THE ANALYST

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PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE Eightieth Annual General Meeting of the Society was held at 4.30 p.m. on Wednesday, March 3rd, 1954, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. D. W. Kent-Jones, F.R.I.C. The financial statement for 1953 was presented by the Honorary Treasurer and approved, and the Auditors for 1954 were appointed. The Report of the Council for the year ending March, 1954 (see pp. 253–260), was presented by the Honorary Secretary and adopted.

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

President—D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.

Past Presidents serving on the Council—Lewis Eynon, G. W. Monier-Williams, J. R. Nicholls and George Taylor.

Vice-Presidents—C. A. Adams, A. J. Amos and T. McLachlan.

Honorary Treasurer—J. H. Hamence.

Honorary Secretary—K. A. Williams.

Honorary Assistant Secretary—N. L. Allport.

Other Members of Council—The Scrutineers further reported that 366 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—J. Haslam, 298; C. L. Hinton, 250; R. E. Stuckey, 250; C. Whalley, 248; D. C. M. Adamson, 227; A. G. J. Lipscomb, 223; W. C. Johnson, 222; B. Bagshawe, 186.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—D. C. M. Adamson, J. Haslam, C. L. Hinton, A. G. J. Lipscomb, R. E. Stuckey and C. Whalley.

A. L. Bacharach, R. C. Chirnside, Miss Mary Corner, D. C. Garratt, H. W. Hodgson and H. M. N. H. Irving, having been elected members of the Council in 1953, will, by the Society's Articles of Association, remain Ordinary Members of Council for 1954.

T. W. Lovett (Chairman of the North of England Section), R. S. Watson (Chairman of the Scottish Section), A. M. Ward (Chairman of the Microchemistry Group), A. A. Smales (Chairman of the Physical Methods Group) and L. J. Harris (Chairman of the Biological Methods Group) will be *ex-officio* Members of the Council for 1954.

After the business outlined above had been completed, the meeting was opened to visitors, and Dr. E. B. Hughes, F.R.I.C., delivered the Bernard Dyer Memorial Lecture (see pp. 261–267). At the close of the meeting the President presented Dr. Hughes with the Bernard Dyer Memorial Medal.

ORDINARY MEETING

AN Ordinary Meeting of the Society, organised by the Biological Methods Group, was held at 2.30 p.m. on Wednesday, April 7th, 1954, at the Wellcome Research Institution, Euston Road, London, N.W.1. Professor J. H. Burn, M.A., F.R.S., was in the Chair.

The meeting was in the form of a Symposium on "The Comparison of Chemical and Biological Estimation of Drugs in Quantitative Pharmacology" and, after the Chairman's introduction, the following papers were presented and discussed: "Digitalis: Chemical Methods," by J. M. Rowson, Ph.D., M.Sc., Ph.C., F.L.S.; "Digitalis: Biological Methods," by G. A. Stewart, B.Sc.; "Vitamin D: Chemical Methods," by J. Green, Ph.D., A.R.I.C.; "Vitamin D: Biological Methods," by M. E. Coates, Ph.D., F.P.S.; "Chemical and Biological Methods for the Estimation of Adrenaline and Noradrenaline," by G. B. West, Ph.D., B.Pharm., Ph.C.; "Routine Methods used in the Quantative Estimation of Adrenaline," by G. F. Somers, Ph.D., Ph.C. (A fuller account will be published later.)

NEW MEMBERS

Ordinary Members Elected March 3rd, 1954

Alfred Bacon, Assoc.Met. (Sheff.); Ronald Ernest Bailey, B.Sc. (Lond.), A.R.C.S.; Geoffrey William Barrell, B.Sc. (Melbourne), A.R.A.C.I.; James Wennington Boyd, B.Sc., A.R.I.C., A.F.Inst.Pet.; Nathaniel Carmichael, B.Sc. (McGill), M.Sc. (West. Ont.), A.R.I.C.; Thomas Joseph Leonard Cuthbert, B.Sc. (Manc.), A.M.C.T.; Harold Ainsworth Harrison, M.Sc., Ph.D. (Manc.), F.R.I.C.; Stephen Claude Jolly, B.Pharm., B.Sc. (Lond.), A.R.I.C., Ph.C.; Frank Mercer Lever, B.Sc. (Lond.), A.R.C.S., F.R.I.C., F.I.M.; Alfred John Maisey, A.R.I.C.; Frederick Cecil Barron Marshall, B.Sc., Ph.D. (Lond.), D.I.C., F.R.I.C.; Miss Adele Mittwoch, M.Sc. (Lond.); Derek Peter Rowlands, B.Sc. (Sheff.), A.R.I.C.; John Paterson Young, B.Sc., A.R.I.C.

Junior Members Elected March 3rd, 1954

Henry Giveen Hamilton Alner, A.R.I.C.; Thomas Joseph Hayes; Ian Peter Forshaw; Emmanuel St. Clair Fitzgerald Jones; Robert Kerr, B.Sc. (Lond.), A.R.I.C.; Ernest Arthur Schofield; William Irvine Stephen, B.Sc. (Aber.), Ph.D. (Birm.), A.R.I.C.; Laurence George Stonhill, B.Sc. (Lond.); Mrs. Mary Patricia Taylor, B.Sc. (Liv.); Thomas Summers West, B.Sc. (Aber.), Ph.D. (Birm.).

Ordinary Members Elected April 6th, 1954

Roy Edward Cockaday, B.Sc. (Leeds); David Gideon Colquhoun; Albert John Nutten, B.Sc. (Aber.), Ph.D. (Birm.), A.R.I.C.; Richard Pickup, B.Sc. (Vic.), F.R.I.C.; Robert Taylor, M.A., Ph.D. (Cantab.).

Junior Members Elected April 6th, 1954

Desmond Ronald Curry, B.Sc. (Dunelm.), A.R.I.C.; Reginald Roy Muir; Bernard Stephen Noyes.

DEATHS

We regret to record the deaths of

Samuel Ernest Melling
Thomas Arthur Nightscales
Dorothy Elsie Stillwell.

SCOTTISH SECTION

An Ordinary Meeting of the Section was held at 7.15 p.m. on Thursday, March 11th, 1954, in the George Hotel, Edinburgh, 2.

A lecture entitled "Applications of Infra-red Spectroscopy" was given by H. A. Willis, B.Sc. (see summary below).

Applications of Infra-red Spectroscopy

Mr. H. A. Willis traced the development of the study of infra-red spectroscopy from the original discovery by Herschel in 1800 of radiation in sunlight beyond the red region that was capable of refraction and that was detectable by its thermal effects. The science advanced with technical achievements in instrument design, *i.e.*, with the production of light sources, of methods of measuring the radiation and of materials suitable for the manufacture of prisms. The study of the absorption of infra-red light by a variety of compounds led to the discovery that similar materials had similar spectra but that there was dependence in detail on the specific molecular structure. This was illustrated by reference to the spectra of methacrylate polymers that differed in the nature of the esterifying alcohol. All possessed absorptions characteristic of the presence of ester groupings, but varied markedly in the regions associated with the hydrocarbon residues.

A comparison of the features involved in the design of single-beam and double-beam spectrometers was made, and the advantages of the double-beam instruments, *e.g.*, the ease of compensation for solvent and for water vapour and carbon dioxide in the air, were stressed. The methods of preparing samples of different physical characteristics were indicated.

The application of the infra-red method to the determination of the structure of an unknown substance was outlined. The first stage was the determination of the spectrum in the region of 2 to 15 μ. The strong absorption bands were used for a

preliminary identification of structural type by reference to correlation tables. The various divisions of these tables were discussed and it was pointed out that, although several interpretations were often possible, many of these could be eliminated by the consideration of such factors as the elementary analysis of the compound. After the various possibilities had been reduced by trial and error methods, the final matching with a spectrum of a substance of known structure led to a complete structural appreciation. The examples were selected from the plastics field and included the identification of a substance, or of substances, used as plasticisers, particularly the alkyl and aryl phosphates and the alkyl phthalates.

The lecture concluded with the description of some methods used in the determination of the components of mixtures by infra-red techniques. These included the use of mixtures of standard composition for comparison and, in the example of the determination of monomer in Perspex, the introduction into the beam of the instrument of both a standard sheet of monomer-free Perspex and solutions of the monomer at different concentrations in a transparent solvent. This gave a calibration curve in which the intensity of a particular absorption due to the monomer, relative to the background due to the polymer, was plotted against the concentration of the standard solution introduced. The concentration of monomer in any sheet of Perspex could then be assessed by examining the intensity of the same absorption peak for that sheet.

A JOINT Meeting of the Section with the Aberdeen and District members of the Chemical Society, the Royal Institute of Chemistry and the Society of Chemical Industry was held at 7.30 p.m. on Thursday, April 1st, 1954, in Robert Gordon's Technical College, Aberdeen. The Chair was taken by Professor R. M. Barrer.

A lecture entitled "Some Applications of the Newer Techniques in Analytical Chemistry" was given by Dr. J. R. Nicholls, C.B.E., F.R.I.C. (see summary below).

SOME APPLICATIONS OF THE NEWER TECHNIQUES IN ANALYTICAL CHEMISTRY

DR. J. R. NICHOLLS said that the classical techniques of analytical chemistry were primarily designed for the separation of the material to be determined in a form capable of measurement either gravimetrically or volumetrically. This involved the application of chemical principles to remove interfering substances and to separate the material in a physical state such that a desired measurement of weight or volume could be made. The newer techniques were concerned with separations effected by the application of recently developed chemical principles or by the use of physical processes, and the final determination might involve the measurement of any physical property.

There were few new chemical principles that had been applied in such a way as to warrant description as new techniques; but physical operations had been so widely developed of recent years that there was a danger of them being regarded as tools of the skilled technician rather than as part of the equipment of an analyst. The modern analytical chemist found it essential to be familiar with at least some of them, as by their means he was able to acquire information unobtainable by classical methods. Such techniques were not in place of, but were complementary and supplementary to, classical ones. They were all specialised tools, and as such had their limitations; but the fully qualified craftsman must have them in his tool-chest so that they could be used either singly or in combination to obtain the maximum information and the best results.

Examples were given of some of the newer techniques involving—

(*a*) for separation: complexing reagents (chelates, sequestering agents and clathrates); extraction with immiscible solvents; distillation (fractional and molecular); adsorption (ion exchange and chromatography); electrophoresis;

(*b*) for identification: microscopy (direct and fluorescent); crystallography (Barker index and X-ray); photography (high-speed);

(*c*) for determination: thermogravimetric analysis; titration of weak acids and bases in non-aqueous solvents; micro-methods; instrumentation; spectrography; ultra-violet rays; infra-red rays; X-rays; flame photometry; polarography; isotopes; radioactivation; gas analysis (conductance and acoustic); mass spectrometry.

Reference was made to the use of statistics and to the employment of approximate and simplified methods. Some applications of several of these techniques in medical chemistry, clinical analysis, plastics analysis and forensic work were described.

PHYSICAL METHODS GROUP

THE Forty-third Ordinary Meeting of the Group was held at 7 p.m. on Tuesday, February 9th, 1954, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by Mr. A. A. Smales, B.Sc., F.R.I.C.

The following papers on "Coulometric Analysis" were presented and discussed: "The Principles of Coulometric Analysis," by E. Bishop, B.Sc., A.R.T.C., A.R.I.C. (see summary below); "An Automatic Coulometric Titrimeter," by N. Bett, B.Sc., G. Morris, Ph.D., F.Inst.P., and W. Nock, M.A., Grad.I.E.E.; "Some Apparatus and Techniques for Semi-micro Coulometric Analysis," by G. Packman, M.Sc., A.R.I.C. (see summary below).

THE PRINCIPLES OF COULOMETRIC ANALYSIS

MR. E. BISHOP said that Faraday's classical laws related the quantity of electricity to the quantity of ion discharged at an electrode in an electrolytic process. Instead of the amount of substance produced at an electrode being weighed, the weight could be calculated from the amount of electricity (ampere-seconds or coulombs) passed and the chemical equivalent of the substance, provided the process proceeded with 100 per cent. efficiency. On this basis were founded the coulometric methods of analysis, in which the number of coulombs required for a reaction was measured. These methods might be direct, when the test material was plated on to or anodically stripped from an electrode, or oxidised or reduced in solution; or indirect, when an intermediate material, such as bromine or ferrous ion, was generated at the electrodes and used to produce a chemical reaction. The first type usually made use of constant-voltage electrolysis and the second made use of constant-current electrolysis.

Instead, therefore, of a standard solution of acid, base, oxidising, reducing or precipitating agent being added from a burette, as in volumetric titrations, the reagent was generated electrolytically and the amount was measured electrically in coulometric titrations. As the quantity of electricity corresponding to 10^{-12} equivalent could be readily measured, the method had a high sensitivity. The principles on which the various methods of electrolysis, reaction and detection of end-point were based were reviewed, and the status of the method was examined.

SOME APPARATUS AND TECHNIQUES FOR SEMI-MICRO COULOMETRIC ANALYSIS

MR. G. PACKMAN said that several types of coulometer, gas, silver and iodine, had been investigated for use in work on a milligram scale, and the last had been found the most satisfactory. An electrolytic cell of 2·5 ml capacity and an indicator-electrode system had been designed, suitable for both controlled-potential and constant-current operation.

A procedure had been devised for when it was necessary to reduce an element before coulometrically oxidising it, and for performing both operations with the same cell and electrodes. Difficulties arose that did not appear in more usual methods in which the sample, already in the lower oxidation state, could be added to a suitable medium (which had been pre-adjusted to end-point conditions) and then oxidised. A combination of controlled-potential reduction and constant-current oxidation had been found satisfactory, and the performance had been tested over the range 5 to 50 micro-equivalents, ferrous ion being used in the first instance as a substitute.

THE Forty-fourth Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, March 9th, 1954, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. Mr. A. A. Smales, B.Sc., F.R.I.C., was in the Chair.

The following papers on "Differential Refractometry" were presented and discussed: "Differential Refractometers: Theory and Construction," by G. H. F. Seiflow, M.A., A.Inst.P.; "An Application of Differential Refractometry," by R. Hill, B.Sc., A.R.I.C.; "Interferometric Refractometry: A Survey of the Methods," by H. G. Kuhn, M.A., D.Phil.; "The Use of a Rayleigh Interferometer for Estimating Trichloroethylene," by R. E. Jahn, M.A.

INTERFEROMETRIC REFRACTOMETRY: A SURVEY OF THE METHODS

DR. H. G. KUHN said that two types of instrument were used for the measurement of refractive indexes by interference. The Jamin refractometer was based on interference alone and used an extended source, whilst the Rayleigh refractometer was

essentially a diffraction grating with a slit source. The latter type of instrument suffered from an extreme smallness of the fringe spacing; this made the use of a fiduciary fringe system necessary, instead of a cross-wire, which complicated the design. The thick, accurately worked glass plates of the conventional Jamin refractometer gave rise to difficulties that could easily be avoided if pairs of thin plates, with spacers, were used instead.

Limitations of interferometric methods making use of compensators and white-light fringes were discussed.

The wide range of applications of interferometric refractometry to problems of chemical analysis of gases and liquids was stressed. It appeared that the method was strangely neglected in this country; this fact might be due to the lack of a sufficiently simple and robust instrument on the home market.

Annual Report of the Council: March, 1954

IMPORTANT changes have been made in the constitution of the Society in the past year, and these reflect the developments that have taken place over the last decade. The formation of an Association of Public Analysts designed to look after the professional welfare and needs of public analysts was foreshadowed in last year's Annual Report, and this body has been formed during the year now under review with support from the Society, this support including financial aid on a substantial scale and office help. It is now felt that the Association on the one hand, and the Royal Institute of Chemistry on the other, can satisfactorily deal with the professional life of all analytical chemists, and that the Society can therefore make the furtherance of analytical chemistry its main concern.

Reflecting this development, an extraordinary general meeting of the Society approved by an overwhelming majority in December, 1953, the change of name to "The Society for Analytical Chemistry." At the same time a new grade of junior membership was instituted to encourage younger chemists to join the Society and enjoy its privileges at a lower subscription than that of ordinary members.

The end of 1953 saw the last issue of *British Abstracts C*, the analytical abstracts published by the Bureau of Abstracts. The Society gave up the production of abstracts in 1949, and from 1950 to 1953 has supplied its members and subscribers to *The Analyst* with *Abstracts C*. Now that these are no longer forthcoming, the Council of the Society has undertaken the production of a journal, to be known as *Analytical Abstracts*, to replace *Abstracts C*. The Editorial Committee of this journal sits under the Chairmanship of Mr. R. C. Chirnside; the Editor of the journal is Dr. Norman Evers, and the Assistant Editor is Mr. B. J. Walby.

The roll of the Society now numbers 1646, an increase of 54 over the membership of a year ago.

CORONATION OF HER MAJESTY QUEEN ELIZABETH II—An Humble Address of congratulation was presented to Her Majesty on the occasion of her Coronation in June, 1953, and this address was graciously received and acknowledged.

HONOURS—The congratulations and good wishes of the Council have been extended to Professor E. C. Dodds on the honour of knighthood conferred on him by H.M. The Queen. Congratulations are also extended to Dr. J. B. Firth on the award of the C.B.E., Mr. F. R. Ennos on the award of the I.S.O. and Mr. W. C. Johnson on the award of the M.B.E.

The Council heard with great satisfaction and delight of the election of Sir Harry Jephcott as President of the Royal Institute of Chemistry during the year.

Their congratulations are also extended to—

Professor Sir Robert Robinson, O.M., F.R.S., on receiving the Priestley Medal, the highest honour in American chemistry.

Dr. F. H. Carr on his election to an Honorary Fellowship of the Imperial College of Science and Technology.

Mr. C. H. Manley on his election as President of the Priestley Club, Leeds.

Professor H. Burton on his election as Honorary Treasurer of the Royal Institute of Chemistry.

Mr. A. Harvey on his election as Honorary Secretary of the International Union of Leather Trades Chemists' Societies.

Mr. R. C. Chirnside on his election as Vice-President of the Analytical Section of the International Union of Pure and Applied Chemistry.

Dr. D. W. Kent-Jones on his election as Honorary Secretary of the newly-formed Foods Division of the Applied Chemistry Section of the International Union of Pure and Applied Chemistry.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to A. E. Brown, T. A. Nightscales and W. H. Simmons, who have completed 50 years of membership of the Society, and to S. G. Clifford, R. H. Ellis, W. A. Gibbings, W. R. Hardwick, J. McLaren and W. H. Woodcock, who have completed 40 years of membership.

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

Mrs. M. B. Craven	P. G. T. Hand	J. Myers
W. Dickson	E. O. Heinrich	J. R. Stubbs
G. E. Forstner	W. C. Hughes	W. Thorp

Mrs. Craven was educated at Ardwick Higher Grade School and the Faculty of Technology, Victoria University, Manchester, 1905–09, holding a post-graduate scholarship under Professor W. J. Pope. She was chemist to the Pilkington Tile and Pottery Co. Ltd., and later to the Clifton and Kersley Coal Co. In 1916 she returned to the College of Technology and remained there until she retired in 1952, becoming Head of the Inorganic Chemistry Laboratories. She joined the Society in 1944 and was elected an Associate of the Institute of Chemistry in 1920.

Dickson was trained at the Glasgow and West of Scotland Technical College, having spent three years with R. R. Tatlock & Thomson, two years in public works and two years in teaching and analytical work at Edinburgh Central School of Pharmacy. He was later Chief Chemist at the Regent Factory, Linlithgow, of Nobel Explosives Co. Ltd., Research Chemist at Ardeer, and Chief Chemist, Eley Bros. (I.C.I.). After 1925 he was transferred to I.C.I. (Metals Division), Birmingham, remaining there until his retirement in 1940. He joined the Society in 1906 and was elected a Fellow of the Institute of Chemistry in 1938. He died at the age of 71.

Forstner was born in 1901 and educated at the West Bromwich Secondary School and the University of Birmingham, where he obtained the degree of M.Sc. He joined J. Lyons & Co. Ltd. in 1925 and worked with them as an analytical and research chemist until his death. He joined the Society in 1936. He was elected A.I.C. in 1925 and F.I.C. in 1943.

Hand was educated at King's College, London, and was an articled pupil of Messrs. Harrison & Self. After the war of 1914–18 he became research assistant, Chemical Warfare Committee, remaining until 1925. He then joined British Xylonite Ltd. as chemist, and at the time of his death was consultant to B.X. Plastics Ltd. He joined the Society in 1930, and was elected A.I.C. in 1921 and F.I.C. in 1925. He died at the age of 58.

Heinrich became B.S. (University of California) in 1908, and lived mainly in California, though he worked for a time in Tacoma, Washington, as City Chemist. He was Research Associate in Police Science in his University and a consulting expert in legal chemistry and microscopy. He joined the Society in 1935 and died at the age of about 72.

Hughes joined Brunner, Mond & Co. at Northwich in 1906. He served in the Special Brigade, Royal Engineers, from 1914 to 1918. After the war he went to Billingham, where from 1922 he was Chief Analyst to I.C.I. (F. & S.P.) Ltd. He joined the Society in 1939 and died at the age of 62.

Myers became a Fellow of the Institute of Chemistry in 1920 and was for many years chief metallurgical assistant to G. Rudd Thompson at Newport, later becoming a partner in the practice. He was elected a member of the Society in 1923 and died at the age of 71.

Stubbs was born in 1880 and educated at Witton Grammar School and University College, Liverpool, where he obtained the degree of M.Sc. He was assistant to Professor Campbell Brown and W. Collingwood Williams, Public Analysts, Liverpool. During the 1914–18 war he was Captain, R.A.O.C., and afterwards became Public Analyst and Official Agricultural Analyst for Lancashire and Public Analyst for various towns in the county. He became a Fellow of the Institute of Chemistry (Branch E) in 1911. He joined the Society in 1920 and served on the Council in 1929–30 and 1932–39. He was a Vice-President of the Society, 1940–42, and Secretary of the North of England Section, 1932–39, and its Chairman, 1940–42.

Thorp was born in 1866. For three years he was private assistant to J. E. Thorpe

and then worked at Leeds under Smithells and at University College, London, under Ramsay. He became B.Sc. (London and Leeds), and F.I.C. in 1900. He was senior assistant to J. A. Voelcker in the laboratory of the Royal Agricultural Society of England, 1891–92. He lectured on agricultural chemistry and dairying in the next two years and became Public Analyst, Limerick, in 1895. He transferred to Dublin in 1907. He joined the Society in 1896.

ORDINARY MEETINGS—Eight Ordinary Meetings of the Society were held during the year, and the following papers were presented and discussed—

April, 1953, in London, on the Determination of Small Amounts of Lead in Foods and Biological Materials:

"A Reversion Method for the Absorptiometric Determination of Traces of Lead with Dithizone." By H. M. N. H. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M., and E. J. Butler, B.A., B.Sc., D.Phil., A.R.I.C.

"Preliminary Procedure for the Preparation of Biological Materials for the Micro-determination of Lead." By R. F. Milton, B.Sc., Ph.D., F.R.I.C.

"Sample Preparation for Determination of Lead in Foodstuffs." By D. A. Elvidge, B.Sc., and D. C. Garratt, B.Sc., Ph.D., F.R.I.C.

May, 1953, in Glasgow, organised for the Society by the Scottish Section and the Microchemistry Group:

"Geochemistry and Microchemistry." By David T. Gibson, D.Sc.

"Micro-analysis of Silicate Rocks. Part IV. The Determination of Alumina." By Christina C. Miller, Ph.D., D.Sc., F.R.S.E., F.H.-W.C., and Robert A. Chalmers, B.Sc.

"Microchemical Determination of Sulphur in Organic Compounds." By William H. Massie, B.Sc., Ph.D., A.R.I.C.

This meeting was preceded by a visit to the Clydebridge steel works of Colvilles Ltd.

May, 1953, in London:

"The Determination of Ergosterol in Yeast. Parts I, II, III and IV." By W. H. C. Shaw, Ph.C., F.R.I.C., and J. P. Jefferies, B.Sc., A.R.I.C.

"The Estimation of Micro Quantities of Calcium." By G. E. Harrison, Ph.D., F.Inst.P., and W. H. A. Raymond.

"The Ultra-violet Spectrophotometric Estimation of the Quality of Mineral Oils Extracted from Bread." By M. A. Cookson, B.Sc., A.R.I.C., J. B. M. Coppock, B.Sc., Ph.D., F.R.I.C., and R. Schnurmann, M.Sc., Dr.Rer.Nat.

October, 1953, in London, on the Destruction of Organic Matter. The subject was introduced by G. Roche Lynch, O.B.E., M.B., B.S., D.P.H., F.C.G.I., L.M.S.S.A., F.R.I.C.

"The Preparation of Biological Material for the Determination of Trace Metals." By G. Middleton, B.Sc., F.R.I.C., and R. E. Stuckey, B.Sc., Ph.D., F.R.I.C.

"Determination of Lead in Foodstuffs." By H. C. Lockwood, Ph.D., F.R.I.C.

October, 1953, in Southampton, organised for the Society by the Physical Methods Group on the subject of Paper Electrophoresis:

"The Analysis of Inorganic Compounds by Electromigration and Electrochromatography." By F. H. Pollard, B.Sc., Ph.D.

"The Use of Paper Electrophoresis in the Study of Nucleic Acids." By Roy Markham, M.A., Ph.D.

"Paper-strip Electrophoresis of Serum Proteins." By A. L. Latner, M.Sc., M.D., F.R.I.C.

This meeting was preceded by a visit to the Fawley Refinery of Esso Ltd.

November, 1953, in London, on the subject of the Determination of Niobium in Minerals and Mineral-dressing Products:

"The Absorptiometric Determination of Niobium in Some African Low-grade Minerals and Mineral-dressing Products." By G. W. C. Milner, B.Sc., F.R.I.C., A.Inst.P., and A. A. Smales, B.Sc., F.R.I.C.

"The Absorptiometric Determination of Niobium in Some African Low-grade Ores." By A. E. O. Marzys, B.Sc., A.R.I.C.

"Spectrographic Determination of Niobium and Tantalum in Sukulu-type Soils." By C. S. Campbell, M.A., and D. Nicholas.

"Inorganic Chromatography on Cellulose. Part XIV. A Shortened Method for the Determination of Niobium and Tantalum in Minerals and Ores." By R. A. Mercer and R. A. Wells, B.Sc., A.R.I.C.

"The Colorimetric Estimation of Niobium and Tantalum with Pyrogallol." By E. C. Hunt, B.Sc., A.R.I.C., and R. A. Wells, B.Sc., A.R.I.C.

"Inorganic Chromatography on Cellulose. Part XV. A Rapid Method for the Determination of Niobium in Low-grade Ores." By E. C. Hunt, B.Sc., A.R.I.C., and R. A. Wells, B.Sc., A.R.I.C.

December, 1953, in London:

"Recent Advances in Medical Chemistry." By Professor C. H. Gray, M.D., D.Sc., M.R.C.P., F.R.I.C.

