THE ANALYST

A Monthly Publication dealing with all branches of Analytical Chemistry: the Journal of the Society of Public Analysts and Other Analytical Chemists

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

ANNUAL GENERAL MEETING

THE seventy-eighth Annual General Meeting of the Society was held at 5 p.m. on Friday, March 7th, 1952, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. J. R. Nicholls, C.B.E., F.R.I.C. The financial statement for 1951 was presented by the Honorary Treasurer and approved, and the Auditors for 1952 were appointed. The Report of the Council for the year ending March, 1952 (see pp. 222–232), was presented by the Honorary Secretary and adopted.

The Scrutineers, Messrs. J. H. Defrates and G. G. Elkington, reported that the following had been elected Officers for the coming year—

President—J. R. Nicholls, C.B.E., D.Sc., F.R.I.C.

Past Presidents serving on the Council—Lewis Eynon, E. B. Hughes, G. W. Monier-Williams and George Taylor.

Vice-Presidents—R. C. Chirnside, D. W. Kent-Jones and Eric Voelcker.

Honorary Treasurer—J. H. Hamence.

Honorary Secretary—K. A. Williams.

Other Members of Council—The Scrutineers further reported that 417 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—N. L. Allport, 311; H. C. S. de Whalley, 271; C. A. Adams, 264; H. E. Monk, 209; N. Heron, 198; B. S. Cooper, 186; W. Cule Davies, 183; Miss M. Corner, 179; C. H. R. Gentry, 173; R. H. Jones, 157; E. G. Whittle, 151.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—N. L. Allport, H. C. S. de Whalley, C. A. Adams, H. E. Monk, N. Heron and B. S. Cooper.

D. C. M. Adamson, A. J. Amos, T. McLachlan, G. H. Osborn and E. C. Wood, having been elected members of the Council in 1951, will, by the Society's Articles of Association, remain Ordinary Members of Council for 1952. Owing to the death of Dr. H. E. Cox it was necessary for only five members of the Council to retire this year and it has been decided, in accordance with Article 35, that A. A. Smales shall remain an Ordinary Member of Council until March, 1953.

A. A. D. Comrie (Chairman of the North of England Section), H. C. Moir (Chairman of the Scottish Section), C. L. Wilson (Chairman of the Microchemistry Group), J. Haslam (Chairman of the Physical Methods Group) and H. O. J. Collier (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1952.

After the business outlined above had been completed, the meeting was opened to visitors, and the Hon. Mr. Justice Lloyd-Jacob delivered the Bernard Dyer Memorial Lecture (see pp. 233–238).

NEW MEMBERS

James Kenneth Bailey, A.R.I.C.; George Henry Bush, B.Sc. (Lond.), A.R.I.C.; Norman Sidney Curtis, B.Sc. (Lond.); Allan Paul Domleo, B.Sc. (Lond.), A.R.C.S., A.R.I.C.; Adam Wilson Fairgrieve, A.H.-W.C., F.R.I.C.; Kenneth Gardner, B.Sc. (Lond.), F.R.I.C., L.I.M.; Cedric James Gawler, A.A.C.I.; Edmund Hayes, B.Sc. (Lond.), A.R.I.C.; Simon Kaminsky, B.Sc. (Lond.), A.R.C.S., A.R.I.C., D.I.C.; Colin James Patrick McGinn, B.Sc. (Lond.), A.R.I.C.; George Frederick Reynolds, B.Sc. (Lond.), A.R.I.C.; John David Ronald Thomas, B.Sc. (Wales), A.R.I.C.

DEATHS

We regret to record the deaths of

Archibald Rayner
Frank Ernest Thompson

NORTH OF ENGLAND SECTION

An Ordinary Meeting of the Section was held at 2 p.m. on Saturday, November 10th, 1951, at the City Laboratories, Mount Pleasant, Liverpool, 3. The Chairman, Mr. A. A. D. Comrie, presided over an attendance of sixty-two.

Mr. J. F. Clark showed films taken at recent Summer Meetings and Mr. N. Heron presented a paper on "Some Analytical Micro-techniques."

PHYSICAL METHODS GROUP

The Thirty-fifth Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, February 19th, 1952, in the meeting room of the Chemical Society, Burlington House, London, W.1. Dr. J. Haslam was in the Chair.

The following papers were presented and discussed: "Electrographic Analysis—A Brief Survey of its Development with Special Reference to Recent British Apparatus," by P. R. Monk, B.Sc., A.R.C.S., A.R.I.C.; "The Identification of Certain Alloys and Stainless Steels by Electrographic Methods," by G. C. Clark, A.R.I.C., and E. E. Hale, A.R.I.C.

Annual Report of the Council: March, 1952

The roll of the Society numbers 1578, an increase of 16 over the membership of a year ago.

Honours—During the year Professor T. P. Hilditch has been awarded the C.B.E., and the Council offers him its congratulations.

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

B. C. Aston	H. E. Cox	W. E. F. Powney
C. W. Bayley	H. T. Cranfield	F. B. Richardson
F. C. J. Bird	E. H. England	B. W. J. Warren
R. V. Briggs	T. H. Fairbrother	C. R. Wilkins
H. A. Caulkin	F. J. Flowerdew	W. Collingwood Williams
N. J. Chalabi	H. Heap	E. W. Wright
A. J. C. Cosbie	A. R. Jamieson	

Aston was educated at Horley Grammar School, Surrey, and at the Boys' High School, Christchurch, New Zealand. He was at the University of Otago from 1892 to 1896. For three years he held the post of analyst to the Milbury Lime & Cement Co. He became chemist in the Agricultural Department, New Zealand, in 1899, and was Chief Chemist from 1903 to 1936. He was elected a Fellow of the Royal Society of New Zealand in 1919, and was awarded the C.B.E. in 1949. He became a member of the Society in 1906 and was made an Honorary Member in 1937.

Bayley was elected a member of the Society in 1928, and died in August, 1951, aged about 71 years. He was a member of the Pharmaceutical Society and was employed for 34 years at the British Malt Products Co. Ltd., for much of this time as Chief Chemist.

Bird, at the time of his election to the Society in 1899, was analyst to Messrs. Harker, Stagg and Morgan. He was a well-known drug chemist and published many papers in the early years of the century. He died at the age of 91.

Briggs became a member of the Society in 1912 and a Fellow of the Institute of Chemistry in 1925. He died at the age of 72 in Calcutta. He was a student at Bradford Technical College and first pupil and then assistant to Mr. C. Rawson. From 1904 to 1909 he was chemist to the Indigo Research Station. He joined Dr. C. Schulten & Co., analytical and consulting chemists, in 1909, and was made a partner in 1910, remaining in Calcutta until his retirement.

Caulkin was a B.Sc. of London University and became an Associate of the Institute of Chemistry in Branch E in 1908, attaining his Fellowship in 1911. He joined the Society in 1912. From 1900 to 1905 he was chemist with Messrs. Southall Bros. & Barclay in Birmingham. In 1908 he worked with T. V. Hughes almost exclusively on metallurgical work, and at the time of his election to the Society had worked under L. Archbutt as assistant chemist to the Midland Railway Co. at Derby for 3 years. He later returned to Southall Bros. & Co. Ltd. as chief analytical and research chemist.

Chalabi became a member of the Society in 1938; and was then Chief Assistant Chemical Analyst in the Government Chemical laboratory at Baghdad, Iraq. He was Bachelor of Arts, Master of Science (London) and gained the Diploma of Imperial College.

Cosbie joined the Society in 1941, when he was Head Chemist to Truman, Hanbury, Buxton & Co. Ltd., Brewers, London and Burton-on-Trent. About this time he joined Mr. Harold Heron, F.C.S., as Consulting Chemist to the Brewing Industry Laboratories at Manchester, Birmingham and London. He has been succeeded in the partnership by Mr. A. A. D. Comrie, Chairman of the North of England Section of the Society.

Cox was educated at St. Paul's School, and after spending 2 years with John Bell & Croyden became assistant in the laboratory of Allen of Sheffield, where he qualified as A.I.C. He joined Rudd Thompson at Newport, Monmouth, in 1917, staying with him until 1923, during which time he became Ph.D. of London University and a Fellow of the Institute of Chemistry. About this time he met Otto Hehner through the agency of Ainsworth Mitchell, and in 1923 he took over his practice and established that of Hehner & Cox. Two years later he was made Public Analyst for Hampstead and later for Cornwall, and the Isles of Scilly. He became D.Sc. of London University in 1934. He joined the Society in 1918, served six periods on the Council as an Ordinary Member and three as a Vice-President. For many years he was Chairman of the Public Analysts and Official Agricultural Analysts Committee of the Society. He served on the Council of the Royal Institute of Chemistry and was an Examiner in Branch E of the Fellowship. He had been a Vice-President of the Society of Chemical Industry, and Chairman of the Food Group. (Obituary, *Analyst*, 1952, **77**, 169.)

Cranfield was trained for four years in the Essex County Laboratories under T. S. Dymond and George Clarke, and from 1906 to 1910 was Assistant Lecturer in Chemistry and Assistant Analyst under V. H. Kirkham. Until he joined the Society in 1912 he lectured on chemistry and agriculture at the Midland Agricultural and Dairy College under J. Golding. In 1912 he was Deputy Agricultural Analyst for Nottinghamshire. He remained at the Midland Agricultural College for many years and was later appointed Provincial Chemist, N.A.A.S., Ministry of Agriculture and Fisheries. He received the O.B.E. in 1950 and was elected a Fellow of the Royal Institute of Chemistry in 1947.

England joined the Society in 1946 and had been engaged in analytical chemistry for the previous thirty years in the laboratories of Boots Pure Drug Co. Ltd. The first 11 years of this time were spent in the general laboratory examining drugs, galenicals, water, fine chemicals, etc., and the later years in the soap department, specialising in work on soaps, oils, fats and waxes.

Fairbrother was educated at Wigan Grammar School and Manchester University, where he gained the Leblanc Medal. He relinquished a Commission in the army during the 1914–18 war to work on explosives and later became manager of H.M. factory at Lytham. He joined Levinsteins in 1918, becoming head of the Fine Chemical Department in the British Dyestuffs Corporation in due course. In 1927 he took the post of chemist to McDougalls Ltd., flour millers, and was promoted to the Board in 1937. He was elected an Associate of the Institute of Chemistry in 1918 and a Fellow in 1922: he joined the Society in 1927. (Obituary, *Analyst*, 1951, **76**, 680.)

Flowerdew joined the Society in 1934. He became an Associate of the Institute of Chemistry in 1933 and a Fellow in 1937. He was Chief Chemist to Bob Martin Ltd. He was a Member of the Pharmaceutical Society and a Bachelor of Science of Birmingham University.

Heap was 29 when he joined the Society in 1915, and sat on the Council in 1922–3. He became an Associate of the Institute of Chemistry in 1908 and a Fellow in 1911. He was first an assistant to R. Ross, Public Analyst for Burnley, and in 1915 was Lecturer in Chemistry, Public Health Department, University of Manchester. He was Official Agricultural Analyst for the County Borough of Manchester and in 1920 became Public Analyst for the City, retaining this post until 1949. He was made Public Analyst for the Borough of Lancaster in 1930 and for the Borough of Glossop in 1933.

Jamieson was a native of Glasgow and was educated at Renfrew High School. He graduated in Science at Glasgow University in 1924 and was elected an Associate of the Institute of Chemistry in the same year. He passed the Fellowship examination in Branch E in 1930. He entered the service of the Glasgow Corporation in 1926 and was made Chief Assistant to the Corporation Chemist in 1935, later becoming Corporation Chemist and Chief Analyst. He joined the Society in 1930 and was a founder-member of the Scottish Section, of which he was, in turn, member of Committee, Vice-Chairman and Chairman. He was a Vice-President of the Society in 1943–4. For a number of years he was Honorary Secretary of the Glasgow and West of Scotland Section of the Royal Institute of Chemistry, eventually becoming its Chairman and the District Member of the Council of the Institute. He was a Chairman of the Scottish Section, and a Member of the Council, of the Institute of Sewage Purification, a Member of the Rotary Club (Glasgow) and of the Trades House (Bonnet-makers). (Obituary, *Analyst*, 1952, **77**, 170.)

Powney was a student of the City and Guilds of London Institute's Technical College, Finsbury, and was bracketed first in the final examination of the three years' course. He joined the Society in 1900 and was elected an Associate of the Institute of Chemistry in 1908 and a Fellow in 1919. At the time of his election to the Society he was Chief Assistant Chemist to Holloway, Lake & Currie, Consulting Chemists. He later became Chief Chemist in the Department of the Electrical Engineer, London Passenger Transport Board. He died at the age of 72.

Richardson came to Oxford as a Rhodes Scholar from Tasmania in 1920 and graduated with honours as B.A. from St. John's College, becoming M.A. in 1928. Before 1920 and from 1924 to 1925 he was in the Research Laboratory of the Electrolytic Zinc Co. at Risdon, Tasmania. From 1925 to the time of his death he was Chief Chemist to Cadbury-Fry-Pascall Pty. Ltd., Claremont, Tasmania.

Warren joined the Society in 1900 and died early this year at the age of 75. He was elected an Associate of the Institute of Chemistry in 1898 and a Fellow in 1901. In 1900 he became an assistant to Otto Hehner, and spent much of his professional life in the food industry, working for a time with E. R. Bolton. About 1928 he became Chief Chemist to the Chelmsford water undertaking, remaining there until his retirement.

Wilkins joined the Society in 1912 and died at the age of 72 last year. He obtained a B.Sc. with second class honours at London University and was for two years a pupil of Mr. H. B. Yardley, chemist to Odam's Chemical & Manure Co. For the next 13 years he was assistant to Messrs. Redwood and de Hailes, of Red Lion Square, London. When he joined the Society he was chemist to the Co-operative Wholesale Society Ltd., Silvertown. He was elected an Associate of the Institute of Chemistry in 1917.

Collingwood Williams died in his 89th year and was probably the last of the original pioneer public analysts. After being apprenticed to one of the London Guilds he studied at London University, graduating B.Sc. with honours in chemistry and physics. He was elected an Associate of Mason College, Birmingham, in 1884. He became assistant to Dr. J. Campbell Brown on leaving Birmingham, and shortly after was appointed jointly with Dr. Brown as Public Analyst for Lancashire, Liverpool and several boroughs. In 1910 he became whole-time Public Analyst for Lancashire, and held this post until his retirement in 1926. He became a Fellow of the Institute of Chemistry in 1893, joined the Society in the same year and served for two periods on the Council. In 1949 he presented a badge to the North of England Section of the Society for the use of its Chairman. (Obituary, *Analyst*, 1951, **76**, 561.)

Wright became a member of the Society in 1918. He was assistant to and later in partnership with A. W. Stokes, Public Analyst for Paddington.

ORDINARY MEETINGS—Five Ordinary Meetings of the Society were held during the year and the following papers were communicated and discussed—

"The Determination of the Relative Availability of the Nitrogen in Nitrogenous Fertilisers. Part II." By J. Hubert Hamence, M.Sc., Ph.D., F.R.I.C.

"The Determination of the Acidity of Milk." By E. I. Johnson and J. King, O.B.E., F.R.I.C.

"An Improved Volumetric Method for the Determination of Hydrogen Sulphide and Soluble Sulphides." By J. A. Kitchener, Ph.D., A. Liberman, B.Sc., Ph.D., D.I.C., and D. A. Spratt, B.Sc., A.R.C.S.

"The Estimation of Boron in Boronised Metals." By G. H. Bush, B.Sc., A.R.I.C., and D. G. Higgs.

"The Determination of Germanium. Part I. Titration of Mannito-Germanic Acid. Part II. Absorptiometric Determination with Phenylfluorone. Part III. Determination in Flue Dust, Coal and Coke." By H. J. Cluley, M.Sc., A.R.I.C.

"A Critical Investigation of the Use of the Silver Reductor in the Micro-Volumetric Determination of Iron, especially in Silicate Rocks." By Christina C. Miller, Ph.D., D.Sc., F.R.S.E., F.H.-W.C., and Robert A. Chalmers, B.Sc.

"A Technique to Improve the Efficiency of Desiccators." By J. King, O.B.E., F.R.I.C.

"Controlled Potential Electrolysis in the Analysis of Copper-Base Alloys." By G. W. C. Milner, B.Sc., F.R.I.C., A.Inst.P., and R. N. Whittem, B.Sc., A.R.I.C.

"Has the Chemical Quality of Milk Deteriorated?" By J. G. Davis, D.Sc., Ph.D., F.R.I.C.

"Some Observations on the Determination of the Activity of Rennet." By N. J. Berridge, B.Sc., Ph.D.

"The Estimation of 2 : 4-Dichlorophenoxyacetic Acid." By S. W. Stroud, B.Sc.

"Some Applications of the Conway Micro-diffusion Technique." By N. Heron, F.R.I.C.

"The Microchemical Determination of Iron in Aluminium Alloys." By W. R. Nall.

"The Microchemical Determination of Vanadium in Steels." By W. R. Nall.

"The Separation of Carbides from Steel and their Analytical Examination." By R. Pemberton.

The February meeting, at which the last four papers were presented, was organised by the Microchemistry Group.

JOINT MEETING—A Joint Meeting was held on December 5th, 1951, with the Food Group of the Society of Chemical Industry, when there was a discussion on

"The Food Standards Issue—What Does the Future Hold?"

with the following special contributions—

"Compositional Standards." By T. McLachlan, D.C.M., A.C.G.F.C., F.R.I.C.

"Microbiological Standards." By C. L. Heller, Ph.C., M.I.Biol.

