnel. The stopcock on the tubing leading to the atmosphere or to the vacuum line is now either closed or opened to a vacuum source whose rate of gas removal is controllable. As titrant is withdrawn from the burette, replacement air enters the separating funnel through the other tube. The depth in the separating funnel to which this tube extends controls the hydrostatic head on the rate-controlling orifice of the burette, as indicated in Fig. 1. The amount of titrant removed from the burette is read from the lower meniscus of the bubble under the piston.

Operation with the controlled-vacuum source connected to the separating funnel tube stopcock assures a more rapid rate of entry of bubbles into the funnel and is preferable when using very slow rates of flow of titrant to smooth out the slight variation in hydrostatic head at bubble entry.

It is true that the bubble height becomes less as the bubble falls in the burette, but under the usual conditions of operation with aqueous solutions this causes a pressure change of at most one part in five-hundred, and this therefore has a negligible effect on the flow rate for most purposes. Substantially none of the liquid above the bubble-piston assembly is removed from the burette in operation, so that it may be considered merely as a counterbalancing liquid and need not have precisely the same concentration as the titrant.

Since the bubble is compressed as it travels down the burette, use of a counterbalancing reservoir of sufficiently large surface area will allow the increase in hydrostatic head due to compression of the bubble to be substantially matched by the drop in head of the counterbalancing reservoir. Thus an alternative to the Mariotte bottle is provided.

Under the normal conditions in which the increase in total pressure on the burette bubble is small when the bubble is allowed to fall from its highest to its lowest position in the burette, the large surface area of the counterbalancing reservoir is substantially independent of the distance through which the bubble falls. This area can, under these conditions, be determined from the equation—

$$A = \frac{P\,a}{h}$$

where $A$ is the area of the liquid surface in the counterbalancing reservoir, $a$ is the surface area of the burette cross-section, $P$ is the total pressure on the bubble at its highest position in the burette expressed in height of titrant and $h$ is the height of the bubble at its highest position.

For the usual 50-ml burette having a cross-sectional area of approximately 1 sq. cm and with a a bubble of height 1 cm, a counterbalancing reservoir of surface area about 1000 sq. cm (about 1 sq. foot) is appropriate for use with aqueous solutions. Under these conditions a maximum error in hydrostatic head of less than 0·5 mm can be expected.

It can also be seen that proper choice of shape and size of the reservoir, bubble size and total pressure on the system would allow great flexibility in arranging for programmed flow-rates with the burette.

A typical example of the burette bubble-piston assembly, which has given satisfactory service with aqueous solutions, is an ordinary 50-ml burette of 11·0 mm inside diameter fitted with a piston consisting of a section of heavy walled glass tubing sealed at one end and having an outside diameter of 10·5 mm, a weight of 1·05 g and a liquid-displacement volume as used of 0·92 ml. The piston is inserted in the burette open end down, and in use is filled with air as well as having a bubble of air beneath it. Bubble heights of about 3 mm or more are satisfactory.

Such a burette, also equipped with a Mariotte bottle to achieve constant head, delivers liquid at constant rate provided temperature at the rate-controlling orifice does not change appreciably during delivery. For reproducible rate control, a small section of tapered polythene capillary tubing, which can readily be drawn from polythene tubing of larger diameter, may be inserted into the burette tip. With several such capillaries at hand and by controlling the head through control of depth of the air-admission tube in the Mariotte bottle, practically any desired slow rate of flow can be selected.

As pointed out by Taylor and Escudero-Molins,[1] the viscosity of aqueous solutions changes by about 2 per cent. per °C, so that, for the best reproducibility of flow rate, temperature at the rate-controlling orifice should be carefully controlled. However, when solutions are used that have come to room temperature in a room of fairly uniform temperature, repeatability is about 0·5 per cent. Moreover, since the flow indicator provides a calibration with each delivery, operation without specific temperature control of the orifice is for most purposes satisfactory.

The amount of liquid delivered by the burette with flow indicator and Mariotte bottle fittings differs by less than 0·1 per cent. from delivery of the same burette without the fittings, provided that the flow rate is slow enough to allow liquid drainage at the bubble wall to be substantially complete. With aqueous solutions in an ordinary 50-ml burette at room temperature, flow rates of less than about 10 ml per minute allow such substantially complete drainage. Even with rapid flow rates, the amount of liquid delivered initially by the burette with fittings or without fittings will be practically the same. Subsequent wall drainage from the unfitted burette will then increase the delivery of this burette compared with its delivery when fitted for indication of rate of flow.

Most liquids may be dispensed with this apparatus provided that they have sufficient surface tension. Thus, acetone, hexane, dioxan, chloroform and other organic liquids, as well as liquids such as 96 per cent. sulphuric acid, can be handled when a piston of proper buoyancy is used. On the other hand, detergent solutions and other solutions of low surface tension do not ordinarily lend themselves to metering with this apparatus.

The burette as modified for constant-rate delivery and flow indication is well adapted to use with a strip-chart recorder for automatic titrations. Ewing[2] has pointed out the desirability of such a device for this purpose. In this use, a solution property whose change is indicative of the equivalence-point is plotted by the recorder against time while titrant is added at constant rate of flow. The chart paper is calibrated for the titrant flow rate by marking time of start and end of addition of titrant on the chart, and noting from the burette the total volume of titrant added. Length of chart paper from start to equivalence-point inflexion of the titration curve then allows volume of titrant necessary to reach the equivalence-point to be determined.

Taylor and Escudero-Molins[1] carried out such a titration by calibrating a constant-head constant-flow burette with respect to rate of delivery of titrant under conditions of close temperature control of the rate-controlling orifice. Volume of titrant added to reach the equivalence point was estimated from the one flow-rate calibration and time measurement, since their burette did not indicate volume delivered directly.

Use of the flow-indicating constant-rate burette has the advantage over their method that each titration provides a separate calibration of flow rate, so that it is unnecessary to return to exactly the same conditions of hydrostatic head and temperature of the rate-controlling orifice with each titration. Moreover, accurate determination of volume of titrant used in reaching the equivalence-point becomes less dependent on an exact calibration of the flow rate the nearer this volume approaches the total volume of titrant added. With close approach of these two volumes, an error in flow-rate calibration or even an appreciable change in flow rate during titration will cause little error in determining the equivalence volume.

The constant-rate burette with bubble-piston flow indicator is generally useful for accurately metering small amounts of liquid at constant slow rates of flow, and, because of its excellent accuracy, wide choice of flow rate and good reproducibility, it can for many applications replace the more expensive motor-driven pumps and syringes.

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## A SIMPLE APPARATUS FOR WINDING SILVER WIRE FOR USE IN MICROCOMBUSTION TUBES

WHEN silver wire plugs or fillings are required for combustion tubes it is often a tedious and time-consuming task to wind the necessary amount of wire. The apparatus described was designed to simplify this operation.

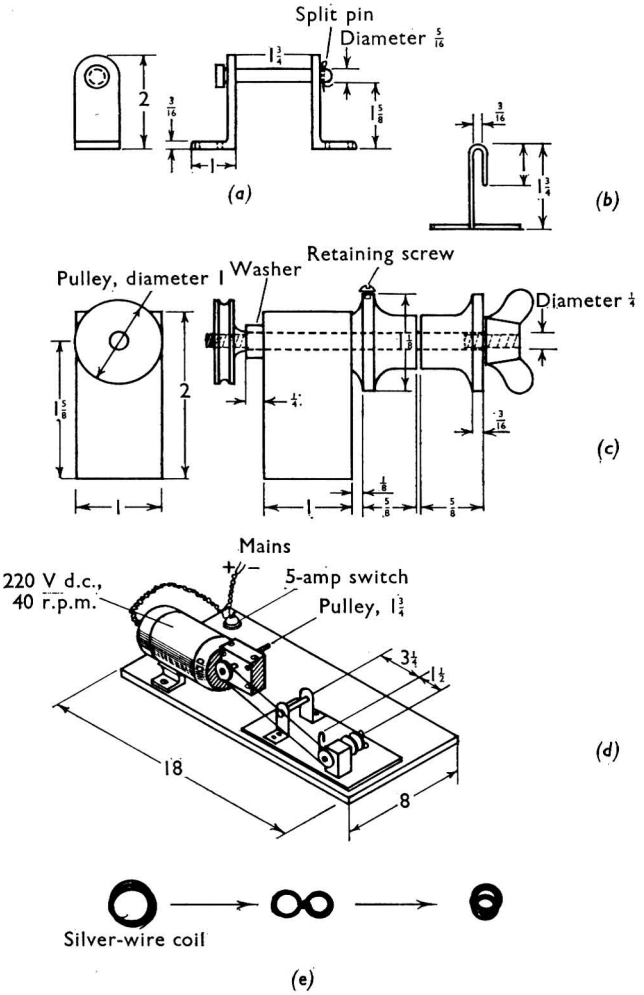


Fig. 1. (*a*) Spindle; (*b*) guide pin; (*c*) split bobbin; (*d*) complete apparatus; (*e*) method of forming plug. (All dimensions are in inches)

### Description of apparatus

The apparatus is shown in Fig. 1; it consists of a spindle (*a*) to hold the reel of silver wire, a guide pin (*b*), a split bobbin (*c*) on which to wind the silver wire, an electric motor to drive the bobbin and a control switch. The whole apparatus (*d*) is mounted on a 6-ply wooden base-board 18 inches × 8 inches.

The spindle is a metal rod of diameter $\frac{5}{16}$ inch; it is mounted in iron supports and permits the reel of wire to turn freely. The guide pin, to prevent the wire running off the bobbin, is of 14-gauge iron wire and is fixed into the base-board. The bobbin, of brass, is supported on a $\frac{1}{4}$-inch diameter iron spindle running through a brass block with a 1-inch pulley screwed to the other end of the spindle. The bobbin is split to permit removal of the silver-wire coil. The half bobbin nearest the block is secured to its spindle by a retaining screw, and the other half is held against it by a butterfly nut. The bobbin is driven by a cord from a Klaxon electric motor, 220 volts d.c. geared to give 40 r.p.m., to which is attached a $1\frac{3}{4}$-inch pulley. A 5-amp tumbler switch permits the motor to be started and stopped.

### Method of operation

Place a reel of silver wire on the spindle, and insert the retaining split pin. Lead the wire under the loop of the guide pin to the bobbin, and clamp the end between the two halves by tightening the butterfly nut. Switch on the motor, and, when sufficient silver wire has been wound on to the bobbin, switch off, and split the bobbin. Remove the coil of silver wire, twist it into a figure of eight, and fold over to form a plug (*e*). The next coil can then be wound.

I thank Mr. F. W. Joy for his assistance in making the apparatus.