January, 1954, in London, organised by the Microchemistry Group:

"Organic Ion Exchange." By L. Saunders, B.Sc., Ph.D., F.R.I.C.

"Inorganic Ion Exchange." By G. H. Osborn, A.M.I.M.M., F.R.I.C.

An exhibition of microchemical apparatus was held in conjunction with this meeting.

JOINT MEETING—A Joint Meeting was held in January, 1954, with the Royal Institute of Chemistry, on the Determination of Alcohol in Blood and Urine, following the presentation of a Report on the subject by a panel of analysts appointed by the Royal Institute of Chemistry to assist the Alcohol and Road Accidents Committee of the British Medical Association. The Report of the panel was surveyed in a paper by D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C., and G. Taylor, O.B.E., F.R.I.C.

NORTH OF ENGLAND SECTION—Including the Summer Meeting at Llandudno, five meetings have been held during the year—one of which was a joint meeting with the Microchemistry Group.

The following papers were read and discussed—

"Principles of Chromatography." By R. L. M. Synge, B.A., Ph.D., F.R.I.C., F.R.S.

"Random Reflections on Food Legislation." By C. A. Adams, C.B.E., B.Sc., F.R.I.C.

"The Society for Analytical Chemistry." By D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.

A discussion on "The Analysis of Waters, Sewages and Effluents" was opened by W. Gordon Carey, F.R.I.C., and J. G. Sherratt, B.Sc., F.R.I.C.

A "Symposium on the Training and Education of Microchemists" included the following papers—

"The Academic Approach." By C. L. Wilson, D.Sc., Ph.D., F.R.I.C.

"Technical Aspects." By G. Ingram, A.R.I.C.

"Industrial Requirements." By R. Rothwell.

SCOTTISH SECTION—In addition to the Annual General Meeting held in Glasgow, four meetings were held during the year, two ordinary meetings in Glasgow and Edinburgh, respectively, the Parent Society meeting in Glasgow, the first in the history of the Section, organised jointly by the Microchemistry Group and the Scottish Section, and including a visit to the Clydebridge Steel Works, and a joint meeting with the Stirlingshire and District Sections of the Royal Institute of Chemistry and Society of Chemical Industry at Falkirk, the first Section meeting held outside Glasgow and Edinburgh.

The following papers were presented and discussed, other than those mentioned elsewhere in this report—

Edinburgh, April 10th, 1953:

"Modern Methods of Analysis in the Training of the Student." By Christina C. Miller, Ph.D., D.Sc., F.R.S.E., F.H.-W.C.

Glasgow, November 10th, 1953:

"Rapid Determination of Glycerol in Fermentation Solutions." By K. Sporek, M.A., and A. F. Williams, B.Sc., F.R.I.C.

"Field Analysis in Connection with Water Treatment Problems." By I. A. Heald, B.Sc.

Falkirk, December 16th, 1953:

"Principles of Chromatography." By R. L. M. Synge, B.A., Ph.D., F.R.I.C., F.R.S.

Following the Council's recommendation, recorders, specialists in individual subjects, are summarising for publication in *The Analyst* those papers of a general nature that do not lend themselves to printing in full.

The Section has become a member of the Federation of Technical Societies in Glasgow, and a representative has been appointed to the Ramsay Dinner Committee.

The membership of the Section has remained stationary at 103.

MICROCHEMISTRY GROUP—Three meetings of the Group have been held during 1953: in London, Glasgow and Southport. The Glasgow meeting was an Ordinary Meeting of the Society organised jointly by this Group and the Scottish Section. The Southport Meeting was organised jointly with the North of England Section and the Liverpool and North-Western Section of the Royal Institute of Chemistry.

The following papers were read and discussed, other than those mentioned elsewhere in this report—

London:

"Microchemistry: An Appraisal." By Cecil L. Wilson, D.Sc., Ph.D., F.R.I.C.

Southport:

"Symposium on the Training and Education of Microchemists," comprising three papers as follows—

"The Academic Approach." By Cecil L. Wilson, D.Sc., Ph.D., F.R.I.C.
"Technical Aspects." By Gerald Ingram, A.R.I.C.
"Industrial Requirements." By Rudolf Rothwell.

Visits were made as follows: Messrs. L. Oertling Ltd., St. Mary Cray, Orpington; Messrs. Colvilles Ltd., Clydebridge Steel Works, Glasgow; Victoria Colliery, nr. Wigan; Simpson's Gold Thread Works, Preston; North-West Gas Board, Southport Gasworks.

The Annual General Meeting in London on January 29th was followed by an Ordinary Meeting of the Society, arranged by the Group. On the same day an Exhibition of Microchemical Apparatus was held at the Sir John Cass College.

The list of "Reference Substances for Use in Organic Micro-analysis," which had been drawn up after careful consultation with users and manufacturers, was published in *The Analyst* for April, 1953.

A specially appointed Sub-Committee completed the script of the proposed film "How to Use a Microchemical Balance."

As more than 40 per cent. of the Group members reside in the London area, it has been decided to recommend the formation of a London Discussion Group for the purpose of holding informal meetings on microchemical matters.

The number of Group members is now 421, an increase of 29 since the last report.

PHYSICAL METHODS GROUP—The Physical Methods Group has arranged six meetings in all during the past year, two of which were on behalf of the Parent Society; one in Birmingham on January 31st on the subject of "Chromatography" and the other in Southampton on October 23rd concerning "Paper Electrophoresis." Three of the Group meetings were held in London, and the remaining one in Ipswich was held jointly with the East Anglian Section of the Royal Institute of Chemistry.

The Polarographic Discussion Panel organised one of the Group meetings held in London. The Chairman of the Panel is Dr. A. J. Lindsey, and Mr. G. W. C. Milner is Honorary Secretary.

The following papers were read and discussed at meetings of the Group—

Annual General Meeting, London, November 25th, 1952. This was followed by an ordinary meeting on Forensic Science.

"The Application of Some Physical Methods in Forensic Science with Particular Reference to the Examination of Materials Relating to Criminal Investigation." By J. B. Firth, D.Sc., F.R.I.C., M.I.Chem.E.

"The Examination of Questioned Documents." By J. A. C. McClelland, B.Sc., Ph.D., A.R.I.C.

Absorptiometry Meeting, London, March 3rd, 1953:

"The Use of High Absorbancy Reference Standards in Absorptiometry." By H. M. N. H. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M.

"The Determination of Titanium by High-precision Absorptiometry." By W. T. L. Neal, M.A., A.R.I.C., and H. G. Short, M.Sc., A.R.I.C.

Polarography Meeting, London, April 14th, 1953:

"The Polarographic Determination of Fluoride." By B. J. McNulty, B.Sc., Ph.D., F.R.I.C., G. F. Reynolds and E. A. Terry.

"The Amperometric Titration of Zinc and its Application to the Determination of Zinc in Lubricating Oils." By D. Pickles, B.Sc., A.R.I.C., and C. C. Washbrook, A.R.I.C.

"A Tentative Method for the Determination of Calcium by Means of the Polarograph." By Mrs. Bertha Lamb, B.Sc.

Emission Spectroscopy Meeting, Ipswich, May 8th, 1953:

"Semiquantitative Techniques in Spectrochemical Analysis." By R. L. Mitchell, B.Sc., Ph.D., F.R.I.C.

"Some Techniques of Presentation of Sample to the Spectrograph." By A. H. C. P. Gillieson, B.Sc., Ph.D.

"Applications of the Porous Cup Technique." By L. G. Young.

The number of Group members is now 446. This represents an increase of 28 since the last Annual Report. Membership of the Polarographic Discussion Panel is 109.

BIOLOGICAL METHODS GROUP—The Group has held four meetings during the year, two of which have been joint Symposia with other societies.

On December 11th, 1952, after the Annual General Meeting, two papers were read and discussed—

"A Method Identifying the Presence or Absence of Splenin 'A' and Splenin 'B' in Serum using Guinea Pigs." By Raymond Greene, M.A., D.M., M.R.C.P., and Josephine Vaughan-Morgan, B.Sc.

"The Application of Large Plate Methods to Microbiological Assays of Antibiotics and Vitamin Products." By K. A. Lees and J. P. R. Tootill.

On March 11th, 1953, a highly successful Symposium on Flavour Assessment was held in collaboration with the Food Group of the Society of Chemical Industry and the Biometric Society (British Region). The Chair was occupied successively by Professor H. D. Kay, Dr. H. O. J. Collier and Dr. K. Coward, and five papers were presented and discussed—

"The Physiological Background of Flavour Assessment." By E. D. Adrian, O.M., P.R.S.

"Basic Considerations in Regard to Flavour Assessment." By H. G. Harvey, M.Sc., A.R.I.C.

"The Objective Approach to Sensory Tests." By A. S. C. Ehrenberg, B.Sc., and J. M. Shewan, B.Sc., Ph.D., A.R.I.C.

"Sensory Tests and Consumer Acceptance." By J. M. Harries, B.A.

"A Biometrician's Viewpoint." By J. O. Irwin, M.A., Sc.D., D.Sc.

The Summer Meeting of the Group took the form of an interesting visit to the Ministry of Agriculture and Fisheries' Veterinary Laboratory at New Haw, Weybridge. Departments visited included Biochemistry, Manufacture of Vaccines, Tuberculin Production, Poultry Diseases and Manufacture of S.19 *Brucella abortus* Vaccine.

On October 2nd, 1953, Organo-phosphorus Insecticides were the subject of a Symposium held jointly with the Crop Protection Panel of the Agriculture Group (Society of Chemical Industry), the Association of Applied Biologists and the Pharmacological Society. Professor V. B. Wigglesworth, C.B.E., M.D., F.R.S., was in the Chair for the morning session, when two papers were presented and discussed—

"Insecticidal and Anti-esterase Activity of Organo-phosphorus Compounds." By K. A. Lord, M.A., Ph.D., and C. Potter, D.Sc.

"Toxic Action of Organo-phosphorus Insecticides in Mammals." By J. M. Barnes, B.A., M.B., B.Ch.

The discussion was opened by B. A. Kilby, M.A., Ph.D., F.R.I.C. For the afternoon session the Chair was taken by J. R. Nicholls, C.B.E., D.Sc., F.R.I.C., and three papers were presented and discussed—

"The Behaviour of Organo-phosphorus Systemic Insecticides in the Living Plant." By G. S. Hartley.

"Some Hydrolytic Aspects of Organo-phosphorus Compounds." By P. R. Carter, B.Sc., Ph.D., A.R.I.C.

"Bio-assay of Organo-phosphorus Insecticides." By J. F. Newman, B.Sc.

Membership of the Group has increased by 13 during the year and now stands at 225.

ANALYTICAL METHODS COMMITTEE—A considerable impetus has been given to the work of the Sub-Committees by the holding of more frequent meetings of the Committee, to which Chairmen and Honorary Secretaries of Sub-Committees and Panels have been invited, to receive and discuss interim reports.

The awaited findings for a standard procedure for determination of lead in foodstuffs have been necessarily delayed. By representation to suppliers of analytical reagents, virtually lead-free reagents have been obtained, thus eliminating one of the most serious sources of error in the determination. However, the Metallic Impurities in Foodstuffs Sub-Committee are not yet satisfied with the reproducibility of results when minimal amounts of lead are present. The amount of experimental work done by the Lead Panel has been very considerable.

The activities of the Vitamin Sub-Committee have resulted in the production of a report on a microbiological assay for thiamine that is in the hands of the Publication Committee. Working Panels have been formed under the Chairmanship of Dr. Amos and Mr. Bacharach, respectively, to establish if possible a standard method for the estimation of vitamin B_{12} and vitamin E.

Following publication of the Interim Report on Pure Meat Extracts, the Meat Extracts Sub-Committee are now dealing systematically with composite products.

STANDARD METHODS COMMITTEE—Dr. Kent-Jones resigned from the Secretaryship of the Committee on his election as President, and Mr. J. B. Attrill has been appointed in his place. Under the Chairmanship of Mr. G. Taylor the Committee is making considerable progress in re-editing the Society's Standard Methods and in putting together standard methods of analysis for a wide variety of materials. These, after final review, will be published section by section.

PUBLIC ANALYSTS AND OFFICIAL AGRICULTURAL ANALYSTS COMMITTEE—The Committee has met on three occasions during the past year. Amongst matters dealt with were the Rag Flock and other Filling Materials Act, 1951; the action taken by certain local authorities with regard to sampling table jellies for the setting test; the freezing point of milk; standards for sausages and the Food and Drugs Amendment Bill.

LIAISON COMMITTEE—During the year the following appointments have been made—

B.S.I. Committees:

Mr. L. A. Haddock, Methods for the Examination of Chemical Products.

Mr. H. Weatherall, Ubbelohde Apparatus.

The President, Mr. R. C. Chirnside and Dr. K. A. Williams, Conference on the Possibility of Making Standards for Analytical Reagents.

Joint Library Committee, Chemical Society:

Dr. J. G. A. Griffiths was again appointed as the Society's representative.

Food Manufacturers' Federation:

Dr. S. G. Burgess was appointed as the Society's representative on a Committee dealing with the determination of fat in canned soups.

British Iron and Steel Research Association:

Dr. J. Haslam and Mr. R. C. Chirnside were appointed as the Society's representatives at the Seventh Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).

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

HONORARY TREASURER'S REPORT—For the first time for a number of years the Society's accounts show a small loss on the year's working. Such a loss was not anticipated in the Spring when the Society's yearly budget was considered by the Finance Committee, but two unexpected factors during the year are responsible for this result. In the first place, sales of the bound volumes of the Proceedings of the International Congress on Analytical Chemistry have not come up to earlier expectations, with the result that the loss on the Analyst and Sundry Publications Account is considerably larger than was expected. The sales of this publication are now improving, and this improvement will be reflected in next year's accounts. Secondly, at the end of the year the Society was called upon to face the cost of setting up an editorial organisation for the publication of *Analytical Abstracts*. This necessitated hiring and furnishing an additional office, and engaging additional editorial staff. The accounts for this new departure now appear as a separate item in the balance sheet as the Analytical Abstracts Account and, quite clearly, the expenses incurred during the preparatory work at the end of 1953 must be borne by the Society and are not offset by any financial return in the year under review.

The publication of *Analytical Abstracts* is an expensive undertaking, and one which may involve the Society in a substantial loss. Very careful costings were made before this project was undertaken, and these were based on an estimated figure for sales of *Analytical Abstracts* to chemists and organisations outside the Society. It is our duty to warn the Society that should the outside sales fall badly short of the predicted figure, the Society may be faced with a loss of anything up to £2,000. The Council of the Society, however, have accepted this possibility in view of the importance of analytical abstracts to its members.

The experiment with the advertisements in *The Analyst*, to which reference was made in the last report, has been a success, as will be seen from the increased revenue to the Analyst Account from this source.

THE ANALYST—The 1953 volume contained 740 pages; the 1952 volume contained 1032 pages, of which 480 pages were the Proceedings of the International Congress on Analytical Chemistry of September, 1952, and 552 pages were usual *Analyst* matter. The numbers of papers and notes published in 1953 were 96 and 54, respectively (a total of 150), against 129 and 28 in 1952 (83 and 28, excluding the Congress papers and lectures). The approximate number of pages of papers and notes was 646, against 970 in 1952, which included the Congress papers and lectures.

Nine issues of the Bulletin have been distributed with *The Analyst*.

The printing number of the monthly issues for 1953 was 4800; it is now 4900.

ANALYTICAL ABSTRACTS—The new journal of *Analytical Abstracts* started in January, 1954, and is already enjoying a wide circulation.

CHEMICAL COUNCIL—During the year the Chemical Council has again distributed large sums of money to assist in the publication of original papers, and the Council acknowledge with thanks the grant of £1500 towards the cost of producing *The Analyst*.

DEVELOPMENT OF THE SOCIETY—For the first time in the history of the Society, a Conference of the Honorary Secretaries of the Sections and Groups was held in May in London. The Conference proved extremely successful, and of great use in promoting the integration of the activities of the various departments of the Society. It is hoped to make this an annual event.

During the year the Council appointed Mr. N. L. Allport as Honorary Assistant Secretary of the Society to assist the Honorary Secretary, primarily as a link between the Council and the Committees of the Sections and Groups.

FOOD LAW INSTITUTE—Advantage was taken of the visit of Mr. C. Wesley Dunn, President of the Food Law Institute of the U.S.A., to this country, by the President to entertain him to an informal dinner at which he could meet members of the Society and discuss problems of food law common to both Great Britain and the United States of America.

D. W. KENT-JONES, *President*.
K. A. WILLIAMS, *Honorary Secretary*.

The Third Bernard Dyer Memorial Lecture

The Contribution of Public Analysts and Other Analytical Chemists to Public Welfare

By E. B. HUGHES

(*Delivered after the Annual General Meeting of the Society, March 3rd, 1954*)

Before giving this Third Memorial Lecture I wish to discharge in a few words my primary duty of paying a tribute to the memory of Dr. Bernard Dyer. His record of lengthy service and of benefit to this Society is unique and will probably remain so. Bernard Shirley Dyer was born in 1856 and died within a fortnight of his 92nd birthday. He was a member of this Society for some 73 years. I do not propose to speak of Dyer's work, for that, particularly his famous contributions to soil analysis and his work in general for agriculture, was so ably described by Sir John Russell in the First Dyer Memorial Lecture, and a faithful word-picture of the man and his character and career can be found in the obituary written by Mr. George Taylor, his colleague, and Mr. Lewis Eynon. Dyer's work will live: indeed, his work on soil acidity, for example, has endured the test of over half a century and, despite modern advances, still provides a practical and useful method.

What I think we should particularly speak of on these occasions is his personality and character. He was not merely a fine chemist and an excellent analyst, but he had the gift of insight into chemical and analytical problems, for he seemed infallibly to choose the surest and most direct method of attack on a problem, whether of research or of analysis.

From his youth he knew what he wished to do and what he could do, and he achieved his objects with seeming ease and happiness. I imagine that his early experience in the laboratory of Dr. Augustus Voelcker must have provided him with a firm foundation of analytical skill and understanding. Nevertheless, it seems almost uncanny that one so young as he was (21 years of age) when he founded his own practice as an analyst and became a member of this Society should have had not only the wisdom and self-confidence that he clearly possessed, but also outstanding ability and foresight. Dyer was modest, courteous and kind, esteemed by all who met him, and generous in his help to the young analyst. He was a great analyst and a stalwart of this Society, and our memory of him is that of a grand and loveable man.

The Contribution of Public Analysts and Other Analytical Chemists to Public Welfare

When your President and Council honoured me with the invitation to give this Third Bernard Dyer Memorial Lecture, I accepted with greater readiness than I have since felt was justified, but I did welcome the opportunity to voice some thoughts that have long been in my mind about the importance and status of analysis, and particularly to say something of my friends the public analysts and of the co-operation that exists between them and other food chemists in furthering knowledge of the analysis of food. At that time I did not know that the Society was so soon to change its title, but this event makes what I have to say even more appropriate to the occasion.

The title I have chosen for this talk is "The Contribution of Public Analysts and Other Analytical Chemists to Public Welfare," but obviously it is impossible in the course of this lecture to discuss adequately the contribution made by analytical chemists in all spheres of industry: I therefore shall refer chiefly to those whose work I know best, namely, analysts in the food industry and public analysts.

The common factor of our interest in this Society is not merely that we are concerned with analysis and like to hear and read something of what is being done in it, but that we *are* analysts: it is the personal factor. The analyst does not drift into his profession, not even on the conclusion of his academic education: he deliberately chooses a career that

necessitates careful and accurate work, that requires the application of any scientifically controllable means of pursuing an enquiry and that gives him the satisfaction and pleasurable anxiety of pitting his knowledge and skill and ingenuity against the complexities of the problem that confronts him. This, to my mind, pictures the essential character of the analyst. No new progress in chemical knowledge can be allowed to escape his attention, for sooner or later it may provide a useful and probably a common line of attack in analysis.

I do not intend to pursue the subject of what the analyst may do—or I think should do—for his own science; this Society provides by its meetings and its Groups and its Analytical Methods Committee ample opportunities for the zealous analyst—and our journal shows that excellent and valuable work is being done. My chief concern this evening is to give some thought to the service of the analyst to mankind.

Sir Robert Robinson, in his foreword to the Proceedings of the International Congress on Analytical Chemistry says—

> "During the earlier decades of the growth of the modern science of chemistry the importance of analytical theory and practice was well understood and the fundamental technique of many of the pioneers was essentially that of analytical chemistry."

Although analysis for a longish period was not of fundamental importance in chemical progress but rather a useful service, it is now again a factor of prime importance, and the growth of chemical knowledge and of analytical science are mutually essential and mutually dependent. Analysis is not merely the handmaiden of industry—although indeed I fear that it is sometimes, if not often, regarded as the Cinderella of chemistry—it is, and particularly in industry, the *sine qua non*, not only for control, but for research.

If the ordinary individual, the layman from our point of view, were given a simple outline of the various applications of our science, I think his greatest interest would be aroused in its application in biochemistry and the allied sciences—chemical pathology, physiological chemistry and pharmacology—for it is in these that a direct personal appeal would be found: the growing knowledge that is so steadily contributing towards understanding of life, and application that can affect health and bodily welfare and lessen fear of disease. The part that analysis plays in these studies—and certainly when they develop into practice—is an important one.

Agriculture and its particularised sciences—pest control, soil analysis, plant nutrition, etc.—also appeal to personal interest and give us faith that they will enable the world for a long time to meet the demands for more and more food. Agricultural chemistry was, in its beginning and growth, chiefly analytical—with a rapid realisation of its benefits. There is now no farmer, nor grower, nor cattle rearer, nor hardly an amateur gardener, to whom such information is not a commonplace of daily life. Dyer, you will remember, made important contributions that are still standard procedures in analysis.

Elements in trace amounts in soil and plants have an astonishing effect on plant growth and health, and a deficiency of this or that element may have a serious effect. Diagnosis in many crops can be made from observation of leaves and growth, but the best means, of course, is chemical or spectrographic analysis. One could wish that as much were known about the effects of trace elements on humans—I mean of beneficial elements: the harmful ones are better known—as is known about the effects on plant life.

The extensive use of chemical substances as pesticides causes anxiety about the possible effects of their residues on crops. Although there is no evidence that any harm has resulted, it is certainly desirable, indeed essential, that methods of analysis should be available for the detection and determination of trace amounts of these substances—a problem that analysts must resolve. I regard this requirement as even more urgent than the precise specification of known methods of analysis to meet the requirement of standards and limits of contaminants in food.

Nowadays, in the manufacturing industries, analysis is an essential service. Without it, rule of thumb would be the only guide; erratic results, faulty products and irregular quality would be commonplace instead of rare; progress would be stultified and by chance and intuition only. We analysts occupy a key position—by no means generally recognised—and although we may be the "back-room boys" of industry, we deserve now and then to be considered worthy of a place in the sun. I will not attempt to name industries in which analysts are necessary: I cannot call to mind an exception.

The greatest need for our modern industries is to produce more goods of reliable and invariable quality and with a greater output per worker. These are not only matters of

management, of factory design and engineering, but they call for the services of chemists, often in a high degree. In the food industry, for example, progress would be uncertain and retarded without such help.

This need is well recognised by government and by industry, and is evidenced by the number of scientific research associations of various trades and by the magnitude of our Department of Scientific and Industrial Research. Nevertheless, it is recognised that there is need for many more scientists in the service of industry. In the U.S.A. the proportion of scientific and technical staff to other workers is very much greater than it is in this country, and if we are to compete successfully in the world market against such well-served industries, we must increase our application of science. Let me quote to you just a few words from a lecture given by a very wise and far-seeing business man, the late S. M. Gluckstein, before the London Section of the Institute of Chemistry in 1927—27 years ago.

> "It is said by advertising people that if business is bad you should increase your advertising in order to improve it, while if it is good you should increase your advertising in order to maintain it as well as improve it. Similarly, I saw recently that an American business man of standing said that when trade becomes bad, you should double your laboratory staff. Although no doubt his remark is not intended to be taken quite literally, nor would I go so far as to agree with him completely, there is more than a grain of business sense behind such advice."

This is not to infer that times are now bad, but the paramount need for expansion of trade is an equivalent condition.

We in this Society hold our meetings, read papers and make such contributions to our science that our journal is of world-wide high repute, but I think we might also occasionally have a meeting where we can learn what the other fellow does. So I put forward for consideration the suggestion of a Symposium on Analysis in Science and Industry—that is, on what we do, not *how* we do it—at which we could learn in some detail what the analyst does in spheres other than our own. (I believe that probably the Society of Chemical Industry would gladly participate with us in a function that would be stimulating and, I am sure, to the credit of all concerned.) Let us tell industry, and the trade associations, and the economists, and the Government, something of the study and zeal that lie, largely hidden to them, in the analysts' contribution to the prosperity of industry and of the nation.

From this short and far from complete appreciation of what the "other analytical chemist" does to further national and human welfare, I pass on to some special reference to the work of my friends the public analysts, with whom food chemists, of whom I am one, have so much in common.

Most of you will know something of the story leading to the establishment of the Food and Drugs Act, as most who speak of food legislation feel impelled to mention it, but in view of what I wish to say I think that just a brief reference here is necessary.

An Act introduced to prevent adulteration of food and drugs could be effective only if there were means of detecting and determining the degree of fraud; and so it is that, though one may consider that the first Food and Drugs Act was much overdue, it could hardly have been made truly effective very much earlier, except, of course, against the cruder forms of adulteration. The speedy and striking success of the 1872 Act was due to the fortunate circumstance that there were then in practice a few analysts who had the wisdom and foresight to realise that for the successful fulfilment of their duties under the Act they should unite to share their knowledge, and with this object they formed a society which, at their first Annual General Meeting in 1875, was constituted as the Society of Public Analysts. The scientific ability, integrity and astonishing zeal of those pioneers in food analysis rapidly made the Act an effective instrument and gave prestige and dignity to their profession and to the Society they had founded. Theirs was indeed a service to the nation and to analytical chemistry, and we in this Society who have inherited what they so well founded have cause to hold them in esteem and gratitude. I need not here go into details of the development of the Society nor of the great names it has left in the history of analysis, such as Redwood, Allen, Adams, Hehner, Dyer, Stevenson, Wanklyn, Bevan and many others: you will find a charming and modest account of these in "Fifty Years of the Society of Public Analysts," published in 1932, wherein Bernard Dyer gave an account of the personalities of the period and the events in their term of office, and C. Ainsworth Mitchell gave a succinct record of the main features of progress in the Society.

It is common, in referring to the introduction of the Food and Drugs Act of 1872, to refer to harrowing stories of openly fraudulent and sometimes harmful adulteration of food in the early part of the nineteenth century, and to refer to Accum's book, "A Treatise on Adulteration of Food and Culinary Poisons," but nevertheless it is pleasing to note that even in those times there were in existence some of the food manufacturing firms whose names are household words to-day and which, I feel sure, were as honourable then as now: there are copies of advertisements of smaller merchants and bakers describing the wholesomeness of their wares, and among them, for instance, one of a baker who claimed that his bread was pure and free from alum (1788). We should remember that, although that period was only about a century ago, there was a general callousness in human treatment that in many respects is equally shocking to us. For example—

1837 (17 years *after* Accum's book was published): up to then some 200 offences on the penal code were punishable by death; in 1861 this was reduced to something like our present law. In 1825 the tax on salt was repealed: it had been as high as £30 a ton (£30 in those days!) for an essential in food, particularly as it was the only means for preserving meat. In 1851 the window tax was repealed: this had been a tax on health and comfort and no doubt contributed to tuberculosis. In 1842 the employment of women and children *underground* in mines was forbidden. In 1875 the practice of boys being sent up chimneys for sweeping was abolished.