NORTH OF ENGLAND SECTION—In addition to the Annual General Meeting, two ordinary meetings were held during the year, and the Section participated in a Joint Meeting of the Microchemistry Group and the Liverpool and North-Western Section of the Royal Institute of Chemistry. Apart from the papers read at the joint meeting, which are recorded below, the following papers were read and discussed—

"Some Applications of the Mass Spectrometer in Analytical Chemistry." By J. G. A. Griffiths, B.A., Ph.D., F.R.I.C.

"Chairman's Address." By J. G. Sherratt, B.Sc., F.R.I.C.

"Some Micro-Analytical Techniques." By N. Heron, F.R.I.C.

"The Use of Laboratory Animals as Analytical Reagents." By A. L. Bacharach, M.A., F.R.I.C.

On the occasion of the joint meeting, visits were made in the afternoon to Lever Brothers (Port Sunlight) Ltd. and to James Bibby & Sons Ltd.

The membership of the Section now amounts to 439.

SCOTTISH SECTION—In addition to the Annual General Meeting three ordinary meetings were held during the year, one in Edinburgh and two in Glasgow. A Symposium, in which the Section participated, of the Microchemistry Group of the Society in conjunction with the Edinburgh and East of Scotland Sections of the Royal Institute of Chemistry and the Society of Chemical Industry was held in Edinburgh. The Section also represented the Parent Society at the Official Opening of the M.O.F. Research Establishment at the Experimental Factory, Aberdeen, by the Minister of Food.

At one Glasgow meeting Dr. H. Dryerre showed the following scientific films—

"Behind the Flame (Coal Gas)."

"Harvest from the Skies (Nitrogen)."

"Ants."

"As Old as the Hills (Oil)."

"The Story of Time (Clocks)."

"Magazine Magic (Four-colour printing)."

The following papers were presented and discussed at the other two meetings—

"The Microscope as an Analytical Aid." By Gordon Rattray, Ph.C., F.R.M.S.

"The Chromatographic Determination of the Acids in Bread." By Hugh C. Moir, B.Sc., F.R.I.C., and A. Kerr.

"The Micro-Determination of Molecular Weights of Picrates by a Spectro-photometric Method." By K. G. Cunningham, A.R.T.C., A.R.I.C., W. Dawson, B.Sc., A.R.I.C., and F. S. Spring, D.Sc., Ph.D., F.R.I.C.

In addition there was an informal discussion on

"The Detection and Estimation of Small Amounts of Acetic Acid,"

including an exhibition of apparatus by W. Anderson and T. A. Eggleston.

There has been an increase in membership of the Section during the year, the total being now 99.

MICROCHEMISTRY GROUP—Three meetings have been held during 1951 in London, Edinburgh and Liverpool respectively. The meeting at Edinburgh was held jointly with the Edinburgh and East of Scotland Sections of The Royal Institute of Chemistry and The Society of Chemical Industry. The Liverpool meeting was held jointly with the Liverpool and North-Western Section of The Royal Institute of Chemistry.

The following papers have been read—

"The Quartz Ultra-microbalance in Radiochemistry." By J. K. Dawson, Ph.D.

"Micromanipulation of Radioactive Gases." By W. J. Arrol, Ph.D.

"The Determination of Trace Quantities of Elements by Radioactivation." By A. A. Smales, B.Sc., F.R.I.C.

"Recent Developments in the Use of Isotope Techniques in Biochemistry." By Professor J. N. Davidson, D.Sc., M.D., F.R.I.C., F.R.S.E.

"The Fractionation of Plasma Proteins and its Clinical Significance." By C. P. Stewart, M.Sc., Ph.D.

"Amino-acid Analysis." By G. R. Tristram, Ph.D.

"Some of the Principles of Quantitative Microscopical Analysis." By J. G. A. Griffiths, B.A., Ph.D., F.R.I.C.

"Some New and Simple Techniques for the Application of Fluorescence Microscopy." By J. King, O.B.E., F.R.I.C.

"Applications of Polarisation Microscopy in Chemical Practice." By N. H. Hartshorne, M.C., M.Sc., Ph.D., F.R.I.C.

An exhibition of microchemical apparatus was held at the Sir John Cass College, London, in January, 1951. In addition to the exhibits shown by Group members a number of manufacturers participated. The Group organised the ordinary meeting of the Society held in February, 1952.

The number of Group members is now 366, an increase of 25 since the last report. The number of members who have returned their index cards showing in some detail their special interests is 56·4 per cent., an increase of 7·9 per cent. during 1951.

The Committee has met three times during the year.

The revised and more exacting specifications for B.D.H. micro-analytical reagents designated "M.A.R.," on which the Committee were invited to advise and assist by the manufacturers, were published in the November, 1951, issue of *The Analyst*. The original recommendations for proposed standard substances for organic micro-analysis were circulated to all members of the Group. Comments were received from a large number of members—some as far afield as New Zealand—and contained much helpful criticism and comments. The collation of this information has now been completed and is being studied by the Committee. It is hoped that the recommendations for these "standards" will be published early in 1952.

Three of the four films dealing with microchemistry belonging to the Group have been handed over to the custody of The British Film Institute. This organisation, which has set up a library of scientific films for use in Universities and by specialists, possesses the necessary facilities for servicing, booking and distribution under ideal conditions. The Committee felt that this would greatly assist in preserving the films for posterity. The titles of the films are—(1) "Microdistillation," (2) "Separations on the Microscope Slide," (3) "Separations in the Centrifuge Cone." Members who may wish to use or show the films should apply to the

Film Distribution Section of The British Film Institute, 4, Great Russell Street, London, W.C.1. (Telephone: Museum 0581.)

A further project in regard to films that the Committee has under consideration is the giving of its support and advice to the making of a new film dealing with use of the micro-balance.

At the New York meeting of the International Union of Pure and Applied Chemistry held in September, 1951, the Chairman, Dr. C. L. Wilson, was elected a member of the Commission on Microtechniques. This Commission is desirous of investigating the interests of microchemists throughout the world, and copies of the Group's "Questionnaire—Index" form have been sent to the Chairman of the Commission in Vienna as a guide to the steps already taken in this direction amongst the Microchemistry Group members.

The Chairman of the Group has been invited to join the Editorial Board of *Mikrochemie* and his name will appear on the cover of future issues.

PHYSICAL METHODS GROUP—The Physical Methods Group has held four meetings in London, one in Leeds and one in Billingham during the past year. The Leeds meeting was held jointly with the Infra-red Discussion Group. All the meetings were well attended.

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

Annual General Meeting, London, November 28th, 1950.

"A Mid-Century Review of Physical Methods of Analysis." By H. M. N. H. Irving, M.A., D.Phil., F.R.I.C.

X-ray Analysis Meeting, London, February 6th, 1951.

"Some Examples of X-ray Analysis in Atomic Energy Research." By J. Thewlis, D.Sc.

"X-ray Diffraction Study of Interfacial Compounds formed in Radio Valve Cathodes." By Y. Budge, B.Sc.

"Some Analytical Uses of X-rays." By H. J. Dothie, B.Sc., A.R.I.C.

Infra-red Spectoscopy Meeting, Leeds, March 9th, 1951.

"The Scope of Infra-red Analysis." By N. Sheppard, Ph.D.

"The Applications of Infra-red Spectroscopy to the Analysis of Polymer Composition." By H. A. Willis, B.Sc.

"Infra-red Spectrometry in the Petroleum Industry." By H. Powell, Ph.D.

Polarography Meeting, London, April 10th, 1951.

"Vibrating Electrodes in Polarography. The Effect of Frequency and Amplitude of Vibration on Diffusion Current." By A. J. Lindsey, M.Sc., Ph.D., F.R.I.C., and E. D. Harris, M.Sc., A.R.I.C.

"The Polarographic Behaviour of Iodo-organic Compounds." By J. E. Page, B.Sc., Ph.D., F.R.I.C.

"Selected Applications of Polarography in Organic Analysis." By G. W. C. Milner, B.Sc., F.R.I.C., A.Inst.P.

Radiochemistry Meeting, London, May 22nd, 1951.

"Radioactive Tracer - Paper Chromatography Techniques." By F. P. W. Winteringham, F.R.I.C., A. Harrison and R. G. Bridges.

"Paper Chromatography of Radioactive Penicillin." By E. Lester Smith, D.Sc., F.R.I.C., and D. Allison.

"The Determination of Sub-microgram Quantities of Arsenic by Radioactivation." By A. A. Smales, B.Sc., A.R.I.C., and B. D. Pate, B.Sc.

"Micro-determination of Sodium and Potassium by Activation Analysis." By R. D. Keynes, M.A.

Physical Methods Meeting, Billingham, October 19th, 1951.

"Physical Methods in the Titanium Pigment Industry." By F. R. Williams, Ph.D., F.R.I.C.

"Rapid Methods of Quantitative Analysis of Rutile - Anatase Mixtures." By W. Hughes, Ph.D., and H. Smith, M.Sc.

"Surface Area Measurements by the High Vacuum Nitrogen Adsorption Method." By C. T. Morley Smith, B.Sc., F.R.I.C.

The number of Group members is now 388. This represents an increase of 32 since the last Annual Report.

During the past year there has been some movement to obtain a liaison between the various groups and discussion panels concerned with spectroscopy. The Physical Methods Group has collaborated with other groups in the production of the *British Bulletin of Spectroscopy*, the first issue of which appeared in September, 1951. This is issued jointly with the Industrial Spectroscopy Group of the Institute of Physics, with the Photo-electric Spectrometry Group and the Infra-red Discussion Group, and will appear quarterly. It is hoped that this may be the first step to the closer international collaboration of spectroscopists.

Polarographic Discussion Panel—The Panel now has 82 members. The Chairman is Dr. A. J. Lindsey and the Honorary Secretary is Mr. G. W. C. Milner.

Two meetings were held during the year, at which the following papers were presented—

"The Determination of Trace Metals in Foodstuffs and Biological Materials." By J. V. Westwood, M.Sc.

"The Determination of Aluminium, Tin and Zinc in Water." By H. W. Hodgson, F.R.I.C., and J. M. Glover, B.Sc., F.R.I.C.

"The Vibrating Electrode in Polarographic Determination of Alkyl Peroxides." By E. R. Roberts and J. S. Meek.

"A Recording Polarograph for Continuous Flow Operation." By K. C. Overton and J. A. Lewis, A.R.I.C.

"An Improved Randles-Type Cathode-Ray Polarograph." By G. F. Reynolds, B.Sc., F.R.I.C., and H. M. Davis.

BIOLOGICAL METHODS GROUP—During the year the Group has held four scientific meetings, at all of which papers were read and discussed, and at one of which demonstrations were given.

On December 19th, 1950, the Annual General Meeting of the Group was followed by an Ordinary Meeting, at which the following papers were presented—

"Assessment of ACTH Activity." By I. D. K. Halkerston, B.Sc., and M. Reiss, D.Sc., M.D.

"*Euglena gracilis* as an Assay Organism for Vitamin B_{12}." By G. E. Shaw, B.Sc., Dip.Bact.

"The Effect of Interfering Agents on the Vitamin B_{12} Plate Assay (*E. coli* mutant method)." By W. F. J. Cuthbertson, Ph.D., F.R.I.C., Valerie Herbert, H. F. Pegler and C. Quadling.

On March 12th, 1951, an evening meeting was devoted to a discussion on "The Evaluation of Drugs in Man," at which the following papers were read—

"The Evaluation of Drugs in Man with Special Reference to Antihistaminics." By W. A. Bain, M.D., M.B., Ch.B.

"Tests on Analgesic Drugs in Man." By C. A. Keele, M.D., M.B., B.S., F.R.C.P., M.R.C.S.

Through the kindness of the Director of the National Institute for Medical Research a Summer Meeting of the Group was held at Mill Hill on June 1st, 1951. The following communications were presented and discussed in the Fletcher Memorial Hall.

"Errors of the Mouse Insulin Assay." By P. A. Young, B.Sc., and G. A. Stewart, B.Sc.

"Simplification in Statistical Computation." By D. C. Gilles, B.Sc., Ph.D., D.I.C.

"Cup-plate Assays of Biotin and Nicotinic Acid." By S. Morris, D.Sc., and A. Jones.

After tea the following demonstrations were given in the Institute's Laboratories—

"Demonstrations of Some of the Less Well-known Methods of Biological Assay in Use at the National Institute for Medical Research." By W. L. M. Perry, Ch.B., M.D.

(*a*) Some Aspects of Plate Assays of Antibiotics. (J. H. Humphrey, B.A., M.D., and J. Lightbown, M.Sc., Dip.Bact., Ph.C.)

(*b*) Assay of Hyaluronidase. (J. H. Humphrey, B.A., M.D., and R. J. Jacques, M.D.)

(*c*) Assay of Tuberculin. (D. A. Long, M.D.)

(*d*) Assay of *d*-Tubocurarine by Rabbit Head-Drop Method. (W. L. M. Perry, Ch.B., M.D.)

(*e*) Assay of Oxytocic Activity of Posterior Pituitary by Fowl Blood-Pressure Method. (R. J. Jacques, M.D., W. L. M. Perry, Ch.B., M.D., and M. Schachter, M.Sc., M.D., C.M.)

(*f*) Pyrogenic Activity of Plasma Dextrans. (W. W. Douglas, M.D., and W. L. M. Perry, Ch.B., M.D.)

"Assay of Digitalis." By G. F. Somers, B.Sc., Ph.D., Ph.C.

"Assay of Vitamin B_{12} with *Euglena gracilis*." By P. Waterhouse, B.Sc.

"Microbiological Assay of Crude Extracts Containing Several Growth Factors." By F. A. Robinson, M.Sc.Tech., LL.B., F.R.I.C., and B. W. Williams, B.Sc.

"Apparatus for Automatic Recording of Blood-clotting Times." By S. S. Randall, M.Sc.

The last meeting of the Session, on October 26th and 27th, 1951, took the form of a Symposium on "The Evaluation of Chemotherapeutic Substances," with Dr. G. M. Findlay in the Chair. After a general introduction by the Chairman, the following papers were presented and discussed—

"The Design of Antibiotic Assays." By W. L. M. Perry, Ch.B., M.D.

"Evaluation of the Biological Properties of Newly-isolated Antibiotics." By J. Ungar, M.D., M.R.C.S., L.R.C.P.

"Factors Determining the Character of Inhibition Zones." By J. H. Humphrey, B.A., M.D.

"Evaluation of Antituberculous Compounds *in vivo*." By J. M. Robson, F.R.S.E., D.Sc., M.D., M.B., Ch.B.

"Practical Aspects of the Routine Testing of Antituberculous Compounds." By A. R. Martin, M.Sc., Ph.D.

"Evaluation of Antiviral Compounds." By L. Dickinson, M.Sc., Ph.D., A.R.I.C.

Next morning, emphasis was on the "Evaluation of Anti-protozoal Substances" and the following contributions were given—

"The Evaluation of Amoebicidal Substances *in vivo*," followed by a film, "The Chemotherapy of Experimental Amoebiasis." By L. G. Goodwin, M.B., B.S., B.Pharm., B.Sc.

"Routine Testing of Amoebicidal and Leishmanicidal Agents." By J. D. Fulton, M.A., M.B.

"The Evaluation of Chemotherapeutic Agents directed against Trypanosome Infections." By E. M. Lourie, M.B., B.S., M.R.C.P., M.R.C.S., L.R.C.P., D.T.M., D.P.H.

"The Evaluation of Antimalarial Substances." By D. G. Davey, M.Sc., Ph.D.

"Problems of Drug Resistance, with Special Reference to Malaria." By A. Bishop, Sc.D.

Membership has increased during the year from 179 to 199. Following the success of the demonstrations at the Summer Meeting, it is proposed to make a laboratory meeting of this type an annual feature.

ANALYTICAL METHODS COMMITTEE—Work of the Sub-Committees has resulted in the publication of several Reports during the year in *The Analyst*. The Chemical Assay of Aneurine in Foodstuffs (p. 127), The Analysis of Meat Extract (p. 329) and an Addendum to the Report on Determination of Esters (p. 387) were typical of the work published by the Committee. The Examination of Detergent Materials (p. 279) was a report not in the usual style; the Sub-Committee were unable to recommend any standard method, but it was considered that the analytical information collected should prove of value if published. It was the opinion of the Chemical Panel of the Vitamin Sub-Committee (p. 58) that a standard chemical method for determination of nicotinic acid was impracticable at present. A Report on the Determination of Carotene in Green-leaf Material other than Grass has been completed.

Sub-Committees continue their activities and work on the Determination of the Freezing Point of Milk and a standard procedure for lead in foodstuffs are nearing completion. The sale of the Bibliography of Standard Methods has been very satisfactory and a reprint has been necessary.

The Committee has reported to Council on the practicability of publication of recommended methods in all fields of analytical work and, as a preliminary, the Secretary of the

Standard Methods Committee has written to contributors to the Bibliography to ask their co-operation in starting work on a book of standard methods.

PUBLIC ANALYSTS AND OFFICIAL AGRICULTURAL ANALYSTS COMMITTEE—The Committee has suffered a very severe loss by the tragic death of the Chairman, Dr. H. E. Cox. Mr. George Taylor has been elected to be the new Chairman.

The Committee has only met once during the past year when the Rag Flock and Other Filling Materials Act, 1951, The Proposed Amendment of the Food and Drugs Acts, 1938 to 1950, Negotiations regarding the remuneration and conditions of service of Public Analysts and the formation of a Professional Association of Public Analysts were discussed. Regarding the last Messrs. Taylor, McLachlan, Clark, Wood, Monk, Hamence, Thin and Voelcker have been appointed as a Committee to formulate more precisely the plans for forming the Association.

As regards the negotiations that have taken place concerning the remuneration of Public Analysts, agreement has been reached for Part-time Public Analysts, but negotiations are still proceeding with regard to Full-time Public Analysts.