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## A SLIDE RULE FOR SPECTROPHOTOMETRIC CALCULATIONS

A fundamental equation of spectrophotometry relates $A_\lambda$, the optical density of a solution of a single absorbing species at wavelength $\lambda$, to its molar extinction coefficient, $\epsilon_\lambda$, measured in litres per mole per centimetre, to its concentration $c$ and to the optical path length, $b$, in centimetres; this equation is—

$$A_\lambda = \epsilon_\lambda cb \quad (1)$$

and the concentration $c$ is expressed by—

$$c = \frac{g}{MV} \quad (2)$$

in which $g$ is the weight of the material in grams, $M$ is its molecular weight and $V$ is the volume of the solution in litres.

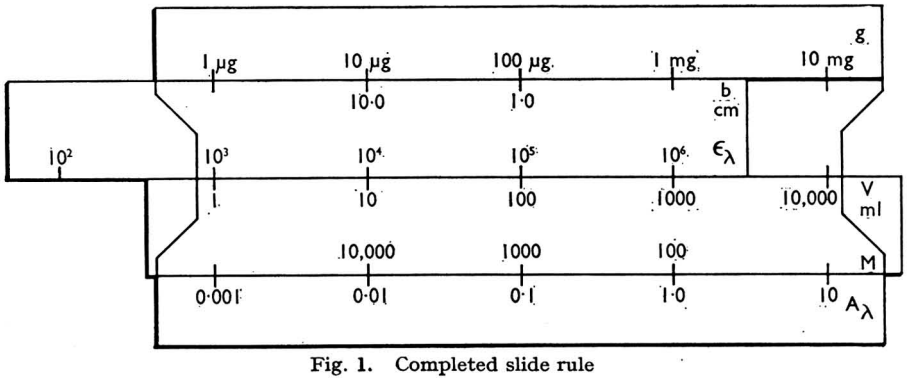


Fig. 1. Completed slide rule

Substitution for $c$ in equation (1) and rewriting in logarithmic form leads to the expression—

$$\text{Log } A_\lambda + \log M + \log V - \log g - \log b - \log \epsilon_\lambda = 0 \quad .. \quad .. \quad (3)$$

Special kits have recently become commercially available, and these permit the construction of slide rules for solving such equations containing up to eight variables. For the solution of equation (3) we use the 2-SLIDE slide-rule blank No. 22, obtainable from the Dyna Slide Company, 600 South Michigan Avenue, Chicago 5, Illinois, U.S.A. The general rules for lay-out of scales[1] were adhered to, and a sketch of the completed slide rule is shown in Fig. 1. The more convenient units milligram and millilitre are substituted for gram and litre. It can be seen that all operations for division are carried out as subtractions of lengths equivalent to the logarithms of the variables; for multiplication, the lengths correspond to the logarithms of the reciprocals of the variables.

The scales may be manually plotted on the slide-rule blanks described by Hedberg,[1] but we found that greater accuracy was achieved by cutting the scales from a single sheet of semi-logarithmic graph paper (four-cycle semi-logarithmic paper No. 359–81, obtainable from the Keuffel and Esser Co.). The scales are pasted to the slide-rule blank with rubber cement and, after drying and labelling, are liberally coated with a plastic aersol spray.

We have not used a special scale for optical path length, $b$, as all our measurements are made with cells of path length either 1 or 10 cm. The two index marks on the $b$-scale are added after complete assembly of the rule by solving a typical equation. Errors in the alignment of the scales are thereby compensated for, and this results in greater accuracy than that attainable by cementing on to the slide an additional $b$-scale.

Fig. 1 shows the solution of an equation. An optical density of 0·1 was measured for a solution of a compound of molecular weight 1000 dissolved in 10 ml of solvent. The extinction coefficient of the compound was $10^4$, and the measurement was made in a cell of length 1 cm. The unknown, the weight of sample, is read from the top scale as being 100 $\mu$g. Naturally, any other variable can be determined equally well, provided that the other five are known.

This investigation was supported by a research contract, NONR 2196 (00), with the United States Office of Naval Research.

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# Reagents for use in Micro-analysis

## SPECIFICATIONS PREPARED BY THE SUB-COMMITTEE FOR MICRO ANALYTICAL STANDARDS OF THE MICROCHEMISTRY GROUP OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

THESE specifications for the commonly used reagents employed in micro-analysis have been drawn up by a sub-committee* representative of the Microchemistry Group and British manufacturers of reagent chemicals.

Ten years have passed since the publication in *The Analyst* of the first quantitative specifications for reagents to be used in micro-analytical practice, but the revision has indicated that the earlier specifications have needed little amendment. In one or two instances limits have been raised; this is a realistic appreciation of manufacturing difficulties: in other instances limits have been reduced.

Certain of the tests described in the specifications are taken from "'AnalaR' Standards for Laboratory Chemicals," issued jointly by the British Drug Houses Limited, and Hopkin and Williams Limited, and are reproduced by permission of the owners of the copyright.

The individual specifications have been drafted so that most of them contain all the information necessary to carry out the acceptance tests. Certain reagents, solutions, etc., are required in the tests for more than one specification. To avoid repetition details of them are given in an Appendix (see p. 409) to the specifications.

Where a figure is given in brackets at the end of a test this indicates the maximum amount of impurity permitted by the given test.

### ASBESTOS

1. **Description**—White or off-white fluffy fibres.
2. **Acid-soluble matter**—Heat 2 g with 30 ml of 1·0 M hydrochloric acid on a steam-bath for 10 minutes. Filter, evaporate the filtrate to dryness, and ignite at 400° to 450° C for 5 minutes. The weight of the residue should not exceed 5 mg (0·25 per cent.).

### CAMPHOR

1. **Description**—Colourless crystals.
2. **Particle size**—All should pass a 30-mesh B.S. sieve.
3. **Solution**—Dissolve 1 g in 10 ml of ethanol. A clear colourless solution should be produced.
4. **Melting-point and suitability for Rast method**—The material should melt between 179° and 179·5° C and show no darkening when maintained at its melting-point for 30 minutes.

### COPPER OXIDE (POWDER)

1. **Description**—A black or nearly black powder prepared by grinding copper oxide (wire form).
2. **Particle size**—All should pass a 30-mesh B.S. sieve; none should pass an 85-mesh B.S. sieve.
3. **Carbon**—Ignite 6 g in a stream of carbon dioxide free air or oxygen, and pass the evolved gases into 20 ml of a solution prepared by diluting 2·5 ml of ammonia solution, sp.gr. 0·880, to 100 ml with carbon dioxide free water. Add 2 ml of 0·5 M barium chloride. Any turbidity obtained should not exceed that produced by the addition of 2 ml of 0·5 M barium chloride to 20 ml of the dilute ammonia solution containing 1 ml of 0·005 M sodium carbonate (0·001 per cent. of C).

### COPPER OXIDE (WIRE FORM)

1. **Description**—Two- to four-millimetre lengths of approximately 24 s.w.g. wire completely oxidised and free from metallic cores.
2. **Freedom from dust**—None should pass a 36-mesh B.S. sieve.
3. **Carbon**—Ignite 6 g in a stream of carbon dioxide free air or oxygen, and pass the evolved gases into 20 ml of a solution prepared by diluting 2·5 ml of ammonia solution, sp.gr. 0·880, to 100 ml with carbon dioxide free water. Add 2 ml of 0·5 M barium chloride. Any turbidity obtained should not exceed that produced by the addition of 2 ml of 0·5 M barium chloride to 20 ml of the dilute ammonia solution containing 1 ml of 0·005 M sodium carbonate (0·001 per cent. of C).

* The sub-committee consisted of: E. Bishop (*Chairman*), A. E. Heron (*Recorder*), P. R. W. Baker, A. G. Hill, T. F. McCombie and J. T. Yardley.

## COPPER SULPHATE

1. **Description**—A blue crystalline powder.
2. **Solution**—Dissolve 10 g in 100 ml of water. A clear blue solution should be produced, which should remain free from sediment after standing for 2 hours.
3. **Chloride**—Dissolve 1 g in 50 ml of water, and add 1 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·001 per cent. of $Cl^-$).
4. **Nitrogen**—Digest 0·6 g with 4 ml of sulphuric acid and 0·5 g of Kjeldahl catalyst (see Appendix, Note 1) until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating a mixture of 0·1 g of the sample and 0·6 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·001 per cent. of N).
5. **Iron**—Dissolve 2 g in 90 ml of water, add 1 drop of nitric acid and 10 ml of sulphuric acid, and electrolyse the solution for 30 minutes at a current density of approximately 0·1 amp per sq. cm between concentric cylindrical platinum-gauze (or similar) electrodes. Remove the copper from the cathode with nitric acid, add 1 g of urea to the solution, and electrolyse for a further 15 minutes at a current density of approximately 0·05 amp per sq. cm. Evaporate 50 ml to 2 ml, and add 15 ml of water, 1 ml of 5 M hydrochloric acid, 1 drop of 0·1 N potassium permanganate and 5 ml of 7·5 M ammonium thiocyanate. Any pink colour produced should not exceed that obtained by adding 5 ml of 7·5 M ammonium thiocyanate to a solution containing 20 ml of water, 1 ml of 5 M hydrochloric acid, 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) and 1 drop of 0·1 N potassium permanganate (0·001 per cent. of Fe).

## *p*-CYMENE

1. **Description**—A clear colourless liquid.
2. **Weight per ml at 20° C**—About 0·86 g.
3. **Distillation range**—Not less than 95 per cent. should distil between 175° and 177° C.
4. **Non-volatile matter**—Evaporate 6 ml (5 g) to dryness. Not more than 0·5 mg of residue should remain (0·01 per cent.).

## DEKALIN

1. **Description**—A clear colourless liquid.
2. **Weight per ml at 20° C**—About 0·88 g.
3. **Distillation range**—Not less than 95 per cent. should distil between 189° and 193° C.
4. **Non-volatile matter**—Evaporate 6 ml (5 g) to dryness. Not more than 0·5 mg of residue should remain (0·01 per cent.).

## DIETHYL ETHER

1. **Description**—A clear colourless mobile liquid.
2. **Ether peroxide**—Place 10 ml of ferrous thiocyanate reagent* in a stoppered 30-ml bottle previously filled with carbon dioxide; completely fill the bottle with the sample of ether, insert the stopper so that no gas is enclosed, shake vigorously, and set aside in the dark for 5 minutes. No pink colour should appear (0·000015 per cent.).
3. **Distillation range**†—Not less than 95 per cent. should distil between 34° and 35° C.
4. **Non-volatile matter**†—Evaporate 140 ml (100 g) to dryness on a steam-bath. Not more than 0·5 mg of residue should remain (0·0005 per cent.).
5. **Water**—Determine by the Karl Fischer method, according to B.S. 2511 : 1954 (0·008 per cent.).