The Food and Drugs Act of 1872 was not introduced as the cure of the one outstanding evil, but was part of the rapid general civic reform of the period.

Be that as it may, those days are passed, and public analysts' work is now the more prosaic—but still important—one of seeking the stray offender or the manufacturer who, generally by mischance, is guilty of a minor infringement of Regulations or of a divergence from the normal not in reality to the prejudice of the purchaser. Thus, taking figures for 1937–38 (the latest I have found available), a total of about 151,370 samples were examined by public analysts and of these more than half (82,357) were milk: the "not genuine" samples amounted to 5·5 per cent., of which nearly 75 per cent. were milk; this shows quite clearly why so much attention is given to the sampling of milk and that, despite the efforts of years, this particularly despicable adulteration is still far too prevalent. These samples taken by public authorities are not all random samples; they represent quite largely a selection of kind and origin in which adulteration might be more suspected, so that, on the whole, the indication is that the occurrence of adulteration of food is slight.

From the point of view of the manufacturer, the extent to which testing of his raw materials and products is necessary is much more exigent than is required for compliance with the Food and Drugs Act. He must do all he reasonably can to ensure that his products are genuine and uncontaminated and, so far as possible, leave nothing to chance; consequently sampling must be more intense. As an indication, I quote a few figures from our own laboratory: in a year, a total of some 70,000 samples are analysed, some fully, some for specific purposes only; also in one year we make about 3000 determinations of arsenic, 1000 of lead, 1000 of copper and 800 of tin. In industry, as with the public analysts, samples generally prove satisfactory, but the occasional faulty sample must be looked for.

A workable, effective and just Food and Drugs Act is a necessity in any civilised community; it not only protects the public but also protects and guides the responsible manufacturer. From my reading of the new Food and Drugs Amendment Bill, I infer that much more control may be exercised in future by specific Regulations promulgated by the Ministries of Food and Health, which might lead one to fear, perhaps, what we all as individuals dislike in our private lives as well as in business, excessive bureaucratism. I hasten to add that, although I know the existing Act of 1938 requires the Minister "to consult with representative organisations as he thinks fit," my experience as a food chemist has been that this requirement is applied widely and generously, and that the officials responsible do seek and consider evidence from the industry—and inspire its co-operation; and I feel that, if this understanding spirit is maintained, there should be nothing to fear but much to be gained from clearly stated needful and useful Regulations, and I stress needful and useful.

Another clause that attracts my attention, as a chemist, is the one stating that methods of analysis may be prescribed and that "evidence of an analysis carried out by the prescribed method shall be preferred to evidence of any other analysis or test." I trust that such prescribed methods will be such as can be approved, and preferably will be produced, by this Society, and that they may be subject to review as circumstances require.

This occasion gives me the opportunity I have often desired—to pay a tribute to the public analysts, and to express the food chemists' appreciation of the co-operation between them and us on the scientific work required for establishment of assured methods of analysis, to the advantage of both. I (and many other food chemists) have been associated with public analysts on many committees on methods of analysis of food and the like, and the experience has been a happy one and, I feel sure, to the benefit of the public and the manufacturer alike.

That the public analysts have relinquished their claim on the name of this Society and have willingly and generously accepted the change necessitated by the many and expanding interests of the Society is worthy of grateful acknowledgment, of which they have had many assurances but which I wish to emphasise once more. In the new Association of Public Analysts we hope that they will find all the professional status and recognition that are their due, but, above all, we hope that they will still be ardent supporters of this Society and maintain their close scientific contact with chemists of the food industry, which becomes more and more necessary to both as the knowledge of the science of food advances.

We are living in an age of manufactured food, and it is futile to pretend that we, or any industrial nation, can revert to the simplicity of, say, even the eighteenth century. What we have to do is to strive to ensure that the food we supply to *countryman* and townsman alike—for nowadays the countryman is a consumer of manufactured food—shall be wholesome and nutritive as well as attractive and pleasing, and capable of withstanding the exigencies of transport and distribution. This is the objective of the food chemist—and I say this as one who has spent what may be considered as the greater part of a working life as such. Chemists are employed in the food industry for the purposes I have stated, and their most important function—and their first duty to their firm—is to use their knowledge and skill to ensure the purity and quality of their product; the food chemist is paid to maintain—if possible, to enhance—the reputation of his firm's goods; certainly he would not—and dare not—be the cause of any harm. The food chemist—one of the "other analytical chemists"—is thus as much a contributor to public welfare as is the public analyst: perhaps I could justly say even more so, because his object is not merely to find any evidence of harm or of infringement of law or regulation, but definitely to prevent such mischance. A food chemist's standard of requirement of purity of a raw material is stringent, for he knows how this or that ingredient or constituent can contribute some desirable or undesirable quality to the manufactured product—and so he works to exacting limits. To him a substance is not necessarily satisfactory solely because it is genuine or pure; it must have certain qualities or characteristics, which are of importance according to the intended use of the substance. You, I think, will realise how this is done; it is by constant application of analysis and microbiological examination, by tests chosen to give the information required and by specifying all the details of the care required in manufacturing processes; by making tests and inspections to verify the observance of them, and finally advising how the product should be packed and specifying how long it will remain in the condition that the customer rightly expects. It is this sort of work that accounts for the testing of some 70,000 samples that I have previously mentioned. To you, analysts and microbiologists, I need not elaborate this or go into details, but I would emphasise that all this control and checking is a very real part of food manufacture.

In the course of such intensive examination, data such as do not come to notice in casual inspection become available, and attention by industrial food chemists results in reduction or elimination of contamination that probably otherwise would have escaped notice. The care that a food manufacturer takes to avoid contamination he naturally requires also of the suppliers of the raw materials, and in this alone there is obviously a public benefit. The sequence of this testing is obvious: it is to see that in the factory there is no contamination, or perhaps more exactly, that there shall be the very minimum, ensured by choice of material for equipment, and that all metals with which the food comes in contact shall be appropriate for the purpose: this applies to plastics as well as to metal—more work for the analyst. Cleanliness is an all-important matter in a food factory and kitchen and must be to a degree well beyond what visual inspection will detect; in fact, to an extent that could hardly be expected in the ordinary household. Cleansing materials are important, and we must know what we use and how they function; also we must know not only their efficacy but their effect on equipment. This necessitates bacterial testing of plant and materials and products, and the formulation of conditions of processing and of cleaning. For this work

we prefer chemists who have been trained in the analytical procedures of bacteriology; they have some consideration for the food as well as enmity towards unwanted micro-organisms. This section of the laboratory will also undertake work on fermentation (*e.g.*, enzyme reactions, treatment of trade waste and the like).

I have given this sketchy description of science applied in the food factory and kitchen only to indicate the great importance of such work, not to describe in detail how it is carried out, and to show that the able analyst—suitably trained and experienced in the industry—is the best man for the job.

In recent years a new name for the food chemist has been used, and seems to be becoming popular, the food technologist. If such a title or grade is to be recognised, and adopted by the food chemist, it must indicate one whose post-graduate scientific training has been concerned with food and food manufacture, and not merely the acquisition of enough knowledge to meet the normal requirements for food manufacturing processes. My opinion is that the analyst, suitably experienced, is the ideal food technologist, as I think it important not to lose sight of the fundamentals. We in our laboratory go further. We like to have our investigational work and research work in the hands of those who have special knowledge of the products being studied and who have had the experience of the analysis and manufacture of those products. There are exceptions, of course, such as in the physical laboratory, X-ray work and the like, although much of such work is contributory to the work in other sections. There is no reason why the analyst should not know all the technology nor why he should not know something of the functioning of the industrial plant and, when he has special knowledge of the product concerned, consult and work with the engineer and the designer and architect. The analyst should not, in industry, be restricted to the laboratory bench. Knowledge gained in the factory helps him to understand better the object of his work and also to be more useful to the industry. We regard analysis as the backbone of our work.

What of the ethics of the chemist in the food industry? I feel impelled to refer to this because this industry so much affects every individual, in purse as well as in welfare; and this being so, it is an industry particularly liable to be criticised, attacked and even maligned. There is the suggestion that the food manufacturer, for convenience and for profit, makes wide use of "chemicals," aided and guided by his food technologists, to the consequent detriment of the consumer. How far this is from the truth is obvious from even a cursory scanning of published abstracts of the scientific literature on food, and too, for example, from the subjects discussed at meetings of the Food Group of the Society of Chemical Industry and in particular the exhaustive presentation and discussion of the subject of Chemicals in Food, including Pharmacological Aspects, in September, 1951, all published and available. I would also especially mention the joint request made by the Society of Public Analysts and Other Analytical Chemists and the Food Group to the Ministry of Food to review the Preservative Regulations and to make needed recommendations. Could we do more? To our satisfaction a Committee, on which medical science is well represented, with such terms of reference—including not only preservatives but other chemical additives—was formed and is now actively considering this matter, and I suggest that we all—including those who, being less responsible and less appreciative, are the more ready to criticise—should await that Committee's recommendations and report. I therefore refrain from any particularisation.

Food chemists in this country have assumed that their meetings, discussions, published work and the abundant evidence of their interest in the purity and quality of food would be ample indication of their aims, but in view of recent trends it would be desirable to *state* the policy as well as carry it out. I have noted such a statement in the 1953 Presidential Address by Professor Bernard E. Proctor to the Institute of Food Technologists (U.S.A.), which Institute is an important body requiring evidence of satisfactory academical and postgraduate training for membership. Here are abstracts therefrom—

"It [the Institute] is a respected champion for improvement in food quality and more efficient food processes and equipment. . . . There is no group in this country in whose hands more responsibility is vested concerning the well-being of the public from the standpoint of its food intake." And, speaking of Chemicals in Food: "The protection of the ultimate food consumer is the first interest of all food technologists." These are sentiments that we can sincerely say represent our views too: they are necessarily the guiding principles of all responsible food chemists. The U.S.A. Food Chemists, in their objective of "the protection of the ultimate consumer," include as a most important matter the necessity for sound evidence of the harmlessness of any proposed chemical additive to food before its use can be

advocated, and I note with considerable interest—and a certain amount of national satisfaction—that they attach great importance to the work of Professor A. C. Frazer in this country and that his opinions are quoted as "exceptionally able statements of the problem."

A very unsatisfactory aspect of the matter of additives in food—preservatives, colours, emulsifiers and stabilisers—is that there should be such variation in different countries in what is considered suitable and in the amount permitted. There is obviously a lack of knowledge and, equally obviously, I suggest, a lack of frankness in making information available. Committees do not provide information: they can only collect what is available, collate it and make the best possible decisions thereon. One would expect that such matters should be recognised as being for the benefit of all peoples and for simplicity in trade, yet the authorities in each country proceed as if they, and they alone, understand what is right and just. Perhaps one day we shall have some international co-operation; the effort would be worth while because then so many could contribute to the provision of essential knowledge.

I know that in what I have said there may be little or nothing new—and no new sentiment or opinion—and if it seems so to you I shall be content, for what I have tried to say was something about ourselves that I believe should be expressed in words and not merely lie dormant in our minds.

The Polarographic Determination of Fluoride

Part II. The Determination of Fluoride in Bromine, Hydrochloric Acid and Hydrobromic Acid

By Miss J. S. BEVERIDGE, B. J. MACNULTY, G. F. REYNOLDS and E. A. TERRY

(*Presented, together with Part I, at a meeting of the Physical Methods Group on Tuesday, April 14th,* 1953)

The application of the method described in Part I to the determination of fluoride in bromine, hydrochloric acid and hydrobromic acid is described. In the application discussed, the cathode-ray polarograph appears to be superior to the conventional type of instrument.

In the course of other work[1] on the determination of fluoride, it became clear that a method was needed to check the fluoride content of halogen acids used as reagents and in control experiments. Separation of fluoride by the standard technique of distilling it as hydrofluosilicic acid seemed unlikely to be satisfactory, for, although it might be possible to remove the halogen acid by a low-temperature distillation at less than 120° C before the steam distillation of the fluoride as hydrofluosilicic acid, such a procedure would at best be tedious and time-consuming and might result in erratic losses of fluoride. In these circumstances a direct method of fluoride determination, more sensitive than those in current use, was required. The polarographic method described in Part I of this series[2] has proved satisfactory for this work.

Experience in the treatment of hydrobromic acid to remove elements likely to interfere in the determination of fluoride had indicated the possibility of free bromine being present after treatment. Experiments were therefore made to find methods of determining fluoride in the presence of this element. Although the question of fluoride determination in the presence of free bromine subsequently proved of no importance with hydrobromic acid, a method of determining fluoride in bromine was developed in the course of the work and is presented here.

In this paper the experimental development and the final details adopted for each of the three materials concerned are described separately and a general discussion of these applications of the general method is given at the end.

Experimental

Determination of fluoride in hydrochloric acid—

The basis of the method was to neutralise as much hydrochloric acid as was compatible with the solubility of the resulting salt and then to add an aluminium - dye complex solution,

prepared as previously described,[2] make up to standard volume, heat to 70° C for 5 minutes, cool and record a polarogram. Ammonium hydroxide was used for neutralising the acid, as this base was the least likely to contain fluoride and other impurities, such as iron or aluminium, that would interfere with the method, although there was no reason why other bases of sufficient purity should not be used.

Preliminary experiments showed that the method could be used in strong salt solution and that no trouble was experienced owing to salting out of the dye, Solochrome Violet R.S. The experiments were carried out in solutions of AnalaR quality ammonium chloride. The ammonium chloride was crystallised twice before use.

Double recrystallisation of salts is sufficient to free them from all detectable traces of fluoride except when contamination is heavy; three recrystallisations may then be required. This was proved in the following way. A saturated solution of ammonium chloride was prepared and the equivalent of 530 μg of fluoride per 50 ml was added as sodium fluoride. The solution was treated in the usual manner and polarograms were made before and after recrystallisation. The results are shown in Table I, from which it is evident that double recrystallisation is sufficient to remove any normal amount of fluoride.

TABLE I

REMOVAL OF FLUORIDE FROM AMMONIUM CHLORIDE BY RECRYSTALLISATION

	Before treatment	After 1st treatment	After 2nd treatment	After 3rd treatment	After 4th treatment
Fluoride, μg per 50 ml of solution	530	35	9	0	0

A similar experiment was carried out with sodium chloride. With this material recrystallisation was achieved by addition of 7 *M* hydrochloric acid; the precipitated chloride was filtered, washed with a little hydrochloric acid and dried at 150° C. In this experiment fluoride content was reduced from 16 μg per 50 ml to nil in two recrystallisations.

The use of strong salt solutions results in a uniform suppression of the aluminium - dye step-height and some loss of reproducibility. The effect on the fluoride determination is exactly parallel to the effect observed with aluminium alone. Hence, under the new conditions, the step-height reduction corresponding to 1 μg of fluoride was of the order of one unit, compared with two units in the absence of salt, *i.e.*, in water; the reproducibility of fluoride concentration was then of the order of $\pm$15 per cent., against $\pm$10 per cent. in the absence of salt, for fluoride contents between 0 and 0·5 p.p.m. At these very low levels this was considered satisfactory.

METHOD FOR DETERMINING FLUORIDE IN HYDROCHLORIC ACID

REAGENTS—

The reagents described in Part I[2] with the addition of—

Ammonium chloride—Purify this by recrystallising AnalaR quality ammonium chloride twice from water.

PROCEDURE—

Measure 16 ml of the hydrochloric acid into a 50-ml beaker, place it in a bath of ice, and carefully neutralise the sample with concentrated ammonium hydroxide, with methyl red as indicator. Add 5 *N* perchloric acid dropwise until the pH is 2, as measured with a pH meter, then add 2 ml of 0·1 per cent. v/v acetylacetone and, after stirring well, re-adjust the pH to 7 with ammonium hydroxide. Pour the solution into a 100-ml separating funnel, add 10 ml of redistilled chloroform and shake the funnel vigorously for 2 minutes. Discard the chloroform layer and repeat the extraction three more times. Transfer the water layer to a 50-ml beaker and warm it to remove traces of chloroform. Cool it and add 3 ml of a solution containing 10 μg of aluminium per ml, 1 ml of proteose peptone and 2·5 ml of 2 *N* ammonium acetate. Adjust the pH to 3·9 with perchloric acid and transfer the solution to a 50-ml calibrated flask. Add 2 ml of Solochrome Violet R.S. and mix well. Make the solution up to the mark with water, heat it in a water-bath at 70° $\pm$ 5° C for 5 minutes, and then cool it.

Place about 4 ml of the solution in a polarographic cell, deoxygenate it for 10 minutes and record a polarogram at 25° C on "half voltage" from —0·15 to —0·8 volt, using the

mercury pool as anode. Measure the height, A, of the aluminium - dye complex step, which occurs at $-0{\cdot}32 \pm 0{\cdot}05$ volt.

Determine the height of the aluminium - dye complex step in the absence of fluoride by dissolving 9·2 g of purified ammonium chloride in about 40 ml of warm water, making the solution just alkaline to methyl red with ammonium hydroxide and proceeding as described above with this solution as the neutralised sample. Measure the step-height, B, of the undepressed aluminium - dye complex step. Then—

$$[\mathrm{F}] = K(B - A).$$

Calibrate with known amounts of fluoride in a base solution containing 9·2 g of ammonium chloride per 50 ml.

Experimental

Determination of fluoride in hydrobromic acid—

Application of the technique already used for hydrochloric acid necessitated calibration in the presence of ammonium bromide, and preliminary experiments gave results of an unexpectedly erratic nature; this rendered the method unusable. Examination of the

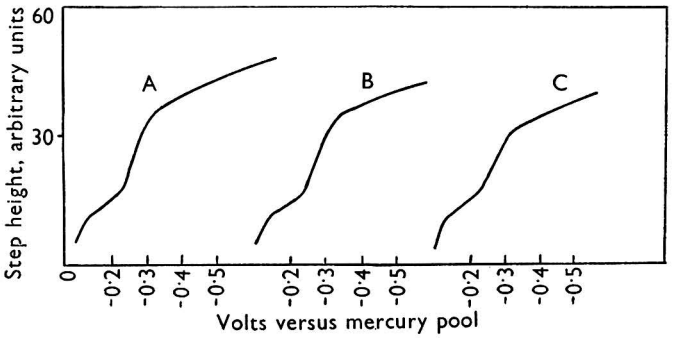

Fig. 1. Calibration for fluoride in ammonium bromide. Curve A, 15 μg of fluoride; curve B, 20 μg of fluoride; curve C, 30 μg of fluoride

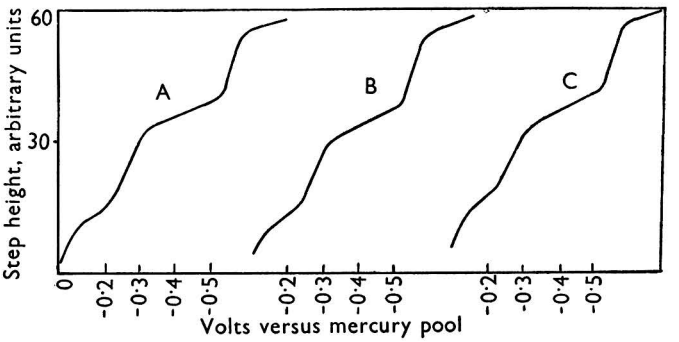

Fig. 2. Calibration for fluoride in ammonium bromide in presence of cadmium. Curve A, 15 μg of fluoride; curve B, 20 μg of fluoride; curve C, 30 μg of fluoride

polarographic traces indicated that the erratic results were due to difficulty in measuring the step-height. This arose from the fact that the top of the polarographic wave was curved and that it did not provide a clear line from which to measure. The introduction of a small amount of cadmium ensured that there was a constant point of inflection in the wave from which measurement could conveniently be made, and with this modification results were satisfactory. Figs. 1 and 2 illustrate typical waves without and with cadmium. It is possible in favourable circumstances to obtain good results without the cadmium, but its presence makes the actual measurement much easier.

Method for determining fluoride in hydrobromic acid

Reagents—

The reagents described in Part I[2] with the addition of—

Ammonium bromide—Purify ammonium bromide of AnalaR quality by recrystallising it twice. Some supplies may not need recrystallising, but new supplies should be tested to see that the untreated material gives the same calibration blank as the recrystallised material.

Cadmium solution, 1 mg per ml—Dissolve 0·25 g of pure cadmium wire in 5 ml of AnalaR quality 16 *N* nitric acid. Evaporate the solution just to dryness, dissolve the residue in 5 ml of AnalaR quality hydrochloric acid and again evaporate it just to dryness. Repeat this evaporation with hydrochloric acid twice. Finally dissolve the residue in water and make the solution up to 250 ml.

Procedure—

Place 3·0 ml of the hydrobromic acid in a 50-ml beaker and neutralise it with 18 *N* ammonium hydroxide, with methyl red as indicator. Dilute the solution to 30 ml and treat it as described in the procedure for hydrochloric acid except that the removal of impurities as their acetylacetonates by chloroform extraction may be omitted and 2 drops of cadmium solution must be added before the solution is heated in a water-bath. The aluminium - dye complex step that is to be measured occurs at $-0{\cdot}30 \pm 0{\cdot}03$ volt and it is followed by that of the cadmium at $-0{\cdot}53 \pm 0{\cdot}02$ volt.

Calibrate the instrument in the presence of known amounts of fluoride, using a 0·2917 g per ml ammonium bromide solution as blank solution.

If the cathode-ray polarograph is used for this determination, cadmium should not be added.

Experimental

Determination of fluoride in bromine—

An obvious method was to convert the bromine to ammonium bromide with ammonium hydroxide and to proceed as described above. However, it was decided first to try a simpler method, which involved placing a small quantity of bromine under a layer of water containing a suitable amount of an aluminium salt, *i.e.*, the amount required in the subsequent polarographic treatment, and carefully evaporating the bromine. It was hoped that by this treatment the fluoride would be trapped in the aluminium solution, which could then be treated in a manner similar to that used for the determination of fluoride in water. This method proved entirely successful.

Method for determining fluoride in bromine

Reagents—

As previously described.[2]

Procedure—

Place 3 ml of the bromine, 15 ml of water and 3 ml of a dilute solution of an aluminium salt (containing 30 μg of aluminium) in a 50-ml beaker fitted with a lifter and a watch-glass. Heat the beaker gently until the solution becomes colourless and then let it cool. Test the solution for the absence of bromine by placing 1 drop on a tile and adding to it 1 drop of a potassium iodide - starch solution. If a blue colour develops, gently boil the solution for 5 minutes and repeat the test. Repeat the heating until the test is negative. Wash the watch-glass, the lifter and the sides of the beaker with a little water and dilute the solution to about 30 ml. Determine the fluoride in the solution as described for the determination of fluoride in water in Part I.[2]

Results

The results obtained by application of the methods described above are shown in Tables II, III and IV. Both the Cambridge photographic and the cathode-ray polarographs were used in this work.

TABLE II

RECOVERY OF FLUORIDE FROM HYDROCHLORIC ACID

Fluoride added, μg	Fluoride found: With Cambridge photographic polarograph, μg	Fluoride found: With cathode-ray polarograph, μg
0	0·0, 0·0, 0·0, 0·0	0·0, 0·0
15	14·5, 14·5, 14·5, 16·0	
20	18·0, 18·0, 23·0, 23·0, 20·0, 20·0, 18·0, 21·0, 18·0, 18·0, 17·0	19·0, 18·0, 18·0, 17·0, 18·0, 21·0
25	25·0, 26·0, 29·0, 27·0, 28·0, 20·0, 20·0	
30	28·0	

TABLE III

RECOVERY OF FLUORIDE FROM HYDROBROMIC ACID

Fluoride added, μg	Fluoride found: With Cambridge photographic polarograph, μg	Fluoride found: With cathode-ray polarograph, μg
0	3·0, 3·0, 4·0, 1·4, 1·4, 3·0, 5·0, 3·0, 5·0, 2·5, 3·0, 4·0, 4·0, 2·0, 3·0	0·0, 0·0
5	10·5, 6·8, 6·8, 7·2, 7·0, 6·4, 6·4, 6·4,	5·0, 5·0
10	14·0, 14·0, 15·0, 10·0, 12·0, 12·0, 8·0, 13·4, 10·6, 12·0, 12·8	10·0, 10·0
15	22·0, 18·0, 18·0, 20·0, 14·0, 14·2	14·0, 14·0
20	21·0, 23·0, 22·0	17·0, 20·0

TABLE IV

RECOVERY OF FLUORIDE FROM BROMINE

Fluoride added, μg	Fluoride found: With Cambridge photographic polarograph, μg	Fluoride found: With cathode-ray polarograph, μg
0	0·0 (nine determinations), 1·0, 0·5, 0·3	0·0, 0·0
5	6·0, 6·0, 6·0, 5·0, 5·0	5·0, 5·0
10	8·0, 11·0, 10·0, 7·0, 7·0, 13·5, 10·0, 9·0, 11·0, 11·0, 10·0, 10·0, 10·0	9·0, 9·0
20	19·0, 19·0, 23·0, 20·0, 17·5, 18·0	

DISCUSSION OF RESULTS

The results are satisfactory, particularly those for hydrochloric acid and for bromine, but for hydrobromic acid there appears to be a factor that causes the spread of results to be rather wide. In general, and particularly with hydrobromic acid, the results with the cathode-ray polarograph appear to be better than those determined with conventional polarographs. Although we have not yet been able to obtain sufficient results with the cathode-ray polarograph to substantiate completely its apparent superiority when these methods are used, it is clear, from practical experience, that the measurement on this instrument of the waves produced is easier and more accurate. It should be noted that different samples of hydrobromic acid were used in the experiments on the photographic and cathode-ray polarographs. It appears that the nature of the hydrobromic acid samples and the shape of the wave produced on the conventional type of polarograph, which make it difficult to measure the wave height even in the presence of cadmium, account for most of the rather wide spread of results with this substance.

That the potentialities of this method for the determination of fluoride have as yet only been touched upon must again be emphasised; ideal conditions have not yet been attained. In the work described here, a small depression of a large wave is measured and all errors are thus greatly enhanced. It seems likely that this fault could be overcome by use of a differential (subtractive) circuit[3] and this method is now being investigated; only when this project is successfully concluded can the full potentialities of the technique be realised.

In conclusion, the authors have to thank the Chief Scientist, Ministry of Supply, for permission to publish this paper, and Mr. A. S. Nickelson for his interest and encouragement.

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NOTE—Reference 2 is to Part I of this series.