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

B.S.I. Committees—

Dr. W. F. Elvidge, Transfusion Equipment for Medical Use Committee.
Dr. J. G. Davis, Bacteriological Technique for Dairying Purposes Committee.
Dr. J. G. Davis, Sampling of Dairy Products Committee.
Dr. J. G. Davis, Dairy Apparatus Committee.
Mr. J. King, Dairying Industry Committee.
Dr. G. H. Walker, Sampling of Dairy Products Committee.
Mr. H. E. Monk, Disinfectant Fluids Committee.
Dr. J. E. Page, Standardisation of Glass Electrodes Committee.
Mr. J. F. Clark, Dr. J. H. Hamence and Dr. K. A. Williams, Methods of Analysis of Condensed Milk and Ice Cream Committee.
Mr. W. Gordon Carey, Dr. J. H. Hamence and Dr. K. A. Williams, Testing of Water Committee.
Mr. H. E. Brookes, Glass Blown, Drawn and Other Volumetric Glassware Committee.

Mr. G. Taylor was appointed as the Society's representative on the Chemical Divisional Council of the British Standards Institution for the next three years in the place of Dr. G. W. Monier-Williams who had completed his three-years' term of membership.

Dr. G. W. Monier-Williams has accepted the Chairmanship of the Committee set up by the British Standards Institution to draft methods for testing water.

Mr. G. F. Hall has taken the place of Dr. W. F. Elvidge on the Regional Advisory Council for the Organisation of Further Education in the East Midlands.

Mr. C. J. Regan was appointed as the Society's representative on the Joint Committee on Analytical Definitions.

The Council of the Society takes this opportunity of thanking all its representatives for the work that they have carried out on the various Committees during the year on behalf of the Society.

HONORARY TREASURER'S REPORT—At the end of 1950 it appeared that the increased subscription rate to the Society and the increased cost of *The Analyst* to outside subscribers had resulted in placing the Society in a satisfactory financial position. Although we began the year 1951 full of optimism, we were soon caught up in the now all too familiar tide of increasing costs and but for a timely grant from the Chemical Council at the end of the year the Society might have finished with an adverse balance. The principal causes of our unexpectedly increased expenditure were substantial increases in the cost of printing *The Analyst* and in postage and the cost of notices of meetings. In spite of the increased costs the Council still hopes to maintain grants to the Sections and Groups of the Society at the rates agreed in 1951, and to give them additional assistance from the Society's office staff.

It is gratifying to report an increase in the sales of *The Analyst* for 1951 and we hope that this will be maintained in the present year.

It is difficult to predict how the ever-rising costs will affect the finances of the Society during 1952, but we are already committed to extra expenditure in respect of office staff.

Efforts are being made to increase the Society's income from advertisements and also to make all possible economies in the Society's office without reducing the efficiency of the organisation.

A further increase in the subscription to the Society is to be avoided if possible, but it must be remembered that the last increase in the subscription rate, although introduced only a short time ago, was in fact considerably overdue, and, moreover, that the increase enabled the Society not only to build up an efficient office organisation in order to cope with the expanding activities of the Society but also to distribute Abstracts C to all members.

THE ANALYST—The volume for 1951 contained 740 pages, compared with 694 in 1950.

The Decennial Index for the years 1936 to 1945, which had suffered delay owing to the loss of the card-indexes for many of the volumes, has now been published and arrangements made to prevent untoward delay of the next general index.

During 1951 the number of papers and notes published amounted to 103 and 47, respectively, against 103 papers and 38 notes in 1950. The number of pages occupied by papers and notes in 1951 was 670 compared with 640 in 1950.

Three issues of a Bulletin covering the activities of the Society and its constituent Sections and Groups have been published during the year and distributed with *The Analyst*. A Table of International Weights printed on card has also been sent out.

The editorial staff has been strengthened by the engagement of Mr. B. J. Walby, B.Sc.

The printing number of the monthly issues is now 4450.

BULLETIN—It has been decided to supplement the pages of *The Analyst*, from time to time, by the issue of a Bulletin containing advance news of the contents of papers accepted for publication and other news items that would not normally be printed in *The Analyst* itself. During the past year three such Bulletins have been published and it is intended that this feature of the activities of the Society shall become a permanent one.

XIITH INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY—In response to an invitation from Sir Cyril Hinshelwood, Chairman of the British National Committee for Chemistry of the Royal Society, the Council nominated Dr. J. R. Nicholls, President, Mr. R. C. Chirnside, Vice-President, and Dr. K. A. Williams, Honorary Secretary, as Delegates to the Congress. The Congress was held in September, 1951, in New York, and about a thousand papers were read to it. The Delegates reported on their attendance at an informal dinner held by the Society in December, 1951.

AMERICAN CHEMICAL SOCIETY.—A congratulatory address was presented to the American Chemical Society by the President on the occasion of the celebration of its 75th Anniversary and thanks have been received for this from Professor N. H. Furman, President of the American Chemical Society.

INTERNATIONAL CONGRESS ON ANALYTICAL CHEMISTRY, 1952—Mr. Taylor has continued to act as Chairman of the Executive Committee of the Congress. Details of the meetings to be held in Oxford in September, 1952, have now been very largely worked out. The proceedings will appear in a special number or numbers of *The Analyst*. The Congress will be held under the patronage of the International Union of Pure and Applied Chemistry and the Board of the Analytical Chemistry Section of the Union, and some of the commissions of the Union will meet during the period of the Congress at Oxford.

MEMBERSHIP OF SECTIONS—Membership of the Sections of the Society has now been extended automatically to all members resident in the relevant areas.

CHEMICAL COUNCIL—The Chemical Council has again made a grant to the Society to help towards the publishing costs of *The Analyst*, for which the Council of the Society expresses its thanks.

POLICY COMMITTEE—The Council of the Society has formed a Policy Committee, under the chairmanship of Mr. George Taylor, to consider various matters connected with the future development of the Society.

SWISS SOCIETY OF ANALYTICAL AND APPLIED CHEMISTRY—An invitation was received, as in past years, from this Society for us to send Delegates to its autumn meeting. Unfortunately this proved impossible this year, owing to the incidence of the International Meetings in New York and Washington at the same time. The Council of the Society has, however, decided to nominate a Delegate to the meeting in future years.

FOOD AND DRUGS BILL—The Ministry of Food asked the opinion of the Society on various amendments it is proposed to make to the Food and Drugs Acts. These have been considered by the Council and by the Public Analysts Committee. The Council has reported that on the whole they are in broad agreement with the proposals in so far as the interests of analytical chemistry are concerned. Detailed comments of various Public Analysts have been forwarded to the Ministry.

BUREAU OF ABSTRACTS—Mr. A. L. Bacharach was nominated to sit on the Board of the Bureau in place of Dr. J. R. Nicholls when the latter became President of the Society.

JOINT LIBRARY COMMITTEE OF THE CHEMICAL SOCIETY—Dr. J. G. A. Griffiths was again nominated to represent the Society on this Committee.

BRITISH STANDARDS INSTITUTION—The Society is now represented by members on no fewer than 75 of the British Standards Institution's Technical Committees, which meet to consider the standardisation of Methods of Analysis. Mr. George Taylor represents us on the Chemical Divisional Council. Dr. K. A. Williams is also a member of this and sits as well on the General Council of the Institution.

J. R. NICHOLLS, *President.*

K. A. WILLIAMS, *Honorary Secretary.*

The Second Bernard Dyer Memorial Lecture

Lines of Development

By the Honourable Mr. Justice LLOYD-JACOB

(*Delivered at the Annual General Meeting of the Society, March 7th*, 1952)

If on a snowy Easter Tuesday thirty-five years ago the German pilot of a yellow-nosed Fokker had deflected his aircraft a little to the left, I might well have been sitting amongst you listening to the lecture and not have been the person giving it. It is only right to add that if he had deflected it a little to the right, I should probably have received the burst of machine-gun fire in a somewhat more vulnerable part, and in all probability I should have been denied the opportunity of either listening or lecturing.

This personal reminiscence will not, I feel sure, be interpreted as a plea for sympathy. I mention it so that you may know that it was my original intention to follow a career in chemistry, and it was the physical disability I sustained in those days that constrained me to seek an alternative occupation. You will therefore understand how deeply sensible I am of the honour that you do me by this invitation, and I hope you will allow me to express my pleasure in being able to be of your company this evening.

As the details of Dr. Bernard Dyer's life and of his great work on soil analysis have been already so elegantly collated by Sir John Russell, the scope for further discussion of such matters is severely limited, and would in any event have been quite beyond my powers to deal with, so that I have chosen to accept the freedom accorded to me when this invitation was extended, to speak on a topic of my own choosing, and, because a title is thought to be desirable, let me call it "Lines of Development." I have prepared it in the hope that the direction of my own thoughts may be of some interest to you who might so easily have been my colleagues. They are primarily, of course, the thoughts of a lawyer, for, despite our normal pretence to the contrary, the primary pre-occupation of our lives must necessarily colour the pattern of our thought; but I hope they will bear in some measure the mark of my early scientific training, for otherwise, even if the demands of courtesy retained for me your superficial attention, I could not expect to establish that mental accord with you without which no real germination of ideas is possible. Moreover, I can think of no more suitable body than your Society with whom to share these musings of mine, for your day-by-day work covers so wide a range, taking you into so many regions not yet fully explored and documented or surveyed by the academic scientists, that you are already conditioned to what is the main theme of the subject I have chosen. Indeed, I would go so far as to say that you are the ideal audience from one point of view, because your work has brought to you a ready acquaintance with the vocabulary, the characteristic intellectual approach and the general field of activity of workers in most aspects of commerce and industry.

You do not need to be reminded, therefore, that it is wholly impossible for any one man to have command of all the scientific activity of our day and generation. We have progressed a good way since the days of Leibnitz. Nor did you need a war, as did some politicians, civil servants and Service chiefs, to make you realise the necessity for teamwork in scientific development.

It happened to be my good fortune in the war to see how in this country and in the United States of America the most formidable problems in meeting the needs of the Services crumbled away before the planned attack of specially selected groups of scientific workers. What perhaps was even more striking was the initial resentment, the disdainful sneer, the rooted disbelief and the final incredulous acceptance when some wholly fresh approach, founded upon scientific hypotheses and pursued with the typical intellectual honesty and diligence of scientific investigation, provided a solution to a problem that rule-of-thumb methods of treatment had effectively hidden from the very people who should have appreciated it.

To mention but one instance will suffice out of the many. In my time in the Royal Flying Corps and for many years thereafter in the Royal Air Force, it was the practice to ordain engine overhauls after a certain specified number of flying hours. If as a consequence

it meant that aircraft were out of service just when they were most wanted, that was a necessary evil. So far as concerned the pilot, who would be perfectly happy in having sweetly running and balanced engines, he had to fume and fret whilst the satisfactory ones were taken out or, worse still, whilst one only of a pair was taken out, and take his chance that the stand-by engine would be equally satisfactory.

You probably all know that it was brilliant work by Waddington and some of his co-workers, developed merely from a study of the statistical data obtained from a number of Service stations, that altered the whole set-up and vastly increased the proportion of aircraft available for operational purposes. That was a striking instance of how scientific concentration upon a problem demonstrated to the people most closely concerned that they were proceeding on wholly wrong lines.

That and a number of other experiences have convinced me that the most promising areas for future scientific growth, if one leaves out of account the very gifted people who happen to strike some wholly new approach, are those that have been neglected as a sort of no man's land, that is to say, those that lie between the various well-established scientific fields; it is in precisely those areas that collaboration is most necessary. But, of course, it has got to be collaboration of the right kind. Perhaps an instance will illustrate exactly what I mean. Let me take an engineering problem that is statistical in its essence. Ten engineers untrained in statistics can be expected to get on no faster than one engineer who has no knowledge of statistics, assuming they are all of substantially equal competence. Moreover, if the engineer, knowing no statistics, has the good fortune to collaborate with a statistician, but finds one to whom engineering is a closed book, then the one will fail to state his problem with the necessary precision that the other requires to contribute his share, and the answers of the other, even if he is able to give any, will not be competently applied because they will be but imperfectly understood.

What is seen to be wanted, therefore, if my diagnosis is an accurate one, is not so much the skill to experiment in the field of another, but the competence to understand and to criticise and to appreciate the experiment and the results that the experiment secures. It was upon such lines that the most useful teamwork was in fact done during the war. It is a tragic thing that the cloaks of security still prevent the publication of the whole truth about the tremendous progress that was made during that time by reason of this collaboration. It is tragic from a wider point of view too, because, had it been otherwise, the concepts and the characterisations of the scientist would not remain so dreadfully unfamiliar to the great majority of his fellow men. He would not then continue to be regarded and often feared, as at present, as a sort of medicine man—a very strange and mysterious creature, possessed of almost magical powers and stuffed with the most recondite knowledge. But some understanding of him, or at any rate some better understanding of him, might save him from the thought of the ignorant that his very power might make him perhaps the most appropriate sacrifice if, in these days of mob hysteria over nuclear fission, some sufficient propitiation is called for.

Do those thoughts give us any guide at all to what is, after all, our mutual problem, namely, the administration of justice in cases where estimations of scientific matters must necessarily be made if the cause is to be fully appreciated? My very dear friend and one of your number, the late Dr. H. E. Cox, used often to reproach me with the apparent uncertainty of the result of patent actions, and he would never be pacified when, I confess somewhat superficially, I used to urge upon him that exaggerated expectations of the possibilities of the isolation of truth were not appropriate to a scientist. There is, of course, no question that in some fields of human activity the unscientific, intuitive method of the historian may be more fruitful of result; but is that true of the administration of justice?

I should like to spend a little time in considering the factors that have to be weighed in arriving at a fair conclusion. There are two distinct aspects of the administration of justice: the first is the laws that are administered; the second is the technique by means of which these legal concepts are made effective.

Of the first, I must content myself with merely stating it, for it would ill-become a High Court judge publicly to question the propriety of the laws that he is called upon to interpret and apply. If you are sufficiently interested in that topic, let me refer you to your Member of Parliament. I may also say that even judges are aware that only bad workmen blame their tools.

The second, however, is a proper field for discussion. Before I embark upon it you will,

I know, allow me to utter a cautionary note. Some of you—possibly many of you—may be smarting under the recollection of your own testimony being disregarded by a Court and nourishing some sort of conviction that injustice appears to be inevitable. Will you allow me to remind you, as I fairly can a scientific audience, that for reliable statistics, long runs under essentially constant conditions are vitally necessary, and where conditions vary substantially, spurious and specious results may well be secured. If you, in retaliation, would remind me of the theory of small samples, let me say that the results obtained by that method of inquiry can only be applied with great caution and then only within the specially defined parameter that the investigation requires. Loose and approximate readings can only be adequate within the limits that experience has shown to be applicable.

If, therefore, you have by any grievous mischance ever found yourself on the losing side, you will not, I am sure, conclude that you have thereby demonstrated the existence of an unjust system. It is conceivably possible that one or other of two alternatives has happened: first, that you may in fact be a bad witness or, second, that you may have come before an incompetent court. Both you, as witnesses, and myself, as a judge, can comfort ourselves by turning to quantum mechanics. There we learn that the whole past of a system does not predicate its future in any absolute sense at all. It merely determines the possible distribution of possible futures of the system. That will encourage us, I have no doubt, to strive on your part to be better witnesses and on my part to be a better judge.

There is another matter we must always keep in mind, and that is the essential difference between the desire for the ascertainment of truth and the desire for logical and consistent thought, because they are by no means the same thing. Of course, all ultimate truth, if ascertainable by our human thoughts, must necessarily be found consistent, because otherwise our minds could not comprehend it. That I accept and understand. But as we all readily acknowledge, if we insist on looking for consistency we are not necessarily making the best approach to a new field. That is rather the mark of the final integration, when from the class of previously unresolved alternatives we can set out in organised fashion all that is demonstrably valid; so that until that moment comes it is better, is it not, to hope that some way may be found to reconcile opinions rather than to accept without demur a conclusion that has only consistency to support it. Here again, an audience of scientists will not find it difficult to follow me, because you all know that so frequently a rampart of apparently impenetrable logic has been built around certain observed phenomena, but that rampart had necessarily to exclude from its ambit phenomena that were imperfectly understood at the time, but subsequently were found to be plainly and normally related to the remainder. It needs the genius of men like Einstein and Planck to show us how vulnerable these Maginot Lines of our thoughts really are.

You can all understand with what deep interest it was that I noted that, as shown in the first lecture, Sir John Russell's thoughts followed rather similar lines to my own. Two years ago he said this: "The nineteenth century was a time of great generalisations, majestic in their comprehensiveness, magnificent in their simplicity." But he went on: "In this century the accumulation of awkward facts that could not be fitted into so simple a scheme broke down the old generalisations." It was on that ground, as you will remember, that he applauded the adoption of the empirical approach. That is what I am going to ask you to do in considering this common problem of ours.

It will help us also, I think, if we remind ourselves of the acknowledged variation in the accuracy of scientific prediction. Let me illustrate that. Whilst we would all readily accept a time and area for, say, a solar eclipse, provided it was published by an acknowledged authority, we cannot restrain our mistrust of the forecasts of a general election based upon polls of public opinion. Why is this? It is because, is it not, that precision of statement in our experience is only found to be possible where there is a high degree of isolation between the observer and the observed phenomena. In astronomy, for example, we consider only a relatively small number of objects, differing widely in size and only loosely coupled together, assumed to have substantially no effect one upon the other, and for all practical purposes wholly independent of the observer himself. In the social sciences, the coupling between the observer and the phenomena he has to observe cannot be avoided and its effect should never be minimised. Indeed, normally the observer finds himself unable to avoid influencing the very thing that he seeks to observe. When he knocks on the door and makes his inquiries as to how the lady of the house proposes to vote, the clothes that he wears and the quality of his speech may easily affect the answer that he gets.