* Ferrous thiocyanate reagent—

Add 3 ml of 2·5 M sulphuric acid to 35 ml of water, and boil to remove oxygen. To the hot solution add 1 g of ferrous sulphate, dissolve, cool, and add 0·5 g of potassium thiocyanate. Remove any pink colour by treating the solution with clean iron wire; decant from excess of iron, and store the reagent in an atmosphere free from oxygen. For use it must be colourless. Remove any pink colour that may have developed by shaking with ether, and discard the ether layer.

† It is dangerous to determine distillation range and non-volatile matter on samples that do not comply with Test 2 for peroxide.

## D (+) GLUCOSE

1. **Description**—A white crystalline or granular powder.
2. **Solution**—Dissolve 10 g in 100 ml of water. A clear colourless solution should be produced.
3. **Chloride**—Dissolve 0·5 g in 50 ml of water, and add 1 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·002 per cent. of $Cl^-$).
4. **Nitrogen**—Digest 0·6 g with 4 ml of sulphuric acid and 0·5 g of Kjeldahl catalyst (see Appendix, Note 1) until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing one drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating a mixture of 0·1 g of the sample and 0·6 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·001 per cent. of N).
5. **Phosphate**—Dissolve 0·5 g in 20 ml of water, add 3 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·002 per cent. of $PO_4^{3-}$).
6. **Sulphate**—Dissolve 5 g in 50 ml of water, add 1 ml of 5 M hydrochloric acid and 1 ml of 0·5 M barium chloride, and set aside for 6 hours. No turbidity or precipitate should appear (0·002 per cent. of $SO_4^{2-}$).
7. **Iron**—Mix 10 g with 0·1 g of anhydrous sodium sulphate and 2 drops of sulphuric acid, heat gently until the glucose is decomposed, and then ignite until no more fumes are produced and any carbon is oxidised. Heat the residue with 1 ml of hydrochloric acid, and evaporate to dryness on a steam-bath. Dissolve the residue by warming with a mixture of 1 ml of 5 M hydrochloric acid and 10 ml of water, add 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl alcohol and amyl acetate, shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·0001 per cent. of Fe).

## HYDRIODIC ACID, sp.gr. 1·7

### (Stabilised with 0·03 per cent. w/w of hypophosphorous acid)

1. **Description**—A colourless liquid when freshly distilled; it may become yellow to red-brown on storage through liberation of iodine.
2. **Weight per ml at 20° C**—About 1·70 g.
3. **Nitrogen**—Mix 0·75 ml (1·3 g) with 4 ml of sulphuric acid, and heat until most of the iodine is removed. Add 0·5 g of Kjeldahl catalyst (see Appendix, Note 1), and re-heat for 5 minutes Cool, add 4 ml of water, continue the digestion until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428: Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing one drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating a mixture of 0·1 g of the sample and 0·6 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0005 per cent. of N).
4. **Sulphur compounds**—Add 1 ml (1·7 g) dropwise, with stirring, to 5 ml of 5 M nitric acid. Add 0·2 ml of 0·5 M sodium carbonate, and evaporate to dryness on a steam-bath. Dissolve the residue in 1 ml of 5 M hydrochloric acid and 50 ml of water, add 1 ml of 0·5 M barium chloride, and set aside for 6 hours. No turbidity or precipitate should appear (0·002 per cent. of S).

## HYDROCHLORIC ACID

1. **Description**—A clear colourless fuming liquid.
2. **Weight per ml at 20° C**—About 1·18 g.
3. **Non-volatile matter**—Evaporate 85 ml (100 g) to dryness on a steam-bath, moisten the residue with 1 drop of sulphuric acid, and ignite at 400° to 500° C for 5 minutes. Not more than 0·5 mg of residue should remain (0·0005 per cent.).

4. **Free chlorine**—Dilute 8·5 ml (10 g) with 20 ml of freshly boiled and cooled water, add 1 ml of 0·25 M cadmium iodide and 1 ml of starch solution (0·5 per cent., aqueous), and set aside in the dark for 10 minutes. Any blue colour produced should be discharged by the addition of 0·05 ml of 0·005 M sodium thiosulphate (0·0001 per cent. of Cl).

5. **Sulphate**—To 168 ml (200 g) add 0·2 ml of 0·5 M sodium carbonate, and evaporate to dryness on a steam-bath. Dissolve the residue in 10 ml of water and 1 ml of 1·0 M hydrochloric acid, filter if necessary, and add 1 ml of sulphate seeding reagent (see Appendix, Note 6). Any turbidity produced should not exceed the standard turbidity (see Appendix, Note 7) (0·0001 per cent. of $SO_4^{2-}$).

6. **Iron**—Evaporate 8·5 ml (10 g) to dryness on a steam-bath, dissolve the residue by heating with a mixture of 2 ml of 5 M hydrochloric acid and 10 ml of water, add 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl alcohol and amyl acetate, shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·0001 per cent. of Fe).

7. **Lead**—Evaporate 5 ml to 1 ml on a hot-plate. Add a little water, and make just alkaline by dropwise addition of 5 M sodium hydroxide. Add 2 drops of 5 M nitric acid (the solution should now be acid), and dilute to 10 ml. Place 5 ml of this solution in a separating funnel, add 1 ml of chloroform, and shake to saturate the solution with chloroform. Reject the excess of chloroform. Add 0·2 ml of 0·1 M sodium metabisulphite, 0·2 ml of 1·0 M ammonium citrate, and adjust to pH 9 with 5 M ammonia solution (about 2 drops are required). Then add 0·1 ml of 1·5 M potassium cyanide, and run in a 0·002 per cent. solution of dithizone in chloroform from a microburette, with vigorous shaking, until a mixed colour (mauve) is produced in the chloroform layer. Carry out a blank experiment, with all reagents being used in a similar manner, and finally add the exact amount of dithizone solution previously used in the test. Titrate the blank with standard lead solution (1 ml ≡ 0·01 mg of $Pb^{2+}$) from a 1-ml microburette, shaking after each addition, until the colour of the chloroform layer matches that of the test. Not more than 0·25 ml should be required (0·0001 per cent. of Pb).

## HYDROGEN PEROXIDE
### (100 volumes)

1. **Description**—A clear colourless liquid.

2. **Acidity**—
   (*A*) *Total acid*—Dilute 10 ml with 20 ml of carbon dioxide free water, and titrate with 0·1 N sodium hydroxide, with phenolphthalein as indicator. Not more than 0·5 ml of 0·1 N sodium hydroxide should be required (0·5 ml of 1·0 N per cent.).
   (*B*) *Steam-volatile acid*—Dilute 10 ml with 100 ml of carbon dioxide free water, and steam-distil until 50 ml of distillate have been collected. Titrate with 0·1 N sodium hydroxide, with phenolphthalein as indicator. Run a blank on the reagents, omitting the hydrogen peroxide. The difference between the two titrations should not exceed 0·1 ml (0·1 ml of 1·0 N per cent.).

3. **Chloride**—Dilute 2 ml with water to 50 ml, and add 1 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·0005 per cent. of $Cl^-$).

4. **Nitrogen**—To 5 ml in a platinum dish add 1 drop of sulphuric acid, and evaporate on a steam-bath to 2 ml. Dilute to 20 ml. Transfer 2 ml of this solution to a Kjeldahl flask with 4 ml of sulphuric acid, add 0·01 g of sucrose, and set aside for 30 minutes. Add 0·5 g of Kjeldahl catalyst (see Appendix, Note 1), heat until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428: Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating a mixture of 0·2 ml of the diluted sample solution and 0·6 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·001 per cent. of N).

5. **Phosphate**—Evaporate 1 ml to dryness in a platinum dish on a steam-bath, dissolve any residue in 20 ml of water, add 3 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·001 per cent. of $PO_4^{3-}$).

6. **Sulphate**—Transfer 36 ml (40 g) to a platinum dish. When the initial reaction has subsided add 0·2 ml of 0·5 M sodium carbonate, and set aside until no more oxygen is evolved; then evaporate to dryness on a steam-bath. Dissolve the residue in 10 ml of water and 1·0 ml of 1·0 M hydrochloric acid, filter if necessary, and add 1 ml of sulphate seeding reagent (see Appendix, Note 6). Any turbidity produced should not exceed the standard turbidity (see Appendix, Note 7) (0·0005 per cent. of $SO_4^{2-}$).

## LEAD CHROMATE

1. **Description**—Fine orange-brown granules.
2. **Particle size**—All should pass a 14-mesh B.S. sieve and not more than 5 per cent. should pass a 22-mesh B.S. sieve.
3. **Carbon**—Ignite 3 g in a stream of carbon dioxide free air or oxygen, and pass the evolved gases into 20 ml of a solution prepared by diluting 2·5 ml of ammonia solution, sp.gr. 0·880, to 100 ml with carbon dioxide free water. Add 2 ml of 0·5 M barium chloride. Any turbidity obtained should not exceed that produced by the addition of 2 ml of 0·5 M barium chloride to 20 ml of the dilute ammonia solution containing 1 ml of 0·005 M sodium carbonate (0·002 per cent. of C).
4. **Nitrogen**—To 130 ml of water in an ammonia-distillation apparatus add 0·8 g of the finely powdered sample, 1 g of aluminium wire and 10 ml of 12·5 M sodium hydroxide. Distil 90 ml into a 100-ml Nessler tube containing 0·1 ml of 0·5 M sulphuric acid. Add 2 ml of Nessler's reagent (see Appendix, Note 2), and set aside for 10 to 15 minutes. Any yellow-brown colour obtained should not exceed that produced by treating 1 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in a similar manner (0·001 per cent. of N).

## MAGNESIUM PERCHLORATE DRIED
## (Anhydrone)

1. **Description**—White granules.
2. **Particle size**—All should pass a 14-mesh B.S. sieve and not more than 5 per cent. should pass a 22-mesh B.S. sieve.
3. **Moisture**—Titrate 1 g by the Karl Fischer method (B.S. 2511 : 1954), with 20 ml of methanol as solvent. Not more than 14 per cent. of water should be indicated.
4. **Reaction**—Shake 5 g with 20 ml of ethanol. The liquor should not be alkaline to phenolphthalein.

## MERCURIC SULPHATE

1. **Description**—White or very pale cream crystalline powder.
2. **Nitrogen**—Digest 1·3 g with 4 ml of sulphuric acid and 0·5 g of Kjeldahl catalyst (see Appendix, Note 1) until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating a mixture of 0·1 g of the sample and 0·6 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0005 per cent. of N).