CHEMICAL INSPECTORATE
MINISTRY OF SUPPLY
STATION APPROACH BUILDINGS
KIDBROOKE, LONDON, S.E.3

November 2nd, 1953

The Separation and Determination of Gallium

BY G. W. C. MILNER, A. J. WOOD AND J. L. WOODHEAD

From a study of the extractability of the halides of gallium from acid solutions with organic solvents, the chloride was found to be more readily extracted than either the bromide or the iodide. In addition, several organic solvents proved to be as efficient as ether for extracting gallium chloride from solution. Diethyl ether was preferred in the analysis of gallium - uranium mixtures. The extracted gallium was then precipitated with camphoric acid after the solution has been buffered with a formic acid - ammonium formate buffer of pH 3·3, this precipitate being separated by filtration through a sintered-glass crucible, washed, dried and finally weighed. The factor for converting the weight of precipitate to weight of gallium proved to be 0·213. The determination of amounts of extracted gallium less than about 3 mg was more satisfactorily accomplished by a potassium ferrocyanide titration with 3:3′-dimethylnaphthidine as indicator.

GALLIUM readily forms stable complexes that are soluble in organic solvents and can, therefore, be applied to its separation from many other elements. For example, in acid solutions it forms, with cupferron, a complex that is soluble in chloroform. This reaction is not specific, however, as several other elements are also extractable under these conditions, including niobium, titanium, iron, zirconium and so on. The ready solubility of gallium chloride in ether is applicable to the separation of gallium from other constituents in chloride-containing solutions.[1] This latter requirement can lead to some difficulty, however, for if gallium metal is directly attacked with hydrochloric acid, some of the gallium may be lost by evaporation.[2] It is possible to overcome this difficulty by dissolving the metal in sulphuric acid with the minimum of nitric acid and then adding an excess of ammonium chloride to the resulting solution to form the gallium chloride ions. After the extraction with diethyl ether, it is necessary to recover the gallium from the combined diethyl ether extracts and at the same time to separate it from any other elements in solution. In early work, Ato[3,4] used camphoric acid for precipitating gallium from solution, the precipitate being ignited to the oxide. Various objections have been raised, however, to determining gallium via the oxide owing to the very hygroscopic nature of gallium oxide unless ignition has been carried out at a temperature of 1200° C.[2]

In developing procedures for the separation of gallium, many organic solvents were investigated and the experiments were extended to include the extraction of gallium bromide and iodide in addition to gallium chloride. These studies were greatly simplified by the use

of the tracer technique with radioactive gallium. Conditions were also developed for completing the gallium determination without the ignition to the oxide.

Full details of these investigations are included in the experimental section.

Experimental

Development of a procedure for separating the gallium from other constituents—

In these investigations suitable gallium solutions were prepared by dissolving weighed quantities of Specpure gallium metal (approximately 100 mg) in a suitable quantity of nitric acid, then adding 20 ml of sulphuric acid, sp.gr. 1·84, and finally evaporating to fumes of this acid to remove the nitric acid completely. After being cooled, each gallium solution was diluted to 100 ml with water and a weighed amount of ammonium chloride, bromide or iodide was added. Then after the addition of a suitable amount of radioactive gallium, the gallium halide was extracted with two separate 25-ml portions of a conditioned organic solvent, the conditioning being accomplished by shaking the solvent with 100 ml of 20 per cent. v/v sulphuric acid containing the same amount of ammonium halide as was present in the gallium solution. A measure of the amount of gallium transferred to the organic layer was obtained from the decrease of the activity of the aqueous solution caused by the extraction procedure. Results obtained with 20-g quantities of the ammonium halides and a wide range of organic solvents are summarised in Table I.

Table I

Gallium extracted by different solvents in presence of ammonium halides

Solvent	Gallium extracted in presence of Ammonium chloride, %	Ammonium bromide, %	Ammonium iodide, %
Diethyl ether	>99	61	2
*iso*Propyl ether	90	27	—
Dibutyl carbitol	>99	—	—
$\beta\beta$-Dichlorodiethyl ether	92	—	—
Methyl ethyl ketone	>99	—	—
Methyl *iso*butyl ketone	>99	77	28
Methyl propyl ketone	>99	90	38
Amyl alcohol	>99	1·5	—
Ethyl acetate	>99	18	10
Amyl acetate	>99	—	—

The results in Table I show that gallium chloride is more readily extracted by organic solvents than either the bromide or iodide, and they substantiate Irving and Rossotti's[6] earlier findings with diethyl ether. In addition, many other organic solvents are just as efficient for this extraction as diethyl ether, especially the ketones. Subsequent experiments were, therefore, limited to gallium chloride, and the effects of the sulphuric acid content of the solution on the extractability of the gallium were next investigated. These experiments were also limited to only a few of the solvents that from the previous work appeared to be as suitable as diethyl ether. The results are given in Table II.

From Table II it is clear that extraction of gallium with diethyl ether is influenced by the final sulphuric acid concentration, whereas the extractions with the ketones are unaffected. The effect of the final concentration of ammonium chloride on the extraction of gallium from 20 per cent. v/v sulphuric acid solutions was next investigated. Again, only a few selected solvents were used and the results in Table III show that methyl ethyl ketone is less influenced by a decrease in the ammonium chloride concentration than the other solvents.

From the results of the above experiments it is clear that certain ketones are as efficient as diethyl ether for the quantitative extraction of gallium chloride and are less affected by variations in the solution conditions. On the basis of experience with the separation of gallium from solutions containing uranium, however, the ketone extractions are not quite as selective as the diethyl ether extraction. In the analysis of uranium - gallium mixtures, about five times as much uranium contaminated the gallium extracted by ketones as compared with the contamination from the diethyl ether extractions, the amount of uranium co-extracted by the ether being generally less than 1 mg from a 2-g sample. Consequently

extractions with diethyl ether were found to be more suitable in the analysis of these particular mixtures.

TABLE II

GALLIUM EXTRACTED FROM 100 ml OF SOLUTION CONTAINING 100 mg OF GALLIUM, 20 g OF AMMONIUM CHLORIDE AND VARIOUS AMOUNTS OF SULPHURIC ACID, SP.GR. 1·84

Solvent	Gallium extracted in presence of 20 ml of H_2SO_4, %	15 ml of H_2SO_4, %	10 ml of H_2SO_4, %
Diethyl ether	>99	85	34
Methyl ethyl ketone	>99	>99	>99
Methyl propyl ketone	>99	>99	>99

TABLE III

GALLIUM EXTRACTED BY VARIOUS SOLVENTS FROM 100 ml OF 20 PER CENT. v/v SULPHURIC ACID SOLUTION CONTAINING APPROXIMATELY 100 mg OF GALLIUM AND VARIOUS AMOUNTS OF AMMONIUM CHLORIDE

Solvent	Gallium extracted in presence of 15 g of NH_4Cl, %	10 g of NH_4Cl, %	5 g of NH_4Cl, %
Diethyl ether	93	24	—
Methyl *iso*butyl ketone	>99	98·5	71
Methyl ethyl ketone	>99	>99	>99
Methyl propyl ketone	>99	>99	80

METHOD

PROCEDURE—

Transfer 2 g of the sample to a 650-ml conical beaker, add to it 25 ml of nitric acid, sp.gr. 1·42, and heat the beaker gently to obtain complete solution. Then add 20 ml of sulphuric acid, sp.gr. 1·84, and cautiously evaporate to fumes of this acid. After cooling, transfer this solution to a 100-ml calibrated flask and dilute it to the mark with water. With a pipette, place a suitable aliquot (Note 1) of this solution in a 250-ml beaker, dilute it to 100 ml with 20 per cent. v/v sulphuric acid and dissolve 20 g of ammonium chloride in this solution. Transfer the solution to a 250-ml separating funnel, using not more than 10 ml of water to wash the beaker. Add 50 ml of conditioned diethyl ether (Note 2), stopper the funnel and shake it well for 30 seconds (Note 3). Transfer the aqueous layer to another 250-ml separating funnel and add a further 50 ml of diethyl ether. Shake well for 30 seconds and transfer the aqueous layer to a third separating funnel. Repeat the extraction with a third 50-ml portion of diethyl ether and then combine all the diethyl ether extracts in the first separating funnel. Wash the combined extracts with 10 ml of the 20 per cent. v/v sulphuric acid - 20 per cent. ammonium chloride solution used for conditioning the diethyl ether and reserve them for the determination of the gallium concentration.

NOTES—

1. Take an aliquot of sample solution according to the gallium content—

Gallium	Aliquot taken, ml
1 to 5 per cent.	100
5 to 10 per cent.	50
10 to 20 per cent.	25
20 to 80 per cent.	10

2. Condition the diethyl ether by shaking 100-ml portions with 100 ml of 20 per cent. v/v H_2SO_4 containing 20 g of ammonium chloride.
3. Care must be taken to release the pressure frequently by removing the stopper.

EXPERIMENTAL

DEVELOPMENT OF SUITABLE PROCEDURES FOR DETERMINING THE EXTRACTED GALLIUM—

After the separation of the gallium from the diethyl ether extracts either by evaporation or by re-extraction into water, it is necessary to determine the gallium concentration by

some convenient procedure. Ato used the insoluble complex, $Ga_2[C_8H_{14}(CO_2)_2]_3$, produced from gallium and camphoric acid, for separating the gallium from solution before completing the determination by igniting the precipitate to gallium oxide. This type of procedure is not very satisfactory, however, unless the precipitate is ignited at a temperature of 1200° C, as gallium oxide residues produced by ignitions at lower temperatures are very hygroscopic. The ignition of gallium camphorate to gallium oxide is therefore to be avoided, if possible, and we attempted to complete the determination by weighing the gallium camphorate directly after filtration and drying.

In the preliminary experiments some difficulty was encountered in attaining the complete precipitation of gallium under Ato's conditions. This discrepancy was traced to lack of control of the pH of the solution at the precipitation stage, and an investigation into the influence of pH by use of buffers prepared from molar solutions of sodium acetate and acetic acid showed that precipitation of gallium camphorate was complete over the pH range from 3·1 to 4·0 (see Fig. 1). Attempts to separate the precipitates produced under

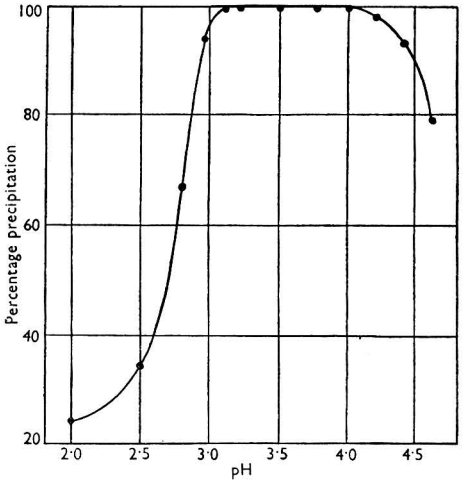

Fig. 1. The effect of pH on the precipitation of gallium camphorate from acetic acid - sodium acetate buffers

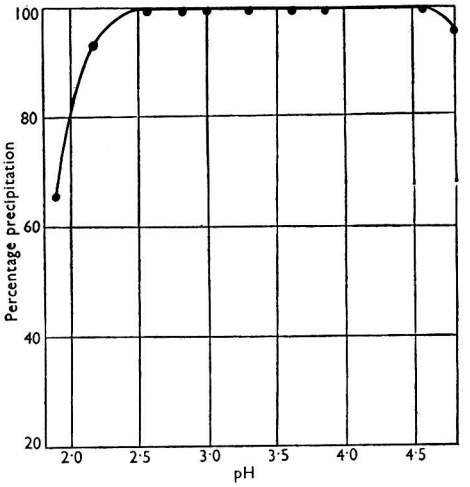

Fig. 2. The effect of pH on the precipitation of gallium camphorate from formic acid - sodium formate buffers

these conditions by filtration through sintered-glass crucibles failed completely, even No. 4 porosity sinters failing to retain the precipitates quantitatively. The replacement of the acetate buffer with a sodium formate - formic acid buffer resulted in better-crystallised gallium camphorate precipitates, which were readily separated by filtration through sintered-glass crucibles. Under these conditions precipitation of the gallium was complete over the pH range from 2·5 to 4·5 (see Fig. 2), and hot water proved to be the most suitable wash solution for this type of precipitate. The gallium camphorate precipitates were always contaminated with sodium salts even after thorough washing. This difficulty was overcome by precipitating the gallium camphorate from a buffer solution of pH 3·3 prepared from molar solutions of formic acid and ammonium formate. Under these conditions the weight of the final camphorate precipitate bore some relation to the weight of the gallium initially taken (see Table IV, columns 1 and 2). As ferric chloride is also extractable by diethyl ether, it is possible for the gallium solutions produced from the diethyl ether extracts to contain ferric iron. The pH of the final formate solution for the precipitation of gallium camphorate is, however, suitable for the reduction of the iron to the ferrous state with hydroxylamine hydrochloride and after this treatment the gallium camphorate precipitates were found to be free from interference by iron.

Method

Procedure—

Transfer the diethyl ether extracts to a 400-ml squat-type beaker. Wash the separating funnels with 25 ml of 20 per cent. v/v sulphuric acid and add it to the beaker. Remove the diethyl ether by evaporation on a water-bath. Cool the solution, transfer it to a 50-ml

calibrated flask and dilute it to the mark with water. With a pipette, place a suitable aliquot containing up to about 50 mg of gallium in a 650-ml conical beaker and add 3 drops of thymol blue indicator. Adjust the solution to pH 2·8 by the dropwise addition of approximately 8 *N* ammonium hydroxide solution, the indicator changing colour from red to yellow. Add 25 ml of a formate buffer solution prepared by mixing 100 ml of *M* formic acid with 50 ml of *M* ammonium formate. Also add 1 g of hydroxylamine hydrochloride, 200 ml of water and 50 ml of boiling formate buffer solution containing 1 g of camphoric acid. Boil the resulting solution for 2 minutes and leave it warm for 1 hour to digest. Filter it through a tared No. 4 sintered-glass crucible and wash the precipitate thoroughly with hot water. Dry at 110° C and weigh the crucible and contents. Use the factor 0·213 for converting gallium camphorate to gallium.

RESULTS WITH THIS PROCEDURE—

The usual factor for converting gallium camphorate, $Ga_2[C_8H_{14}(CO_2)_2]_3$, to gallium is 0·189. But, on applying this factor to the weights of camphorate precipitate in column 2 of Table IV, the recoveries for gallium were consistently low (see column 3). These low recoveries were rather inexplicable and the applicability of this factor under these new conditions was therefore checked by igniting weighed amounts of the camphorate precipitate to gallium oxide, Ga_2O_3, in platinum dishes at very high temperature and then re-weighing after cooling. The results from three separate experiments are given in Table V and show that the factor under these conditions should be 0·213. When this factor was applied to the results in Table IV, the figures for recovery of the gallium were good (see column 4).

TABLE IV

RECOVERIES OF GALLIUM AFTER PRECIPITATION AS GALLIUM CAMPHORATE

Weight of gallium taken, mg	Weight of camphorate, mg	Weight of gallium recovered, mg	
		Factor 0·189	Factor 0·213
2·5	11·7	2·2	2·5
5·0	23·5	4·4	5·0
7·5	36·1	6·8	7·7
10·0	47·1	8·9	10·0
20·0	95·0	17·5	20·2
30·0	143·5	27·1	30·6
40·0	190·7	36·1	40·6
50·0	235·2	44·4	50·0

TABLE V

DETERMINATION OF THE FACTOR FOR CONVERTING GALLIUM CAMPHORATE TO GALLIUM

Weight of gallium camphorate, g	Weight of Ga_2O_3, g	Weight of gallium, g	Factor
0·2909	0·0834	0·0620	0·214
0·2855	0·0822	0·0611	0·214
0·2941	0·0840	0·0624	0·212

The factor 0·213 was confirmed by the examination of a thermolysis curve determined for the camphorate precipitate. This curve (Fig. 3) also showed that the composition of the camphorate was retained for temperatures up to 135° C and that it was completely converted to Ga_2O_3 at 450° C. The gallium precipitate from the formate solution must therefore have a composition different from that corresponding to the formula $Ga_2[C_8H_{14}(CO_2)_2]_3$. The analysis of typical specimens of the camphorate precipitate produced under the above conditions gave the following percentage composition: Ga, 21·3; C, 43·3; H, 5·46; O, 29·94 (by difference). The empirical formula corresponding to this composition is $GaC_{12}H_{18}O_6$, but so far the exact structural formula for this precipitate has not been established.

Typical results obtained on applying the diethyl ether extraction followed by the camphorate precipitation to the analysis of gallium - uranium mixtures are shown in Table VI.

TABLE VI

THE ANALYSIS OF GALLIUM - URANIUM MIXTURES

Nominal gallium content, %	Percentage gallium	Composition uranium*	Impurities	Total
75	74·6	24·6	0·03	99·23
50	53·2	46·6	0·01	99·9
10	11·45	87·75	†	99·2
1	1·23	98·5	0·07	99·8

* The uranium was precipitated as ammonium diuranate and ignited to U_3O_8.[5]
† Not determined.

The determination of the smaller amounts of gallium was better accomplished by the potassium ferrocyanide titration, with 3:3′-dimethylnaphthidine as indicator. Belcher[6] first used this indicator in the direct determination of small amounts of gallium in organic com-

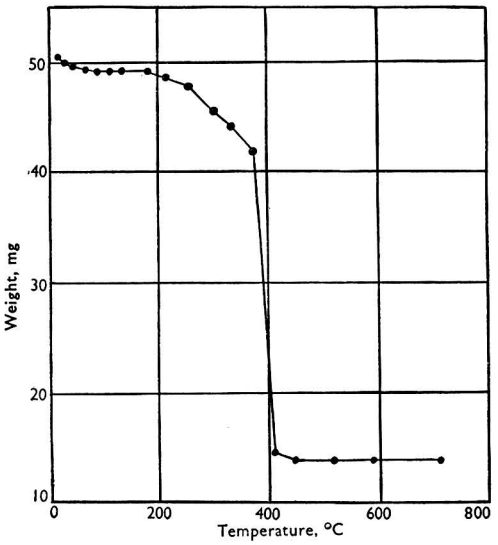

Fig. 3. Thermolysis of gallium camphorate

pounds. After the extraction of gallium with diethyl ether, however, the conditions of the resultant gallium solution differed considerably from those recommended by Belcher for the ferrocyanide titration. When known amounts of gallium were taken through such a procedure, the recoveries were always low owing to the difficulty of detecting the end-point of the titration. The titration conditions were therefore investigated. The influence of the pH value on the titration of 1·47 mg of gallium is shown in Fig. 4, the optimum pH range for complete recovery being from pH 2·2 to 2·5. Known amounts of gallium were next taken through the diethyl ether extraction procedure and the pH values of the resultant aqueous solutions were adjusted to the optimum pH range each time before the ferrocyanide titration. The gallium recoveries were good under these conditions for concentrations from about 0·3 to 3·6 mg of gallium, as shown by the results in Table VII.

It was noticed that the titration end-point progressively became more indeterminate for amounts of gallium greater than 2 mg owing to the rapid re-oxidation of the indicator. The addition of a larger volume of absolute ethanol was found to suppress this effect, and the end-point was fairly sharp when 15 ml of ethanol were used, the end-point being reached when the red colour of the indicator did not return for about 5 seconds. No interference was

encountered in the determination of gallium by the complete procedure of ether extraction followed by titration, from similar amounts of uranium, iron, vanadium, copper, zinc, cadmium, lead and aluminium. Details of the titration are as follows.

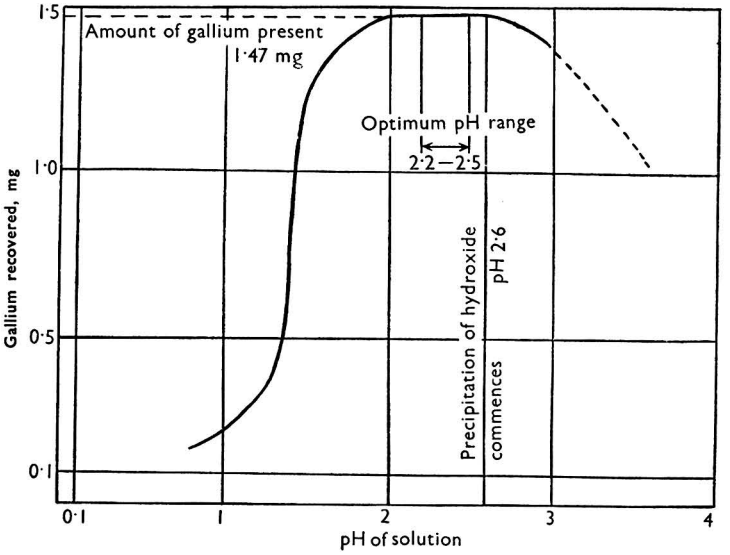

Fig. 4. The effect of pH on the titration of gallium chloride with potassium ferrocyanide

TABLE VII

RECOVERY OF KNOWN AMOUNTS OF GALLIUM

Gallium taken, mg	Gallium recovered, mg	Error, %
0·307	0·305	−0·6
0·735	0·735	nil
1·105	1·108	+0·3
1·44	1·44	nil
1·83	1·82	−0·5
2·17	2·20	+1·3
2·51	2·56	+2·0
2·87	2·90	+1·0
3·59	3·57	−1·0

REAGENTS—

Potassium ferrocyanide, 0·0075 M—Dissolve 3·167 g of AnalaR potassium ferrocyanide in 1 litre of distilled water containing 0·2 g of sodium carbonate. Standardise the solution against a pure zinc solution with 3:3′-dimethylnaphthidine as indicator.

1 ml of 0·0075 *M* $K_4Fe(CN)_6 \equiv$ 0·6972 mg of gallium.

Potassium ferricyanide, 0·5 *per cent. w/v*—Dissolve 0·5 g of potassium ferricyanide in 100 ml of distilled water and store the solution in a dark bottle. Prepare a fresh solution daily.

3:3′-*Dimethylnaphthidine*—Dissolve 0·200 g of 3:3′-dimethylnaphthidine in 100 ml of ethanol.

PROCEDURE FOR DETERMINING GALLIUM—

Take the aqueous gallium solution (volume about 30 ml) obtained from the combined diethyl ether extracts and adjust its pH to a value of 2·3, with the aid of a pH meter, by the addition of ammonium hydroxide. Transfer the solution to a 100-ml titration flask and rinse the beaker with two separate 7·5-ml portions of ethanol. Add 1 drop of the potassium ferricyanide solution, 2 drops of indicator solution and then titrate by adding the standard ferrocyanide solution from a 5-ml burette. Titrate rapidly until the red colour of the indicator

begins to fade and then dropwise until a pale green colour persists for 5 seconds whilst the solution is being shaken. Carry out a blank titration on the reagents. Calculate the gallium concentration in milligrams from the expression (sample titre — blank titre) × 0·6972 × molarity of ferrocyanide/0·0075.

PROCEDURE FOR STANDARDISATION OF POTASSIUM FERROCYANIDE SOLUTION—

Prepare a standard zinc solution by dissolving 3·269 g of Specpure zinc metal in 15 ml of hydrochloric acid, sp.gr. 1·16. Then to it add 100 ml of diluted sulphuric acid (1 + 1) and evaporate to fumes of this acid. Accurately dilute this solution to a volume of 1 litre with water and mix it thoroughly. With a pipette, place 100 ml of this solution in a 500-ml calibrated flask and dilute it to the mark with water.

Transfer 20 ml of the zinc solution to a titration flask and make it up to 50 ml with water. Add 2·5 ml of 10 per cent. ammonium sulphate solution, 4 drops of 0·5 per cent. potassium ferricyanide and 2 drops of the indicator solution prepared by dissolving 50 mg of 3:3′-dimethylnaphthidine in 10 ml of glacial acetic acid. Rapidly add the potassium ferrocyanide solution to give an excess of about 25 per cent. (normally about 25 ml). Shake the solution and leave it to stand in the dark for not less than 5 minutes. Titrate the excess of ferrocyanide with the standard zinc solution, the end-point being marked by the first permanent pink coloration. Calculate the molarity of the ferrocyanide solution from the expression—

$$\frac{\text{total volume of zinc solution (ml)} \times 0{\cdot}0006538 \times 2000}{\text{volume of ferrocyanide solution (ml)} \times 3 \times 65{\cdot}38}.$$

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The Spectrophotometric Determination of Magnesium with Thiazol Yellow Dyes

By T. A. MITCHELL

A critical examination of the thiazol yellow method for the colorimetric determination of magnesium has shown the following. (*i*) The fading of the thiazol yellow - magnesium hydroxide complex is caused by "ageing" of the magnesium hydroxide. This change in the structure of the colloid, which takes place both in the presence and in the absence of thiazol yellow, is inhibited by the addition of glycerol and concentrated sodium hydroxide. (*ii*) The solubility of magnesium hydroxide and hence of the coloured complex is greatly increased by the colloid protectors, starch and polyvinyl alcohol. Starch, however, is preferable to polyvinyl alcohol for this purpose, because, unlike the alcohol, it does not itself affect the colour of the dye or dye-complex. (*iii*) Numerous cations and organic compounds interfere, and neither their removal by precipitation nor the use of "compensating solutions" satisfactorily controls this effect.

A method is accordingly proposed in which the magnesium is precipitated from solution as magnesium ammonium phosphate, the precipitate is redissolved and the colorimetric determination is carried out on the resulting solution, starch being used as the protective colloid and glycerol as the colour stabiliser. The absorptions of the solutions are measured at a fixed brief interval after colour development.

When sodium hydroxide solution is added to a dilute solution of a magnesium salt in the presence of certain yellow thiazol dyestuffs, a red coloration, related in intensity to the magnesium concentration, is produced. The object of the investigation reported in this paper was to develop a reliable general photometric procedure for determining magnesium by this reaction, and to apply the method to the estimation of magnesium in plant and soil extracts. Since Kolthoff's discovery of the reaction in 1927, numerous papers describing its use in the colorimetric estimation of magnesium have appeared in the literature, and the following facts are now well established—

(1) Numerous other substances give the same colour change as magnesium under the same conditions.[1,2]

(2) Certain metal ions and organic compounds in solution alter the intensity of the colour due to magnesium.[1,3,4,5,6,7,8,9,10,11]

(3) At concentrations of magnesium above 3 μg per ml a precipitate rapidly settles from the test solution.[3,12]

(4) The coloured complex is not stable and a decrease in colour intensity occurs with time.[3,4,12]

Many methods for eliminating or standardising these effects have been proposed. Among those for dealing with interfering substances are—

(*a*) Their removal from solution by precipitation (calcium as oxalate,[4] iron and aluminium as phosphates[13] or hydroxides,[6,11,14] and phosphate as the uranyl salt[15]), ignition (ammonium ion[13,14]) and separation as complexes (iron, aluminium, manganese, copper, titanium and vanadium as acetylacetonates[16]).

(*b*) Standardisation of their effects by the use of "compensating solutions."[5,7,8,10,11] This involves the addition of fixed amounts of the various ions to each test solution; it is assumed that the effects of these ions are constant when they are present at more than a certain concentration.