It is also the fact that he must rely upon very short statistical runs for his data, because the events into which he is inquiring are usually very short-term events.

I need not pause here to remind you of how the genius of the British people intuitively appreciated the undesirability of such couplings in the administration of the law. I do not pretend, even to myself, that it was due, in any sense, to a scientific approach. It was no doubt, and indeed necessarily must have been, an empirical approach, but that in no way detracts from the credit that must be given to the race to which we belong for that great discovery. What was it that they insisted upon? They insisted upon the independence of the judiciary, the development of disinterested advocacy, the formulation of most precise rules as to corroboration and, above all, upon the isolation of the jury who were to find the facts. All those requirements, when you come to think about it, were not only desirable but practically essential if you were ever to obtain satisfactory proof. But that is rather a different thing from the ascertainment of truth itself. In that desire, which is after all an overriding desire in any judicial system, to arrive at the truth as between party and party, was it wrong when that same genius of our people led us to insist upon oral testimony in public, confrontation of the parties, the whole investigation to be in open court, the presence of any interested member of the public, and to attach, as it did, the greatest weight to findings of fact by a judge who had both heard and seen the witnesses? I am myself convinced that it was all part of the same genius, because equally with those other matters I have mentioned, it shows an appreciation of the fact that, quite independently of the language used, social animals do possess an active, intelligent and flexible means of communication one with the other that can vary tremendously, far more widely than we normally suppose, both in content and complexity. I hope I can make my meaning plain by taking an extreme case. Let me suppose that I am alone with an intelligent foreigner, and that neither of us has any appreciation whatever of the language of the other and that our *amour propre* denies us the opportunity of using sign language; making those assumptions, how much is there that he and I could share? It is plain, when you think about it, that, if we remain alert to each other's movements, we can detect interest or emotion just as readily as if we had language to disclose our thoughts and feelings. I postulate, of course, an intelligent foreigner, because my reading of his expressiveness is likely to be more fruitful than if he were moronic; but even the moron will disclose something, even if it is only his imbecility.

So it is that the visual observation of a witness, the inflections of his voice, the readiness or hesitancy of his answers, apart altogether from the words he uses, are very cogent factors in the estimation of the reliability of his testimony. Indeed, in many instances they may well transcend in value the verbal significance of his answers. I hope no one will think that I am disparaging either lucidity of thought or precision of expression when I say that understanding what a witness is really trying to say far outstrips the mere definition of the terms that he uses. So often the meaning that he intends to convey is much more easily detected in the general sense of his evidence, taken as a whole, than in any close examination of the particular way in which he frames his statement. That, incidentally, is why an inability precisely to formulate a definition of a word or an expression that we use is by no means a sign that we do not know its meaning or that we are in the habit of using it in anything but its true sense.

Let me sum up what I have to say in this way. The perception of the judge—for this purpose I am including also the juryman—is through his sense organs. Within his mind the information so perceived is co-ordinated, passing through the steps of storage, collation and selection, and then consciously related to the particular legal frame of reference that the particular occasion requires.

So far so good; but although the application of that technique in the resolution of ordinary issues of fact is plainly satisfactory, assuming it to be competently applied, it is subject to certain stresses when it is applied to so-called expert evidence, at any rate where such evidence consists of expressions of opinion, as it so often does and, indeed, frequently must.

Like any other witness, an expert witness giving evidence on oath has a moral and legal responsibility for what he says; but in technical cases the working tolerance for expert opinion, assuming it to be honestly held, seems to be in striking contrast to the precision of expression that is normally expected in matters scientific. Indeed, in one's ordinary experience, much so-called expert testimony is frequently unsatisfactory and there are occasions when it borders on the disgraceful.

It is idle to pretend that, because we have secured some academic qualification in a

scientific field, we are necessarily immune from the temptation to colour our testimony, a temptation that is notoriously and rightly allowed for when the evidence of an actual party to a cause is being weighed. Were it not so, there would be an even stronger bias in our ancient universities in favour of the natural sciences against the humanities. Consider how our police court administration would be simplified and improved if a statement by a Bachelor of Science of the speed of his car or of his sobriety could be treated as a scientifically ascertained fact.

That leads up to the core of the problem. The difficulty, of course, is that in the vast majority of cases the expert witness is really retained by a party as an advocate and we tend, possibly unconsciously, to blur the sharp differentiation that intellectual honesty demands that we should draw between the role of an advocate and that of an independent witness. So far from incurring odium, it is a *tour de force* for an advocate to develop with equal brilliance mutually inconsistent arguments. Upon that ability many great reputations have been built up. This he may fairly do, for notionally at any rate these arguments are presented to a judge upon whose mental anvil their validity can be tested. But it is not so with an expert witness. The *ipse dixit* of the expert witness is not in any sense in like case. Subject only, of course, to human fallibility, his statement of scientific fact is, so to speak, oracular, an exposition of the immutable laws of nature that it would be impiety to question.

So it comes about—we all know it—that the anxious litigant, anticipating that his opponent is going to call some such witness, turns to the same priesthood in order that he may obtain an authoritative rebutter, with the result that we all know. Even if justice is substantially done, it is only done at the price of denigrating the status of the expert witness.

Perhaps the least unkind of the many current definitions of expert evidence, which I might share with you, is this. I have heard it labelled as a costly and ponderous progress from an unwarranted assumption to a foregone conclusion. Those of us whose daily work has brought us into touch with expert witnesses will know how grievously that sort of criticism maligns the vast majority of them. How much of that is due to a defective sense of humour on the part of the people who criticise expert witnesses, I can only guess. I well remember a story that was current in my early days at the Bar about one of the greatest experts whom I had the good fortune to meet, a most distinguished engineer. He had been retained in an action about nuisance by smell. His Puckish spirit urged him to write to the Director of the National Physical Laboratory to the effect that he wished to eliminate, so far as he possibly could, the subjective element in his evidence, and he felt the need in consequence for some up-to-date instrument of precision. Unhappily the anti-German spirit that was then obtaining, of which placards demanding "Hang the Kaiser" and expressions of a like nature were instances, made it unbecoming for him to depend upon the only instrument that he had in his laboratory, a pre-war Charlottenburgische Smellungskunk; could he, therefore, have on loan from the National Physical Laboratory a calibrated badger? For some technical reason unconnected with the subject-matter, the request was not in due form, and his letter was returned to him with a covering note that satisfied him that his request had never been considered by the N.P.L. Accordingly, he indented officially in triplicate for his requirement, and this demand, accompanied by dockets, minutes and occupying a vast file, eventually found its way into the in-tray of the then Director, who, I believe, was Glazebrook.

I ought also to acknowledge that in my own experience I have known instances of the utmost fairness on the part of expert witnesses. Let me tell you of one experience I had of that kind. I was appearing for a defendant in an action that was being heard in the courts. My expert witness, having heard his opposite number in the witness box and the exposition of the art that witness had given, then frankly came to me and admitted that he had not sufficiently considered the matter when giving his original report to the clients and he begged me to arrange that he should be excused from supporting his report on oath. That was perfectly honest, and it is what I should expect of the majority of expert witnesses. But consider the position if he had been the first expert to be called. He would not then have had an opportunity of adopting that course. Even assuming that a witness possesses the moral courage, after committing himself to one line of reasoning, to acknowledge its inaccuracy, none the less the very circumstance that his prepared conclusion appears to him to be no longer convincing will cause him to question his judgment and probably make him

less likely to accept an alternative that was being put to him by way of questions in cross-examination by counsel on the other side. It is natural enough that he will fence and will try to take refuge behind a smoke screen of technical expressions, ambiguities, abstractions and the like, to develop a breathing space until the court rises and he can think afresh about it.

I have not sought to deal in detail with the difficulties that have emerged in practice with expert evidence; nor have I developed, as I should, the more complete justification for the role of expert witness that can fairly be made. Possibly you know all that as well as I do; but in any event I trust you will allow me to consider it as said. I want to get on to something that interests me perhaps a little more.

I have said enough to justify the attention that has been directed to this particular aspect of our jurisprudence. Various suggestions for improvement have been made. One that at one time was thought to provide a satisfactory answer was to appoint court assessors, that is to say, scientific gentlemen who were drawn from a panel, who would take no part whatever in the conduct of the case, who would sit through the hearing and would be available to inform the judge upon such technical or scientific matters as had arisen in the course of the case. In practice, parties were not found willing to surrender their right of calling an expert of their own choosing, so that the assessor made a sort of third cook in the devil's kitchen. But more importantly perhaps, the discussions between the assessor and the judge were in secret; they were not exposed to the test of public cross-examination. When that is added to the natural tendency to put upon the panel only the most conservative and elderly of our scientists, you can well understand that in practice it did not work out very successfully, if for no other reason than that, without an assessor, at any rate one party went away happy, but with an assessor that result hardly ever followed.

There was another method we tried, and that was to endeavour to get the scientific issues reduced to writing and agreed before the hearing. That merely provided a most glorious battleground for the Pundits. When there was added to our ordinary legal jargon the vocabulary of the scientists, you can well imagine the result. In addition to the ordinary issues in the case, there were thus introduced a number of additional issues, and hence, so far from saving time and expense, which was its avowed purpose, this method made patent actions the luxury only of the great corporations.

The legislature has now decided to try a different approach by providing for the trial of patent cases by a judge who is expected to have some general familiarity with the modes of scientific examination and is thought to have some general understanding of the discipline of scientific reasoning. If that is successful, it is, is it not, an instance of that collaboration to which I have already referred when speaking of the value of real teamwork. It is, of course, much too early yet to assess the results and, indeed, as I am the judge selected, I am not the person even to endeavour to make such an assessment; but it most certainly provides the opportunity, if expert witnesses desire to avail themselves of it, to relinquish once and for all any tinge of advocacy in the presentation of their testimony. That this will restore the prestige of scientific exposition in our Courts of Justice I do not myself doubt for one moment. In doing so, it will underline the responsibility of the judge himself for erroneous decisions, but that he will have to bear with such fortitude as he can command.

I have read somewhere that a characteristic of a paper read by Bernard Dyer was that "it commenced without any introduction and finished without any peroration." It is perhaps only in that respect that I could have hoped to emulate him. Let his memory, therefore, excuse the abruptness of my termination.

The Grammar of Units of Biological Activity

By N. T. GRIDGEMAN

(*An Address presented at the Annual General Meeting of the Biological Methods Group on Thursday, December 13th, 1951, by the Retiring Chairman.*)

Divers weights and divers measures, saith the Proverb, both of them alike are an abomination to the Lord. And anything that will restrict their diversity is a boon to His people. Yet the branches of science scatter new ones like chestnuts in autumn. The "jiffy," we read, is a unit of time, being the time taken for light to travel 1 centimetre. The atom of oxygen weighs 16 "daltons." An awkward "half-value" is urged as a useful photometric unit. For computational convenience in horticultural work, I have recently been using the hybrid "milliton." These, and countless other examples, seem at first sight to call for a ruthless wielding of Occam's razor. But second thoughts will suggest judiciousness rather than ruthlessness, for beyond necessity lies, once we forsake the realm of pure philosophy for that of natural philosophy, a large area where convenience has undeniable claims. The convenience of even the most bizarre-looking units of measurement must be soberly examined. What follows is such an examination of units of biological activity.

There are biological units of all manner of things, so if I mostly draw on one particular group of substances, the vitamins, the reason is partly because I happen to be more at home in that group and partly because some special features are to be found there. Vitamins, which came late into the field of biological standardisation, are nutrients, which means that there is not the same call for accurate knowledge of the biological activity of particular preparations of them as there is for drugs. A confidence of ± 5 per cent. or less may be necessary in the dose or injection of a drug; but an error of even 50 per cent. in a vitamin dose would hardly be of physiological consequence. None the less, in practice, and for a number of reasons not germane to clinical risk, estimation in the two groups is on the same footing in regard to accuracy, but we are, I think, more ready to abandon biological units and to substitute physico-chemical analysis for vitamins than we are for drugs. Coupled with this is the tendency for vitamins to have smaller molecules than occur in many other compounds, and the smaller the molecule, the easier is characterisation and, consequently, standardisation and analysis without reference to biological systems. To assert, therefore, that anything said about vitamin standardisation will apply, other things being equal, to that of all other groups, would be unwise, although we may be sure that there will be more correspondence than discrepance.

The system of international standardisation of biologically active substances that grew out of Paul Ehrlich's work on diphtheria antitoxin over half a century ago has not only been, and continues to be, of inestimable practical value in the fields of medicine and nutrition, but has stimulated and entrained important work on the logic of the concepts of unitage and measurement. These concepts are in themselves ancient, having been fundamental to the affairs of life and to scientific investigation long before the action *in vivo* of certain biochemicals called for quantification. Broadly speaking, units are of three kinds: those that are defined functions of the three fundamental (but arbitrary) units of mass, length and time (these include most physical and local units); those that, being ratios, are independent of the fundamental units (for instance, the decibel and a degree of temperature); and those that depend on non-fundamental arbitrary standards (certain colorimetric units fall into this group). Biological units occupy a special position; they are fully orthodox in that they are directly linked to one of the three primary units, that of mass; but unorthodox, and indeed unique, in that they are additionally and necessarily linked to the *behaviour*, under certain conditions, of the particular substance or substances concerned, and usually, although not necessarily, linked to *ad hoc* material standards carefully preserved by official bodies. An International Unit of a particular hormone or drug or vitamin is the activity of a given weight of a Standard Preparation. There are national and pharmacopoeial units of the same genus.

Few of the definitions of the thirty or so International Units qualifies the word *activity*, nor is qualification necessary, but two adjectives, *specific* and *biological*, are always implicit or explicit. The second is obvious enough, but the first needs elucidation. Let us start with

the dictum that the proper subject of a particular standardisation is not a certain substance but the activity of a class of biologically indistinguishable substances. More precisely, the class is that within which there is no evidence, in any biological system, of qualitatively different reactions of any kind, under identical experimental conditions. Standardisation is of the activity of a class; the reference standard is a preparation of one, or of a complex, of the members of the class; and the unit is the activity of a given weight of this standard. There is an official unit of vitamin-D_3 activity; this is improper, because vitamin D_3 is only one member of a class and has, as we say, no specific activity. The International Unit is "of vitamin D," which is better; the impeccable wording would be "of vitamin-D activity." There is a redundant unit of provitamin A, which is also without specific activity. If there is only one standardisable substance, this scheme still applies; we here conceive of a class that consists of only one known member.

We must now digress to the estimation of activity. This means biological assay against the standard, and the methodology concerned has been so highly developed that there is little of further interest I can here add to the twice-told and well-told tale. Deferring for the moment a discussion of categories, I shall merely take for granted that whatever type of assay is used, whether with a continuous variate, with a quantal response or based on reaction time, the conditions of validity are complied with. (We may parenthetically note that the responses, which may be expressed as mass, length, time or enumeration, are always relative and so independent of the primary standards.) The immediate interest lies in the choice of reaction to be measured. This is dictated, not by whatever is commonly associated with the class, but by considerations of convenience and precision. Formally, the best is that involving the smallest cost per unit coefficient of variation of the resultant estimate of activity. Cost will include the type of organism and the work, time and maintenance involved. This is a sufficient criterion. Within the practicable limits, the nature of the chosen reaction or response is immaterial. Very often this will prove to be related to a well-known biological characteristic of the class. Antirachiticity, for example, the property for which the vitamins D are best known and used, happens also to provide the best bio-assay response. On the other hand, many vitamins can be assayed by their effect on growth, although growth promotion is always a secondary effect, itself non-specific. Again, the nurture or stasis or death of a particular micro-organism may be used for the assay of more than one class of biochemical. The point that emerges is that the specificity of the activity of a class resides in the aggregate biological behaviour, and no one property, no matter how characteristic, has a prior methodological claim to be used for activity measurement; the only meaningful criterion is sensitivity. *Specific activity*, then, is that belonging uniquely, under all conceivable biological circumstances, to the class of substances concerned. A rider to this outlook is the desirability of naming the activity in terms of the substances rather than of a property; thus, for example, antiscorbutic and antirachitic are rightly absent from most official definitions of units.

Let us now scrutinise this peculiar feature of activity evaluation—the reference standard. Perhaps the first thing to be said is that if any one member of a standardised class is a characterised chemical compound, there is no logical necessity for the maintenance of a reference preparation; a verbal definition of the standard and, consequently, the unit, will suffice. Although every International Unit is now bound to a reference preparation, and although the existence of a "free" Unit does not seem ever to have been contemplated, in some ways the "freeing" of the Unit is a consummation devoutly to be wished. The release of some of the elaborate machinery of custody would be a good thing; further, a descriptive standard has a permanence and an inviolability that a material standard cannot hope to achieve. There are, in fact, some International Standards that are not used because the assays are done by chemical or physical methods, although the results are expressed in International Units. And there are other instances where the Rubicon has been crossed, the assays being done non-biologically and expressed, as in normal analytical notation, by percentage content. An advanced view is indeed often taken in this respect, and the now classical remark of Sir Henry Dale, that "the ultimate aim of all progressive work on biological standardisation, as in all progressive medicine, may be regarded as self-extinction," has been quoted as approbation of a future dropping of biological units. This is disputable teleology, although whether Sir Henry meant to be taken that way is uncertain. The point will be returned to later. In the meantime, noting in passing that some qualities of a characterisable standard, for instance, scarcity or difficulty of preparation in a stable form suitable for bio-assay,

may make the maintenance of a material standard practically desirable, even although theoretically unnecessary, we must glance at the requirements of a good standard preparation.