## NITRIC ACID

1. **Description**—A clear colourless fuming liquid.
2. **Weight per ml at 20° C**—About 1·42 g.
3. **Non-volatile matter**—Evaporate 70 ml (100 g) to dryness, and ignite at 400° C for 5 minutes. Not more than 1 mg of residue should remain (0·001 per cent.).
4. **Chloride**—Dilute 10 ml (14·2 g) with 40 ml of water, and add 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·00007 per cent. of $Cl^-$).
5. **Sulphate**—To 140 ml (200 g) add 0·2 ml of 0·5 M sodium carbonate, and evaporate to dryness. Dissolve the residue in 10 ml of water and 1 ml of 1·0 M hydrochloric acid. Filter if necessary, and add 1 ml of sulphate seeding reagent (see Appendix, Note 6). Any turbidity produced should not exceed the standard turbidity (see Appendix, Note 7) (0·0001 per cent. of $SO_4^{2-}$).
6. **Lead**—Evaporate 5 ml to 1 ml on a hot-plate. Add a little water, and make just alkaline by dropwise addition of 5 M sodium hydroxide. Add 2 drops of 5 M nitric acid (the solution should now be acid), and dilute to 10 ml. Place 5 ml of the solution in a separating funnel, add 1 ml of chloroform, and shake to saturate the solution with chloroform. Reject the excess of chloroform. Add 0·2 ml of 0·1 M sodium metabisulphite and 0·2 ml of 1·0 M ammonium citrate, and adjust to pH 9 with 5 M ammonia solution (about 2 drops are required). Then add 0·1 ml of 1·5 M potassium cyanide, and run in a 0·002 per cent. solution of dithizone in chloroform from a microburette, with vigorous shaking, until a mixed colour (mauve) is produced in the chloroform layer. Carry out a blank experiment, with all reagents being used in a similar manner, and finally add the exact amount of dithizone solution previously used in the test. Titrate the blank with standard lead solution (1 ml ≡ 0·01 mg of $Pb^{2+}$) from a 1-ml microburette, shaking after each addition, until the colonr of the chloroform layer matches that of the test. Not more than 0·25 ml should be required (0·0001 per cent. of Pb).

## POTASSIUM NITRATE

1. **Description**—Colourless crystals or crystalline powder.
2. **Solution**—Dissolve 10 g in 50 ml of water. A clear colourless solution should be produced.
3. **Chloride**—Dissolve 2 g in 50 ml of water, and add 1 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·0005 per cent. of $Cl^-$).
4. **Nitrite and iodate**—Dissolve 1 g in 10 ml of water, add 1 ml of 2·5 M sulphuric acid, 1 ml of starch solution (0·5 per cent., aqueous) and 1 ml of 0·25 M cadmium iodide, and set aside for 1 minute. No blue colour should appear (0·0001 per cent. of $NO_2^-$; 0·00005 per cent. of $IO_3^-$).
5. **Phosphate**—To 5 g add 20 ml of hydrochloric acid, and evaporate to dryness in glass or porcelain on a steam-bath. Add a further 20 ml of hydrochloric acid, and again evaporate to dryness. Dissolve the residue in 60 ml of water. (Retain 40 ml of the solution for Test 6.) To 20 ml of the solution add 3 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·0006 per cent. of $PO_4^{3-}$).
6. **Sulphate**—To the remaining 40 ml of the solution from Test 5 add 10 ml of water, 1 ml of 5 M hydrochloric acid and 1 ml of 0·5 M barium chloride, and set aside for 6 hours. No turbidity or precipitate should appear (0·003 per cent. of $SO_4^{2-}$).
7. **Iron**—Dissolve 5 g in 10 ml of water, add 1 ml of 5 M hydrochloric acid and 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl alcohol and amyl acetate. Shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·0002 per cent. of Fe).

## POTASSIUM SULPHATE

1. **Description**—Colourless crystals.
2. **Solution**—Dissolve 10 g in 50 ml of water. A clear colourless solution should be produced.
3. **Chloride**—Dissolve 2 g in 50 ml of water, and add 1 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·0005 per cent. of $Cl^-$).
4. **Nitrogen**—To 2 g in a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) add 0·5 g of aluminium wire and 35 ml of 5 M sodium hydroxide. Pass steam into the distillation flask, and collect any distillate in 5 ml of water containing 1 drop of 2·5 M sulphuric acid. Continue to pass steam until the liquid boils; disconnect the steam supply, allow the reaction to proceed for 1 hour, and then steam-distil so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard in the same manner, with 1·25 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in place of the sample. To each distillate add 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0005 per cent. of N).
5. **Calcium and magnesium**—Dissolve 5 g in 100 ml of water, and add 1 ml of standard magnesium solution (1 ml ≡ 0·1 mg of Mg). Add sufficient (about 2 ml) borate buffer solution* to adjust the pH to 10·5 to 10·7, the measurement being made with a pH meter. Add about 0·1 ml of Eriochrome black T solution,† and titrate slowly, with shaking, with 0·01 M EDTA (ethylenediaminetetra-acetic acid, disodium salt) from a microburette until a pure blue colour is obtained. Not more than 1·6 ml of 0·01 M EDTA should be required (0·01 per cent. of Ca + Mg).
6. **Iron**—Dissolve 2 g in 10 ml of water, add 1 ml of 5 M hydrochloric acid and 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl alcohol and amyl acetate, shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·0005 per cent. of Fe).

* Borate buffer solution—

| | | |
|---|---|---|
| Sodium borate .. | .. .. | 40 g |
| Sodium hydroxide | .. .. | 10 g |
| Sodium sulphide .. | .. .. | 5 g |
| Water .. .. | To produce | 1000 ml |

† Eriochrome black T solution—

Dissolve 0·5 g of Eriochrome black T (Colour Index No. 14645) in a mixture of 1 ml of 0·5 M sodium carbonate and 30 ml of isopropyl alcohol; dilute with water to 100 ml. This solution has poor keeping qualities.

7. **Lead**—Dissolve 0·25 g in 10 ml of water, and transfer to a separating funnel. Add 1 drop of 5 M nitric acid and 1 ml of chloroform, and shake to saturate the solution with chloroform. Reject the excess of chloroform. Add 0·2 ml of 0·1 M sodium metabisulphite and 0·2 ml of 1·0 M ammonium citrate, and adjust to pH 9 with 5 M ammonia solution (about 2 drops are required). Then add 0·1 ml of 1·5 M potassium cyanide, and run in a 0·002 per cent. solution of dithizone in chloroform from a microburette, with vigorous shaking, until a mixed colour (mauve) is produced in the chloroform layer. Carry out a blank experiment, with all reagents used in a similar manner, and finally add the exact amount of dithizone solution previously used in the test. Titrate the blank with standard lead solution (1 ml ≡ 0·01 mg of $Pb^{2+}$) from a 1-ml microburette, shaking after each addition, until the colour of the chloroform layer matches that of the test. Not more than 0·25 ml should be required (0·001 per cent. of Pb).

## SELENIUM

1. **Description**—Very dark red to black powder.
2. **Solution**—Dissolve 1 g in 5 ml of nitric acid, and dilute to 50 ml with water. A clear colourless solution should be produced.
3. **Non-volatile matter**—Ignite 5 g gently at first, then slowly increase the temperature to 750° to 800° C. Not more than 2 mg of residue should remain (0·04 per cent.).
4. **Total nitrogen**—Digest 0·2 g with 4 ml of sulphuric acid and 0·5 g of Kjeldahl catalyst (see Appendix, Note 1) until the mixture is colourless, and then for a further 30 minutes. Cool, transfer to a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) with 10 ml of water and 15 ml of 12·5 M sodium hydroxide containing 0·5 g of sodium thiosulphate, and steam-distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard by treating 0·6 ml of a standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in the same manner and with the same amounts of reagents. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0025 per cent. of N).

## SILVER GAUZE

1. **Description**—30 to 60 meshes per linear inch. Prepared from silver wire containing not less than 99·99 per cent. of silver after degreasing.

## SILVER WOOL

1. **Description**—Fine silver wire containing not less than 99·99 per cent. of silver after degreasing.

## SODA ASBESTOS, 14 to 22 MESH

1. **Description**—Light brown granules containing indicator material giving a greyish white colour when the absorptive capacity is exhausted.
2. **Particle size**—All should pass a 14-mesh B.S. sieve and not more than 5 per cent. should pass a 22-mesh B.S. sieve.
3. **Water content**—The loss of weight when dried at 150° C should be between 2 and 4 per cent.

## SODIUM CARBONATE, ANHYDROUS

1. **Description**—A white powder.
2. **Solution**—Dissolve 10 g in 100 ml of water. A clear colourless solution should be produced.
3. **Moisture**—Ignite 1 g for 1 hour at 300° C in a platinum crucible. The loss in weight should not exceed 10 mg (1·0 per cent.).
4. **Chloride**—Dissolve 1 g in 45 ml of water, and add 5 ml of 5 M nitric acid and 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·001 per cent. of $Cl^-$).
5. **Nitrogen**—To 2 g in a micro-Kjeldahl distillation apparatus (*e.g.*, B.S. 1428 : Part B1 : 1953) add 0·5 g of aluminium wire and 35 ml of 5 M sodium hydroxide. Pass steam into the distillation flask, and collect any distillate in 5 ml of water containing 1 drop of 2·5 M sulphuric acid. Continue to pass steam until the liquid boils; disconnect the steam supply, allow the reaction to proceed for 1 hour, and then steam-distil so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard in the same manner, with 1·25 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in place of the sample. To each distillate add 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0005 per cent. of N).
6. **Phosphate**—Dissolve 2 g in 20 ml of water in a platinum dish, and neutralise with 2·5 M sulphuric acid. Add 2 ml of acid in excess and dilute to 40 ml. To 20 ml (retain the remainder for Test 7), add 2 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·001 per cent. of $PO_4^{3-}$).

7. **Silicate**—To 2 ml of the solution retained from Test 6 add 20 ml of water, 1 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·005 per cent. as $SiO_2$).
8. **Sulphate**—Dissolve 10 g in 40 ml of 5 M hydrochloric acid, add 10 ml of water and 2 ml of 0·5 M barium chloride, and set aside for 6 hours. No turbidity should appear (0·002 per cent. of $SO_4^{2-}$).

## SODIUM HYDROGEN SULPHITE SOLUTION, 35 per cent. w/v

1. **Description**—A clear solution free from extraneous particles.
2. **Chloride**—To 7 ml add 20 ml of water and 10 ml of nitric acid dropwise. Boil, cool, dilute to 50 ml with water, and add 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·0001 per cent. of $Cl^-$).
3. **Assay**—Dilute 5 ml to 100 ml with water, and transfer 10 ml of this solution by pipette into 50 ml of 0·1 N iodine. Titrate the excess of iodine with 0·1 N sodium thiosulphate, with starch as indicator.