(*c*) Suppression of their effects by formation of complexes in the test solution. Thus cyanide[1,9,17] reduces interference by copper, cobalt, nickel, zinc, cadmium and mercuric ions, hydroxylamine has been used to prevent manganese interference and sucrose to reduce that of calcium.

To prevent the precipitation of the magnesium hydroxide - dye complex, protective colloids, such as starches,[5,8,12,15] dextrins,[15] gums,[4] agar,[18] polyvinyl alcohol[10] and a number

of commercial polymers, have been recommended, while additions of hydroxylamine hydrochloride[3] and glycerol[14] have been claimed to reduce or prevent fading of the colour.

However, in this laboratory, analyses of plant extracts by a variety of the published procedures, which incorporate these refinements, have given results that were generally unreliable. Therefore, the reaction itself, factors affecting the production of stable and reproducible coloured solutions, and methods for eliminating interferences have been investigated, and the proposed method is based on the findings from these experiments.

Method

Apparatus—

Coleman model 14 spectrophotometer with matched 13-mm square cuvettes.

Capillary tube of 1 mm bore, bent back along its own length by 1 to 2 mm.

Reagents—

Ammonium chloride—Dissolve 50 g of ammonium chloride in distilled water and dilute to 1 litre.

Ammonium oxalate—Dissolve 10 g of crystalline ammonium oxalate in distilled water and dilute to 1 litre.

Citrate - phosphate reagent—Dissolve 5 g of sodium citrate dihydrate and 25 g of ammonium dihydrogen phosphate in distilled water and dilute to 1 litre.

Acetic acid—Dilute 60 ml of glacial acetic acid to 1 litre with distilled water.

Ammonium hydroxide—Concentrated and 0·1 *N*.

Sodium hydroxide, 3 N.

Thiazol yellow (General Aniline Works, Rensselaer, N.Y., or Antara Products, N.Y.)—Dissolve 0·10 g of the solid in water and dilute to 100 ml. This stock solution keeps indefinitely if stored away from light.

Soluble starch—Mix 2·5 g of analytical-reagent grade starch to a paste with water, add 80 ml of boiling water, boil for 2 minutes, filter and, when cold, make up to 100 ml. This solution should be prepared every 2 or 3 days.

Dye - stabiliser reagent—Mix together 50 ml of glycerol, 50 ml of soluble starch solution and 15 ml of the thiazol yellow solution. Dilute to 500 ml. This solution must be prepared daily.

Magnesium standards—Dissolve 1·230 g of magnesium sulphate, $MgSO_4.7H_2O$, in water and dilute to 1 litre. This solution contains 120 μg of magnesium per ml, and is diluted to give standards of 90, 60 and 30 μg of magnesium per ml.

Procedure—

Into a 15-ml tapered centrifuge tube put, from a pipette, an aliquot of the solution to be analysed, containing between 15 and 120 μg of magnesium. From micro-burettes add 0·1 *N* ammonium hydroxide to bring the pH to between 4 and 6 and water to make the volume of solution in the tube to a total of 2 ml. (The amount of ammonium hydroxide is determined, for a particular series of samples, by titrating an aliquot of one of them against the 0·1 *N* ammonium hydroxide, methyl red being used as indicator.) Next add 1 ml of ammonium chloride solution and then 1 ml of ammonium oxalate reagent. Set the tube aside for 10 minutes, then centrifuge it for 5 minutes at 3000 r.p.m. at a radius of 15 cm and take 3 ml of the supernatant liquid by pipette and put it in a second centrifuge tube.

To this tube add 2 ml of the citrate - phosphate reagent and 2 ml of concentrated ammonium hydroxide. Set this aside overnight, then centrifuge it for 5 minutes and, by means of the bent capillary tube, draw off as much of the supernatant liquid as possible without disturbing the magnesium ammonium phosphate precipitate. Without washing it, dissolve the precipitate in 1 ml of 6 per cent. acetic acid, and add 8 ml of the dye-stabiliser reagent and 1 ml of 3 *N* sodium hydroxide. Mix the solution, set it aside for 1 minute, and then transfer it to a spectrophotometer cuvette and measure the optical density at 520 mμ against a reference cell containing distilled water.

Construct a calibration graph relating optical density to concentration by using solutions containing 0, 30, 60, 90 and 120 μg of magnesium, prepared by the same method and at the same time as the test samples. A uniform variation in the optical density values of the standards of up to $\pm$2·5 per cent. occurs from day to day.

Discussion of results

Fading—The rapid decrease in intensity of the red colour of the magnesium hydroxide - dye complex, on standing, was again confirmed. Investigation showed the effect to be associated with an "ageing" of the magnesium hydroxide. The change responsible for fading starts as soon as the magnesium hydroxide is formed in solution and is independent of the presence or absence of the dye or complex. A number of substances were found to inhibit the fading. They included sodium hydroxide in high concentrations (about 1·25 *N* in the final solution), polyvinyl alcohol, and calcium ion at a specific concentration of 125 μg per ml of the final solution. Hydroxylamine[3] was without effect, but glycerol[14] showed pronounced effects. As, however, calcium and polyvinyl alcohol have other undesirable

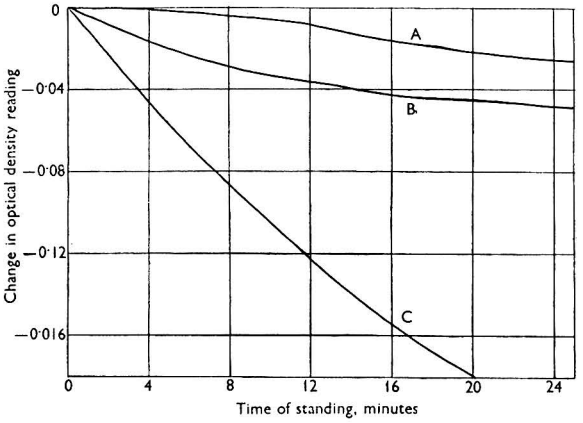

Fig. 1. Fading of solutions containing 120 μg of magnesium, 0·0025 per cent. w/v of thiazol yellow and 0·2 per cent. w/v of starch in addition to the following: curve A, 1·25 *N* sodium hydroxide; curve B, 8 per cent. v/v of glycerol and 0·4 *N* sodium hydroxide; curve C, 0·4 *N* sodium hydroxide. The solutions were prepared by mixing solutions of the reagents to give the concentrations required

properties, their use as colour stabilisers is not recommended. Increased concentrations of sodium hydroxide reduce the range of the optical density measurements, so that the use of glycerol and moderate concentrations of sodium hydroxide was considered the most practical compromise. In addition, measurement of each solution at a fixed interval (between 1 and 2 minutes) after colour development gave results of improved consistency and accuracy.

Protective colloids—As magnesium has been shown to be present in some samples of gum arabic, tragacanth and agar,[15] work on protective colloids was confined to analytical-reagent grade soluble starch and polyvinyl alcohol. Both protected the colloidal complex adequately, but starch was preferred because it has no other effect on the coloured solution. Polyvinyl alcohol itself reddened the dye, and though it also increased the ability of magnesium hydroxide to redden it, the resultant effect was a marked reduction in the range of optical density measurements. The soluble starch used (Baker's C.P. Analysed "Lintner," 0·2 per cent. w/v) increased the "solubility" of magnesium hydroxide from 7 or 8 μg per ml to 275 to 300 μg per ml. This increased value, measured turbidimetrically on a series of solutions ranging in concentration from 0 to 900 μg of magnesium hydroxide per ml, was confirmed by estimating the residual magnesium hydroxide left after centrifuging to remove the precipitate formed on the addition of sodium hydroxide to a solution of starch and magnesium ion (600 μg per ml). As the sensitive range of the method described in this paper is 0 to 25 μg of magnesium hydroxide (0 to 10 μg of magnesium) per ml, this starch clearly gives adequate protection. It must be remembered, however, that the protective abilities of starches vary greatly, depending on their original source and subsequent preparation.[19] Anomalous results may therefore occur unless a good grade of soluble starch is used. The opalescence that forms in a starch solution after a few hours is no objection to its use, as it is completely dispersed when the concentrated sodium hydroxide is added.

Dyestuff—A number of commercial thiazol dyes, Titan Yellow, Clayton Yellow, Thiazol Yellow, Mimosa and Chlorazol Yellow, have been used for the determination of magnesium.

These vary somewhat in constitution according to the source and the mode of preparation, and show marked differences in sensitivity.[20]

Interferences—Routine determinations of magnesium are generally required for materials containing substances capable of interfering with the determinations. In the present work the marked effects of small concentrations (25 μg per ml of test solution) of copper, manganese, cobalt, nickel, iron, zinc and especially aluminium were again demonstrated. The effect of calcium was irregular, both intensification and reduction of the magnesium hydroxide - thiazol yellow colour being observed. The effect was dependent on the concentrations of magnesium and calcium in solution and varied with temperature. Where calcium caused a reduction in intensity, it was followed, when the solution was set aside, by a gradual increase. For all the elements examined the effects increased markedly with concentration, and no maximum was ever observed. It was considered, therefore, that "compensating solutions" could effect no practical control of interferences. In addition to the effects of metal cations,

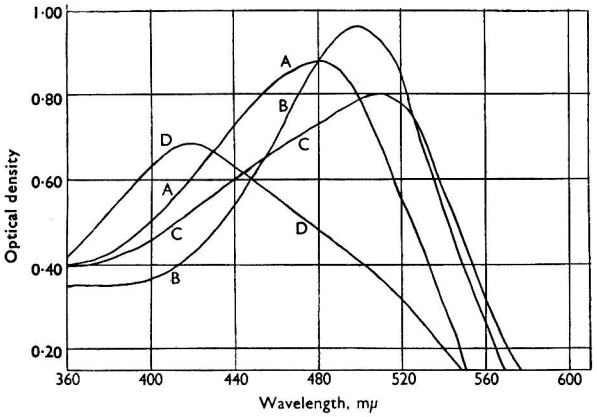

Fig. 2. Absorption spectra of solutions containing 0·0025 per cent. w/v of thiazol yellow, 0·2 per cent. w/v of starch and 0·25 *N* sodium hydroxide in addition to the following: curve A, 10 per cent. v/v of ethanol; curve B, 0·2 per cent. w/v of polyvinyl alcohol; curve C, 120 μg of magnesium; curve D, no additional reagent

the interference by many organic compounds was studied, and it was confirmed that small amounts of citrate ion (10 to 50 μg per ml of test solution) and tartrate ion suppress colour formation. An examination, by the method of Natelson, Pincus and Lugovoy,[21] of the citrate content of extracts of fresh plant tissue in 2 per cent. acetic acid showed it to be appreciable in many instances, and sufficient to cause large errors (50 per cent. and greater) in the magnesium determination. Absorption curves plotted for solutions containing 0·2 per cent. w/v of starch, 0·0025 per cent. w/v of thiazol yellow, 0·25 *N* sodium hydroxide and various alcohols showed that alcohols also redden the dye (see Fig. 2). The use of ethanol as a dye solvent[3,10,18] is therefore inadvisable. Because the dye and complex are so sensitive to the presence of other compounds, it was considered essential to separate the magnesium from all interfering substances before proceeding with the colorimetric determination. Earlier methods involving purification by precipitation of these substances are frequently time-consuming, only specific substances are removed, and magnesium may be lost in the precipitate. Precipitation of the magnesium itself, as magnesium ammonium phosphate, was therefore tried. Preliminary trials showed that large amounts of phosphate and ammonium ion (100 and 200 μg, respectively, per ml of the final solution) did not affect the colorimetric determinations, nor was there any effect when these amounts were combined in one solution. Calcium, ferric iron, aluminium and manganese also give precipitates with phosphate and concentrated ammonium hydroxide. Calcium was therefore removed as oxalate, and iron and aluminium were held in solution with citrate. No simple convenient control for manganese was found, but a minimum amount of 50 μg in the aliquot of solution taken is necessary to cause appreciable interference.

Accuracy

The addition, individually, of 2500 μg of calcium or 1000 μg each of aluminium, copper, cobalt, nickel, zinc or ferric iron to standards containing 0, 30, 60, 90 and 120 μg of magnesium gave results which did not differ significantly from those with the pure standards.

Up to 50 μg of manganese did not interfere, but above that level considerable increases in colour intensity occurred.

From a bulk plant-ash extract, in 0·1 *N* hydrochloric acid, containing 116 μg of magnesium per ml (determined gravimetrically as pyrophosphate), ten solutions were prepared, ranging in strength from 0·1 to the full strength of the original solution. Magnesium was determined in each of these ten solutions 10 times, and the results are shown in Table I. Spectrographic analysis showed the following major elements to be present also: calcium, 633 μg per ml; potassium, 1280 μg per ml; manganese, 3·0 μg per ml; sodium, 117 μg per ml; magnesium determined spectrographically was 111 μg per ml. At all levels there was good agreement with the gravimetric figure.

Table I

Results of replicate determinations of ten solutions prepared by diluting a solution of known strength

Dilution	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
Magnesium found, μg per ml	12·0	25	35	47	59	68	83	90	104	117
	11·5	26	34	47	61	74	82	87	108	120
	11·0	26	34	49	59	70	83	87	105	112
	11·0	21	35	47	59	69	78	97	107	119
	13·0	22	35	50	60	69	80	94	104	114
	11·5	22	34	47	61	72	78	97	104	116
	12·0	21	37	47	60	72	79	95	104	117
	12·0	21	35	47	61	72	79	95	108	117
	11·5	22	36	48	63	69	81	89	107	117
	12·0	23	35	48	60	67	80	89	107	118
Mean	11·8	23	35	48	60	70	80	92	106	117
Concentration found for original solution, μg per ml	118	115	117	119	120	117	115	115	118	117
Standard deviation	1·2	3·5	1·6	1·9	2·2	3·8	3·3	6·9	3·0	4·0

A series of extracts of fresh plant tissue in 2 per cent. w/v acetic acid were analysed with and without additions of known amounts of magnesium, with the results shown in Table II. Recoveries ranged from 93 to 107 per cent. and averaged 101 per cent.

Table II

Recoveries of magnesium added to plant extracts

Material	Magnesium originally found, μg	Magnesium added, μg	Total magnesium found, μg	Difference, μg	Recovery, %
Tomato petiole	63	30	95	32	107
Cauliflower leaf	30	30	61	31	103
Cauliflower leaf	57	45	102	45	100
Cauliflower petiole	55	30	85	30	100
Cauliflower petiole	51	45	96	45	100
Cauliflower petiole	63	60	123	60	100
Cabbage petiole	73	45	115	42	93
Cabbage petiole	43	60	105	62	103
Cabbage petiole	45	60	105	60	100
Ryegrass leaf	61	60	122	61	102
Ryegrass leaf	51	60	112	61	102
Ryegrass leaf	57	60	120	63	105
Clover petiole	44	45	89	45	100
Clover petiole	48	60	108	60	100

The author wishes to thank Mr. J. E. Allan for the spectrographic analysis.

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DEPARTMENT OF AGRICULTURE
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The Determination of O:O-Diethyl O-*p*-Nitrophenyl Thiophosphate Residues in Tomatoes

BY R. BUCKLEY AND J. P. COLTHURST

A method is described for the separation and colorimetric determination of parathion residues in tomatoes. Residues on the surface are removed by washing the fruit with alcohol, plant pigments are oxidised with hydrogen peroxide and the parathion is hydrolysed to *p*-nitrophenol, which is determined colorimetrically. Residues in the whole fruit are determined by extraction of the macerated tomato with *n*-hexane, removal of plant pigments by oxidation and extraction, and colorimetric determination of *p*-nitrophenol after hydrolysis.

SEVERAL papers have been published on the determination of traces of the insecticide O:O-diethyl O-*p*-nitrophenyl thiophosphate, known generally as parathion. Averell and Norris[1] reduced it to the corresponding amine, which was diazotised and coupled with N-(1-naphthyl)ethylenediamine dihydrochloride to yield an intense magenta colour. The method has been used extensively in America.[2] It is very sensitive, but a great number of compounds give the same reaction and the danger of error from contamination is increased.[3,4] The method of Gage[5,6] is similar in principle, but we have found it very sensitive to the presence of inhibitors in some grades of toluene. Even when this difficulty was overcome, the results were variable with tomato pulp containing known added amounts of parathion.

Ketelaar and Hellingman[7] describe a method for the analysis of parathion and parathion formulations; this consists in a colorimetric determination of *p*-nitrophenol after alkaline hydrolysis. This, the simplest colorimetric method, was used throughout the work described in this paper.

Preliminary tests were confined to the determination of parathion on the surface of sprayed tomatoes.

The fruit was washed with ethanol and the washings were hydrolysed with sodium hydroxide. Alkali produces a bright yellow colour with the plant pigments present, but

this colour can be destroyed by hydrogen peroxide, after which the *p*-nitrophenol can be determined colorimetrically.

A method was also worked out for determining the total parathion residue in the whole fruit. Extraction of tomato pulp with organic solvents removes too much pigment to be readily oxidised by hydrogen peroxide. The remaining pigment is removed from the alkaline aqueous solution by ether extraction.

Experimental

When Gage's method was applied to parathion residues in tomatoes, the results were unsatisfactory. A known amount of parathion was added to 100 g of macerated tomato contained in a conical flask. The pulp was shaken with 200 ml of *n*-hexane and allowed to stand overnight. The *n*-hexane was decanted and an aliquot was taken for parathion determination. After the *n*-hexane had been removed by distillation under reduced pressure, the parathion was determined as described by Gage. As Table I shows, the recovery was very poor at low levels, but increased steadily with increased parathion content. No further work was done on this method.

Table I

Recovery of parathion by Gage's method

Parathion added, μg	Volume of hexane recovered, ml	Parathion (from graph), μg	Parathion (corrected), μg	Recovery, %
27	140	5	7	27
114	170	46	54	48
228	130	141	217	95

Method for the determination of surface residue

Reagents—

All reagents should be of recognised analytical grade.
Ethanol—Distilled from sodium hydroxide.
Hydrogen peroxide, 100-*volume*.
Ether.
n-*Hexane*.
Sodium hydroxide—A 5 *N* solution.

Preparation of standard curve—

Prepare a solution of parathion in ethanol to contain 10 μg of parathion per ml. From a micro-burette add 0·0, 1·0, 2·0, 3·0, 4·0, 5·0, 6·0, 7·0, 8·0, 9·0 and 10·0 ml to separate boiling tubes and make up each to 20 ml with ethanol. Add 1 ml of sodium hydroxide and 1 ml of hydrogen peroxide and heat under a reflux air condenser for 15 minutes. Cool, then transfer to a 25-ml calibrated flask. Wash the tube with a few millilitres of distilled water and add the washings to the flask. Make up to 25 ml with distilled water. Filter the solution and determine the optical density with the Spekker absorptiometer, using 4-cm cells and Ilford blue filters No. 601. Plot a curve with absorptiometer reading as ordinate and μg of parathion as abscissa.

Procedure—

Place the tomato in a 3-inch diameter funnel and wash it with 20 ml of ethanol, collecting the washings in a boiling tube with a B24 socket. Add 1 ml of sodium hydroxide and 1 ml of hydrogen peroxide. Fit the boiling tube with a reflux air condenser having a B24 ground-glass cone and boil the solution gently for 15 minutes. Cool and transfer the solution to a 25-ml calibrated flask. Wash the tube with a few millilitres of distilled water and add the washings to the flask. Make up to volume with distilled water. Filter the solution and measure the optical density on the Spekker absorptiometer, using 4-cm cells and Ilford blue filters No. 601.

Some of the tomatoes were washed with a further 20 ml of ethanol and the washings were analysed to determine whether one washing was sufficient to remove all the parathion

from the surface. Provided the first washing is carefully done, the amount of parathion in the second washing is not measurable.

The method is sensitive to 10 μg and the blank is negligible.

METHOD FOR THE DETERMINATION OF TOTAL RESIDUE

PREPARATION OF STANDARD CURVE—

Prepare a solution of parathion in 50 per cent. v/v aqueous ethanol containing approximately 50 μg of parathion per ml. From a micro-burette put aliquots into a series of boiling tubes and prepare a standard curve, as before, for 0 to 400 μg of parathion.

RECOVERY OF PARATHION FROM TOMATO PULP WITH HEXANE—

Macerate the tomatoes thoroughly in a high-speed macerator and weigh 100-g portions of the pulp into 500-ml conical flasks each fitted with a ground-glass stopper. Add to each flask, from a micro burette, an aliquot of the parathion solution containing 50 μg or a multiple of 50 μg of parathion. Mix the contents of each flask thoroughly and allow them to stand for 30 minutes. Add 200 ml of *n*-hexane to each flask and shake each vigorously by hand, then shake them on a mechanical shaker for 30 minutes, allow them to stand for at least 2 to 3 hours to settle, then decant the *n*-hexane through a small cotton-wool filter into a measuring cylinder. Note the volume of *n*-hexane recovered and transfer it to a clean dry 250-ml flask with a B24 socket. Usually about 160 ml of hexane are recovered.

METHOD FOR THE DETERMINATION OF PARATHION: HYDROLYSIS TO *p*-NITROPHENOL AND REMOVAL OF PLANT PIGMENTS

Add 20 ml of water and 1 ml of 5 *N* sodium hydroxide to the *n*-hexane solution; evaporate the *n*-hexane under reduced pressure at a bath temperature of 35° to 45° C. Subsequent oxidation with hydrogen peroxide will be ineffective unless the *n*-hexane is completely removed. Add a further 1 ml of 5 *N* sodium hydroxide and boil the aqueous solution under a reflux condenser for 30 minutes. During this time, add about 6 ml of 100-volume hydrogen peroxide through the condenser, in small portions to avoid excessive frothing; the solution, which is cloudy at this stage, should then be pale yellow in colour owing to the *p*-nitrophenol formed by hydrolysis of the parathion, most of the pigment having been destroyed. To remove the remaining pigments and to clarify the solution, cool and transfer the solution with the washings from the condenser and flask to a 150-ml separating funnel; acidify with concentrated hydrochloric acid and extract with 25 ml of ether, which has previously been used to wash the condenser and flask. Separate the aqueous layer and extract once more with 25 ml of ether. To the combined ethereal extracts in a 150-ml separating funnel, add about 1 g of sodium chloride to break the emulsion, 20 ml of water and 1 ml of 5 *N* sodium hydroxide; shake the funnel vigorously and allow the layers to settle. Run the aqueous layer into a separating funnel and extract the ether layer as before with water, alkali and salt in the same quantities; acidify the combined aqueous extracts with concentrated hydrochloric acid and extract twice with 25-ml portions of ether. Extract the combined ether extracts with the following solution: 20 ml of water containing about 1 g of sodium chloride and 1·0 ml of 5 *N* sodium hydroxide. Allow time for the aqueous and ethereal layers to separate as completely as possible, then run the aqueous layers into a 25-ml calibrated flask. Wash the ether solution with a few millilitres of distilled water and make up to volume. Filter the solution and determine the optical density on the Spekker absorptiometer, making use of a 4-cm cell and an Ilford blue filter No. 601.

Determine the blank on the reagents and parathion-free tomato pulp and deduct it from the reading for the sample. From the standard curve read the quantity of parathion present, in μg, in the aliquot of *n*-hexane solution used in the determination. Correct this figure to the 200-ml volume of *n*-hexane used to extract the tomato pulp, and from the figure for the parathion present calculate the percentage recovery of the known amount of parathion added.

RESULTS

Table II shows the recovery over a range of approximately 50 to 400 μg (0·5 to 4 p.p.m.).

The reproducibility of the method is shown in Table III, which gives figures for recoveries from seven samples of tomato pulp, each containing about 2·5 p.p.m. of parathion.

Discussion of results

In all determinations of parathion residues on plant material one of the most difficult problems is the removal of interfering biological pigments from the solution to be analysed.

Averell and Norris, using benzene as stripping solvent, found that plant pigments could be sufficiently removed by pouring the benzene extract through a column of Attapulgus clay. In Gage's method separation is achieved when the reduced parathion is extracted from toluene with dilute hydrochloric acid. Jones and Riddick[8] claim that methyl cyanide selectively extracts many insecticides, including parathion, from *n*-hexane.

In the course of this work we have found that the yellow pigment is most conveniently removed from surface residues by oxidation with hydrogen peroxide. When oxidation alone is not sufficient, solvent extraction after hydrolysis will remove the remaining pigment.

Table II

Recovery of parathion from 100 g of tomato pulp containing from 50 to 400 μg

Parathion added, μg	Volume of hexane recovered, ml	Parathion (from graph), μg	Parathion (corrected), μg	Recovery, %
49·5	150	32·5	43·3	87·5
99·0	150	60·0	80·0	80·0
99·0	150	62·0	82·7	83·5
148·5	150	92·0	122·7	82·6
198·0	150	128·0	170·6	86·2
198·0	150	110·0	146·7	74·1
396·0	150	250·0	333·4	84·1

Table III

Recovery of parathion from 100 g of tomato pulp containing 250 μg

Parathion added, μg	Volume of hexane recovered, ml	Parathion (from graph), μg	Parathion (corrected), μg	Recovery, %
247·5	150	150·0	200	81
247·5	150	152·5	203	82
247·5	150	150·0	200	81
247·5	160	162·5	203	82
247·5	140	125·0	179	72
247·5	160	160·0	200	81
247·5	160	160·0	200	81

The blank has always been of the order of 4 to 5 μg of parathion.

Averell and Norris examined a number of solvents to select the most suitable for stripping. We have chosen *n*-hexane, as it appears to fill all the requirements without having the toxicity of benzene. The same authors report a slow, steady loss of parathion in proportion to the volume of benzene evaporated. In evaporating the hexane under reduced pressure we have found losses of the same order, *i.e.*, roughly 2 to 3 per cent. for each 100 ml of solvent evaporated.

Attempts to shorten the method by omitting one of the extractions or the hydrogen peroxide oxidation were not successful, as separation of pigments was incomplete.

The specified quantities of alkali and salt must be adhered to closely, otherwise separation of the ethereal and aqueous layers will be slow and incomplete.

Although the method is not as sensitive as that of Averell and Norris or that of Gage, it can be used to determine 0·5 p.p.m. and is capable of detecting 0·2 to 0·3 p.p.m. of parathion. No official limits have yet been specified for parathion in foodstuffs, but Lehman[9] considers that 2 to 5 p.p.m. is not likely to constitute a hazard to health. The method is sufficiently accurate for the determination of quantities of this order, and any loss of sensitivity is compensated by its simplicity and relative rapidity.

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PLANT PROTECTION LTD.
YALDING, KENT

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The Micro-determination of Picric Acid in Picrates

BY P. R. W. BAKER

Three methods for the determination of picric acid in organic picrates, on a micro scale, have been examined. Neither Bolliger's method of titration with methylene blue, nor the method of titration with sodium hydroxide, is of universal application. The macro method of Busch and Blume, involving precipitation with nitron, gives satisfactory results on a micro scale, and is applicable to all the compounds examined. The solubility of the precipitate and the effect of chloride on its purity have also been examined.