These are simple enough: that the preparation (*i*) is stable, (*ii*) exhibits the appropriate class activity in association with the least possible amount of any other kind of activity and (*iii*) is available in a form and at a strength convenient for the assayist. The minimisation of "other activity" clearly implies that a pure compound makes the best reference preparation. Still, there is no logical objection to a mixture of more than one compound from the same class. Nor is the presence of inhibitors or enhancers (of the specific activity) a serious flaw; the only consequence would be that the main compound present was, respectively, more or less potent than was at first believed, and this would not effect assessment of activity.

From the standard, whether preparative or descriptive, comes the definition of the unit of class activity. To define a unit as the activity of a certain weight of the standard is simple enough, but a definition alone does not endow a unit with reality. To be real and unequivocal, two conditions must be fulfilled: (*i*) that the area of application, if not unlimited, be defined and (*ii*) that the unit be both usable and used. Now, in most standardisations, these conditions are fulfilled; the first because no limitations are known, and the second, by virtue of general acceptance and repute. Yet there are standardisations in which their non-recognition had led to confusion. Superficially, both conditions may seem baffling, yet they are demonstrably essential to the logical framework of the subject. Let us expand them.

The first concerns areas of application, by which is meant the biological systems. If the relative activity of the members of a standardised class is found not to be the same for all pertinent systems, the unit needs qualification to allow for this. Vitamin-D activity is a perfect illustration, for the relative activities of two leading members of this class differ in chicks and rats. The ratio of the activities in rats is almost certainly the same as that in humans and is possibly representative of a mammalian ratio, just as the ratio in chicks is possibly representative of an avian ratio. (Incidentally, there are unexplored zoological, and perhaps evolutionary, implications here.) One of the two leading members, vitamin D_3, is currently the International Standard; the other is vitamin D_2. Now to say that vitamin D_2 contains, or even that the biological activity of vitamin D_2 is, 40 i.u. per μg is an incomplete statement, because by chick assay only about a twentieth of this potency would be exhibited. To be precise all statements of vitamin-D potency should have appendaged "by rat assay" or "by chick assay." This means, I think, that the International Unit of vitamin-D activity is not an unequivocal entity; and in spite of the stigmata attached to "animal unit" (because the term once described a nebulous concept, now abandoned, in the early days of biological standardisation) I think there is a strong case for the re-introduction of animal qualification in this new context. An International (Rat) Unit and an International (Chick) Unit of vitamin-D activity would be perfectly rational entities. Both would share the present definition, the activity of 0·025 μg of vitamin D_3, but each would be shackled to the appropriate test animal.

Mention may here be made of the arguments sometimes adduced for the specification of the type, or even the details, of bio-assay. The only circumstance justifying such a step would be evidence that two members of a class exhibited different relative activities by different responses in the same organism. I think I am right in saying that no such evidence is known. If there were any, the remedy would seemingly lie in another subdivision of the unit—"by method X" and "by method Y"—although this dichotomy might seriously weaken the fabric of the particular standardisation. Let us hope that the situation never arises. Meanwhile, the principle of leaving the assayist to choose his own technique stands cardinal. But he cannot, in all standardisations, be given freedom of choice among test organisms.

The second condition, that a unit is real only when used, is easily exemplified, for units of all kinds, whether biological or not, are so conditioned, although the fact is rarely noticed—for much the same reason that the Parisian does not notice the Eiffel Tower. Suppose we require a new unit of length. We make two minute scratches on a metal bar and draw up our definition of the unit accordingly. Shortly afterwards, and before being taken into use, the bar is lost at sea; *ipso facto*, the unit, being unusable, ceases to exist—despite the definition and despite the continued existence of the standard, in perpetual safety, at the bottom of the sea. We should in consequence create a new unit roughly the same size as the old, and nobody would suggest a submarine expedition to try to correlate the new unit with the old.

Transposed to biological activity, the condition becomes this: a unit is a reality only when used directly, by way of biological assay, or indirectly, by way of non-biological assay of established adequacy. From 1934 onwards vitamin A was assayed by a non-biological method whose adequacy was not established; in that year, therefore, the International Unit ceased to exist. In 1949 a new and real International Unit was created.

The spinosities of vitamin-A standardisation, replete with valuable lessons on the logic of activity units, are worth closer examination, especially as the history of the subject is still being reviewed in terms giving the impression of rational and progressive development within the limits of contemporary knowledge; whereas closer examination of the facts shows that this is not so. Moreover, original papers embodying misconceptions of units of vitamin A continue to appear.

A parable may help. In a certain community peanuts began to be an important commodity and the king decreed that they be measured in units of capacity, one such unit to be called the Imperial Nuttle. A scoop of this capacity was accordingly prepared. Unfortunately, and for reasons irrelevant to the story, the scoop, being wide-mouthed and shallow, proved inaccurate in use, and trade could not flourish. Then someone invented the balance and suggested that peanuts be weighed. This was approved, but as the Imperial Nuttle was the official measure, some accommodation was necessary. So a ton of peanuts was scooped with the official scoop by several independent observers. Each produced a different result, so an average was taken; this was 1600 Imperial Nuttles to the ton. Thereafter, with royal approval, all peanuts were weighed in 1600ths of a ton and expressed as Common Nuttles. Nobody at the time was aware that, whereas the weighings included all the foreign bodies in the crude peanuts, the scooping procedure was confined to the clean nuts. Certain consignments of nuts that came from one particular source were, however, observed to contain sizable amounts of foreign bodies, so some special scoopings were done on this material and, as a result, trading in nuts from this source was carried out on a basis of 1200 Common Nuttles per ton.

The official scoop was not thrown away. From time to time a curious merchant would come along and scoop a ton of peanuts, and rates ranging from 1000 to 3000 Imperial Nuttles per ton were reported. No action was taken, however, because the "true" capacity, whatever that might mean, of the Imperial Nuttle now had as little to do with the case as the flowers that bloom in the spring. The Imperial Nuttle, lying unused and virtually unusable, no longer existed as a unit; the Common Nuttle, although imperfect, was the real unit.

Nevertheless, on three special occasions, a working party tried scooping a ton of nuts and got different results each time, this being due in part to the differing amounts of foreign bodies in the three lots. The party pooled all the results and urged that because these three particular tons of nuts had, on average, filled 1740 Imperial Nuttles each, the traders should devalue their Common Nuttle from one 1600th of a ton to one 1740th of a ton. This advice was declined for the implicit reason already stated, namely, that the Imperial Nuttle simply was not a unit of peanuts. All estimates and all requirements everywhere were in Common Nuttles; none of them were or could have been assessed in Imperial Nuttles because the imprecision of the scoop overwhelmed the advantage of being able to handle nuts pure and unsullied. The work thus had no point of contact with the problem of peanut assessment; the estimation attempted was not, as assumed, that of the Common Nuttle in terms of the Imperial Nuttle, but *vice versa*. Whatever the result obtained, the status of the Common Nuttle could not have been affected. Indeed, a native of another community (where, incidentally, crude peanuts were assessed in 2000ths of a ton, a unit known as the Amernuttle) once demonstrated that, skilfully manipulated, the official scoop could be made to hold twice as many nuts as the working party had made it hold, corresponding to fewer than 1000 Imperial Nuttles per ton.

Eventually, the situation was transformed by a simple stratagem: cognisance was taken of the observation that foreign bodies normally made up about 15 per cent. of the weight of crude peanuts, so that the creation of a new unit, the Alsob Nuttle, defined as the capacity of one 1900th of a ton of clean peanuts, rationalised the position and ensured a reasonable continuity between the Alsob Nuttle and the Common Nuttle (but not, of course, the chimerical Imperial Nuttle). Capacity measurement was still unfeasible because nobody could devise an accurate scoop; but this did not seriously matter, as the density of clean nuts was reasonably constant. The problem of assessing peanuts switched to the efficient removal of foreign bodies before weighing.

An interesting commentary on the intricacies of the theory of units lies in the fact that the establishment of the Alsob Nuttle, which plainly could have been done by a stroke of the pen on the day that the first batch of clean peanuts was prepared, was, in the event, thought to be justified by the results of yet another vast scooping trial, whose pooled results, most charitably interpreted, lent strong support to the proposition that, if you remove all non-peanut from a batch, what you have left is—just peanuts.

This parable, in which, almost needless to say, capacity, scooping and balance, respectively represent biological activity, rat-growth bio-assay and spectrophotometer, is, like all parables, a little misleading. The parallel events in the real world differed in two respects. Firstly, there was a semantic entanglement: the analogy would be closer if Imperial Nuttle had been used as a blanket term for the three different things, Imperial Nuttle, Common Nuttle and Alsob Nuttle, just as the term International Unit had three distinct referents, one of which, the defined (1934) unit of biological activity, never existed as an entity. Secondly, there is special significance to be attached to the fact that the parable has been constructed without reference to more than one kind of nut. The peanut represents the main member, vitamin A_1, of the class of vitamin-A-active substances; yet the actual set-up was complicated by the employment of another member, β-carotene, as the standard preparation. A common assumption, on which much of the investigational work was carried out, is that the major cause of imperfection was the existence of a standard bearing a dubious biological relation to vitamin A. This was a cause, but only a minor one. The major cause lay deeper, in the fact that the imprecision of the bio-assay so overshadowed the inaccuracy of spectrophotometry that the accurate but virtually inaccessible unit of activity had to give way to an inaccurate but precise weight unit (via spectrophotometry). Unfortunately, the official unit got hopelessly mixed up with the working unit. The absence, at the time, of a clear-cut organon of activity measurement led to an unclear view of the significance of the excellent and necessary work that the decisions of 1934 were based on.

At this point someone may well remark that there must be a biological link somewhere in the nexus of the evaluation of a vitamin, and that the above attitude to vitamin-A standardisation sacrifices scientific probity to the exigencies of commerce. Further, the question has been asked whether the old standard did not provide a reference point from which the shortcomings of non-biological tests could be, and in fact were, made manifest. As this is not a paper on vitamin A, the temptation to enlarge on these points must be resisted, and I shall confine myself to pointing out that the answers can be found in the foregoing parable and to asking that the implications of the following statement be considered: (*a*) that sodium chloride, an essential near-micro nutrient, could be, yet is not, biologically standardised and assayed; (*b*) that if, years after the originally recommended conversion factor of 1600, relating physical assay of vitamin A to International Units, had been taken into use, the discovery was made that the experimental data behind the recommendation had (through an error, confirmed by re-assay) been wildly misinterpreted, then the 1949 redefinition of the Unit, involving a conversion factor of 1900, would still have been proper and valid; (*c*) that, without exception, all food and animal-organ contents and veterinary and human requirements of vitamin A have been assessed non-biologically (*i.e.*, there has never been any distinction of method between "commercial" assay and field-research assay); and (*d*) that the inaccuracies of the physical assay could have been shown up far more easily, economically and precisely if the use of the old carotene standard had been made a capital offence, for then the discrepancies would have been assessed by direct bio-assay comparisons. One side of a triangle is invariably shorter than the sum of the other two. All in all, thus did we, as Polonius, with unwitting prescience, called to us across the centuries,

with assays of bias
By indirections find directions out.

The course of vitamin-A standardisation is, however, a special case only by historical accident; there is nothing unique about the standardisation as such—although, as we shall have occasion to note later, the position of the provitamins A needs careful consideration. The unit is a typical unit, and shares the paradoxical yet almost ineluctable fate of all biological units, that of losing title, as measures of activity, with the advance of time and knowledge. Eventually, a stage in a standardisation is reached at which the chemical nature of the compounds possessing activity becomes known and biological assay is then retained only if more economical than chemical or physical assay. At this stage units per

gram simply means parts per n, where n is the reciprocal of the weight of the unit in grams, and as this is a metrically obnoxious convention, the question arises whether the normal analytical convention of parts per 100 should not then be substituted. In support of an affirmative answer we may point to the existence of the hundreds of physiologically active compounds that have always been measured in normal analytical terms, because appreciation of their activity did not happen to precede their identification—and among them are some, for example, the amino-acids, that are biologically assayed. As no criterion is available whereby the relative importance of all active compounds can be rated, the retention of the unitage convention for what is physiologically an arbitrary selection of them may be said to invest that selection with a spurious dignity. Finally, the pure-minded bio-assayist will here stress his contention that biological assay is logically defensible only as a branch of quantitative analysis, and he may argue that a unit of activity is to that extent a misleading description.

In touching earlier on the role of bio-assay in unitage assessment we deferred discussion of categories. This must now be faced. There are three categories of bio-assay: (*i*) that in which the standard preparation and the test preparation contain the same class member in inert media, (*ii*) that in which the two preparations are different class members in inert media and (*iii*) that in which the test preparation is in a medium that is not inert.

The first category presents no methodological puzzles. The only difference between the standard preparation and the test preparation is between the concentrations of the active substance in them; the assay is straight-forward analysis in which the reagent happens to be a living organism, and the conditions of validity demanded by our pure-minded bio-assayist are fully met.

The second category poses the question whether we can assume that the relative activity of the class members is a constant. If we can, there is a case to be made for the retention of units of activity even when bio-assay is abandoned and a standard preparation is no longer maintained—simply because the statement "this sample contains x units of substance-M activity" is more concise and convenient than the alternate statement, "this sample contains a weight y of substance M and a weight z of substance N, which are together biologically equivalent to a weight w of substance M." If, on the other hand, the assumption cannot be made, the use of the unit convention is hazardous and had better be dropped. Strictly speaking, the assumption is altogether too sweeping ever to permit its adoption with perfect confidence. Nobody can say that any two members of a class have the same relative activity over the whole range of possible conditions of health and disease in any one organism. Nevertheless, I think that in some instances (the class of vitamin-D activity is one) the limits of confidence are sufficiently wide to justify keeping the unit convention. By contrast the limits of confidence of the vitamin-A activity of certain carotenoids (dependent on alimentary environment), as compared with vitamin A_1, are much too narrow to justify a common unitage.

The third category holds the greatest interpretive difficulties. What is to be done about the analysand that contains, in addition to the active substance or substances, other compounds that modify the activity *in vivo*? Is there, for example, a measurable and meaningful vitamin-B_1 activity of a live yeast that also contains a vitamin-B_1 depletor? In the limited sense that a biological assay on a selected test organism, against the pure vitamin or against the corresponding dead yeast, can yield valuable information on the degree of depletion, an affirmative answer may be given. But in the wider sense that the results of such assays will be of little help to anyone wishing to make statements about the contextual nutritive value of the yeast, the answer must be negative. Nutritional science is full of complexities of this kind: to know the analysis of a food is one thing, but to assess the biological value, in context, of the individual component factors is another and very different matter.

We can now begin to see the dangers of ever assuming a unit of activity to mean anything other than a unit of weight or, in some circumstances, of equivalent weight. A logical positivist might well be persuaded that the whole notion of activity units is sophistical. Yet I think that a compromise view is best. The unit convention can often give usable, if not infallible, information that would be cumbrously conveyed within the framework of the normal analytical conventions. Nor must we forget that, in many activity classes, the unravelling of the chemical problems has occupied so many years that the unit convention has had time to become firmly established in the literature, the laboratory and the dispensary.

and to change this convention may be ill-advised. The important thing is that the nature of an activity unit be clearly understood and in particular be not taken as implicative of a fixed behaviour pattern under any condition of administration or usage. The onus of physiological interpretation does not lie on the assayist, be he biologist or chemist or physicist.

The conclusions to be drawn from this survey can be summarised as follows—

1. Whereas most chemical compounds come to be known and characterised directly in the ordinary course of research, the existence of some is first inferred from their biological activity; identification comes later. When the estimation of such compounds is required before the identification stage, they must be standardised in terms of their biological activity.

2. Biological activity is estimated relative to an arbitrary standard. This procedure is almost identical, in effect, with ordinary quantitative analysis, but, largely because of the existence of different compounds exhibiting the same kind of biological activity, a unit of activity may come to mean something more than a simple weight unit.

3. A close-knit logic of biological activity as a measurable entity that is not a simple function of weight is probably impossible, but the concept can be pragmatically justified over a wide field.

4. Biologically active compounds can be grouped into classes of common specific activity.

5. "Specific activity" means the aggregate behaviour of the class in all relevant circumstances.

6. Each such class can be singly standardised. Any one member, or complex of members, of the class will serve as a standard. A single member, in an inert medium, makes the best standard.

7. If one member is a characterised compound, a material standard is superfluous; description alone will suffice. A material standard, kept in a stable form and in a medium suitable for bio-assay purposes, may, however, be convenient even when the active principle is characterised. If the active principle is not characterised, a material standard is essential.

8. A unit of activity is the activity contained in a given weight of the standard.

9. The unit of activity can be an unambigous entity only if the members of the class concerned exhibit the same relative potency in all biological systems. If there are differences, the unit must be subdivided according to the representative assay animals or organisms that are appropriate.

10. The unit of activity can be real only if used, either directly by bio-assay or indirectly by means of non-biological assay of established validity in terms of biological activity.

11. If the relative biological activity of several members of a class is established within a certain biological system, the unit of activity, as a complex weight function of all the members, is a convenient entity whose use could be justified even in the absence of either a material standard or the use of biological assay.

12. In some instances, the activity unit has acquired a tradition that is not easily broken. Nor is there need for breakage, provided that the meaning of the unit is fully understood.

13. Items 11 and 12 would constitute a case against the view that biological standardisation is an interim device to be abandoned as soon as possible. The material paraphernalia can be jettisoned, yet the unit system remain to serve a useful purpose.