**1 ml of 0·1 N iodine ≡ 0·0052 g of $NaHSO_3$.**

(Not less than 34 or more than 36 per cent. should be indicated.)

## SODIUM PEROXIDE

1. **Description**—A fine cream-coloured powder.
2. **Solution**—Add 5 g in small portions to 100 ml of water. A clear solution should be produced. (Retain this solution for Test 3.)
3. **Chloride**—To 4 ml of the solution produced in Test 2 add 45 ml of water and 1 ml of 5 M nitric acid. Boil, cool, and add 1 ml of 0·25 M silver nitrate. No opalescence should appear within 5 minutes (0·005 per cent. of $Cl^-$).
4. **Phosphate**—Dissolve 3 g in 20 ml of water in a platinum dish. Neutralise the solution with 2·5 M sulphuric acid, with litmus paper as the indicator, and add 2 drops of the acid in excess. Evaporate the solution to dryness on a steam-bath, and dissolve the residue in 30 ml of water. This is solution A; (portions of this solution are used for tests 5 and 7 below). To 20 ml of solution A add 3 ml of 2·5 M sulphuric acid, 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·0005 per cent. of $PO_4^{3-}$).
5. **Silicate**—Dilute 1 ml of solution A to 20 ml with water, and add 1 ml of 2·5 M sulphuric acid. Add 1 ml of phosphate reagent No. 1 (see Appendix, Note 3) and 1 ml of phosphate reagent No. 2 (see Appendix, Note 4), and place in a water bath at 60° C for 10 minutes. Any blue colour produced should not exceed the standard colour (see Appendix, Note 5) (0·005 per cent. as $SiO_2$).
6. **Sulphate**—Add 8 g in small portions to 70 ml of water, and then add 48 ml of 5 M hydrochloric acid. Boil, cool, add 2 ml of 0·5 M barium chloride, and set aside for 6 hours. No turbidity should appear (0·003 per cent. of $SO_4^{2-}$).
7. **Iron**—Dilute 2 ml of solution A to 20 ml with water, add 1 ml of 5 M hydrochloric acid and 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl acetate and amyl alcohol, shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·005 per cent. of Fe).

## SODIUM SULPHIDE

1. **Description**—Moist colourless crystals.
2. **Solution**—Dissolve 10 g in 100 ml of water. A clear colourless solution should be produced, which should not deposit any sediment on standing for 2 hours.
3. **Ammonia**—Dissolve 1 g in 40 ml of water in an ammonia-distillation apparatus, and add 5 ml of 12·5 M sodium hydroxide. Distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard in the same manner, with 1·0 ml of a standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in place of the sample. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any colour produced in the test should not exceed that of the standard (0·001 per cent. of $NH_3$).
4. **Sulphite and thiosulphate**—Dissolve 1 g in 100 ml of water, and add 2 g of zinc sulphate dissolved in 100 ml of water; set aside for 30 minutes, filter, and titrate the filtrate with 0·1 N iodine. Not more than 0·15 ml of 0·1 N iodine should be required (0·05 per cent. as $SO_2$).

## SODIUM THIOSULPHATE

1. **Description**—Colourless crystals free from white powder.

2. **Solution**—Dissolve 10 g in 50 ml of freshly boiled and cooled water. A clear colourless solution should be produced.

3. **Ammonia**—Dissolve 5 g in 40 ml of water in an ammonia-distillation apparatus, and add 10 ml of 12·5 M sodium hydroxide. Distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard in the same manner, with 1·0 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in place of the sample. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0002 per cent. of $NH_3$).

4. **Sulphate and sulphite**—Dissolve 1 g in 10 ml of water, add 0·1 N iodine in slight excess (about 40 ml) and 1 ml of 0·5 M barium chloride. No turbidity or precipitate should appear within 5 minutes (0·01 per cent. as $SO_4^{2-}$).

5. **Sulphide**—Dissolve 1 g in 20 ml of water, and add 0·05 ml of 0·5 M cupric sulphate. The solution should not darken in colour (0·0005 per cent. of $S^{2-}$).

6. **Calcium**—Dissolve 2 g in 20 ml of water, add 2 ml of 5 M ammonia solution and 2 ml of 0·25 M ammonium oxalate, and set aside for 2 hours. No turbidity or precipitate should appear (0·005 per cent. of Ca).

7. **Iron**—Dissolve 4 g in 20 ml of water, and add 0·2 g of sodium citrate; when it has dissolved add 2 drops of thioglycollic acid and 5 ml of 5 M ammonia solution. Match any red colour obtained with the colour produced by treating portions of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) by the whole of the procedure described above. Not more than 2 ml of the standard iron solution should be required to match the colour obtained in the test solution (0·0005 per cent. of Fe).

8. **Lead**—Dissolve 1 g in 40 ml of water, and transfer 10 ml to a separating funnel. Add 1 drop of 5 M nitric acid and 1 ml of chloroform, and shake to saturate the solution with chloroform. Reject the excess of chloroform. Add 0·2 ml of 0·1 M sodium metabisulphite and 0·2 ml of 1·0 M ammonium citrate, and adjust to pH 9 with 5 M ammonia solution (about 2 drops are required). Then add 0·1 ml of 1·5 M potassium cyanide, and run in a 0·002 per cent. solution of dithizone in chloroform from a microburette, with vigorous shaking, until a mixed colour (mauve) is produced in the chloroform layer. Carry out a blank experiment, with all reagents being used a similar manner, and finally add the exact amount of dithizone solution previously used in the test. Titrate the blank with standard lead solution (1 ml ≡ 0·01 mg of $Pb^{2+}$) from a 1-ml microburette, shaking after each addition, until the colour of the chloroform layer matches that of the test. Not more than 0·25 ml should be required (0·001 per cent. of Pb).

9. **Assay**—Dissolve 1 g in 30 ml of water, add 1 ml of 5 M acetic acid, and titrate with 0·1 N iodine, with starch as indicator.

1 ml of 0·1 N iodine ≡ 0·02482 g of $Na_2S_2O_3.5H_2O$.

(Not less than 99 and not more than 101 per cent. should be indicated.)

## SULPHURIC ACID

1. **Description**—A clear colourless oily liquid.

2. **Weight per ml at 20° C**—About 1·84 g.

3. **Non-volatile matter**—Evaporate 55 ml (100 g) to dryness, and ignite at 400° to 500° C for 5 minutes. Not more than 1 mg of residue should remain (0·001 per cent.).

4. **Ammonium salts**—Add 2·7 ml (5 g) to 40 ml of water in an ammonia-distillation apparatus. Cool, add 20 ml of 12·5 M sodium hydroxide, and distil into 5 ml of water containing 1 drop of 2·5 M sulphuric acid so that a total volume of 50 ml is obtained during about 6 minutes. Prepare a standard in the same manner with 1·0 ml of standard ammonium chloride solution (1 ml ≡ 0·01 mg of $NH_4^+$) in place of the sample. To 40 ml of each distillate add 10 ml of water and 2 ml of Nessler's reagent (see Appendix, Note 2). Any yellow-brown colour produced in the test should not exceed that of the standard (0·0002 per cent. of $NH_4^+$).

5. **Nitrate**—Add 5·5 ml (10 g) to 2 ml of water. Cool to about 60° C, and add 1 drop of hydrochloric acid and 1 ml of diphenylamine reagent.* No blue colour should be produced (0·00002 per cent. of $NO_3^-$).

* Diphenylamine reagent—

| | |
|---|---|
| Diphenylamine .. .. .. | 80 mg |
| Water .. .. .. .. | 20 ml |
| Sulphuric acid (nitrogen-free) .. | 45 ml |

6. **Iron**—To 5·5 ml (10 g) add 0·1 g of anhydrous sodium sulphate, heat until the sulphuric acid has volatilised, and finally ignite. Heat the residue with 1 ml of hydrochloric acid, and evaporate to dryness on a steam-bath. Dissolve the residue by warming with a mixture of 1 ml of 5 M hydrochloric acid and 10 ml of water. Add 1 drop of 0·1 N potassium permanganate, and mix. Add 5 ml of 7·5 M ammonium thiocyanate and 10 ml of a mixture of equal volumes of amyl alcohol and amyl acetate, shake vigorously, and allow to separate. Any pink colour obtained in the upper layer should not exceed that produced by treating 1 ml of standard iron solution (1 ml ≡ 0·01 mg of $Fe^{3+}$) in a similar manner (0·0001 per cent. of Fe).

7. **Lead**—Evaporate 2·7 ml (5 g) to 1 ml on a hot-plate. Add a little water, and make just alkaline by dropwise addition of 5 M sodium hydroxide. Add 2 drops of 5 M nitric acid (the solution should now be acid), and dilute to 10 ml. Place 5 ml of this solution in a separating funnel, add 1 ml of chloroform, and shake to saturate the solution with chloroform. Reject the excess of chloroform. Add 0·2 ml of 0·1 M sodium metabisulphite and 0·2 ml of 1·0 M ammonium citrate, and adjust to pH 9 with 5 M ammonia solution (about 2 drops are required). Then add 0·1 ml of 1·5 M potassium cyanide, and run in a 0·002 per cent. solution of dithizone in chloroform from a microburette, with vigorous shaking, until a mixed colour (mauve) is produced in the chloroform layer. Carry out a blank experiment, with all reagents being used in a similar manner, and finally add the exact amount of dithizone solution previously used in the test. Titrate the blank with standard lead solution (1 ml ≡ 0·01 mg of $Pb^{2+}$) from a 1-ml microburette, shaking after each addition, until the colour of the chloroform layer matches that of the test. Not more than 0·50 ml should be required (0·0002 per cent. of Pb).

### TOLUENE-*p*-SULPHONIC ACID

1. **Description**—White crystals or crystalline powder.
2. **Solution—Dissolve 2·5 g in 10 ml of water. A clear and almost colourless solution should be produced.**
3. **Volatile acid**—Measure 100 ml of water into a distillation apparatus. Distil and discard 10 ml, then rapidly distil a further 25 ml. Add 2 drops of phenolphthalein indicator to the distillate, and titrate with 0·01 N sodium hydroxide. Place 5 g of sample in the distillation flask, collect a further 25 ml of distillate, and titrate with 0·01 N sodium hydroxide as before. The difference between the two titres should not exceed 0·1 ml (0·02 ml of 1·0 N per cent.).
4. **Assay**—Dissolve 3 g in 50 ml of water, and titrate with 1·0 N sodium hydroxide, with phenol red as indicator.