BOLLIGER[1] has described a micro method for the determination of picrates by titration with methylene blue. It is also claimed[2] that picrates can be titrated with sodium hydroxide, with ethyl bis-2:4-dinitrophenylacetate[3] as indicator, but no experimental details have been given. A macro-gravimetric method involving precipitation with nitron has been described by Busch and Blume[4] and recommended by Cope and Barab,[5] who reviewed the literature up to 1917.

Preliminary experiments carried out in this laboratory some years ago suggested that this last method might be successfully adapted to a micro scale, and the work here described was undertaken to substantiate this and to assess the relative merits of the three methods.

When this work was nearing completion, a further method, described by Stöhr and Scheibl,[6,7] came to our notice. In this, the picric acid is reduced to picramic acid, which is determined colorimetrically. The results quoted, given in terms of the molecular weights of the parent compounds, are within about ± 10 per cent. of the theoretical values.

DETERMINATION WITH METHYLENE BLUE

The procedure followed was essentially that of Bolliger.[1]

REAGENTS—

Methylene blue, 0·01 N—Dissolve 3·8 g of methylene blue in water and make up to 1000 ml. Store over a few ml of chloroform in a dark bottle.

Methylene blue, 0·001 N—Dilute the above stock solution as required.

Chloroform—Analytical-reagent grade.

Pyridine—Analytical-reagent grade.

PROCEDURE—

Weigh 3 to 6 mg of the sample into a 50-ml separating funnel. Dissolve it in 5 drops of pyridine and add 4 to 5 ml of water and 20 ml of chloroform. Titrate with 0·001 *N* methylene blue, shaking after each addition to extract the colour into the chloroform. Replace the chloroform when it becomes saturated with methylene-blue picrate. Replace the chloroform more frequently near the end-point, which is reached when addition of methylene blue produces in the aqueous phase a blue colour that is not extractable with chloroform.

Standardise the methylene blue against pure picric acid.

Determination with sodium hydroxide

It is said[2] that picrates can be titrated with standard sodium hydroxide, with ethyl bis-2:4-dinitrophenylacetate[3] as indicator.

With 0·01 *N* sodium hydroxide and pure picric acid, the end-points were very vague in aqueous solution, but there was a great improvement on dissolving the sample in a mixture of equal volumes of acetone and alcohol, the solvent in which it is recommended that the indicator should be made up.[2] The use of more than 5 ml of solvent also rendered the end-point indistinct.

Reagents—

Solvent—Acetone and ethanol (1 + 1).

Indicator—Ethyl bis-2:4-dinitrophenylacetate, 1 per cent. solution, in the above solvent.

Sodium hydroxide, 0·01 N.

Procedure—

Dissolve 20 to 30 mg of the sample in 3 to 5 ml of solvent. Add 3 or 4 drops of the indicator and titrate with 0·01 *N* sodium hydroxide to a pale green colour. (The colour will revert to yellow on standing, owing to absorption of carbon dioxide.) Standardise the sodium hydroxide against pure picric acid.

1 ml of 0·01 *N* sodium hydroxide ≡ 2·291 mg of picric acid.

Determination with nitron

Nitron (2:5:6-triphenyl-2:3:5:6-tetra-aza*bicyclo*[2:1:1]hex-3-ene) was first made by Busch[8] and later used by him for the determination of picric acid on a macro scale.[4] It is of interest, in view of the fact that nitron nitrate is more soluble than the picrate, to note that Utz[9] determined picric acid by a two-stage oxidation to nitrate, followed by precipitation as nitron nitrate. The method here described was adapted from that given by Busch and Blume.[4]

Reagents—

Nitron reagent—A 5 per cent. w/v solution of nitron in 5 per cent. v/v acetic acid. Filter this solution before use.

Sulphuric acid, 2 N.

Procedure—

Dissolve 8 to 10 mg of the sample in 10 ml of water. Add 2 or 3 drops of 2 *N* sulphuric acid and 1 ml of nitron reagent. Heat the solution on a steam-bath for 5 minutes and set it aside for at least 2 hours. Collect the precipitate on a sintered-glass filter of porosity 4 with the aid of a syphon tube,[10] transferring the precipitate with water only, and dry it at 105° C.

1 mg of nitron picrate ≡ 0·4231 mg of picric acid.

Solubility of nitron picrate

Busch and Blume[4] stated that even if picric acid is at as great a dilution as 1 in 250,000, a precipitate is still formed. Cope and Barab[5] incorrectly assumed this to mean that the solubility of nitron picrate is 1 in 250,000. (They have made the same mistake in translation for the other limiting dilutions quoted by Busch.) We find the solubility of nitron picrate, under the conditions of determination, to be of the order of 1 in 800,000. We had at our disposal no direct method of determining such a low solubility and hence the following method was adopted. Ten millilitres each of a series of dilute aqueous picric acid solutions were treated with 2 drops of 2 *N* sulphuric acid and 1 ml of nitron reagent. After being heated on the steam-bath for 5 minutes they were set aside, and the formation of any precipitate was noted. The results are shown in Table I.

It appears from these results that, under our conditions, approximately 6 μg of picric acid will remain in solution, equivalent to 14 μg of nitron picrate. These figures are equivalent to solubilities of 1 in 1,800,000 for picric acid, or 1 in 800,000 for nitron picrate.

Busch and Blume[4] also stated that the precipitate is almost insoluble in alcohol and gave

a result for a solution in 50 per cent. alcohol that is only slightly low (found by them, 63·44 per cent.; required, 63·96 per cent. of picric acid). Under our conditions it was at once apparent that the solubility is far too great to permit the use of alcohol in micro work, and quantitative determinations showed that the solubility of nitron picrate in ethanol, at room temperature, is about 0·4 mg per ml.

TABLE I

PRECIPITATION OF DILUTE PICRIC ACID SOLUTIONS WITH NITRON

Amount of picric acid present, μg	
20	Precipitate formed within 15 minutes
13	Precipitate formed within 30 minutes
10	Precipitate formed within 1 hour
7	Precipitate formed within 2 hours
6·5	Very slight precipitate after 3 hours
6	No precipitate after 24 hours; slight trace after 72 hours

EFFECT OF OTHER ANIONS

Previous workers have given lists of anions that may or may not interfere with the precipitation. Busch and Blume[4] state that bromide, iodide, chlorate, perchlorate, nitrite, nitrate and chromate must be absent. Visser[11] claims that oxalate and salicylate interfere, but that sulphate, chloride, formate, acetate, borate, benzoate, tartrate, citrate and phosphate do not.

There appears, however, to be some doubt about the effect of chloride. Dealing with its effect on the precipitation of nitron nitrate, Busch[12] found that the presence of a small amount of chloride (giving a solution 0·05 *N* with respect to chloride) gave a precipitate slightly contaminated with chloride. Flagg[13] states that "results obtained in the presence

TABLE II

COMPARISON OF RESULTS

Picrate of	Picric acid required, %	Picric acid found with: Methylene blue, %	Sodium hydroxide, %	Nitron, %
(Picric acid)	100·0	—	—	99·8
Naphthalene	64·1	63·8	64·1	63·8
2-Methylnaphthalene	61·7	61·9	62·5	61·3
1-Naphthol	61·35	61·2	61·3	61·05
4-Acetylpyridine (R)	65·4	65·2	65·1	64·55
3-Dimethylamino-2-methyl-1:1-diphenylpropane (R)	47·5	44·0 to 45·2	10·0	46·8
3-Dibutylaminopropylamine (dipicrate) (R)	71·1	68·0 to 69·3	31·6	70·5
Triethylamine	69·35	65·6 to 68·6	14·7	69·0
Ammonia	93·1	93·2	7·2	93·0

The compounds marked (R) were research compounds that had previously given satisfactory elementary analyses. The remainder were prepared by us and had melting points in agreement with the literature values.

of chlorides are generally high, presumably because of co-precipitation." On the other hand, Booth[14] found that up to 100 ml of *N* hydrochloric acid did not interfere.

We have investigated the effect of chloride and find that it depends on the concentration of both reagents. If nitron reagent is added dropwise to 10 ml of dilute hydrochloric acid, a gelatinous precipitate is formed at concentrations greater than 0·2 *N* with respect to hydrochloric acid. On the other hand, if 1 ml of nitron reagent is diluted with 10 ml of water, no immediate precipitate is obtained by adding 35 ml of 2 *N* hydrochloric acid, although clusters of white needles are deposited if the solution is set aside for several hours. The addition of more than 0·1 ml of concentrated acid gives a gel, as described by Busch,[8] which slowly crystallises as white needles, m.p. 225° C, with decomposition and previous shrinking (Busch gives m.p. 242° C). (Found on material dried at 110° C *in vacuo*: C, 68·65 per cent.; H, 4·6 per cent. Calculated for $C_{20}H_{16}N_4.HCl$: C, 68·8 per cent.; H, 4·9 per cent.) The dried

substance is hygroscopic (loss at 110° C *in vacuo* after exposure to the atmosphere for 24 hours is 6·6 per cent.). It is evident, therefore, that chloride should be absent.

Results

Results by the three methods are shown in Table II.

Discussion

The methylene-blue method gave low and erratic results for three of the compounds examined (see Table II), owing, it was suspected, to the compounds themselves being extracted by the chloroform. To check this, 1 mg of each of the compounds examined was shaken with 2 drops of pyridine, 1 ml of water and 1 ml of chloroform. It was seen that the five compounds that gave good results were all extracted slightly by chloroform. Picric acid itself was extracted to about the same extent, and it seemed therefore that the results were good by a compensation of errors. The three compounds that gave low results were all extracted to a far greater extent; with 3-dibutylaminopropylamine picrate the intensity of colour was about the same in both phases. Attempts to overcome the extraction effect by adding methylene blue to within 1 ml of the calculated end-point before replacing the chloroform gave results that were slightly improved but still not satisfactory. Bolliger[1] appreciated that some substances would be more soluble in chloroform than in water, as he suggested that substances not readily soluble in water should be dissolved in chloroform, but he did not mention the possible effect on his results, which are, in general, slightly low.

The sodium hydroxide method gave good results for the picrates of neutral or weakly basic compounds, but not for those of strong bases. This is not unexpected, as the method is merely an acid - base titration. The procedure described above, with relatively large sample weights, is obviously capable of refinement, but owing to the inherent limitations of the method it was not further investigated.

The nitron method is applicable to all the compounds examined, but the results are, in general, about 0·4 per cent. low. If a correction is made for the solubility of the precipitate, as found above, they are only increased by about 0·07 per cent. It is evident, therefore, that either the solubility error is greater than is indicated by the figures in Table I, or there is another, undetected, source of error. The uncorrected results are sufficiently accurate for most purposes, but if greater accuracy is required, an empirical correction, based on results with pure picric acid or a reference picrate, can be applied.

Conclusions

The nitron method is the only one of the three examined that is applicable to all the compounds used, and it has the additional advantage of being an absolute method, since no standardisation is required. In general, therefore, it would be the method of choice. The simple and rapid sodium hydroxide titration would be preferable, however, if analyses were required for a series of picrates known to be derived from non-basic substances.

The author wishes to thank Mr. J. C. H. Stephens for technical assistance.

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Automatic Recording of Ion Concentration in Flowing Solution

By J. A. LEWIS* and K. C. OVERTON

An apparatus, consisting essentially of two polarographs in opposition, automatically and continuously records the concentration in flowing or stationary solutions of metallic ions that give discrete and well-formed polarographic waves. The instrument can also be used as an ordinary polarograph and for differential or derivative polarography.†

Polarographic control of solutions of metals, the concentrations of which vary, has hitherto consisted in intermittent sampling and analysis, or the reading of a polarogram, rapidly, but still intermittently, produced on an oscillograph.[1] Muller[2] has shown that ordinary polarograms can be derived from flowing solutions, but the compositions must remain constant. Polarographs have been used for continuous recording of concentration,[3] but only in circumstances in which one wave alone is present in the polarogram for the solution, so that one electrode is sufficient.

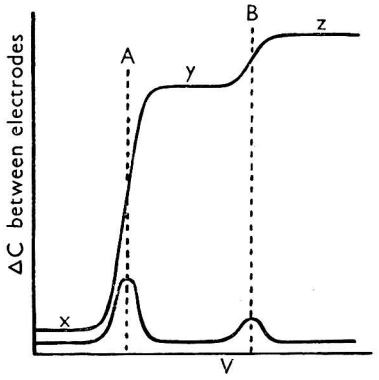

Fig. 1. Polarograms for two reducible species in solution

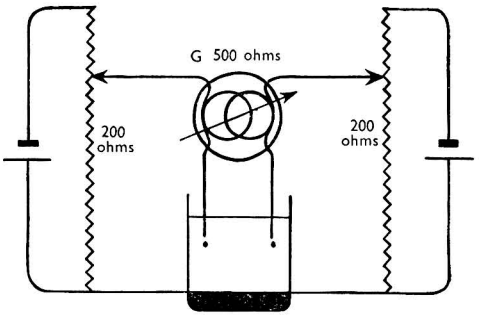

Fig. 2. First circuit: single polarographic cell, differential galvanometer

Various uses have been made of polarographic circuits involving two dropping-mercury electrodes, and the instrument described applies this device; it avoids the difficulty of current flowing in the wrong directions by the use of a separate source of potential for each electrode. Airey and Smales[4] devised a method of synchronising mercury drops, which has been adopted here. Preliminary work is described on a differential polarograph (one in which waves prior to any desired wave can be compensated out) in which the compensation varies as the unwanted section of the polarogram, a property not provided in previous compensation techniques, such as those of Airey and Smales[4] or Semerano and Riccoboni.[5] The obvious method of achieving this was to make the solution self-compensating, and this has been found possible by the principle of two polarographic circuits "back to back." Each cathode is in one of the circuits and the various current recording devices used have been applied to the current difference between the two.

Theoretical principles

The principle is illustrated by reference to a polarogram for two ions in solution, as in the upper curve in Fig. 1. If both electrodes are set at x and the negative voltage on

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† The author (J. A. L.) has elsewhere advocated a different polarographic terminology (see *Chem. & Ind.*, October 10th, 1953, p. 1093).

one is allowed to increase, the record of current difference traces out the normal polarographic waves A and B. If both are set at y and one is allowed to proceed to z, only the wave B is traced out; this gives the first pre-requisite—a differential instrument.

If one electrode is set at y and the other at z on a well-shaped wave, the current difference recorded is proportional to the concentration of B in solution. If this concentration varies, the apparatus will record a proportional variation. If the concentration of A varies, it will affect both electrodes equally and the nett effect is nil.

As a by-product of this work, derivative polarography is possible with the instrument. If the two electrodes are set with a voltage difference between them of, say, 50 millivolts in the neighbourhood of x, and the negative voltage on both is increased at equal rates, the current difference between them will be at a minimum at x, y and z and a maximum at A and B. The record will then present peaks at the half-wave potentials of the elements, as in the lower curve, Fig. 1.

Apparatus

Cathodes—

The work was started with stationary lead micro-electrodes. It was found that reproducible waves were possible, but the work of Airey and Smales on synchronisation of mercury drops, which was privately communicated, was adopted. In place of their motor-driven mechanism, a valve-operated repetitive relay has been used, and the drop time can be varied

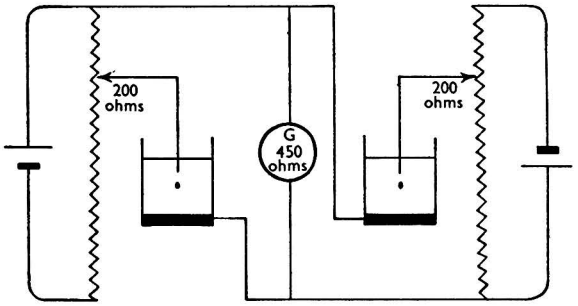

Fig. 3. Second circuit: two polarographic cells, simple galvanometer

accurately over fairly wide limits by changing the time constants. It is important that the two mercury cathodes should have very similar natural drop times for the best results.

Circuits—

The first successful circuit is shown in Fig. 2. The galvanometer, G, is differentially wound (Gambrell Bros.), but is a student-demonstration model and not very sensitive, so that high ionic strengths had to be used to test the circuit. The building of an electronic circuit to replace the differential galvanometer has had to be put in abeyance owing to heavy demands on the National Physical Laboratory electronics section. The chief merit of the circuit is that only one vessel of solution is required; this avoids the division of a solution into two parts, as is necessary with the alternative system.

The second circuit is shown in Fig. 3. It needs only an ordinary, sensitive, long-period galvanometer, but requires two identical solutions with no direct electrical connection between them and this involves special apparatus. The galvanometer used had a resistance of 450 ohms, with 170 mm deflection per μA. The potentiometers in Figs. 2 and 3 were wire-wound, and had a resistance of 200 ohms.

In the second apparatus, which was used for most of the work, a d.c. amplifier and recorder finally replaced the galvanometer. The amplifier was composed of four CV138 pentodes, triode-connected, d.c. coupled throughout with over-all feedback from the cathode of the output valve to the input grid. It was arranged with three sensitivity ranges, namely 1, 5 and 10 μA, to give an output suitable for a Murday 5-mA recorder. There is provision for variable electrical damping and for adjusting the zero of the recorder.

The solutions under examination and all metal frame parts were earthed to prevent stray currents. The leads to the drop synchroniser had to be screened and a condenser

was connected between one side of the coil and the frame. The recorder chart speed was 5 inches per hour.

GLASS APPARATUS—

Apparatus for entrainment of solutions with the sample solution—This apparatus consists of an 8 cm × 1 cm glass tube with a sintered-glass disc fused into the base, as shown in Fig. 4. The solutions are led in at a point just above the disc, which distributes the nitrogen used for removing oxygen and also mixes the solution. The solution from the mixing tube spills over into an annular tube, which separates the bulk of the gases from the solution before it passes to a second small vessel that removes the residuum of gases and smoothes out the small variations in the flow of solution.

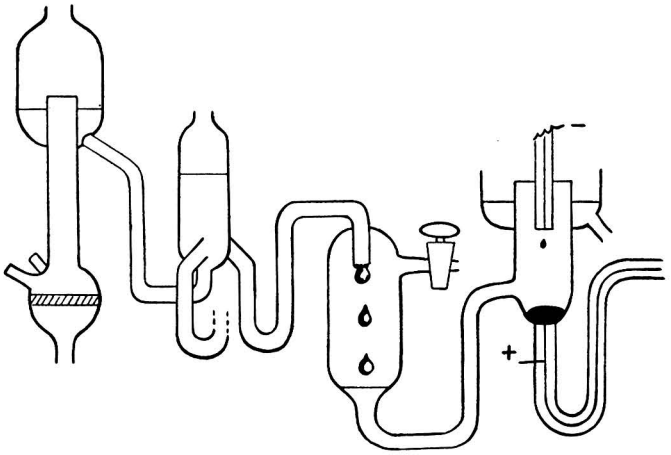

Fig. 4. Mixer - deoxygenator, electrical isolator and continuous-flow polarographic cell (not to scale)

A system for electrical isolation of one stream from the other—If the second type of electrical circuit, Fig. 3, is used, it is necessary to divide the solution and break electrical contact between the two resulting flows. This is accomplished by allowing them to fall dropwise through air. One dropping vessel is illustrated in Fig. 4. The amount of gas in this tube can be controlled by a tap sealed to it.

Polarographic cells—These consist of two glass vessels, one of which is joined, via its attendant dropping vessel, to each arm of the flow divider, when this is in use. If the first type of electrical circuit is used, a single cell is attached directly to the exit from the de-oxygenator - mixer. Solution flows up past the electrode and then to waste. Mercury, building up from the cathode drops, is run to a residues bottle via a capillary U-tube. No thermostat was used.

EXPERIMENTAL

PRELIMINARY TESTS—

All the early work was carried out with galvanometers and with stationary solutions.

Normal polarography—The *N* hydrochloric acid solutions containing gelatin and cadmium and bismuth in various amounts were used and it was found that the apparatus, with one cathode set at zero volts, behaved as an ordinary polargraph. Waves were similar, wave height was linear with concentration, repeatability was good and accuracy was ±2 per cent. No differences were observed between the two types of circuit (Figs. 2 and 3) except those dictated by the respective galvanometer sensitivities.

Differential polarography—With one cathode set on the "head" of the first (*i.e.*, the bismuth) wave, the other electrode traced out the second wave, which was always an improved reproduction of its counterpart on the normal run. In differential polarography, high sensitivity can be applied to the second wave without causing interference from the first and without undue exaggeration of the drop wave. These advantages were shown to apply.

It was found that cadmium waves could easily be produced when the bismuth concentration was so high (of the order of 1000 times the cadmium concentration) that it was not advisable to put the uncompensated current through the galvanometer at the sensitivity required for a good cadmium wave height.

Derivative polarography—This aspect was tested under difficulties inherent in hand operation of the two potentiometers. The same types of solution were used as in the foregoing experiments. The electrodes were moved along the voltage scale in steps of 0·025 volt, with a difference between them of 0·025 volt in one experiment and 0·05 to 0·2 volt in others. It was shown that two peaks were produced each time and that the relation between their heights was approximately that between the ionic concentrations. With the smaller voltage differences there was excellent resolution but extremely small peak heights. With wider differences there was a better peak height with these solutions and resolution was still good. With lead and cadmium, however, the smaller voltage differences were necessary for resolution.

CONTINUOUS RECORDING OF CONCENTRATION—

When the background conditions were stabilised, the simple galvanometer was replaced by a d.c. amplifier and a pen recorder. The previous work was repeatable with this arrangement and simple tests showed that continuous concentration recording was possible with flowing solutions. For this latter purpose, aspirator stock-bottles were fixed about 6 feet above the general apparatus to supply sample solutions and complexing agent separately.

METHOD

The procedure is as follows. The amplifier is switched on to allow the valves to warm up. The flow of nitrogen to the electrode system is started; a suitable rate of flow has been found to be 150 ml per minute. Base and test solutions are allowed to flow and the rate is adjusted to approximately 20 ml per minute for each solution. Nitrogen is forced through the electrode system by closing both gas escape tubes of the mixer for a few moments. The mixed solutions are then allowed to flow through the cells. The rates of flow of the components of the mixture are conveniently equalised by taps and rotameters, while rates of flow through the individual cells are equalised by adjusting the relative heights of the cells and the amount of gas in the separators.

After allowing 5 minutes for the rate of flow to become steady and for the mercury-drop synchroniser to warm, the latter is adjusted to give a drop-rate of 30 per minute. This drop-rate was more satisfactory than the usual, rather slower, polarographic drop times. The amplifier sensitivity is turned to a minimum, and the zero is adjusted with the main potentiometers set on 0. Both potentiometers are then advanced to equal voltages at the foot of the required wave, when the reading of the meter should remain stationary. Any shift in indication shows that the drops are forming at different rates and adjustment is necessary. This adjustment may take the form of a change in the relative mercury heights in the reservoirs or, in serious cases, thorough cleaning or replacement of the electrodes.

A polarogram is recorded by a method similar to that used with a manual polarograph. The sensitivity of the amplifier is adjusted to accommodate the wave whose height is to be recorded. The two potentiometers are then set to give the appropriate part of the wave.

The recorder is calibrated by an experiment on a solution containing a known amount of the ion under examination.

RESULTS

A solution of fixed composition was sent past the electrodes at a rate of 20 ml per minute for each component. The electrodes encompassed the second wave and recorded a difference reading for 6 hours. The maximum variation in reading was $\pm 3{\cdot}4$ per cent. It was found necessary to set the electrodes on flat portions of the wave to avoid variations presumably due to alterations in anode and cathode potential.

On recording normal and differential polarograms for flowing solutions of constant composition, it was found that a slope was imposed on the graphs that increased with the rate of flow, which must, therefore, be kept constant for continuous recording. A total liquid-flow rate of 40 to 150 ml per minute gave stable and satisfactory readings.

The complexing solution contained 3 per cent. w/w of sodium potassium tartrate with 5 per cent. v/v of sulphuric acid and 0·01 per cent. v/v of hydrochloric acid. The

test solution was a mixture of bismuth and cadmium chlorides in dilute hydrochloric acid (these give waves at −0·15 and −0·60 volt, respectively, against the mercury pool, in the complexing solution).

The concentrations of the solutions were varied from 0 to 500 μg of the metals per ml; the method of altering the concentrations was by switching, by stopcock, from one aspirator stock-bottle to another. A change of bismuth concentration should not affect the record, but alteration in cadmium content should give a proportional change in the current.

When the concentration of a solution was changed, it was 1·8 minutes before the alteration was reflected in the pen deflection and 3·0 minutes before a steady new reading was obtained. This delay was due to the distance of the source of sample from the polarographic cells and mixing of new solution with old; it would be almost eliminated in a system in which the deoxygenator was close to the main stream from which the sample was derived.

Table I demonstrates that the instrument follows changes in concentrations. Twelve minutes were allowed between changes, so that each reading was steady for 9 minutes and the whole run occupied about 3 hours. The values for k should be constant;

$$k = \frac{\text{(concentration in } \mu\text{g per ml)}}{\text{(deflection} - \text{deflection at zero concentration)}}.$$

The mean deflection at zero concentration in this example is 9 units.

TABLE I

INSTRUMENTAL READINGS FOR VARIOUS ION CONCENTRATIONS

Ion concentration, μg per ml	0	125	250	500	250	125	250	500	250	0	500	125	250	0	500
Steady deflection ..	8	24	42	75	39	25	42	76	42	10	76	26	42	9	77
k	—	8·3	7·6	7·6	8·3	7·8	7·6	7·5	7·6	—	7·5	7·3	7·6	—	7·3

These results were considered sufficiently promising to suggest that the principles had been proved. The constant is sensitive to variations, and the apparatus could be modified to reduce these sources of error, *e.g.*, by use of external anodes, the reduction of mixing of the different concentrations and so on.

The readings of the continuous recorder could be used to indicate variations with time of concentration of a metal that is being used up, as for instance in plating baths, or the quantity being taken into solution, for example, in leaching from ores. The amount of a given ion in a flowing sample could be determined, if changes were slow, by a standard addition process.

We are indebted to Messrs. E. A. Newman and A. I. Williams for their provision of a d.c. amplifier to replace the ordinary galvanometer and for their work towards a differential amplifier that will, it is hoped, enable the more convenient single cell to be used.

This work was carried out on behalf of the Ministry of Supply and is published by permission of the Director of the Chemical Research Laboratory.

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September 1st, 1953

An Improved Apparatus for the Micro-determination of Unsaturation in Organic Compounds by Catalytic Hydrogenation

By A. F. COLSON

A description is given of an improved form of the apparatus devised by Johns and Seiferle for the micro-determination of unsaturation by catalytic hydrogenation. The improved apparatus can be used for the hydrogenation of solid or volatile liquid samples at temperatures ranging from 0° C (or lower) to about +50° C. The final measurement of the volume of hydrogen absorbed has been made more accurate and precise by simple modification of the original apparatus and by housing the entire assembly in a constant-temperature cabinet.