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The Measurement of Diffusion Current with a Pen-Recording Polarograph

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(*Presented at the meeting of the Physical Methods Group on Tuesday, April 8th,* 1952)

The Tinsley polarograph (model V3211) can be used with capacitance damping to record the average diffusion current during the life of successive mercury drops; alternatively it can be used with no damping to trace approximately the instantaneous values of diffusion current at maximum drop size. With capacitance damping, precision depends upon the time-constant of the pen-recorder circuit, and accuracy is limited by the quality of the electrolytic condensers. For a given drop-rate with no damping, the peak values traced by the pen-recorder depend mainly upon the viscosity of the dash-pot oil. Some limitations and advantages of the two methods in practical polarographic analysis are briefly discussed, and an oil of suitable viscosity is suggested.

The relationship of the peak values, as recorded under various conditions, to the corresponding values for the average diffusion current has been investigated with the aid of a silver voltameter. For several electro-reducible substances in specified supporting electrolytes, the ratio of the average diffusion current to the instantaneous current at maximum drop size differs significantly from the fraction 6/7 derived theoretically by Ilkovič; moreover, the observed values of the ratio vary from one electro-reducible substance to another, diminishing with increasing values of the diffusion coefficient. The extent of the variation is greater than would have been predicted from the recent equation of Lingane and Loveridge, but the change is in the expected direction.

The measurement of a limiting polarographic diffusion current at the dropping-mercury electrode involves either a determination of the average current during the life of each drop or a determination of the instantaneous value of the current at some specified time during the formation of the drop.

Drop times of 3 to 5 seconds are customary, and if a galvanometer of period 15 seconds or more is connected in series with the dropping electrode the magnitude of its oscillations amounts to no more than 10 per cent. of its average deflection. In the past it was generally assumed that the mid-points of these oscillations coincided with the average diffusion current; no doubt this was approximately true, although Taylor, Smith and Cooter[1] recently found it necessary to stress the importance of using a highly-damped galvanometer to minimise the error from this source. It was indeed a timely step forward when Lingane and Kerlinger[2] in 1940 applied capacitance damping to reduce the amplitude of the galvanometer oscillations. They inserted the condenser across the galvanometer and its shunts, but, as the setting of the shunt must be variable, it is advantageous to connect compensating resistances in series, in order that the time-constant of the circuit can be maintained over a wide range of shunt settings. Such a circuit was described by Fill and Stock[3] in 1944.

As the quantity of electricity stored by the condenser must be provided by the reaction proceeding at the dropping-mercury electrode, the slope of a polarographic wave (di/dE) is always smaller when recorded automatically than when plotted manually. To prevent undue distortion, there must be some limit on the rate of change of applied e.m.f., and the time-constant of the galvanometer circuit must be regulated with discretion. Controls of this kind are all the more necessary if it is required to record automatically two or more polarographic waves whose half-wave potentials are close.

In the Tinsley polarograph (model V3211) the current at the dropping-mercury electrode is amplified and then fed to a fast pen-recorder. The movement of this recorder is oil-damped, but provision is also made in the output circuit of the amplifier for capacitance damping of the oscillations resulting from the growth and fall of mercury drops at the capillary. Although there are certain applications of polarography where capacitance damping is essential or desirable, *e.g.*, in the compensation method of measuring small diffusion currents or for the measurement of diffusion current at extremely negative potentials, there are many other

applications in which the polarogram consists of a simple current - voltage curve, or of two or more such curves that can be recorded adequately at the same sensitivity. For these applications, capacitance damping would not normally be used in conventional polarograph circuits, yet, because the natural period of the Tinsley pen-recorder is so very short, capacitance damping provides the only means by which the Tinsley polarograph can measure the average values of diffusion currents at the dropping electrode.

In the simple applications just referred to, the performance of the Tinsley polarograph can be improved in several respects by dispensing with capacitance damping and by measuring the current recorded at the instant of maximum drop size. Values for average limiting diffusion currents are, however, frequently required for comparisons of the results of several investigators, so a method has been devised by means of which the peak values traced by the Tinsley pen-recorder can be correlated accurately with the average diffusion current. It will further be shown that the ratio of the average diffusion current to the diffusion current at maximum drop size is smaller than would be expected from the Ilkovič equation and is not constant for all electro-reducible substances.

Recording of polarograms with capacitance damping

The Tinsley polarograph (model V3211) was used with a rate of change of applied e.m.f. of −0·5 volt per minute. The pen-recorder circuit was modified (Fig. 1) by connecting a

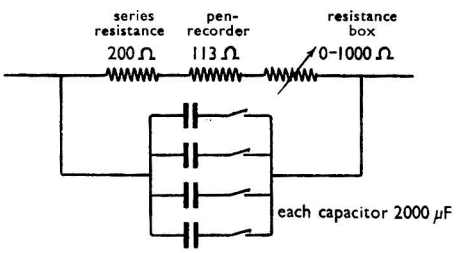

Fig. 1. Circuit providing variable-capacitance damping for Tinsley pen-recording polarograph

resistance-box in series with the recorder and by providing electrolytic condensers that gave a total possible capacitance of 8000 μF. The resistance of the pen-recorder itself was 113 ohms, and to the pen-recorder an external series resistance of 200 ohms had been connected by the makers. In these first experiments the dash-pot of the pen-recorder was nearly completely filled with an oil of viscosity 310 centistokes at 20° C; room temperature was maintained at this value within one or two degrees.

With these matters arranged, polarograms were recorded for a solution of lead nitrate (2·183 millimolar) in 0·2 *N* potassium nitrate with methylene blue (0·005 per cent.) as maximum suppressor, after dissolved oxygen had first been removed by means of a stream of purified nitrogen. The H-type of polarographic cell, previously described,[4,5] was used in a thermostat maintained at 25·0° ± 0·1° C. The rate of flow of mercury from the capillary was 1·90 mg per second and the drop time at −0·7 volt against the saturated calomel electrode was 3·26 seconds, giving for $m^{\frac{2}{3}} t^{\frac{1}{3}}$ the value 1·87 $mg^{\frac{2}{3}}$ $sec.^{-\frac{1}{2}}$ Two series of polarograms were recorded with capacitances of 2000 and 4000 μF, whilst in each series the values in the resistance box were varied between 0 and 1000 ohms (Fig. 2).

At the lower values of capacitance and resistance, the crests of the oscillations are always pointed and the troughs rounded, so that the average limiting diffusion current can hardly be expected to coincide with a horizontal line drawn midway between the upper and lower extremities of the recorded oscillations. Such a line would indicate a diffusion current of 15·4 microamperes. The amplitude of the oscillations diminishes with increasing capacitance or resistance so that, with 500 ohms in the resistance box and a capacitance of 2000 μF (CR_{total} = 1·6 seconds) or with 200 ohms and 4000 μF (CR_{total} = 2·0 seconds), their magnitude does not exceed 2 per cent. of the average diffusion current. Under these conditions the average limiting diffusion current can be read with greater precision, the observed value being 15·1 microamperes. By increasing still further the product of capacitance and

resistance the magnitude of the oscillations can again be reduced. However, a limit is soon reached, for, if the current through the recorder is 15 milliamperes for full-scale deflection and the maximum permissible D.C. potential across the condenser is 12 volts, the value in the resistance box should not greatly exceed 500 ohms. In the last polarograms of each series (Fig. 2) the recorded values of diffusion current are smaller than the true average value because of appreciable D.C. leakage across the condenser.

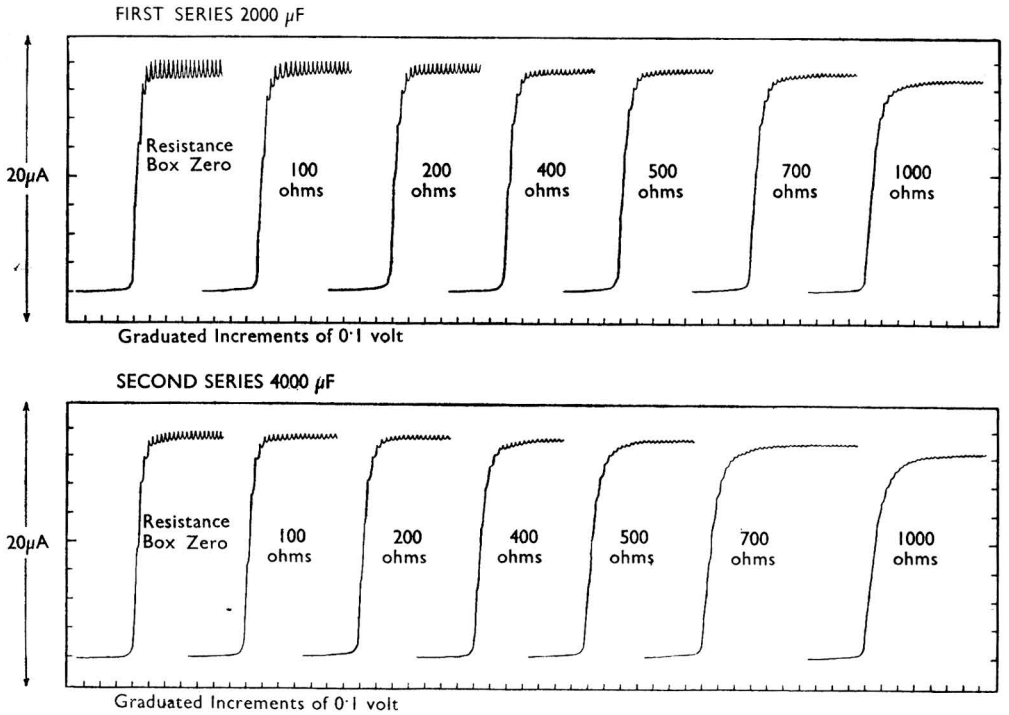

Fig. 2. Effects of progressive increases in capacitance damping on the polarogram recorded for lead nitrate (2·183 millimolar) in 0·2 *N* potassium nitrate with 0·005 per cent. of methylene blue

Temperature = 25·0° C. $m^{\frac{2}{3}}t^{\frac{1}{6}}$ = 1·87 $mg^{\frac{2}{3}}$ $sec.^{-\frac{1}{2}}$
Rate of change of applied e.m.f. = −0·5 volt per minute

It is also clear from Fig. 2 that the slope (di/dE) of the polarographic wave appears smaller as the time-constant of the recorder circuit increases. This effect reduces the accuracy with which the half-wave potential can be determined by simple inspection of the polarogram, although it is more relevant here to investigate its bearing on the resolution between two polarographic waves whose half-wave potentials lie close together.

In Fig. 3 is shown another series of polarograms for lead (1·037 millimolar) together with cadmium (1·092 millimolar), in a supporting electrolyte of 0·2 *N* potassium nitrate with methylene blue (0·005 per cent.) as maximum suppressor. Throughout this series, the rate of change of applied e.m.f. was constant at −0·5 volt per minute, but the values of capacitance and resistance were varied in accordance with the explanatory notes beneath Fig. 3. In polarogram 1, where the product of capacitance and resistance is equal to 0·63 second, the waves are not sufficiently damped to permit precise reading of the average diffusion currents whilst in polarogram 8, where this product is equal to 6·5 seconds, the slopes of the polarographic waves are such that hardly any separation between the lead and cadmium waves can be discerned. No intermediate combination of capacitance and resistance gives a satisfactory polarogram at −0·5 volt per minute, although it should be mentioned that a great improvement does result if this rate is decreased to −0·2 volt per minute or less.

Recording of polarograms without capacitance damping

In consequence of the foregoing remarks it is profitable to investigate the recording of polarograms without capacitance damping, and so to take advantage of the speed of which the recorder is capable when only oil-damped.

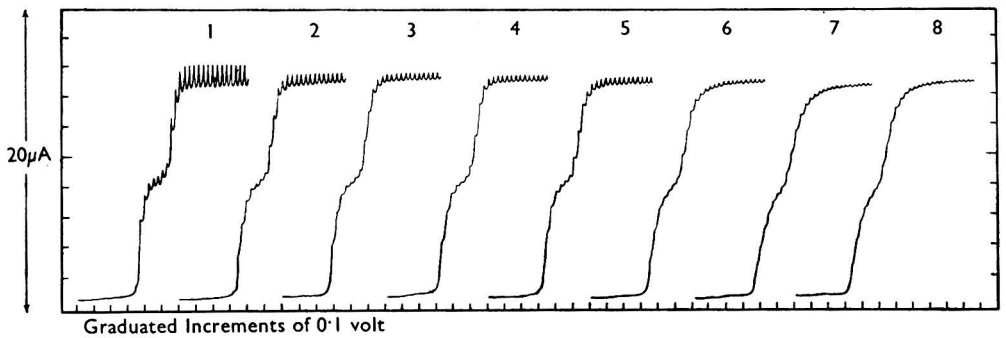

Fig. 3. Effects of progressive increases in capacitance damping on the polarogram recorded for lead (1·037 millimolar) with cadmium (1·092 millimolar) in 0·2 *N* potassium nitrate with 0·005 per cent. of methylene blue

Temperature = 25·0° C. $mt^{\frac{2}{3}}t^{\frac{1}{6}}$ = 1·87 $mg^{\frac{2}{3}}$ $sec.^{-\frac{1}{2}}$
Rate of change of applied e.m.f. = −0·5 volt per minute

Polarogram	1	2	3	4	5	6	7	8
Product of CR (seconds) ..	0·6	1·3	1·9	2·5	1·6	3·3	4·9	6·5

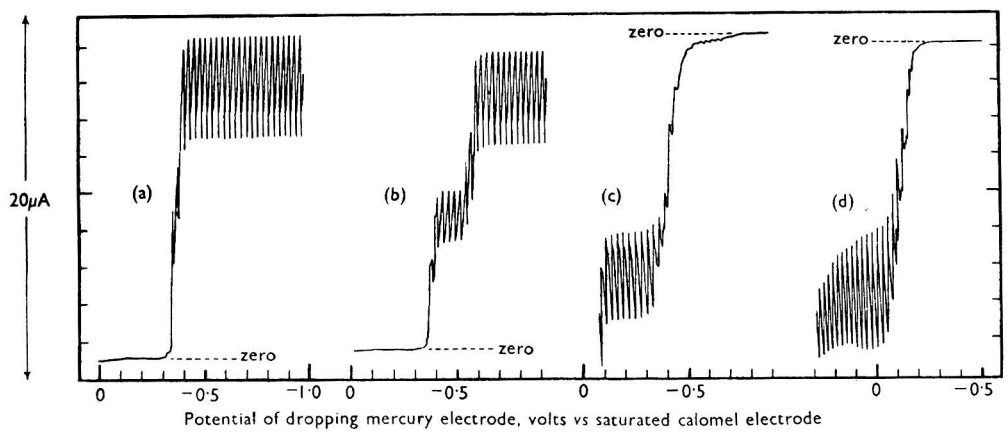

Fig. 4. Examples of polarograms recorded without capacitance damping, the rate of change of applied e.m.f. being −0·5 volt per minute

(*a*) Lead nitrate (2·183 millimolar) in 0·2 *N* potassium nitrate with 0·01 per cent. of gelatin
(*b*) Lead nitrate (1·037 millimolar) and cadmium nitrate (1·092 millimolar) in 0·2 *N* potassium nitrate with 0·002 per cent. of methylene blue
(*c*) Sodium dithionite ($Na_2S_2O_4$, 2·0 millimolar) in 0·5 *M* di-ammonium phosphate, *M* ammonium hydroxide with 0·01 per cent. of gelatin
(*d*) Sodium thiosulphate (3·98 millimolar) in 0·2 *N* potassium nitrate

Some examples of polarograms recorded in this manner appear in Fig. 4. For cathodic waves, such as those of lead and cadmium, the limiting diffusion currents are recorded as a series of peaks corresponding to the maximum size of successive mercury drops; for anodic waves as exemplified by those of the dithionite (S_2O_4'') or thiosulphate anions, these peaks are inverted. In both types, the shape of the envelope that encloses all the peaks very nearly coincides with the current - voltage curve obtained as a manual polarogram with the same solution. Of the practical advantages attaching to this consideration it may be mentioned that, when capacitance damping is dispensed with, the values of half-wave potentials can be

found with an accuracy of ± 20 millivolts by simple inspection of the pen recording (provided also that the iR correction is known); furthermore, the polarographic waves of ions whose half-wave potentials are close are more readily resolved, *e.g.*, those of lead and cadmium. No longer is there any danger of error from D.C. leakage across electrolytic damping condensers, and it is readily shown that the peak deflections, as measured across the entire width of Murday Recorder Chart No. 1360 H, are strictly proportional to the concentration of a reducible ion (such as thallous ion) so long as a siphon pen is used.* Lastly, the use of the Tinsley polarograph without capacitance damping sometimes facilitates the detection and elimination of polarographic maxima as shown, for example, by Davies and Furness[6] in the polarography of nitrilotriacetic acid.

Whilst using this method for the automatic recording of polarograms it is important to be able to correlate the results obtained with those of other workers. For this reason alone, the ratio between the average diffusion current and the peak current traced by the recorder at maximum drop size must be known. These quantities will be denoted by the symbols i_{average} and i_{peak} respectively.

Significance of peak values traced by pen-recorder at maximum drop size

Method of investigation—

With an oil of viscosity 310 centistokes (at 20° C) as supplied by the makers for the dash-pot of the pen-recorder, observations with many electro-reducible ions showed that the ratio of the limiting diffusion current recorded with capacitance damping to the peak current traced at maximum drop size without capacitance damping was close to 6/7. Always, however, the accuracy of these measurements of the average diffusion current was in doubt, for, if the oscillations were only moderately damped, it hardly seemed justifiable to accept a value midway between their pointed crests and rounded troughs, and yet if the effectiveness of capacitance damping were increased by adding resistance in the recorder circuit, the danger of D.C. leakage across the electrolytic condensers could not be ignored. In the further experiments to be described, therefore, the measurement of average diffusion current was made in a different manner, without recourse to capacitance damping.