**1 ml of 1·0 N sodium hydroxide ≡ 0·1902 g of $CH_3{\cdot}C_6H_4{\cdot}SO_3H.H_2O$.**

**(Not less than 99 per cent. should be indicated.)**

## Appendix

1. Kjeldahl catalyst—

| | |
|---|---|
| Potassium sulphate | 84 g |
| Mercuric sulphate | 13 g |
| Selenium | 2·6 g |

Mix thoroughly.

2. Nessler's reagent—

| | |
|---|---|
| Potassium iodide | 35 g |
| Mercuric chloride | 12·5 g |
| Water | 800 ml |

Dissolve, and add a cold saturated solution of mercuric chloride until a slight permanent precipitate is produced; then add:

| | |
|---|---|
| Sodium hydroxide | 120 g |

Dissolve, and add sufficient mercuric chloride to produce a slight permanent precipitate and sufficient water to produce 1000 ml. Shake the mixture occasionally for several days; allow to settle, and decant the clear liquid for use.

3. Phosphate reagent No. 1—

| | |
|---|---|
| Ammonium molybdate (powdered) | 5 g |
| 0·5 M Sulphuric acid | 100 ml |

Dissolve without heat.

4. Phosphate reagent No. 2—

| | |
|---|---|
| *N*-Methyl-*p*-aminophenol sulphate (Metol) | 0·2 g |
| Potassium metabisulphite | 20 g |
| Water | 100 ml |

Dissolve without heat.

5. Standard colour for phosphate or silicate test—

Mix 1 ml of standard phosphate solution (1 ml ≡ 0·01 mg of $PO_4^{3-}$) with 20 ml of water, 3 ml of 2·5 M sulphuric acid, 1 ml of the phosphate reagent No. 1 and 1 ml of phosphate reagent No. 2, and place in a water bath at 60° C for 10 minutes.

6. Sulphate seeding reagent—

Dissolve 2 g of barium chloride in 75 ml of water, and add 20 ml of absolute industrial methylated spirit and 5 ml of standard sulphate solution (1 ml ≡ 0·1 mg of $SO_4^{2-}$).

This reagent should be freshly prepared daily.

7. Standard turbidity—

To 8 ml of water add 2 ml of standard sulphate solution (1 ml ≡ 0·1 mg of $SO_4^{2-}$), 0·2 ml of 0·5 M sodium carbonate, 1·2 ml of 1·0 M hydrochloric acid and 1 ml of sulphate seeding reagent. Mix, and use as a comparison standard after 5 minutes.

# Book Reviews

JOINT SYMPOSIUM ON FERTILISER ANALYSIS, HELD IN LONDON ON 21ST AND 22ND APRIL, 1960, BY THE FERTILISER SOCIETY AND THE SOCIETY FOR ANALYTICAL CHEMISTRY. *Proceedings No.* 62. Pp. 215. 44 Russell Square, London, W.C.1: The Fertiliser Society. Price 21s.

The symposium was the outcome of ten years' collaborative work organised by the two Societies after the reconsideration of the official methods of fertiliser analysis by Mr. George Taylor and Dr. J. H. Hamence at the request of the Fertiliser Manufacturers Association.

After the opening address by Mr. R. C. Chirnside, a paper presented by Dr. Hamence was read, describing the background of the investigations on which the symposium was based.

The first section of the symposium, introduced by Mr. C. J. Regan, dealt with the determination of trace elements. Dr. R. F. Milton discussed methods and modifications recommended for determining molybdenum, iodine, fluorine, cobalt and copper; Mr. S. M. Boden dealt with those for determining boron, magnesium, manganese and zinc; and those for determining iron, chromium and nickel were considered by Mr. J. B. E. Patterson.

On the second day were presented papers on the determination of nitrogen by Mr. H. N. Wilson, of potassium by Messrs. E. W. Schwehr and H. R. Conan, of phosphorus by Messrs. P. Craven and E. W. Schwehr and of the phosphorus content of rock phosphate by Dr. H. L. Davies, Mr. J. Lacey, Dr. H. A. E. Mackenzie, Dr. A. Mendelowitz and Mr. J. Rijkheer.

In general, the emphasis in all the papers is on comparisons of known techniques with recommended modifications suitable for the routine examination of fertiliser materials. Discussions of the various papers are recorded.

The volume represents an extremely valuable contribution towards increasing either the precision, speed or general suitability of analytical methods for this specialised purpose. It is not too much to anticipate that agreement on a long-overdue international system of fertiliser evaluation may be hastened by, and perhaps founded on, the work recorded in these Proceedings.

A. G. POLLARD

ANALYSE DER METALLE. Volume II: BETRIEBSANALYSEN. By the Chemikerausschuss der Gesellschaft Deutscher Metallhutten- und Bergleute e.V. Second Edition. Pp. (Part I) xvi + 726; (Part II) iv + 727–1568. Berlin, Göttingen and Heidelberg: Springer-Verlag. 1961. Price DM 158.

The first edition of this book was so popular that within five years it was sold out, and now a completely revised edition has taken its place, although the third part of the book, dealing with sampling, does not appear to have been revised since 1956.

The advantage of a publication like *Analyse der Metalle* is that it draws on the expert knowledge of a team of analysts, each making a specialised contribution to the analytical chemistry of about

fifty elements ranging from aluminium to sulphur in the first volume and from selenium to zirconium, including physico-chemical methods, in the second volume.

*Analyse der Metalle* is primarily intended for the industrial analyst, and this second edition, although in many respects following the lay-out of the first, is intended to bring the book up to date, particularly in so far as it aims at including the latest innovations in physical methods of analysis. It also aims at providing improved analytical procedures for all the elements previously covered; in particular, however, the analytical chemistry of such elements as titanium, zirconium and uranium, which have grown rapidly in commercial importance over the past decade, has received special attention.

Although the authors have given special attention to the use of procedures involving emission spectrography, polarography, spectrophotometry, absorptiometry, potentiometry, etc., they have not overlooked the needs of the more humble analyst and have given special attention to a revision, when necessary, of conventional gravimetric and volumetric determinations that continue to be of special interest to analysts working in small laboratories.

In many respects this publication can be regarded as a reference book containing a vast collection of accredited analytical methods typical of current practice in Germany.

The title of these volumes may be misleading, especially to anyone not familiar with the earlier edition, because the information is by no means restricted to the analysis of metals; it should be useful not only to analysts in conventional ferrous and non-ferrous laboratories, but to anyone interested in the analytical chemistry of inorganic substances in general.

The book deals with each element in turn, giving relevant information, such as occurrences, qualitative tests, etc.; details are then given for determining the element at various levels and in various naturally and industrially occurring materials. Under the same main heading appears information pertinent to the analysis of materials in which the element predominates, *e.g.*, under "Aluminium," analytical procedures are given for the detailed examination of bauxite. Special sections are devoted to such subjects as the preparation of standard buffer solutions and high-frequency titrations, although in this section the emphasis is on external references, about 180 of which are listed. Other miscellaneous chapters include sections on conductimetric and potentiometric titrations, the examination of metallic and non-metallic coatings, the determination of oxygen in metals, the examination of refractories, oils (for calorific value, flash-point, etc.) and industrial and naturally occurring gases and the determination of toxic gases in the atmosphere.

Like all comprehensive books of this nature, many miscellaneous sections are included, for example, the preparation of standard solutions and Tables relating specific gravity with concentration of regularly used reagents, such as hydrochloric, nitric, acetic and orthophosphoric acids; there is also a Table of atomic weights, which, incidentally, is the 1955 version, but this should serve only to indicate the time taken to prepare such an extensive book.

This publication should be of great value in small laboratories where the analyst is frequently called upon to carry out work outside his particular specialised field. There are, of course, other equally good books on allied subjects printed in English, but in these days when analysis is expensive, the purchase of a comprehensive book like *Analyse der Metalle* could soon justify its cost.

W. T. ELWELL

ANALYSIS OF GASES IN METALS. By Z. M. TUROVTSEVA and L. I. KUNIN. Authorised translation from the Russian by JAMES THOMPSON, B.Sc. Pp. x + 374. New York: Consultants Bureau Inc. 1961. Price $21.50.

To anyone unfamiliar with the problem of determining gases in metals, it should be emphasised that the gases involved are usually restricted to oxygen, hydrogen and nitrogen, present either in the gaseous form or in chemical combination, usually with the parent metal. For example, oxygen may be present as gaseous oxygen or as oxide, and to differentiate between these various conditions is the exception rather than the rule.

The subject matter of this publication is of direct interest to all analysts associated with the examination of metallurgical materials, because of its wide coverage of related subjects. The authors' objective has been to correlate and present information on current analytical practice within the U.S.S.R.; for that reason it is not surprising that the extensive bibliographs at the end of each section contain the names of many Russian authors.

The book is divided into three sections under the headings: (*i*) Theoretical Principles in the Determination of Gases in Metals, (*ii*) Methods of Analysis and Apparatus and (*iii*) The Determination of Gases in Metals, According to the Groups of the Periodic Table.

The first section lays the foundation for a better understanding of the underlying physico-chemical theories involved and contains much theoretical information that will prove as useful to the metallurgist as to the analyst.

In the second section, and elsewhere throughout the book, the determination of gases, based on the principle of "Vacuum Fusion," receives special attention; this technique is obviously highly favoured by Russian analysts. Other methods receiving due consideration and comment include those based on extraction of oxygen into a gaseous phase, fusion in an argon atmosphere, the bromine - carbon reaction, chlorination, mercury-extraction (inclusions), spectrography, isotopic dilution and radioactivation.

The determination of nitrogen by chemical procedures is also discussed in detail in this section, and one statement of particular interest, and doubtful validity, appears on page 214: "Experiments showed that the optimum time of distillation (of ammonia) was 1½ hr."

In the final section (the classification refers to the material being analysed), the following are among those to which special references are made: sodium, copper, beryllium, magnesium, boron, aluminium, titanium, zirconium, niobium, uranium and iron (steels).

Apart from the unacceptable use of the word "Analysis" in the title ("Determination" is correctly used almost exclusively elsewhere in this context) the standard of English throughout is good, and only on a few occasions is there a faint suggestion of too literal a translation. For example, on page 326 ". . . is analysed in a platinum bath with sample weights of 5 g" where, in fact, the 5 g is more likely to be the weight of the platinum bath.

The authors' aim has been to provide a balanced comprehensive account of the theoretical and practical aspects of the determination of gases in a wide variety of metals, and this has been achieved, perhaps at the expense of more detailed practical information, but to anyone with an interest in this subject, the book is well worth purchasing. W. T. ELWELL

A TEXTBOOK OF PHARMACOGNOSY. By GEORGE EDWARD TREASE, B.Pharm., D. de l'U., F.P.S., F.R.I.C., F.L.S. Eighth Edition. Pp. viii + 808. London: Baillière, Tindall and Cox. 1961. Price 45s.