The procedure for making a determination is described in detail, and some results for pure organic compounds are given. The maximum relative error to be expected in routine determinations is about ±2 per cent.

An apparatus capable of giving results with a relative error of about ±2 per cent. was required for the micro-determination of unsaturation in organic compounds by catalytic hydrogenation.

The simple form of apparatus described by Johns and Seiferle[1] was tried out and found to require improvement in certain directions. In common with many other types of hydrogenation apparatus described in the literature, it could not be used conveniently with volatile liquid samples, it did not permit convenient variation of the temperature of the reaction vessel over the range desired (0° to 50° C), and the volume of hydrogen absorbed by the sample could not be measured with the required accuracy and precision.

In the apparatus described in this paper an attempt has been made to eliminate these defects by suitable modification of the original design.

The apparatus

The assembled apparatus is shown diagramatically in Fig. 1, and certain components are illustrated in greater detail in Figs. 2, 3, 4, 5, 6 and 7.

The reaction vessel, B, gas-measuring burette, A, lute, O, saturator, P, heating (or cooling) bath, S, and the shaking mechanism are mounted on a single wooden stand, M, and the complete assembly is housed in a constant-temperature cabinet. The controls for the electrically operated components and the mechanism for raising or lowering the mercury reservoir, N, are outside the cabinet.

Reaction vessels—

Two suitable reaction vessels, one for use with solid (or non-volatile liquid) samples and the other for volatile liquids, are shown in Figs. 3 and 2, respectively.

Sample containers—

Solid or non-volatile liquid samples are weighed into the vessel shown in Fig. 4. Volatile liquid samples must be weighed in thin-walled capillary tubes of the dimensions indicated in Fig. 5.

Gas-measuring burette—

This consists essentially of a 4-mm uniform-bore glass tube, A (Fig. 1), graduated from 0·0 to 5·0 ml in 0·02-ml divisions. The tube is numbered at each 0·1 and 1·0-ml graduation, the 5·0-ml mark being placed at the upper end. The burette is connected to the reaction vessel, B, through the 1·0-mm bore tube, C, and the B.S. B12 cone, D.

The lower end of the burette is sealed to the branch tube, E, and to the extension, F, terminating in the B.S. B7 joint, G. The branch tube carries unnumbered graduations coinciding with each 0·02-ml division on the burette. These graduations, together with the

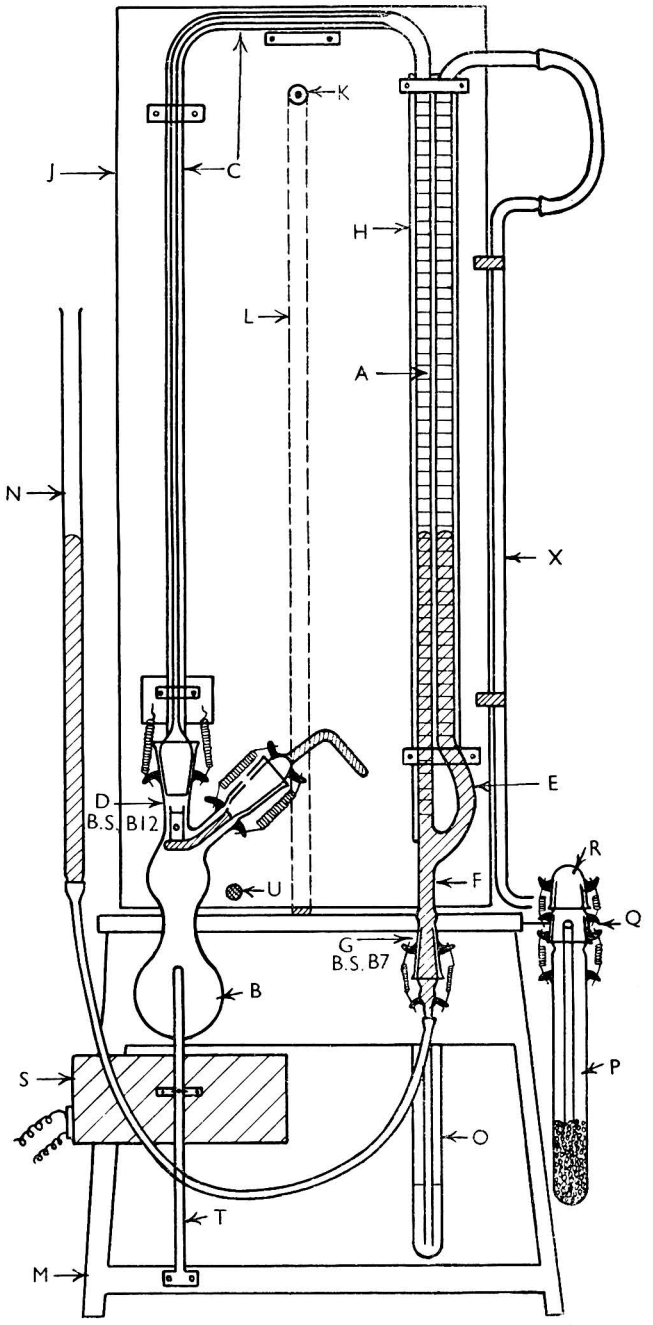

Fig. 1. Assembled apparatus for micro-hydrogenation

mirror, H, assist in the accurate adjustment and reading of the position of the mercury meniscus.

The burette and its connecting tubes are supported on a sheet of Perspex, 20 inches × 8 inches × $\frac{1}{4}$ inch. This support, J, is suspended from a pivot, K, located at the top of a metal pillar, L, 19 inches × $\frac{3}{4}$ inch diameter, welded to a metal plate, which in turn is screwed to the top of the wooden stand, M. The lower end of the capillary tube, C, is bent outwards to give a clearance of about 3 cm between the joint, D, and the Perspex support, J.

LEVELLING TUBE—

This tube, shown at N in Fig. 1, is 36 cm long and of 1·0 cm internal diameter. It is suspended on a thin cord, which can be raised or lowered from outside the constant-temperature cabinet by a suitable combination of pulley wheel and rotating drum.

THE LUTE (O, FIGS. 1 AND 6)—

This is supported on the stand, M, by a Terry clip. It is connected on the inlet side to a cylinder of hydrogen and on the outlet side to the "saturator," P (Figs. 1 and 7). A precision screw clip on the rubber connection between the lute and the "saturator" serves to control the flow of hydrogen.

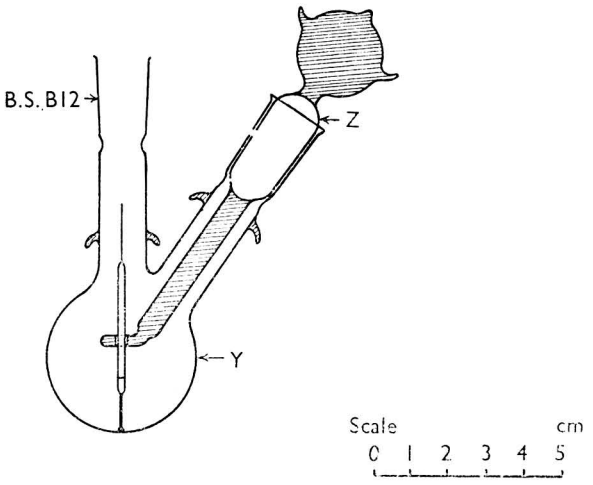

Fig. 2. Reaction vessel for volatile liquids

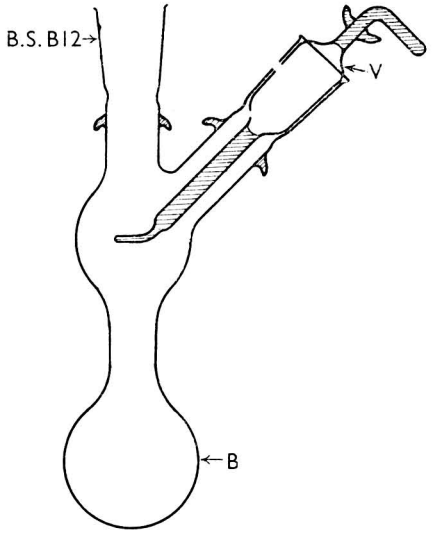

Fig. 3. Reaction vessel for solids or non-volatile liquids

THE "SATURATOR" (P, FIGS. 1 AND 7)—

This vessel contains glass beads covered with the same solvent as that used to dissolve the sample in the reaction vessel; its function is to ensure the saturation of the hydrogen with the solvent vapour. The "saturator" is so designed that the glass beads and solvent can be removed and returned to the vessel without difficulty. The vessel, P, is detached from the joint, Q, cleaned out and replaced. The clean dry beads and the chosen solvent are then returned through the ground-glass joint, R.

THE HEATING (OR COOLING) BATH (S, FIG. 1)—

This is a rectangular copper vessel, 7·5 cm deep, 13 cm long and 5·5 cm from back to front. An electric soldering-iron heating element housed in the base is connected to the mains supply through a Variac transformer outside the constant-temperature cabinet. The bath can be raised or lowered on the rod, T.

MECHANISM FOR SHAKING THE REACTION VESSEL—

Thorough agitation of the contents of the reaction vessel is effected by oscillation of the Perspex support, J, about its point of suspension, K. The back of the support is connected at a point, U (Fig. 1), on the lower left-hand side, to a small electric motor coupled to a worm reduction gear, screwed to the top of the wooden stand, M. The speed of the motor is controlled by a Variac transformer outside the constant-temperature cabinet.

THE CONSTANT-TEMPERATURE CABINET—

The cabinet (a fume cupboard adapted to the purpose) is 3 feet 6 inches high, 2 feet 10 inches wide and 2 feet 6 inches from front to back. It is closed at the front by a sash window and is equipped with an electric fan, electric heater, toluene regulator and a relay. To reduce the time taken to raise the initial temperature of the cabinet to the required value

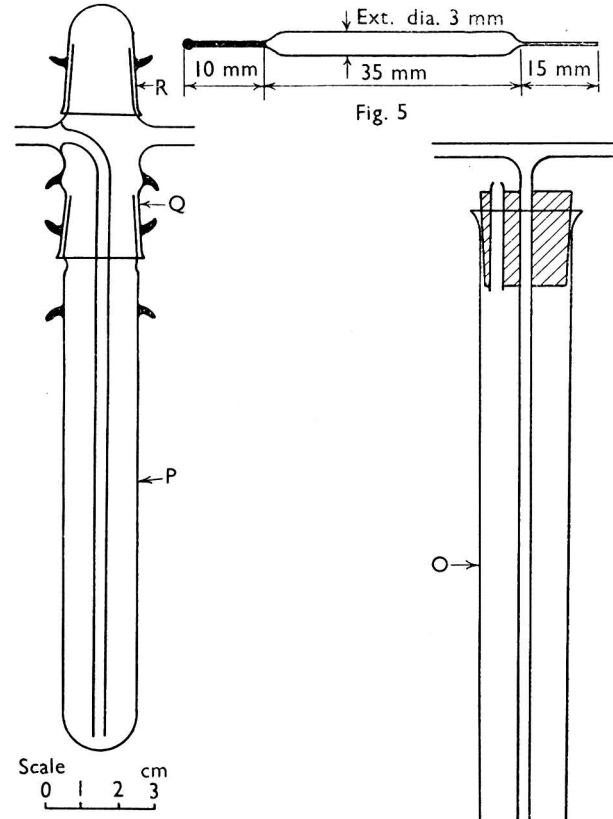

Fig. 5

Fig. 7

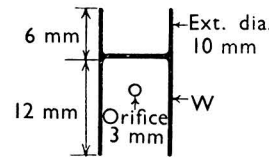

Fig. 4

Fig. 6

Fig 4. Sample container for solids
Fig. 5. Sample container for liquid
Fig. 6. Lutes
Fig. 7. Saturator

(25° to 30° C, according to the laboratory temperature) an additional heater is provided. This is switched off when the selected temperature has been attained. With this equipment any temperature in the range 25° to 30° C can be maintained within $\pm 0{\cdot}1$° C over long periods.

METHOD OF OPERATION

REAGENTS—

Catalysts—For the work described in this report, the catalyst used was Adams' platinic oxide.[2]

Solvents—Pure glacial acetic acid, and methanol purified by distillation.

Hydrogen—Cylinder hydrogen freed from oxygen by passage through a "Deoxo" catalytic purifier (laboratory model: Baker Platinum Ltd.) and dried over anhydrone. Analysis by a sensitive method has shown that the oxygen content of the hydrogen purified in this manner is less than 5 p.p.m.

PROCEDURE FOR SOLID OR NON-VOLATILE LIQUID SAMPLES—

Remove the plug, V, from the side-arm of the reaction vessel, B (Fig. 3). From a long-handled micro weighing-tube transfer about 3 mg of the selected catalyst to the reaction vessel, add 4·0 ml of the required solvent and replace the lubricated plug, V (Apiezon Grease M is a suitable lubricant). Weigh out a suitable amount (3·0 to 10·0 mg) of the sample into the vessel, W (Fig. 4), place the vessel on the platform at the end of the plug, V, and attach the reaction vessel, B, to the lubricated joint, D (Fig. 1). Turn the plug, V, to the open position and lower the mercury reservoir, N, until the mercury level in the gas-burette falls to a position just below the junction of the burette with the branch tube, E. Connect the inlet tube, X, to the saturator, P (containing about 2·0 ml of the same solvent as is used in the reaction vessel), and sweep out the apparatus with oxygen-free hydrogen for about 20 minutes. Detach the tube, X, from the saturator, raise the levelling tube, N, until the mercury in the burette stands near to the 1·0-ml graduation, and then turn the plug, V, until the exit orifice on the reaction vessel is just closed. Switch on the shaking mechanism; when no further contraction is observed on levelling up the mercury in the tubes A and E (shaking for about 40 minutes should be sufficient), record the position of the mercury in the gas-burette.

Turn the plug, V, in the "closed" direction until the sample container falls into the solvent, shake the apparatus until no further contraction is observed, and again record the position of the mercury meniscus in the burette, to acertain the volume of hydrogen absorbed by the sample.

Calculate the "hydrogen number" of the sample from the expression—

$$HN = \frac{22{\cdot}4 \times W}{V}$$

where HN = "hydrogen number" (weight of sample in mg that absorbs 1 millimole of hydrogen),
W = weight of sample in mg, and
V = volume of hydrogen absorbed in ml at N.T.P. (corrected for the vapour pressure of the solvent).

PROCEDURE FOR VOLATILE LIQUIDS SAMPLES—

Transfer the required amount of catalyst and solvent to the reaction vessel, Y (Fig. 2), as described in the procedure for solid or non-volatile liquid samples, and replace the lubricated plug, Z.

Introduce a suitable quantity of sample (3·0 to 10·0 mg) into a weighed capillary tube of the type shown in Fig. 5, seal the tip of the tube, and reweigh it on a micro-balance.

Insert the capillary tube, handle downwards, through the glass ring at the lower end of the plug, Z.

Fill the apparatus with hydrogen and saturate the catalyst as already described.

Finally, break the sample tube by rotating the plug, Z, hydrogenate the sample, and calculate the "hydrogen number" as before. Should it be necessary to cool the contents of the reaction vessel before breaking the sample tube, immerse the bulb of the reaction vessel in a suitable cooling mixture contained in the bath, S (Fig. 1). This procedure was in fact adopted for the hydrogenation of *cyclo*hexene in the determinations recorded in this paper. In this determination the cooling bath (ice and water) was retained during the first few minutes of the hydrogenation process. The same vessel has on occasion been used as an electrically-heated water-bath for hydrogenation experiments at 40° to 50° C.

Results

A series of determinations carried out with the apparatus and procedure described in this paper gave results within about ±2 per cent. of the calculated values for the hydrogen numbers of the compounds examined. The substances used in the tests were sorbic acid, cinnamic acid and *cyclo*hexene. The results are presented in Tables I and II. The required corrections for the vapour pressure of the solvent were obtained from data given by Stull.[3]

Table I

Determination of unsaturation in solid organic compounds

Catalyst used: Adams' platinic oxide. Temperature: 29·5° C

Compound used	Weight taken, mg	Solvent used	Hydrogen number found	Hydrogen number calculated	No. of double bonds found	No. of double bonds present
Sorbic acid	3·861	Acetic acid	58	56·06	1·93	2·0
"	3·828	"	57	"	1·97	"
"	3·498	Methanol	56	"	2·00	"
"	3·467	"	56	"	2·00	"
"	4·063	"	58	"	1·93	"
"	3·128	"	57	"	1·97	"
"	3·860	"	57	"	1·97	"
"	4·000	"	55	"	2·02	"
"	4·000	"	57	"	1·97	"
"	4·394	"	57	"	1·97	"
Cinnamic acid	7·558	Methanol	149	148·15	0·99	1·0
"	7·029	"	147	"	1·01	"

Table II

Determination of unsaturation in volatile organic liquid compounds

Substance tested: *cyclo*hexene. Solvent: methanol. Catalyst: Adams' platinic oxide
Temperature: 27·1° C

Weight taken, mg	Hydrogen number found	Hydrogen number calculated	No. of double bonds found	No. of double bonds present
3·862	82·0	82·0	1·00	1·0
3·530	81·0	"	1·01	"
3·684	81·0	"	1·01	"
3·966	83·0	"	0·99	"
3·901	83·0	"	0·99	"
4·107	81·0	"	1·01	"
4·607	82·0	"	1·00	"
5·074	82·0	"	1·00	"
4·167	83·0	"	0·99	"
3·672	83·0	"	0·99	"
3·318	83·0	"	0·99	"
3·897	82·0	"	1·00	"

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Notes

DETERMINATION OF THE IODINE VALUE OF PHOSPHOLIPIDS

It has become customary to determine the iodine value of purified phospholipid fractions and of fatty acids derived from them, as well as those of crude phospholipid extracts of tissues, by the method of Yasuda.[1] Thus, lecithins (phosphatidylcholine) isolated from egg yolk, beef heart or yeast by the cadmium chloride method,[2] by low-temperature fractionation from solvents[3] or by chromatographic separation on alumina,[4,5,6] have all been characterised by iodine value determinations according to Yasuda's method, while Folch utilised the same procedure in the description of

TABLE I

COMPARISON OF THE YASUDA AND ROSENMUND - KUHNHENN METHODS WITH THE WIJS METHOD FOR PURE FATTY ESTERS AND PHOSPHOLIPIDS

Substrate	Iodine value			
	Theoretical	Wijs	Rosenmund - Kuhnhenn	Yasuda
Methyl oleate	85·6	86·0 (85·7*)	84·3 (98%)	82·6 (96%)
Methyl linoleate	172·4	173·2 (171·8*)	164·0 (95%)	153·4 (89%)
Methyl linolenate	260·4	259·4 (258·8*)	233·8 (90%)	222·0 (86%)
Methyl ester fraction from cottonseed oil	—	150·2	141·4 (94%)	—
Egg lecithin†	—	76·4	69·0 (90%)	—
Egg phospholipid‡	—	74·5	67·0 (90%)	62·0 (83%)
Egg phospholipid via the isolated fatty acids§	—	75·6	68·0 (90%)	64·4 (85%)

* As determined by the Hormel Foundation on the original batch of ester.
† Phosphatidylcholine.
‡ Consisting essentially of 80 per cent. phosphatidylcholine and 20 per cent. phosphatidylethanolamine.
§ Determined on the fatty acids recovered after hydrolysis and calculated back to the phospholipid basis by use of the determined phosphorus content and fatty acid to phosphorus ratio of the phospholipid.

his preparations of phosphatidylethanolamine,[7] phosphatidylserine[8] and diphosphoinositide[9] from brain. Pangborn also used this method to determine the iodine value of cardiolipin[10] and of the fatty acids recovered from it after hydrolysis,[11] concluding, largely on the basis of the iodine value found in the latter experiment that the chief fatty acids of cardiolipin are linoleic and oleic in the approximate ratio of 5 to 1.

The Yasuda technique is a micro version of the Rosenmund - Kuhnhenn pyridine sulphate - bromine method and differs from it in employing a weaker reagent (0·05 *N* in place of 0·1 *N*) and a longer time of contact (15 minutes in place of 5 minutes).

About the determination of iodine values by macro methods, Williams[12] states that the Wijs, Hanus and Rosenmund - Kuhnhenn methods give similar results with most ordinary oils and fats, but that the Wijs and Hanus reagents are too "fierce" for sterols and unsaponifiable material and give high results owing to substitution. For such substances the milder pyridine sulphate - bromine method is satisfactory. Hilditch[13] states that with fats the Rosenmund - Kuhnhenn method is said to give somewhat lower values than the Wijs or Hanus method.

Yasuda[1] claimed that his micro procedure gave the same results as the macro Rosenmund - Kuhnhenn method on oleic, ricinoleic and (deteriorated) linoleic acids, whereas the macro method gave the same results (near to theoretical) as the Hanus method on oleic and ricinoleic acids but was 3 to 4 per cent. lower for linoleic acid. For cholesterol and cholesteryl palmitate the Rosenmund - Kuhnhenn method gave nearly correct results, while those by the Hanus method were much too high. Fairbairn,[14] quoting Riley,[15] states that Yasuda's method has been found to give only 90 per cent. of the theoretical value with highly unsaturated compounds such as methyl linoleate.

In our hands the macro Rosenmund - Kuhnhenn method has given results that are perceptibly too low, 2 per cent. on pure methyl oleate and increasing to 5 and 10 per cent., respectively, for linoleate and linolenate. With the Yasuda method the observed errors were considerably greater, ranging from 4 to 14 per cent. for the three esters.

As phospholipids from natural and particularly from animal sources often contain considerable quantities of highly-unsaturated fatty acids, it would appear that iodine values obtained by the Yasuda method on phospholipids or on fatty acids or esters recovered from them after

hydrolysis must frequently be much too low. Results obtained by the three methods on egg phospholipids confirm this expectation, see Table I, although the values themselves are not particularly high. The absorption spectrum of the mixed acids after isomerisation with alkali shows clearly the presence of fatty acids with 2, 3, 4, 5 and 6 double bonds in the lecithin used, which was from eggs of hens receiving a diet containing a commercially normal proportion of fish meal.

There seems no reason, on the basis of these results, why the Yasuda method should be preferred to the Wijs (or Hanus) procedures (suitably scaled down to semi-micro quantities when necessary), except perhaps for the examination of crude lipid extracts of tissues containing sterols in quantity. It is also apparent from Table I that with any of the three methods used the iodine value of egg phospholipid is the same whether it is determined directly on the phospholipid or by calculation from the iodine value of the fatty acids recovered after hydrolysis, the figures obtained being identical within the rather wide limits of accuracy of the determination of the fatty acid to phosphorus ratio and of the Yasuda iodine value.

The work described in this note has been carried out as part of the programme of the Food Investigation Organisation of the Department of Scientific and Industrial Research.

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CRETA PRAEPARATA AS A SOURCE OF THE IRON IN FLOUR

The Flour Order, 1953, prescribes the addition of creta praeparata at the rate of 14 oz per sack (280 lb) to all flours except true wholemeal (100 per cent. extraction). The same order stipulates that flour of less than 80 per cent. extraction must be fortified to minimum levels with three nutrients, *viz.*, vitamin B_1, nicotinic acid and iron. The level for iron is 1·65 mg per 100 g of flour.

The iron content of eight samples of creta praeparata has been determined using the method developed by Pringle[1] for cereals. The results ranged from 57 to 91 mg per 100 g. Added to flour at the rate of 14 oz per sack, creta praeparata therefore may itself increase the iron content of the flour by approximately 0·25 mg per 100 g (range 0·18 to 0·28 mg per 100 g). A representative figure for the natural iron content of a 70 per cent. extraction flour is 1·0 mg per 100 g, so that the creta praeparata addition could supply one-third of the amount required to raise this natural level to the minimum statutory level.

The figures for the iron content of creta praeparata represent the total content including that obtained after decomposition of silicious material insoluble in hydrochloric acid. The amount extracted by treatment with hot diluted hydrochloric acid only was 85 to 90 per cent. of these figures.

It is of interest to note that Jones and Moran[2] in a careful analysis of National (80 per cent. extraction) flour concluded that a fraction of the iron in this flour was adventitious, although from a different cause, *viz.*, from the wear of the milling machinery.

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A COLOUR TEST FOR NYLON 66 AND FOR TERYLENE

A COLOUR test, providing a distinction between nylon 66 (polyhexamethylene adipamide) and Terylene (polyethylene terephthalate) and differentiating them from other commercial fibres, is given by a reaction between alkaline *o*-nitrobenzaldehyde and the pyrolytic vapours from the test materials.

Positive results are also given by any polyamide containing adipic acid residues (also from adipic acid itself and from certain of its derivatives, notably *cyclo*pentanone), from non-fibrous Terylene and related polyesters derived from ethylene glycol, and from polyvinyl alcohol.

PROCEDURE—

The test is conducted by placing a few milligrams of the sample in the bottom of a 2-inch × $\frac{3}{8}$-inch ignition tube, clamping the tube in a vertical position and gently heating the lower end with a small flame until, at 350° to 400° C, heavy vapours rise to the upper portion. A narrow strip of filter-paper, moistened with a freshly-prepared saturated solution of *o*-nitrobenzaldehyde in 2 *N* sodium hydroxide, is then brought into contact with the vapour.

The colours produced on the test paper, by the vapour from pyrolysed fibres, are indicated in Table I.

TABLE I

COLOURS PRODUCED ON BRINGING A TEST PAPER MOISTENED WITH ALKALINE *o*-NITROBENZALDEHYDE SOLUTION INTO CONTACT WITH THE VAPOUR FROM PYROLYSED FIBRES

Fibre	Initial colour produced on test paper	Colour on test paper after being washed with dilute sulphuric acid and rinsed in water
Nylon 66	Deep mauve - black (fades in air unless the initial alkalinity is maintained)	Colour washes out
Terylene*	Greenish blue (margin is yellow)	Blue or pale indigo
Other commercial fibres, including nylon 6 (Perlon L) and nylon 11	No colour, or at most grey or brownish colorations	—

* Similar but much less pronounced results are given by calcium alginate fibres and by insolubilised polyvinyl alcohol fibres (*e.g.*, Kanebiyan and Vinylon). Soluble polyvinyl alcohol—sometimes encountered as a size on textile yarns—gives a positive result (see text).

As a matter of routine the test was applied, with negative results, to fibres of the following types: cotton, wool, silk, viscose and proteinaceous rayons, cellulose acetate, polyamides (nylons 6, 11 and 610) and a polyurethane (Perlon U), polyacrylonitrile, polyvinyl chloride and polyvinyl acetate - chloride, and polyvinylidene chloride. The following non-fibrous polymers also gave negative results: polyethylene, polytetrafluoroethylene, polystyrene, polyindene and polymethyl methacrylate; polyvinyl acetate, polyvinyl formal, polyvinyl acetal and polyvinyl butyral; aniline -, urea -, melamine - and phenol - formaldehyde resins, and various cross-linked epoxy-type esins; natural rubber (vulcanised and unvulcanised) and its various derivatives; also chloroprene (Neoprene) and butyl, nitrile, styrene (GR-S), polysulphide and silicone rubbers.