Given a solution of lead, for example, in a suitable supporting electrolyte free from dissolved oxygen, we can apply through a large non-polarisable saturated calomel electrode a steady potential difference between the solution and the dropping-mercury electrode such that the limiting diffusion current flows. For lead ions in a potassium nitrate supporting electrolyte containing a maximum suppressor, the potential of the dropping electrode might suitably be set at $-0{\cdot}7$ volt against the saturated calomel electrode, and then the pen-recorder, if fitted with a siphon pen, will begin to trace a series of oscillations of uniform height and amplitude. The circuit switches are so arranged that for a measured interval of time a silver voltameter can be connected in series with the pen-recorder. The cathode of the voltameter used in these experiments was a 25-ml platinum crucible, on the interior surface of which a smooth coating of silver had first been electrolytically deposited from potassium silver cyanide solution. A rectangular piece of pure silver gauze, 10 cm $\times$ 2 cm, welded to a pure silver wire of 16 S.W.G. and twined spirally about it, served as anode. The septum was formed from a sintered-glass disc (porosity No. 3), of diameter 1·0 cm, fused into a 4-cm length of Pyrex tube, and was provided with three hooks to rest over the edge of the crucible. In the anode and cathode compartments the electrolyte consisted of a 15 per cent. solution of silver nitrate prepared according to the directions of Rosa and Vinal.[7]

The pen-recorder, already calibrated as a milliammeter, is allowed to trace the successive values of the amplified diffusion current at maximum drop size, whilst the mass of silver deposited in a measured period gives the average value of the amplified diffusion current. The latter quantity, after correction for the amplified average residual current, is denoted by I_{average}. The solution through which the mercury drops were falling was quiet throughout the experiment, its volume being approximately 14 ml. During the hour of each experiment the peak values fell gradually by between 1 and 3 per cent., doubtless owing to local depletion in the concentration of electro-reducible substance. For each one-minute interval the mean peak value traced by the pen-recorder was noted, and from these records an estimate was obtained for the mean recorded value of the amplified diffusion current at maximum drop size. This quantity, after correction for the amplified peak residual current, is denoted by

* This is not strictly true for certain kinds of pen in which the weight of ink carried may vary.

I_{peak}. But as the amplification factor throughout the life of single mercury drops can be considered constant, the ratio $I_{average}/I_{peak}$ must be equal to the ratio $i_{average}/i_{peak}$.

DEPENDENCE OF PEAK VALUES ON VISCOSITY OF DASH-POT OIL—

In the earlier stages of this work it had been recognised that the value of $i_{average}/i_{peak}$ might be dependent upon the viscosity of the oil in the dash-pot of the pen-recorder and at this point the results of experiments with a number of different oils will be described.

The viscosity of the oil supplied by the makers was 430 centistokes at 15·5° C, 310 centistokes at 20·0° C, and 222 centistokes at 25·0° C. Approximately 15 ml of oil in the dash-pot of the recorder were sufficient to cover the moving vane. With a solution in the polarographic cell consisting of lead nitrate (4·37 millimolar) in 0·2 *N* potassium nitrate with 0·01 per cent. of gelatin as maximum suppressor, and applying to the dropping-mercury electrode a steady

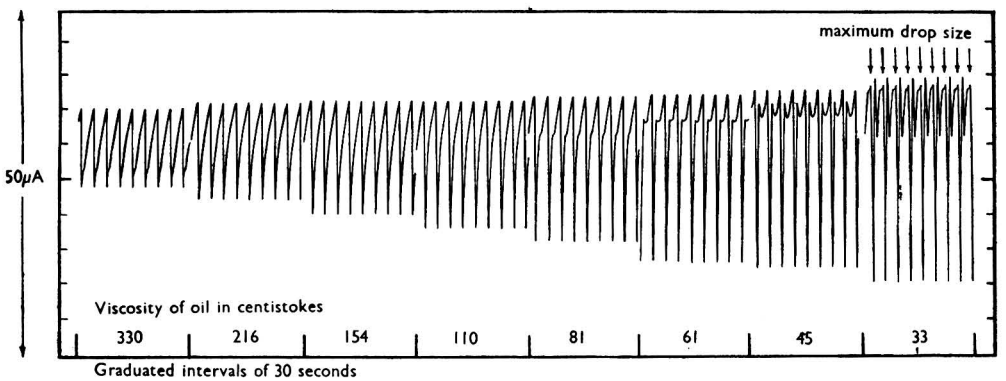

Fig. 5. The effects of changes in viscosity of the dash-pot oil on the oscillations as traced by the pen-recorder in the polarographic reduction of lead nitrate (4·37 millimolar) in 0·2 *N* potassium nitrate with 0·01 per cent. of gelatin. The drop time was 3·42 seconds

potential of −0·70 volt against the saturated calomel electrode, the amplitude of the oscillations traced by the pen-recorder was shown to increase with increasing temperature of the oil. With the oil at 25° C, the peak values traced for the amplified diffusion current were 3 per cent. higher than at 15·5° C. With the oil at temperatures between 18° and 22° C the ratio $i_{average}/i_{peak}$ was 0·86 ± 0·01, a value that, although it lay close to the ratio 6/7 required by the Ilkovič equation, seemed likely to be diminished if oil of lower viscosity were substituted.

By starting with the oil supplied by the makers, then substituting in turn oils of lower viscosity, and by using lead as the electro-reducible ion with a steady applied e.m.f. of −0·70 volt against the saturated calomel electrode, the pen-recorder was allowed to trace, as best it could, the growth and fall of diffusion current for successive drops. The drop-time was 3·42 seconds, and for the sake of clarity in reproduction the speed of the recorder chart was increased to 2·25 inches per minute, so that each of the sections shown in Fig. 5 represents a period of 30 seconds. The temperatures of the oils all lay within 0·2 degrees of 19·0° C, and their viscosities in centistokes at this temperature are shown on the sections of Fig. 5.

By using an oil of a viscosity of 61 centistokes, the momentum acquired by the recorder movement in the early life of the drop (when the rate of increase in diffusion current is greatest) causes the pen to overtake the growth of the diffusion current, and when this momentum is spent the pen moves back slightly until the diffusion current catches up and carries the pen to the point of its maximum deflection. This effect is more pronounced with oils of even lower viscosity; indeed, when the viscosity is 33 centistokes the acceleration of the pen in the early life of the drop is so great that it overshoots the values (indicated by arrows in Fig. 5) finally recorded at maximum drop size. These undesirable excursions of the pen can be prevented by substituting an oil having a viscosity of at least 81 centistokes, but with the use of oils of increasing viscosity there is a trend for the maximum values reached by the pen to become smaller. Although this trend is clearly shown in Fig. 5, too much reliance must not be placed on the precise values recorded there for the diffusion current

at maximum drop size because, although these recorded values were known to be influenced slightly by the weight of ink carried by the pen, it was not practicable on this occasion to use the siphon pen.

For each oil represented in Fig. 5 the ratio $i_{average}/i_{peak}$ was determined preferably by means of the silver voltameter and by the pen-recorder fitted with the siphon pen. The temperature of the oils varied slightly from one experiment to another, so that the figures reported in Table I for viscosity differ somewhat from those given in Fig. 5. From the data of the second column of Table I the precision attainable in the amplification of a polarographic diffusion current and its measurement by means of the silver voltameter can be estimated. Thus, the mean deviation from the arithmetic mean of 10·78 milliamperes for $I_{average}$ was $\pm 0{\cdot}04$ milliampere. The precision of the values recorded for I_{peak} cannot be computed from Table I, but on the grounds of general experience it is probable that it lies between five and ten parts per thousand. The precision of the results expressing the ratio $i_{average}/i_{peak}$ for oils of different viscosities should, therefore, approach ten parts per thousand.

TABLE I

VARIATION OF THE RATIO $i_{average}/i_{peak}$ WITH DECREASING VISCOSITY OF THE DASH-POT OIL

Data obtained with a solution of 2·06 millimolar lead nitrate in 0·2 *N* potassium nitrate with 0·01 per cent. of gelatin

Applied e.m.f. −0·70 volt *vs.* S.C.E.

$t = 3{\cdot}42$ seconds, $m = 1{\cdot}957$ mg per second, $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}92$ mg$^{\frac{2}{3}}$ sec.$^{-\frac{1}{2}}$

Temperature = 25·0° C

Viscosity, centistokes	$I_{average}$, milliamp.	I_{peak}, milliamp.	$i_{average}/i_{peak}$
310–380	—	—	0·868*
280	10·89	12·78	0·852
175	10·71	12·87	0·832
172	10·82	12·80	0·845
172	10·77	12·82	0·840
128	10·76	12·88	0·835
124	10·72	12·95	0·828
85	10·78	13·02	0·828
83	10·74	13·06	0·822
65	10·81	13·12	0·824
64	10·73	13·09	0·820
45	10·75	13·12	0·819
42	10·79	13·24	0·815
40	10·82	13·18	0·821
32	10·77	13·34	0·807

* Mean of four results with lead nitrate at different concentrations.

In selecting a suitable dash-pot oil for the pen-recorder the data of Table I and the results shown in Fig. 5 all have to be considered. On the one hand, the oil should permit the widest fluctuations of laboratory temperature with the minimum effect on the ratio $i_{average}/i_{peak}$. If this were the only consideration the oil of lowest viscosity would be chosen. On the other hand, it is desirable that the pen-recorder should trace a smooth curve up to the instant of maximum drop size, for, when half-wave potentials are to be determined, it is imperative to ascertain that maximum polarographic current coincides with maximum drop size. This may not always be so when polarographic maxima are incompletely eliminated. Thus, an oil having a viscosity between 110 and 150 centistokes is most generally satisfactory. The viscosity of a sample of Shell Tellus Oil 29 was found to be 110 centistokes at 21·5° C and 150 centistokes at 16·0° C, and this oil was chosen for general use in the dash-pot of the pen-recorder.

DETERMINATION OF THE RATIO $i_{average}/i_{peak}$ FOR SOME SELECTED ELECTRO-REDUCIBLE SUBSTANCES

A more general interpretation of the data of Table I must be that the real value of the ratio of average diffusion current to instantaneous diffusion current at maximum drop size is, for lead ions in 0·2 *N* potassium nitrate, significantly smaller than the fraction 6/7. As this result cannot be reconciled with the Ilkovič equation, further experimental work was

undertaken to determine the ratio $i_{average}/i_{peak}$ for some other electro-reducible substances. Before presenting these further results it is desirable to acknowledge the work of other investigators in this field.

In a discussion following a lecture by Heyrovský,[8] experiments were reported by Steghart indicating that diffusion currents at the dropping-mercury electrode increase during the life of each drop not as the $\frac{1}{6}$ power of time but as the $\frac{1}{3}$ or $\frac{2}{3}$ power.* McKenzie[9] also

TABLE II

OBSERVED VALUES OF THE RATIO $i_{average}/i_{peak}$ FOR SELECTED SUBSTANCES REDUCIBLE AT THE DROPPING MERCURY ELECTRODE

Viscosity of dash-pot oil is between 120 and 140 centistokes

m = 1·95 mg per second Temperature = 25·0° C

Experiment	Electro-reducible substance	Concentration, millimoles per litre	Supporting electrolyte	Applied e.m.f., volts *vs.* S.C.E.	Drop time, seconds	$i_{average}/i_{peak}$
1	Cadmium	1·22	0·1 *N* KCl, 0·005% methylene blue	−0·80	3·39	0·843
2	"	2·44	"	"	3·39	0·840
3	"	4·88	0·2 *N* KCl, 0·01% gelatin	"	3·40	0·852
4	"	9·76	"	"	3·40	0·838
5	"	3·64	0·2 *N* KNO_3, 0·01% gelatin	"	3·40	0·850
6	"	5·46	"	"	3·40	0·843
7	Lead	2·06	0·2 *N* KNO_3, 0·01% gelatin	−0·70	3·42	0·835
8	"	2·06	"	"	3·42	0·828
9	Thallium	2·40	0·2 *N* KNO_3, 0·01% gelatin	−0·80	3·40	0·819
10	"	7·2	"	"	3·40	0·804
11	"	14·4	0·4 *N* KNO_3, 0·01% gelatin	"	3·43	0·805
12	Lead + Thallium	2·06 + 3·21	0·2 *N* KNO_3, 0·01% gelatin	−0·80	3·30	0·824
13	Cupric complex with ethylenediamine tetraacetic acid	6·09	0·2 *N* KNO_3, 0·01% gelatin	−0·70	3·40	0·841
14	Tetrathionate	1·26	1·0 *M* $(NH_4)_2HPO_4$, 0·002% methylene blue	−0·60	3·43	0·828
15	Methyl orange	0·87	0·05 *M* citric acid, 0·05 *M* sodium citrate, 10% dioxan, 0·005% methylene blue	−0·60	3·26	0·788
16	"	0·87	"	−0·50	3·26	0·790
17	Cadmium	2·44	0·1 *N* KCl, 10% dioxan, 0·01% gelatin	−0·80	3·26	0·841

reported current - time curves for lead, cadmium and oxygen that were approximately $\frac{1}{3}$-order parabolas and which, on graphical integration, gave a value of 1·29 for the ratio of maximum to average diffusion current. In a paper describing the design and performance of a polarograph incorporating a current recording system of negligible damping, Schulman, Battey and Jelatis[10] reported for the ratio of maximum to average current values of 1·24 for

* Mr. Steghart elaborated his statement at a meeting of the Polarographic Discussion Panel of the Physical Methods Group of the Society on December 12th, 1947.

cadmium ions and 1·26 for thallous ions. By means of a cathode-ray oscillograph, Taylor, Smith and Cooter[1] recorded instantaneous values of diffusion current throughout the life of successive mercury drops. For the ratio of average diffusion current to the instantaneous value at maximum drop size they gave the value 0·81 for cadmium ions in a potassium chloride supporting electrolyte, and by a slight variation in technique a value of 0·80 was given for lead ions.

The work of the authors cited here casts doubt upon the validity of the Ilkovič equation as an expression for relating the average diffusion current to the instantaneous diffusion current at maximum drop size. For the electro-reducible substances included in those studies the observed value for this ratio is close to 0·80, but the results reported so far do not permit a decision as to whether this value should be regarded as a new constant, or as a variable depending upon the identity of the electro-reducible substance or upon the composition of its supporting electrolyte. Hence it is important to collect data for a wider variety of electro-reducible and electro-oxidisable substances in various supporting electrolytes. In the next part of this investigation, therefore, several new results are presented.

ELECTRO-REDUCIBLE SUBSTANCES CHOSEN FOR INVESTIGATION—

The Tinsley polarograph with a silver voltameter in series with the pen-recorder was again used in the manner that led, as already described, to the results for $i_{average}/i_{peak}$ of Table I, except that the viscosity of the oil in the dash-pot of the recorder was now regulated within the limits 120 to 140 centistokes. It is recognised that the values so recorded for i_{peak} are smaller than the real instantaneous values of diffusion current at maximum drop size, yet the $i_{average}/i_{peak}$ ratios so obtained must be comparable amongst themselves. For this study there were chosen lead, cadmium and thallous ions as examples of divalent and monovalent cations reversibly reduced at the dropping mercury electrode, the complex salt formed from cupric ions with ethylenediamine tetra-acetic acid, which undergoes irreversible reduction,[11] and the tetrathionate anion, which is irreversibly reduced. Also, as an example from organic polarography, the reduction of methyl orange was studied. These electro-reducible substances were so chosen that the limiting values of their cathodic diffusion currents could all be measured at potentials between −0·5 and −0·8 volt against the saturated calomel electrode, so that in each instance the drop time was almost constant, although a number of different supporting electrolytes were used.

RESULTS—

The data from these experiments are reported in Table II. In experiments 1 to 6, the ratio $i_{average}/i_{peak}$ for the cadmium ion was determined for concentrations within the range 1 to 10 millimolar in potassium chloride and potassium nitrate supporting electrolytes with gelatin or methylene blue as maximum suppressor. The mean value for the ratio is 0·844, and the mean deviation 0·004. Hence it appears that the ratio is not significantly affected by the changes in concentration of the cadmium ion or by the changes in the nature of the supporting electrolyte or maximum suppressor as specified in Table II.

The values for lead (experiments 7 and 8) are taken from Table I, their mean, 0·832, being smaller than that for cadmium by 1·4 per cent. (The values for cadmium and lead reported by Taylor, Smith and Cooter[1] differed similarly by 1·4 per cent.) For thallous ion (experiments 9, 10 and 11) the ratio is even smaller, the mean value being 0·809. For a solution containing both thallous and lead ions, an intermediate value for the ratio was found.

The results of experiments 13 and 14 do not call for special comment. In the reduction of methyl orange (experiments 15 and 16), however, the ratio $i_{average}/i_{peak}$ was smaller than in any other experiment. With a supporting electrolyte consisting of a 0·1 *M* citrate buffer, pH 4·40, with 10 per cent. of dioxan added to increase the solubility of the methyl orange, the cathodic wave exhibits a polarographic maximum that is difficult to suppress with gelatin, but which is readily suppressed by the addition of 0·005 per cent. of methylene blue. For a 0·87 millimolar solution of methyl orange the half-wave potential is then approximately −0·28 volt against the saturated calomel electrode. If the low value of 0·788, first obtained at an applied e.m.f. of −0·60 volt against the saturated calomel electrode (experiment 15), had been due to incomplete suppression of the polarographic maximum, such a cause would have been manifest to a different degree at an applied e.m.f. of −0·50 volt, yet at this latter voltage the value of the ratio was not significantly altered (experiment 16). Otherwise, if

the presence of dioxan were supposed responsible for such a low result, it could reasonably be anticipated that the addition of dioxan to the supporting electrolytes of other electro-reducible substances should produce a similar effect. However, when dioxan was added to the supporting electrolyte for cadmium (experiment 17) the resulting value of the ratio $i_{average}/i_{peak}$ did not differ significantly from the results of experiments 1 to 6.