This is one of those students' text-books containing so much information that it serves also as a most useful work of reference. In this edition additional space has been found for discussion of the historical development of pharmacognosy, for the constituents of drugs and also for more specialised aspects of the subject, such as chemical races, the biogenesis of active constituents and the uses of radioactive isotopes.

The work is divided into six parts, the number of pages appertaining to each being given in brackets: Historical Introduction (47), From Plant to Crude Drugs (38), Drugs of Vegetable Origin (457), Drugs of Animal Origin (21), Chemistry (90) and Microscopy (123). The classification of drugs for study is discussed at considerable length, there being five possibilities, namely, alphabetical with either Latin or English names, chemical, in which the drugs are grouped according to their most important constituent (alkaloids, glycosides, etc.), therapeutic use, morphological (the drugs being divided into groups such as leaves, barks and roots) and, finally, taxonomic, wherein the arrangement follows the system of botanical classification. Professor Trease has chosen the last-mentioned method for the study of whole drugs, but wisely adopts the morphological arrangement when discussing the microscopical examination of powders and the chemical classification in the section on the constituents of drugs.

Generally, the monographs include an account of collection, preparation, macroscopical and microscopical characters, therapeutically active constituents, uses and allied drugs. The accounts of similar drugs and substitutes are, unfortunately, somewhat inadequate; for example, under Nux Vomica, *Strychnos potatorum* and *S. nux-blanda* are mentioned but not described; again, under Cardamom Fruit (and Seed) allied species are merely listed. It is surely as important for the student as for the consultant to have substantial guidance in the recognition and precise definition of these substitutes, which from time to time are offered in place of the genuine material. Within the last few months the reviewer has had samples consisting of *Strychnos nux-blanda*, false Cardamom Seeds that proved to be *Anomum aromaticum* (Bengal Cardamom) and Gluta Wood (family Anacardiaceae) offered as Red Sanders Wood, all having been purchased by clients as genuine. In preparing a report it is not sufficient for the consultant merely to state that a consignment is not what it is purported to be; he must give the precise scientific name of the substitute if his opinion is to carry the necessary weight to effect satisfactory financial compensation for his client.

The parts devoted to chemistry and microscopy are clear expositions of the subjects in relation to pharmacognosy and convey a remarkable amount of information in small space; in this respect the chapter on cell structure is singularly impressive. The book is illustrated by 267 figures, many of them comprising several separate drawings of histological or morphological structures, while others are photographs illustrating the cultivation and commercial handling of drugs. The publishers are to be congratulated on the fine quality of production at such modest cost, and students and all others concerned with pharmacognosy owe a debt of gratitude to the author for this valuable aid to the understanding of a difficult subject. NOEL L. ALLPORT

COLORIMETRIC METHODS OF ANALYSIS: INCLUDING PHOTOMETRIC METHODS. Volume IIIA. By FOSTER DEE SNELL, Ph.D., and CORNELIA T. SNELL, Ph.D. Assisted by CHESTER ARTHUR SNELL, Ph.D. Pp. x + 576. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Co. Inc. 1961. Price 96s.

Volume III of Snells' "Colorimetric Methods of Analysis" covered about half the field of organic compounds (reviewed *Analyst*, 1955, **80**, 405), and this work is concerned with new matter published since 1953 in relation to the organic groups dealt with in the volume to which this is a supplement. It should be mentioned that volume IV covered the remainder of the organic field, and, presumably, it is intended to publish a further "A" volume in due course, although this point is not made clear in the preface.

The scope of volume IIIA is best indicated by listing the headings of the nineteen chapters as follows: Introductory; Hydrocarbons; Alcohols and Their Esters; Phenols; Quinones; Oxygen Cycles, Oxides and Peroxides; Tetroses and Pentoses; Hexoses and Heptoses; Polysaccharides; Glucosides; Aldehydes; Ketones; Unsubstituted Monobasic Aliphatic Acids and Their Anhydrides, Esters and Lactones; Substituted Monobasic Aliphatic Acids and Their Esters; Polybasic Aliphatic Acids and Their Esters; Cyclic Acids, Their Esters and Their Anhydrides; Complex Acids and Derivatives; Sulphur Derivatives; Halogen Compounds.

That this volume is nearly as large as the one to which it is a supplement is some indication of the growth of the subject and of the difficulty of maintaining a complete coverage. The character of the work may be indicated by quoting the first sentence under the sub-title Glucose: "Many modifications of the anthrone method (Vol. III, p. 207) for determining hexoses have been introduced to eliminate errors and reduce interferences from pentoses." Here, as throughout, references are conveniently set at the foot of the page. Descriptions of analytical procedures are given as briefly as is possible consistent with clarity, and the text is in effect a classified compilation of working abstracts. This supplement can be unreservedly recommended to all analysts working in the organic field, and the authors merit our grateful thanks for their continued efforts in bringing their monumental work up to date. NOEL L. ALLPORT

DOSAGES COLORIMÉTRIQUE DES ÉLÉMENTS MINÉRAUX: PRINCIPES ET MÉTHODES. By G. CHARLOT. Deuxième Édition Entièrement Refondue. Pp. iv + 379. Paris: Masson et Cie. 1961. Price 45 NF.

This volume deals with the colorimetric determination of inorganic substances. As is usual with books of this type, the first portion gives the theoretical application of Beer's law and a description of some types of photo-electric instruments, together with the technique involved in their usage. It also contains a short description of the principles of fluorimetry and of nephelometry.

The second portion of the book deals with methods of separating inorganic substances from complex mixtures before colorimetric determination, including solvent extraction, the use of selective reagents, ion exchange, chromatography and electrolytic separation.

The elements are then listed in alphabetical sequence, and a recommended method for colorimetric determination is given for each. The technique as described is extremely sketchy, and I am sure that any practising analyst would not get far with the methods unless he consulted the original, which is in every instance given as a reference.

I think that there are a number of books on the topic, in languages other than French, that treat the subject more liberally and therefore would be chosen before this volume by any practical worker. R. F. MILTON

FICHES TECHNIQUES D'ANALYSE BROMATOLOGIQUE. By J. A. GAUTIER, J. RENAULT and F. PELLERIN. Pp. viii + 394. Paris: Société d'Édition d'Ensignement Supérieur. 1961. Price 52 NF.

Messrs. Gautier, Renault and Pellerin have produced a book of analytical methods for use in a food laboratory and, in particular, an official laboratory. In the preface, Dr. R. Fabre comments on the absence of good books on food analysis in French and on the advantages of the lay-out adopted, by which each method is printed on separate sheets, using one or more pages for each method, so that the book can be extended or amended as necessary. It is, therefore, a pity that the authors and publishers did not go the whole way and make the volume into a loose-leaf book with entirely separate sheets instead of paging, cutting and binding as a normal volume. The types of food dealt with comprise flours, sugars, molasses, milk, fats, butter, wine and vinegars. The extent of the examinations described varies according to the food. For sugars, only the determinations of moisture, ash, sucrose and reducing sugars are considered necessary, whereas with milk, provision is made for the determination of the specific gravity, freezing-point, acidity, total solids, ash, examination for dichromate, alkalinity of ash, fat, nitrogen, chlorides, lactose, added water, preservatives and hygienic and bacteriological examinations, including cleanliness, methylene blue test, bacteriological count, indole-producing bacteria, pasteurisation control and leucocyte count. The order in which these determinations are given is different from that adopted in the average British laboratory, as are the actual methods of carrying out the tests, but the volume should serve three useful functions in many laboratories. First, it will encourage many who feel that they should have laboratory methods made out in some simple form of card-index system. Secondly, the French is simple and will encourage a study of the language. Thirdly, it will provide information about certain methods employed in other countries and practically unknown here, for example, the determination of fat in milk by the ether - acetic acid method. By this method, the fat is entrained in an acid curd suspended in a large volume of dilute acetic acid to remove lactose, and, after drying, is extracted by ether. T. MCLACHLAN

CHROMATOGRAPHIC REVIEWS: PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS. Volume 3. Edited by MICHAEL LEDERER. Pp. viii + 187. Amsterdam, London, New York and Princeton: Elsevier Publishing Co. Ltd. 1961. Price 50s.

This third volume of Chromatographic Reviews differs slightly from the previous volumes published in 1958 and 1959. Most of the reviews appeared earlier in the *Journal of Chromatography*, but this volume includes two reviews not previously published. Another new feature is that three papers are continuations of reviews published in earlier volumes. The international character is well maintained, with eight papers from seven countries.

The first paper, by R. A. Keller and J. Calvin Giddings, is on multiple zoning in chromatography. Allowing for my bias on finding my own work commended in the opening sentences, this still seems a limitation of chromatography that needs re-emphasising. A single zone does not guarantee homogeneity, but nor does a double zone necessarily prove heterogeneity. Half-a-dozen different causes can produce two or even three zones from a single substance.

H. Bloemendal provides Parts II and III of "Starch Electrophoresis." He concludes that electrophoresis in vertical starch columns is usually less satisfactory than the block technique reviewed in Volume 2. Electrophoresis in cooked starch gels has analytical but not preparative value for some protein problems, but gel-filtration and molecular-sieve effects are superimposed on electrophoresis, making interpretations uncertain.

Z. Pucar contributes a comprehensive 50-page review (with 150 references and 50 figures) on continuous electrophoresis; this has been competently translated from the original German. It assesses critically all the designs in the literature and those available commercially and goes into some detail on the principles involved. Many examples are cited of the separation of dyes, proteins and inorganic ions, but only on a laboratory scale.

In Volume 1, L. Reio reported his own extensive work on the paperc hromatography of phenolic and other compounds and their identification by $R_F$ values in several solvent systems and colours with different spray-reagents. This work is here extended to many more compounds of biochemical interest (270 in all); the results fill 15 closely printed Tables.

Chromatography of lipids on silica is reviewed exhaustively by J. J. Wren, in a highly condensed, but readable style, with almost more references than text on some pages.

The editor, M. Lederer, has this time included a short paper himself, a progress report on inorganic paper chromatography during the last 3½ years. This is packed with information on separations of anions and cations on plain, impregnated and modified papers, developed with aqueous or organic solutions. Incidentally, this paper provides several more examples of multiple zoning by different ionic species of the same element.

Finally, separation of inorganic ions by electromigration in paper is critically reviewed by R. A. Bailey and L. Yaffe. Most of the information is conveniently conveyed in nine long Tables.