NATURE OF THE COLOURED PRODUCTS

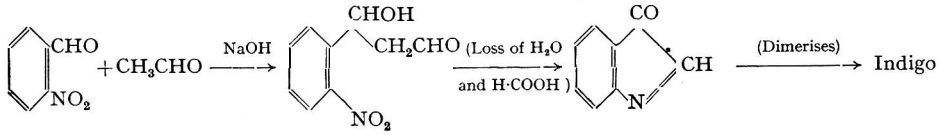
THE PRODUCT FROM NYLON 66—

The deep mauve, almost black, colour produced on the test paper is specific, among commercial fibres, for nylon 66. The same result is obtained on pyrolysis of adipic acid, or derivatives such as adipamide, or nylon copolymers having an adipic component. The reactive material deriving from these pyrolyses appears to be *cyclo*pentanone (adipic ketone); this substance has been reported by Achhammer, Reinhart and Kline[1] in the thermal decomposition products of nylon 66, and the vapour of pure *cyclo*pentanone has been found to produce the required result on *o*-nitrobenzaldehyde test paper.

*cyclo*Pentanone dissolves *o*-nitrobenzaldehyde, but reacts with it only under strongly alkaline conditions of pH 12 or more. The mauve colour of an aqueous alkaline solution of the product changes to yellow (and the solution becomes highly fluorescent) on acidification, or on sufficient dilution with water, but can be restored by addition of enough alkali. The exact nature of this product has not, however, been elucidated.

THE PRODUCT FROM TERYLENE AND RELATED RESINS SUCH AS POLYETHYLENE PHTHALATE AND FROM POLYVINYL ALCOHOL—

A yellow component is largely removed by water or dilute acids, but an insoluble blue or greenish blue pigment remains on the paper. The pigment appears to be indigo; it is unaffected by concentrated sulphuric or hydrochloric acids but is changed to yellow by concentrated nitric acid, and when warmed with alkaline sodium dithionite ($Na_2S_2O_4$) solution the blue colour is bleached but slowly reappears on exposure to air. Indigo is formed (as described by Feigl[2]) when *o*-nitrobenzaldehyde is exposed to acetone vapour, but this does not seem to be the reactive material in the present instance. Small quantities of acetaldehyde have been reported by Marshall and Todd[3] in the thermal degradation products of Terylene, and the vapour of acetaldehyde, although less reactive than acetone, has been found to produce a deep green colour on *o*-nitrobenzaldehyde test paper. Pyrolysis of polyvinyl alcohol also yields acetaldehyde (by rearrangement of the hypothetical monomer, $CH_2{:}CH{\cdot}OH$) and it therefore seems likely that, by analogy with the sequence given by Feigl for acetone, the colour develops as follows—



It is to be noted that whereas polyvinyl alcohol gave a positive result, commercial fibres of insolubilised polyvinyl alcohol gave an almost negligible blue colour. Fibres of calcium alginate (pyrolysis of which might be expected to yield traces of calcium acetate and, in turn, acetone) also gave an indefinite colour, more obscured by yellow products than that from Terylene.

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THE VOLUMETRIC DETERMINATION OF CERIC PERCHLORATE

IT is known that ceric sulphate solutions can be accurately determined by titration with standard ferrous sulphate (and *vice versa*) with the ferrous - *o*-phenanthroline complex as indicator.[1] Several workers[2,3] have extended this method, apparently without modification, to the titration of ceric perchlorate, although Kolp and Thomas[3] point out that it is not particularly good. Heidt and Smith[4] also used the *o*-phenanthroline indicator, but found it necessary to add considerable amounts of sulphuric acid to the ceric solution before titration; they also resorted to heating some of the solutions.

Sometimes the disadvantages of the method can be tolerated, especially in 0·1 *M* or stronger solutions, but in some experiments recently carried out in this laboratory, which required the titration of approximately 1×10^{-3} *M* ceric perchlorate, the *o*-phenanthroline method was found to be useless. When the indicator[5] is added to a perchlorate solution, a scarlet precipitate appears and then immediately dissolves to give a solution having the same colour characteristics as a sulphate solution. Unfortunately the titration end-point is reached only extremely slowly and the indicator blank may be considerable. Heating or the addition of sulphuric acid does not improve the end-point in dilute solutions.

These difficulties can be overcome by the following procedure. An excess of standard ferrous sulphate is run into an aliquot of ceric perchlorate and titrated back with standard ceric sulphate, 2:2′-dipyridyl being used as indicator.[6] In this way a very sharp end-point can be attained and indicator corrections are negligible. As pointed out by Nieuwenburg and Blumendal,[6] the titration must be carried out in approximately *M* hydrochloric acid solution, otherwise the indicator does not develop its colour correctly. The indicator consists of 0·5 g of 2:2′-dipyridyl in 100 ml of ammonium hydroxide, sp.gr. 0·880, and 100 ml of water. About 0·1 ml of this solution is generally suitable.

If the ferrous solution contains a fairly large excess of ferric salt, the yellow - brown ferric chloride complex may cause the end-point to be rather indistinct. This can be remedied by the addition of phosphoric acid[7] just before the end-point, which is then perfectly sharp. The phosphoric acid should not be added before titration, as it considerably increases the rate of autoxidation of ferrous ions. The solution should be stirred during titration to avoid local excesses of the titrating agent, as the indicator is not strictly reversible.

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CONDUCTIMETRIC DETERMINATION OF CARBON IN METALS

IN our paper on "Conductimetric Determination of Carbon in Metals" in the January issue,[1] we referred to a conductimetric apparatus devised by Gardner, Rowland and Thomas.[2]

In listing some features of our own apparatus we implied that the conical joint used at the entrance to the combustion tube in their apparatus was a greased joint. We have been informed that this is not so, but that a dry joint has been found to be perfectly satisfactory, the steel cone being accurately machined.

We are glad to have the opportunity of correcting the statement in our paper. As no mention was made in the earlier paper of the presence or absence of lubricant or of accurate machining of the steel cone, we had assumed that the joint was greased according to the usual practice with joints required to be gas-tight.

We apologise for the misconception on which we based this particular claim to have effected an improvement on the apparatus of Gardner *et al.*

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Book Reviews

STANDARD METHODS OF CLINICAL CHEMISTRY. Volume I. By the American Association of Clinical Chemists. Editor-in-Chief: MIRIAM REINER. Pp. xii + 142. New York: Academic Press Inc.; London: Academic Books Ltd. 1953. Price $4.50; 36s.

For thirty years successive volumes of "Organic Syntheses" have taken an honoured place on the book-shelves of organic chemists, and more recently "Biochemical Preparations" has supplemented these volumes in the laboratory of the biochemist. The "Official and Tentative Methods of Analysis" published by the Association of Official Agricultural Chemists has also provided an invaluable reference book for analytical chemists. No such compendium of tested methods has been available to the clinical chemist. It is hoped that the first volume of "Standard Methods of Clinical Chemistry" and its successors will fill the gap.

The rapid advances that have been made in this field must render well-nigh impossible the production of a new edition of the methods volume of Peters and Van Slyke—the standard book of reference for many years. The American Association of Clinical Chemists are to be congratulated on their intention to produce a series of small volumes that would allow revisions of individual methods from time to time without the necessity of delay for a new edition.

As in "Organic Syntheses" and "Biochemical Preparations," each method has been thoroughly examined in the laboratory of the submitter. Independent workers have thoroughly tested the methods in their own laboratories, and their results, suggestions and criticisms have been included in the published account. Each method, too, has been checked with a large number of normal and pathological blood samples.

The methods described in the first volume are of those analyses most frequently carried out in hospital laboratories. It is intended that specialised investigations should be covered in later volumes. The reviewer has had personal experience of most of the methods that have been chosen to combine satisfactory precision with the speed and simplicity required for hospital routine work. The modification of the Malloy and Evelyn method for bilirubin is new and should do much to meet the disadvantages of the original method, in which the optical density of the final solution is measured after a dilution of serum of one in twenty. The mercurimetric determination of chloride is also unfamiliar to the reviewer, who has a personal preference for the latest modification of the Sendroy silver iodate method, as well as for the Trevan acidimetric technique for calcium, which is more accurate than any of the procedures involving permanganate. It is an interesting sign of the times that both of the methods for determining glucose in blood are photometric. That of Folin and Wu is given because it is widely used in clinical laboratories everywhere although, as the authors point out, it has many disadvantages. The photometric technique of Nelson and Somogyi is in every way the equal of the old titrimetric Somogyi and Schaffer - Hartmann methods. Protein is determined by a photometric biuret method. The thymol turbidity test has been described in full, but it is surprising that the turbidity standards described by Shank and Hoagland, in which barium sulphate is used, are recommended; workers in this country have not had with them the success that has been claimed in the United States. The recommended method for uric acid is the old original method of Folin as modified by Brown in 1945.

The American Association of Clinical Chemists are to be congratulated upon their editor-in-chief. Dr. Miriam Reiner published an invaluable little practical book of methods in 1941. The excellent quality of that book has been maintained in the present volume of this series, with the added advantage that each method has been independently checked. Each method has been prefaced by a brief account of its scientific basis and ends with an equally short account of its practical applications. It is a pity that these applications are so briefly dealt with. This may be why there is no mention of the increase in blood amylase occurring in mumps and in the early stages of certain cases of perforated peptic ulcer. To practising clinical chemists the comments at the end of each method will be specially valuable. C. H. GRAY

FEDERAL FOOD, DRUG, AND COSMETIC LAW. ADMINISTRATIVE REPORTS, 1907–49. Food Law Institute Series. Pp. xvi + 1446. New York: Commerce Clearing House, Inc. 1951. Price $22.50; 161s.

The Food Law Institute was founded in the United States of America in 1949 with functions based on the 1948 recommendations of the Committee on Food, Drug and Cosmetic Law in the American Bar Association, as a non-profit making corporation financed by executives of the food industry to stimulate basic education and research in food law at University schools of law. The

membership of the Institute is mainly legal, but food chemists take a keen interest in its objects. The President of the Institute is Mr. Charles Wesley Dunn, and he has done much voluntary work to foster greater understanding in Great Britain and the United States of America of the food and drugs legislation of the two countries. He was a guest of the President of our Society at a dinner held last summer to enable members of the Society to meet him and exchange ideas.

The Food Law Institute not only sponsors the publication monthly of "The Food, Drug, and Cosmetic Law Journal," but is also engaged in producing a series of volumes to supplement a growing programme of research in American universities into these laws and their administration. The book now under review is the first of this series. It comprises an indexed and complete compilation of the annual reports of the Federal Food and Drug Administration, Washington, on the administration of the original Federal Food and Drug Act of 1906 and subsequent legislation. It has an introduction by Dr. Paul B. Dunbar, formerly U.S. Commissioner of Food and Drugs, and a foreword by Mr. Dunn. In this country we know both Dr. Dunbar through his hospitality to visitors to his country, and, as has been indicated, Mr. Dunn through his visits here.

The book is of deep and absorbing interest to all food chemists, manufacturers and exporters, and its value is enhanced by a very complete index. The early reports recorded in it were the work of that famous and courageous public servant who did such outstanding work in furthering analytical chemistry early in this century, Dr. Harvey W. Wiley. Their historical value cannot be over-estimated, and it would appear that the more recent reports will point the way to further progress.

The reports cover a wide range and, besides dealing with all the common foods, devote space to "economic cheats," to dangerous substances in food and to filth and decomposition. In his introduction Dr. Dunbar states: "With the passage of the Act of 1938, the F.D.A. was again confronted with innumerable enquiries from manufacturers which required it to form day-to-day opinions interpreting the revised law and new regulations. At first these opinions were issued as a mimeographed series for the guidance of the staff, to promote uniformity throughout the country. While they were not distributed to the public, they were available for public inspection at the administrators' offices in Washington and the field stations." This enlightened outlook is commended to the Ministry of Food as commentary on its recent retrograde step in abandoning an official advisory service on food legislation here, which had done much to protect the public and to assist food manufacturers.

It is in their favour that these reports are not overloaded with tabular matter, and their readability and value as critical comment is enhanced thereby. The style is direct and almost provocative. It may be noted that the 1949 report contains critical comment on the necessity for food standards and on their advantage to consumer, producer, distributor and law enforcement officer, all of which seems particularly pertinent to the changes at present under consideration in our own food and drug law.

C. A. ADAMS

CHEMISTRY OF THE LANTHANONS. By R. C. VICKERY, D.Sc., Ph.D. Pp. viii + 296. London: Butterworth's Scientific Publications. 1953. Price 35s.

The lanthanons, which are known more familiarly to chemists as the metals of the rare-earth series, although they are by no means rare, represent a unique group of elements of atomic numbers 57 to 71 inclusive in the Periodic Classification of the Elements. The special feature of this group of metals is the close similarity of its members in chemical and physical properties. This peculiarity has attracted the attention of chemists from the earliest days of their discovery, which was greatly complicated by the difficulty of identifying individual elements. Interest has been considerably enhanced in recent years by the important part played by the lanthanons in atomic energy, both as undesirable impurities in nuclear fuels and as substantial constituents in fission work. This volume, written by an expert who has made many contributions to the chemistry of the lanthanons, is most timely, as there are few books dealing solely and fully with this group of elements and none of recent date.

The first chapter of the book deals with historical development, and this is followed by an interesting survey of the modes of occurrence of the lanthanons in minerals and ores. The next two chapters cover certain physical aspects of the lanthanons, such as atomic structure, spectroscopy, paramagnetism, isotopic constitution, radioactivity and valency. The following eight chapters, occupying nearly half the text of this work, deal with separation and purification techniques. The detailed consideration of these methods is a particularly valuable aspect of this book and shows very clearly the great difficulties inherent in obtaining individual metals

in a high state of purity. It is shown that a combination of methods, which may involve several such devices as precipitations, crystallisations, oxidations, reductions, solvent extractions or ion exchange, is necessary in the long train of procedures from crude lanthanons to a purified product. The properties of the lanthanons and their compounds are reviewed in two chapters, and in some respects it seems that this work has been unduly condensed; for example, complex compounds are dealt with in just over one page, while the heavier lanthanons, terbium to lutecium, receive only five pages. Even so, the essential features of the properties are brought to light, if only very briefly in some instances. The chapter on analytical methods reveals that a great deal of work is still needed in this field. Spectrophotometry and emission spectroscopy are the main general methods for identification and determination, with polarography and volumetric and gravimetric methods being used for a limited number of special elements, such as cerium. The newer techniques making use of ion exchange, chromatography and radioactivation analysis are still in the preliminary stages of development, but should in time provide valuable keys to analysis among these closely allied metals. The book concludes with a short account of the uses and applications of the lanthanons and an appendix on yttrium, which, although not a true lanthanon, invariably appears with this group of metals.

Although this book is not comprehensive, it provides a reliable and readable account of the lanthanons and, as such, is cordially recommended to all chemists who want to know more about this fascinating branch of chemistry than appears in books on inorganic chemistry. There is an adequate index, and a number of selected references to original literature are recorded at the end of each chapter. It is the best book of its kind that I have read on the subject. The price is moderate and the production is very good. It is hoped that the reading of this work will stimulate further activity, particularly among analytical chemists, in this branch of chemistry.

F. H. BURSTALL

ELECTROANALYTICAL CHEMISTRY. By JAMES J. LINGANE. Pp. x + 448. New York and London: Interscience Publishers Inc. 1953. Price $8.50; 68s.

No book surveying the field of electro-analytical chemistry has been published since H. J. S. Sand's "Electrochemistry and Electrochemical Analysis" appeared in three volumes in the years 1939, 1940 and 1941. It is, therefore, particularly satisfactory that a new book has been written to summarise the many advances made during the last decade.

The author, already well known for his electrochemical researches and scholarly writing, has produced a most satisfactory survey of the principles and practice of electrochemical analysis. In the preface it is stated that the original plan was to limit the scope to newer methods based upon controlled-potential analysis and to coulometric titrations. This intention is still obvious, for about two-thirds of the book are given to these subjects, and other branches of the subject have a far less thorough treatment. I regret that when the author decided "to broaden the treatment to include nearly the whole field" he did not adjust the balance so that equally important branches received approximately equal space. Professor Lingane could, with advantage, have extended the scope to include "the whole field" without increasing the size and cost of the book, for he has shown himself to be a master of brief and lucid exposition.

The book is well arranged and indexed and deals with all branches of electrochemical analysis except polarography. The selective bibliographies are well chosen, but it was surprising to see reference to the 1922 edition of W. M. Clark's "Determination of Hydrogen Ions"; the third and last edition was published in 1928. After a brief introduction, chapters are devoted in turn to Measurement of the E.M.F. of Galvanic Cells, Interpretation of the E.M.F. of Galvanic Cells, pH and its Measurement, Potentiometric Acid - Base Titrations, Potentiometric Precipitation Titrations, Potentiometric Oxidation - Reduction Titrations, Automatic Potentiometric Titrations, Conductometric Analysis, Electrolysis, Electrical Instrumentation for Controlled Potential Electrolysis, Methodology of Controlled Potential Electrogravimetric Analysis Procedures, Controlled Potential Electrogravimetric Analysis Procedures, Controlled Potential Electrolytic Separation of Metals Prior to Other Determinative Methods, Internal Electrolysis, Electrographic Analysis, Controlled Potential Coulometric Analysis and Coulometric Titration with Constant Current.

Several parts of the book deserve the highest praise; particularly Chapters III and X, dealing with the interpretation of cell e.m.f. and electrolysis, respectively. I have never read a clearer discussion of e.m.f. sign conventions than that in Chapter III. Over 30 pages are given to descriptions with circuit diagrams of potentiostats: the major development in controlled potential electro-deposition since the year 1940.

After the excellent discussion on elimination of liquid junction potential (p. 47) it was disappointing not to see mention of the use of mixed junction electrolytes to reduce these unwanted errors still further.

The production, printing and binding are of the high quality usually associated with the name of its publishers.

A. J. LINDSEY

STANDARD X-RAY DIFFRACTION POWDER PATTERNS. Volumes I and II. National Bureau of Standards Circular 539. Volume I by HOWARD E. SWANSON and ELEANOR TATGE. Volume II by H. E. SWANSON and RUTH K. FUYAT. Pp. ii + 95; ii + 65. Washington: U.S. Government Printing Office. 1953. Price 45 cents; 45 cents.

The value of the X-ray diffraction method of chemical identification is widely recognised. Considerable assistance to the method has been afforded by the Card Index of X-ray Diffraction Data published by the American Society for Testing Materials. Inevitably the necessity for rapid expansion to cover as large a range of materials as possible has led to various mistakes in the data. For example, for many substances, duplicate cards, differing in certain details, have been allowed, and the user has been left in doubt about the correct choice. In other instances, errors of chemical identity of the specimen used for the X-ray pattern have been discovered.

These mistakes have given rise to criticism and even some misgivings about the general reliability of the Index. A programme of investigation at the United States National Bureau of Standards has therefore been sponsored by a Joint Committee of the American Crystallographic Association, the American Society for Testing Materials, and the British Institute of Physics, with the aim of producing high-grade patterns of carefully purified substances by a counter-spectrometer technique.

The present volumes contain the results obtained in the course of this work on 84 different inorganic substances. Very nearly all the substances are of simple structure types, for example, Al, Si, ZnO, TiO_2, but the second volume contains information on one or two compounds not previously included in the A.S.T.M. Index.

The introductory pages of both volumes refer to the technique of measurement and the general presentation procedure. Analytical details and crystallographic features of each substance investigated are discussed in the text adjoining the tabulated data.

The books are of primary interest to those actually engaged on X-ray work and indicate the real difficulties of compiling and selecting irreproachable X-ray spacing lists and structure-cell dimensions for reference purposes. It seems unlikely that the books will be of much permanent value, as all the X-ray lists will eventually be issued on starred A.S.T.M. cards. The stiff paper covers and rather insubstantial binding can therefore be considered adequate.

H. P. ROOKSBY

Publications Received

CHEMISTRY OF CARBON COMPOUNDS. Volume II, Part B. ALICYCLIC COMPOUNDS. Edited by E. H. RODD, A.C.G.I., D.I.C., D.Sc., F.R.I.C. Pp. xvi + 489–1091. Amsterdam and New York: Elsevier Publishing Co. Ltd.; London: Cleaver-Hume Press Ltd. 1953. Price 105s.

FLUORESCENCE ANALYSIS IN ULTRA-VIOLET LIGHT. By J. A. RADLEY, M.Sc., F.R.I.C., and J. GRANT, M.Sc., Ph.D., F.R.I.C. Fourth Edition. Pp. xvi + 560. London: Chapman & Hall Ltd. 1954. Price 52s. 6d.

SPOT TESTS. Volume I. INORGANIC APPLICATIONS. By F. FEIGL, Eng., D.Sc. Translated by R. E. OESPER, Ph.D. Fourth Edition. Pp. xii + 518. Amsterdam and New York: Elsevier Publishing Co. Ltd.; London: Cleaver-Hume Press Ltd. 1954. Price 45s.

DIE CHEMISCHE ANALYSE IN DER STAHLINDUSTRIE. By R. WEIHRICH. Fourth Edition by Prof. Dr. A. WINKEL. Pp. viii + 223. Stuttgart: Ferdinand Enke. 1954. Price (paper) DM 29.50; (cloth boards) DM 32.

APPROVED METHODS FOR THE PHYSICAL AND CHEMICAL EXAMINATION OF WATER. Second Edition. Pp. ii + 59. London: The Institution of Water Engineers. 1953. Price 7s.

HER MAJESTY'S COLONIAL RESEARCH SERVICE, NIGERIA

A VACANCY exists for a Scientific Officer (Chemist) for Sokoto Malaria Control Pilot Project (CDE 87/14/03). *Qualifications*: Candidates, male, must possess at least a 2nd class honours degree. *Duties*: The project will be conducted in Northern Nigeria, the experiment being designed to test house applications of modern insecticides for control of mosquitoes. The chemist will be required to follow up spraying operation by chemical studies of the persistence of insecticidal deposits and reasons for their disappearance. *Terms of Appointment*: Temporary for one tour of 12 to 24 months in first instance with basic salary according to experience in the scale £400–£650 p.a., plus U.K. pay addition of between £40 and £57 10s. and Overseas Research allowance of between £250 £350 p.a. Gratuity at rate of 15 per cent. of total basic salary drawn payable on satisfactory termination of appointment. *Outfit Allowance*: £60. Free passages for officer, wife and all children under 13; leave of 7 days for each completed month of resident service; quarters, if available, at rental of 10 per cent. of basic salary; income tax at local rates. Apply in writing to the Director of Recruitment, Colonial Office, Great Smith Street, London, S.W.1, giving briefly age, qualifications and experience. Mention the reference number CDE.87/14/03.

SCHWEPPES LTD. require a Chemist in their London analytical laboratory. Duties include the examination and analysis of raw materials and water. Minimum qualifications degree (or equivalent), together with experience in similar work. Initial salary within the range £450–£750. Write for application form to Personnel Manager, 1–4, Connaught Place, London, W.2.

ARMSTRONG SIDDELEY MOTORS require three Laboratory Assistants for Metallurgical Laboratory. Applicants must have Higher National Certificate, A.I.M. or Degree in Metallurgy. Also a Chemist possessing Higher National Certificate, A.R.I.C., or Degree in Chemistry. Apply by letter stating age and full details of experience and qualifications to Reference CAD., Personnel Manager, Armstrong Siddeley Motors, Coventry.

SENIOR ANALYTICAL CHEMIST, F.R.I.C., with experience in food chemistry, required to take charge of the Association's Analytical and Microbiological Assay Section. Some knowledge of bacteriology would be an advantage. Commencing salary of the order of £1,000 per annum according to age and experience. F.S.S.U. Pension Scheme. Apply, as soon as possible, to the Director of Research, British Baking Industries Research Association, Chorleywood, Herts.

LARGE INDUSTRIAL undertaking in the West of England requires, for its expanding Research Department, Physical and Organic Chemists with an interest in plant products. Candidates (within age group 23–30) should have good Honours Degree and preferably some research experience. Salary according to experience and qualifications. Applications, giving full particulars, will be treated in confidence. Write Box No. T. 4365, Haddons, Salisbury Square, London, E.C.4.

CHEMIST required to assist in laboratory dealing with members' day-to-day production problems. Initial salary up to £650. Superannuation (F.S.S.U.). Five-day week. Application forms from Printing, Packaging and Allied Trades Research Association, Randalls Road, Leatherhead, Surrey.

HER MAJESTY'S COLONIAL SERVICE

A VACANCY exists for a Government Chemist in Zanzibar. *Qualifications*. Degree in Agricultural Chemistry; knowledge of soils and soil analysis.

Duties. General chemistry of agricultural products; small amount of forensic work; analysis and survey of soil, routine analysis of coconut oil, mangrove bark.

Appointment. On contract for two tours (24–36 months each tour) with basic salary according to qualifications and experience in the scale £585–£1,320 per annum plus cost of living allowance of between £190 and £350 per annum according to salary. Gratuity of 13½ per cent. of basic salary, payable on satisfactory completion of contract. Outfit allowance £30. Free passages; quarters at rental of 10 per cent. of basic salary; leave of 5 days per month of resident service; income tax at low local rates.

Apply in writing to the Director of Recruitment, Colonial Office, Great Smith Street, London, S.W.1, giving briefly age, qualifications and experience. Mention the reference number CDE.97/10/01.

ALBRIGHT & WILSON LIMITED have a further number of vacancies for Junior Shift Chemists at their factory at Barry, Glam., which is engaged in the manufacture of Silicone products. Applications are invited from persons, preferably with Inter. B.Sc. or equivalent, under 30 years of age and who have completed their National Service.

The posts are of two types:—

(*a*) *For Plant Work*. Duties involve assisting in all aspects of plant operation and control.

(*b*) *For Laboratory Work*. Duties consist of quality control and laboratory scale production of new products.

The company possesses a non-contributory pension scheme. Commencing salary according to age, qualifications and experience. Applications to Appointments Officer, Albright & Wilson Limited, Oldbury, Birmingham.

THOMAS TYRER & CO. LTD., Chemical Manufacturers, Stratford, London, E.15, which is associated with Albright & Wilson Ltd., have vacancies in their laboratories for Research and Development Chemists. Duties involve investigational work concerning new products, both organic and inorganic, pilot plant research and technical service on the application of the company's products. Candidates under 30 years of age with Honours degree or A.R.I.C. and some experience of applicational research or analytical control are preferred, but applicants with qualifications of Inter. B.Sc. or National Certificate and some experience would be considered. Salary according to age, qualifications and experience. There is a non-contributory pension scheme. Apply to Appointments Officer, Albright & Wilson Limited, Oldbury, Birmingham.

ANALYTICAL CHEMIST—Genatosan Limited, Loughborough, have a vacancy for a Qualified Analytical Chemist of B.Sc. or A.R.I.C. standard. Duties include the analysis of pharmaceutical and fine chemicals. Applications, stating age, qualifications and experience, should be addressed to the Personnel Officer.

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