The volume is well produced and commendably free from errors. With the previous two, it constitutes an invaluable reference work, and the editor promises that subsequent volumes will complete the coverage for the whole field of chromatography and electrophoresis.

E. Lester Smith

Carbon-14 Compounds. By John R. Catch. Pp. viii + 128. London: Butterworths Publications Ltd. 1961. Price 30s.

The publication of this book has been sponsored by the United Kingdom Atomic Energy Authority. The stated object of the book is to serve as a guide to the literature and use of carbon-14 compounds. It is directed primarily at the newcomer to this field, but with the hope that it will profit even the experienced reader. Carbon-14 compounds are mainly used in tracer studies. If, as I believe, tracer studies properly constitute a branch of analysis, then this book is of practical interest to the analyst.

After a brief introduction, a short chapter is devoted to the production of carbon-14. Then come three chapters, which in sum comprise nearly half the book. These relate to chemical synthesis, biological methods of labelling and peculiar features of carbon-14 compounds; the "peculiar features" discussed include the effects of single and multiple labelling of organic compounds, behaviour of small quantities, radiation decomposition and nomenclature. Three further chapters deal with analysis (of labelled compounds), measurement of carbon-14 and precautions in the use of carbon-14 compounds. Finally, a short appendix draws attention to publications of particular interest that have appeared during preparation of the book. In all, some six hundred references, grouped at the end of the relevant chapters, are given.

The author's work at the Radiochemical Centre has no doubt provided an unusually extensive background of knowledge and experience of carbon-14 compounds. Certainly he has succeeded in producing a lucid and authoritative treatment of the subject. Only an occasional error or anomaly is apparent, *e.g.*, the maximum permissible total body burden for carbon-14 is quoted as 300 $\mu$C on p. 107 and 260 $\mu$C on p. 109. The book amply fulfils its objective as an introduction to work with carbon-14 compounds and as a guide to the literature. H. J. Cluley

Submicrogram Experimentation. Edited by Nicholas D. Cheronis. Microchemical Journal Symposium Series. Volume I. New York and London: Interscience Publishers Inc. 1961. Price (paper) $10.75; 81s.: (cloth boards) $12.75; 96s.

Since the pioneer work of Emich and Pregl at the start of the present century microchemistry has become widely employed in both academic and industrial spheres. Investigations in nuclear chemistry leading to the advent of the atomic bomb, etc., focused attention on a level of working below that involving but a few milligrams of material. Since then, ultra-micro or sub-micro experimentation has become increasingly important in other fields, notably that of biochemistry, where single-cell analysis is the obvious ultimate goal. Such eminent names as Alimarin (U.S.S.R.), Belcher (England), Kirk (U.S.A.) and Wilson (N. Ireland), to give but a few, have become associated with sub-micro work.

This book represents the first volume of the Microchemical Journal Symposium Series and contains the proceedings of a conference on Submicrogram Experimentation sponsored by the U.S. National Academy of Sciences—National Research Council and the U.S. Army Chemical Corps in 1960. After the introductory remarks come 18 papers by American authors—all acknowledged authorities in their various fields—a summary of the symposium, three short papers and finally an evaluation of the symposium findings and of new fields for research. Widely separated areas of the physical and biological sciences are covered by the papers, as is readily seen from a few of the titles: Submicrogram Methods used in Studies of the Synthetic Elements; the Determination of Pesticide Residues—Enzymatic Methods of Analysis; Chemical Studies with

the Electron Microscope on Structurally Intact Cells. I found the reported discussion after each paper as interesting and informative as the paper itself. Incidentally, the book contains an index to discussors in addition to a short subject index.

Although the symposium was apparently restricted to 29 participants, its subject is of interest to many more people and must inevitably become even more so as the trend towards investigation of smaller and smaller samples continues in the future. In general, therefore, the publication of the symposium proceedings has been well worth-while. The price of the book may for the present, however, tend to keep it from having the wide circulation it deserves.

M. WILLIAMS

# Publications Received

THE RADIOCHEMISTRY OF SILICON. By W. T. MULLINS and G. W. LEDDICOTTE. Pp. vi + 30. Washington, D.C.; U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.
*Nuclear Science Series: NAS–NS-3049.*

FLUORESCENCE ASSAY IN BIOLOGY AND MEDICINE. By SIDNEY UDENFRIEND. Volume 3 of MOLECULAR BIOLOGY, An International Series of Monographs and Textbooks. Edited by N. O. KAPLAN and H. A. SCHERAGA. Pp. x + 505. New York and London: Academic Press Inc. 1962. Price 100s.

A TEXTBOOK OF PURE AND APPLIED CHEMISTRY. By JAMES E. GARSIDE, M.Sc.Tech., Ph.D., F.R.I.C., F.I.M., F.Inst.F., and R. F. PHILLIPS, M.A., B.Sc., Ph.D., F.R.I.C., M.Inst.F., A.M.I.Chem.E. Second Edition. Pp. x + 1091. London: Sir Isaac Pitman & Sons Ltd. 1962. Price 32s. 6d.

ORGANIC SYNTHESES. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 41. Editor-in-Chief: JOHN D. ROBERTS. Pp. x + 118. New York and London: John Wiley & Sons Inc. 1961. Price 30s.

HANDBUCH DER MIKROCHEMISCHEN METHODEN: Band III: ANORGANISCHE CHROMATOGRAPHISCHE METHODEN. ANORGANISCHE CHROMATOGRAPHIE UND ELEKTROPHORESE. By M. LEDERER, H. MICHL, K. SCHLÖGL and A. SIEGEL. GASCHROMATOGRAPHISCHE METHODEN IN DER ANORGANISCHEN ANALYSE. By G. KAINZ. Pp. iii + 225. Vienna: Springer-Verlag. 1961. Price 120s.

TREATISE ON ANALYTICAL CHEMISTRY. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. Part I. THEORY AND PRACTICE. Volume 3. Pp. xviii + 442. New York and London: Interscience Publishers Inc. 1961. Price 126s.

PROGRESS IN POLAROGRAPHY. Volume I. Edited by P. ZUMAN and I. M. KOLTHOFF. Pp. xiv + 355. New York and London: Interscience Publishers Inc. 1962. Price 90s.

PROGRESS IN POLAROGRAPHY. Volume II. Edited by P. ZUMAN and I. M. KOLTHOFF. Pp. x + 450. New York and London: Interscience Publishers Inc. 1962. Price 113s.

ENCYCLOPAEDIC DICTIONARY OF PHYSICS. Volume I. Editor in Chief: J. THEWLIS. Pp. xvi + 800. Oxford, London, New York and Paris: Pergamon Press. 1961. Price per set of 9 volumes £106; $298.

CHEMISTRY IN NON-AQUEOUS SOLVENTS. By HARRY H. SISLER. Pp. viii + 119. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1961. Price 16s.

THE RADIOCHEMICAL MANUAL. Part 1: PHYSICAL DATA. Pp. vi + 102. Amersham, Bucks.: The Radiochemical Centre. (Also available from Her Majesty's Stationery Office.) 1962. Price 15s.

MOLECULAR STRUCTURE AND THE PROPERTIES OF LIQUID CRYSTALS. By G. W. GRAY. Pp. vii + 314. London and New York: Academic Press Inc. (London) Ltd. 1962. Price 63s.

*Classified Advertisements continued on page xviii*

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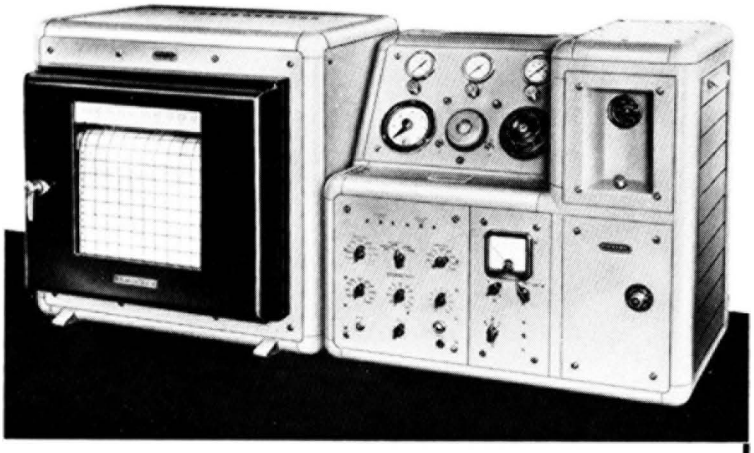

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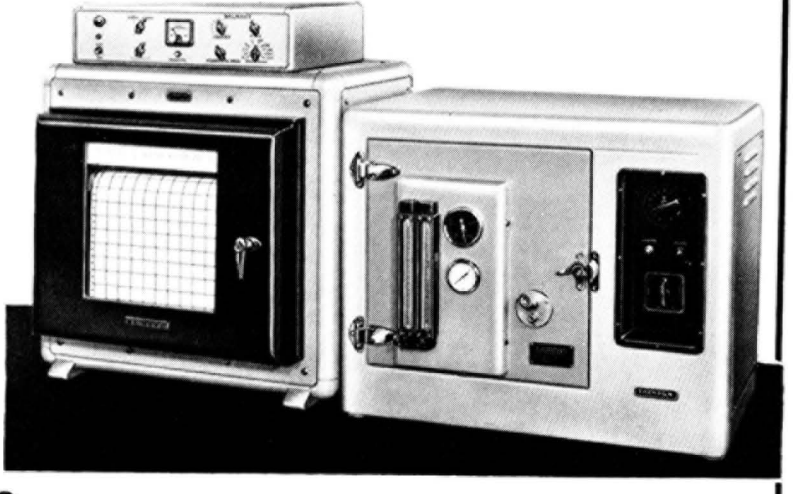

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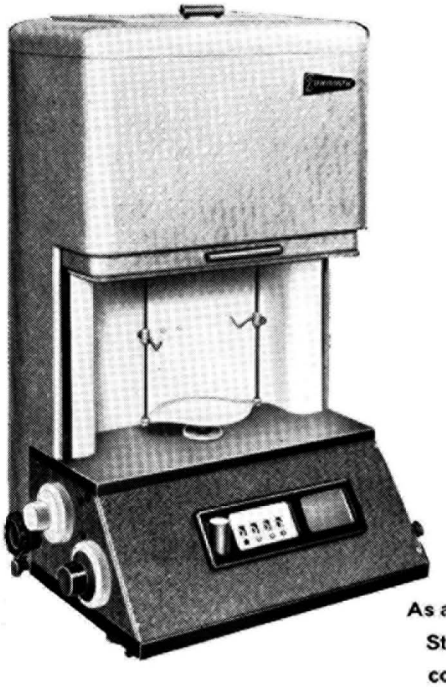

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