The available results show that the ratio of the average diffusion current to the diffusion current at maximum drop size has not the same numerical value for all electro-reducible substances. The value of this ratio at the dropping electrode when polarographic maxima are suppressed is dependent on the identity of the ion undergoing electrochemical change and is not influenced in any determinable way by the nature of the supporting electrolyte.

Summary and conclusions

Whenever the compensation technique is used for measuring small diffusion currents, or whenever the drop time becomes very short, as at extremely negative potentials, the use of capacitance damping provides an expedient method for recording diffusion currents at the dropping-mercury electrode. With the Tinsley instrument, however, it is difficult to tell precisely which point between the crests and troughs of the oscillations does represent the average diffusion current and, as the possibility of leakage across the electrolytic condensers cannot be ignored, this method provides at best only an approximate measurement of diffusion current.

When polarograms are automatically recorded the use of capacitance damping is accompanied by distortion of the polarographic wave. If the rate of change of applied e.m.f. is equal to or greater than 0·5 volt per minute, appreciable errors arise in the recording of half-wave potentials, so that effective separations between polarographic waves whose half-wave potentials are close can no longer be accomplished. In these respects, as well as in the detection of polarographic maxima, the performance of the Tinsley polarograph is improved by recording instead the peak values of the diffusion current at maximum drop size, capacitance damping in the recorder circuit not then being required.

The peak values traced in this way are not, however, simply related to the average diffusion current at the same potential by the factor 6/7: their ratio is best calculated from a measurement of the amplified value of the average diffusion current with a silver voltameter and from the corresponding values of the amplified diffusion current traced by the pen-recorder at maximum drop size. By such means, the extent to which the numerical value of this ratio depends upon the viscosity of the oil in the dash-pot of the recorder has been investigated. For most purposes the optimum viscosity is close to 130 centistokes, although an oil of this viscosity prevents the pen ever recording the real maximum values of diffusion currents when the drop time approximates to 3 seconds. Under these conditions it was found that the ratio of the average diffusion current ($i_{average}$) to the recorded value of the diffusion current at maximum drop size (i_{peak}) varied from 0·84 with cadmium ion as the electro-reducible substance to 0·79 in the reduction of methyl orange, intermediate values having been obtained with certain other electro-reducible substances.

The practical significance of this work is that investigators who use the Tinsley polarograph without capacitance damping and who wish to compare their own results with those of other polarographers must determine with their own instrument the ratio $i_{average}/i_{peak}$ for the electro-reducible or electro-oxidisable substance concerned.

Since the conclusion of the experimental work reported here, Lingane and Loveridge[12] have suggested a new expression for the diffusion current at a dropping-mercury electrode. By using the familiar notation, this expression is given in two forms: the one for the average diffusion current i_d and the other for the instantaneous diffusion current i_t at any instant during the life of a drop, as follows—

$$i = 607\, n\, D^{\frac{1}{2}} C\, m^{\frac{2}{3}}\, t^{\frac{1}{6}} + 23670\, n\, DC\, m^{\frac{2}{3}}\, t^{\frac{1}{3}}$$
$$i_t = 709\, n\, D^{\frac{1}{2}} C\, m^{\frac{2}{3}}\, t^{\frac{1}{6}} + 31560\, n\, DC\, m^{\frac{2}{3}}\, t^{\frac{1}{3}}.$$

From these equations a calculation of the ratio of average diffusion current to diffusion current at maximum drop size can be made. The ratio should always be smaller than the fraction 6/7 (or 0·857), and for given values of the capillary constants m and t its value should diminish with increasing values of D. In accordance with this general rule the observed values of the ratio $i_{average}/i_{peak}$ for the reversibly reducible ions of cadmium, lead and thallium are found to decrease in order of increasing diffusion coefficients as shown in Table III.

When making comparisons between the observed values of $i_{average}/i_{peak}$ and the calculated values of $i_d/i_{t(max.)}$ it must be remembered that, whilst the terms $i_{average}$ and i_d are identical, the observed values of i_{peak} are always a little smaller than those of $i_{t(max.)}$, on account of the

TABLE III

COMPARISON OF OBSERVED VALUES FOR $i_{average}/i_{peak}$ WITH VALUES OF $i_d/i_{t(max.)}$ CALCULATED FROM THE EQUATIONS OF LINGANE AND LOVERIDGE

Electro-reducible substance	D, $cm^2sec.^{-1} \times 10^5$	m, mg per second	t, seconds	$i_d/i_{t(max.)}$, calculated	$i_{average}/i_{peak}$, observed
Cadmium	0·73	1·95	3·40	0·845	0·844
Lead	0·95	1·95	3·42	0·843	0·832
Thallium	2·01	1·95	3·41	0·839	0·809
Cupric complex with ethylene-diamine tetra-acetic acid	0·51	1·95	3·40	0·847	0·841
Tetrathionate	0·96	1·95	3·43	0·843	0·828
Methyl orange	1·00	1·95	3·26	0·843	0·789

slight inertia of the pen-recorder. For this reason, the discrepancies between values of the ratio calculated from the equation of Lingane and Loveridge and the values indicated by experiment are a little greater than Table III shows.

Still more recently, Delahay[13] has demonstrated that when polarographic currents are controlled by reaction rates as well as by diffusion processes, the ratio $i_d/i_{t(max.)}$ may even approach the low value of 0·60. The ratio for pyruvic acid was found to be 0·65 under certain conditions. The earlier work of Brdička and his collaborators, referred to by Koutecký and Brdička,[14] indicates that many other examples of rate-controlled polarographic currents are to be encountered.

During the course of this work I have had many helpful discussions with Dr. W. Cule Davies. His friendly advice and encouragement are gratefully acknowledged.

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An Extrapolation Procedure for the Assay of Aneurine

By S. J. PROKHOVNIK

A procedure for the determination of aneurine in the presence of inhibiting factors is outlined. It involves only an acidified water extraction and the oxidation of the aneurine with mercuric chloride under carefully controlled conditions. The aneurine concentration is obtained by a simple extrapolation of the "apparent aneurine" readings given by the test substance at various dilutions.

The method is quick and simple, although special care must be taken over reagents and technique. It gives results reproducible to within 5 per cent. and gives good agreement with other methods.

THE Holman[1] method for determining aneurine, as modified by Patrick and Wright,[2] has been used in these laboratories for the past four years. The method has proved to be efficient and accurate in its application to the measurement of aneurine in pharmaceutical products such as tablets and solutions that contain several vitamins.

With many substances, however, such as yeast products and chocolate - malt based granules, containing vitamins A, B_1, C and D, and vanillin, interfering substances cause not only extraneous residual fluorescence, but also inhibition of the thiochrome formed. Patrick and Wright[2] used a zeolite adsorption technique to isolate the aneurine from these substances. Lately it has been found that they can be assayed directly by this method without any preliminary adsorption or non-aqueous extractions. Experience with the two preparations mentioned above is described.

The extraneous fluorescence can be measured by a blank determination in which water is substituted for the mercuric chloride and therefore no thiochrome is formed. The difference between fluorimeter readings for blank and sample gives the quantity of apparent aneurine present. From assays on samples of various concentrations it was noticed that there was a comparative increase in apparent aneurine with increasing dilution, or conversely, that the proportion of inhibited thiochrome increased with concentration, and in fact, above a certain concentration the inhibition was complete and the apparent aneurine zero.

On plotting the apparent aneurine reading per constant weight of sample against the dilution of the sample, the resulting points linked up in a straight line sloping upwards towards zero concentration. This indicated that there existed a simple linear relationship between the concentration of test sample and the proportion of thiochrome inhibited, and hence that extrapolation to zero concentration would give the apparent aneurine when there is theoretically no inhibition, that is, the true aneurine concentration.

METHOD

PROCEDURE—

With the products mentioned it is found convenient to make an extract of 1 g in 100 ml of water acidified with hydrochloric acid. After thorough shaking, filter the extract through a No. 5 Whatman paper and label the resulting solution as 10 mg per ml. Dilute part of this solution in stages to give solutions of 5, 2·5 and 7·5 mg per ml. Transfer 1-ml duplicate portions of each dilution and also of standard aneurine solutions containing 1 μg per ml and 2 μg per ml into 6 × 1-inch test tubes by means of a pipette. Add in turn 6·00 ml of a 25 per cent. w/v potassium chloride solution, 1·00 ml of 0·8 per cent. w/v mercuric chloride and 4·00 ml of 0·04 *N* sodium hydroxide to the standards and half the sample tubes; mix before and immediately after adding the sodium hydroxide. With the other sample tubes, which are marked "blank," follow the same procedure but substitute 1·00 ml of distilled water for the mercuric chloride. Place the tubes in a thermostat bath at 40° C for 15 minutes and, after cooling, add 12·00 ml of acetone to each tube. Determine the fluorescence of the resulting solutions on a Klett fluorimeter with an aneurine photo-cell filter and a solution of 0·2 μg per ml of salacrin (1-methyl-5-aminoacridine hydrochloride) as standard. The apparent aneurine is equivalent to the difference in fluorimeter readings between sample and blank at each dilution.

Draw a graph of apparent aneurine readings per 10 mg of sample against the dilutions, that is, 2·5, 5·0, 7·5 and 10·0 mg per ml. The four points should lie on a straight line that can be extrapolated to 0 mg per ml. The apparent aneurine reading at zero concentration represents the true concentration of aneurine per 10 mg of sample.

An illustration of the extrapolation procedure is shown in Table I and Fig. 1, from an assay on a yeast product.

TABLE I

RESULTS OF AN ASSAY ON A YEAST PRODUCT TO ILLUSTRATE THE EXTRAPOLATION PROCEDURE

Sample	Concentration in 1-ml sample, mg per ml	Fluorimeter reading	Apparent aneurine readings	
			per ml	per 10 mg
Aneurine	1×10^{-3}	36·0		
"	2×10^{-3}	71·5		
Yeast product	2·5	12·0, 12·0	4·25	17·0
"	2·5 (blank)	7·7, 7·8		
"	5·0	19·8	6·9	13·8
"	5·0 (blank)	12·9		
"	7·5	25·7	7·7	10·3
"	7·5 (blank)	18·0		
"	10·0	29·1	7·0	7·0
"	10·0 (blank)	22·1		

EXPERIMENTAL

Burettes are now used in these laboratories for adding all reagents. This procedure has been found to be accurate and time saving. For the potassium chloride and the acetone, 100-ml burettes are used.

The purity of the potassium chloride is critical. Certain brands were found to be responsible for precipitating a white gelatinous suspension when the sodium hydroxide was added. Of those tested, Baker's Analysed C.P. and Morson's A.R. are the most satisfactory.

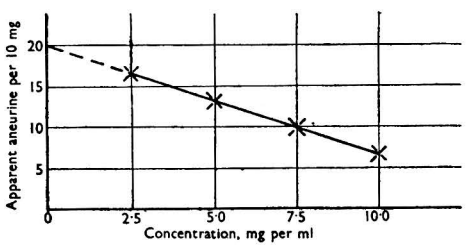

Fig. 1. Extrapolation of readings of apparent aneurine to zero concentration

Extrapolation to zero concentration gives apparent aneurine per 10 mg = 20·3

Hence, aneurine per 10 mg of test substance = 20·3/36·0 = 0·57 μg, and aneurine content = 57 μg per g

Heating time and temperature—At the heating stage of the assay, neither the temperature nor the time is critical. A minimum time of about 15 minutes at 38° to 42° C is required to complete the oxidation. Longer times (up to 1½ hours) have been tried and no difference in assay results was noted; neither more nor less thiochrome was formed.

The purity of the acetone is critical. Fresh commercial acetone should be boiled under reflux with activated carbon, preferably Norit Granule, for 2 hours and then distilled in an all-glass apparatus. Recovered acetone that has been similarly treated is less satisfactory and should be avoided in work when high accuracy is required.

If the acetone is added slowly a precipitate often forms. This dissolves on gentle shaking and does not affect the final fluorescence.

Results

Reproducible results can be obtained with the chocolate - malt product. Three samples from one batch, for instance, assayed 98, 97 and 94 μg per g, averaging 96 μg per g. An independent assay based on orthodox procedure, *i.e.*, by extraction and ferricyanide oxidation, gave 96 μg per g. These results also agree with the work done by Patrick and Wright[2] on this product, with a zeolite column adsorption technique as a preliminary to the mercuric chloride assay. The quantity of pure aneurine incorporated in this product is 98 μg per g.

With yeast products (12 samples), reproducible results were also obtained, and generally there was good agreement with the results of independent assays by the ferricyanide method. It is probably not surprising that the poorest agreement occurred with samples in which the aneurine concentration was very low and in which the interference also was greater than usual.

Discussion of the method

The accuracy of assays by the proposed extrapolation method is clearly impaired a little by the smallness of the apparent aneurine differences and by the arithmetic involved, which tends to multiply small errors. This is somewhat offset by the fact that the assay is quick and simple and avoids non-aqueous extraction or adsorption losses. Moreover, duplication of the procedure, particularly for the lowest concentration, enhances both the precision and the accuracy considerably.

Theoretically, the proportion of inhibition should also be measurable by adding a known amount of aneurine to a sample and by determining the inhibition produced by the increment. This increment method was applied simultaneously with the extrapolation procedure. It led to results of the same order as those from independent assays, but agreement between results was generally poor. Experiments with various increments of pure vitamin to extracts of the same concentration show that the proportion of aneurine inhibited under such conditions is not constant. The work done seems to support Ridyard's theories[3] on the limitations of this method.

Digestion of the samples with either acid or enzymes is not needed in this method, as aneurine esters, if present, dissolve in water easily and react similarly to the unesterified vitamin. Assays performed on the yeast product both after digestion with acid at 98° C and after digestion with takadiastase at 47° C confirmed this.

The fact that the proportion of thiochrome inhibited decreases with dilution of the test substance presents a puzzling phenomenon. *A priori*, one might expect a linear relationship between the quantity—not the proportion—of thiochrome inhibited and the concentration of extraneous material, and that consequently the same relative proportions of aneurine and extraneous material would always result in the same proportion of aneurine being inhibited, no matter what the dilution.

However, it would appear that it is some constant factor of the assay—possibly the oxidation reaction itself—which is affected by the extraneous material. Such an interpretation would explain why the inhibition decreases with dilution. It does not, however, help us to understand the mechanism of the interference, which must remain in doubt until the chemical reactions involved are determined exactly. Nevertheless, the phenomenon is useful from the analytical point of view, and it would be interesting to learn whether it occurs in any other fields of chemistry.

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The Determination of Higher Alcohols in Whisky and other Potable Spirits

By G. H. OSBORN and O. E. MOTT

A critical examination of the method for the determination of higher alcohols, recommended in the report of the Royal Commission on Whisky and Other Potable Spirits (1909 Appendix Q), has been carried out. The cause of the discrepancies in reported results has been found and a modified method that gives consistent results is described. The colour developed by higher alcohols in presence of furfural and sulphuric acid can be measured photometrically or visually and can be related to the amounts of higher alcohols present.

The Royal Commission on Whisky and Other Potable Spirits (1909)[1] laid down a method for the determination of higher alcohols as follows—

> Dissolve 1 g of a standard mixture of higher alcohols (see below) in 100 ml of pure 50 per cent. ethyl alcohol and make the solution up to 1 litre with 50 per cent. alcohol. To estimate the amount of higher alcohols in the sample, place 10 ml of the 50 per cent. alcoholic distillate in a small flask of about 75 ml capacity, or a smaller quantity made up to 10 ml with pure 50 per cent. ethyl alcohol if the amount of higher alcohols exceeds 0·1 per cent. Place 10-ml portions of pure 50 per cent. spirit containing from 0·5 to 10 ml of the standard 0·1 per cent. solution in similar flasks. Add 0·5 ml of a 1 per cent. aqueous solution of furfural to each of these solutions and slowly add 10 ml of concentrated sulphuric acid to each flask so that the acid forms a layer at the bottom. Place the flasks, one by one, on a water-bath containing ice-cold water, stir the contents by shaking each flask for 30 seconds and set them aside for about an hour at room temperature. In the presence of an appreciable amount of higher alcohols a reddish-violet colour develops and the proportions of the various alcohols are estimated by comparison with the standards.
>
> The standard higher alcohol mixture used for comparison in the Government Laboratory, and in terms of which the results of this test are expressed, contains: 1 part of propyl alcohol, 2 parts of *iso*butyl alcohol, 3 parts of amyl alcohol and 1 part of capryl alcohol. These are the usual alcohols other than ethyl alcohol found in ordinary fermentations, and the composition of the mixture is some approximation to the average composition of the "fusel oil" alcohols of pot-still spirits as determined by a number of experiments in the Government Laboratory.

This method is still widely used, but the discordant results by workers in different laboratories with the same sample or even by the same analyst in duplicate estimations has produced a tendency for discredit to be cast on the method. In May, 1951, a request was made to the Analytical Methods Committee of the Society for an investigation into the causes of these discrepancies. One of the authors (G. H. O.), who was familiar with the problem, was asked to carry out the work; the following investigations and recommendations are the result of this request.

Experimental

Experiments along the lines suggested by the Royal Commission were first tried. Half of a millilitre of a freshly prepared 1 per cent. aqueous solution of furfural was added to 10 ml of 50 per cent. ethyl alcohol in a 50-ml stoppered tube and then 10 ml of AnalaR concentrated sulphuric acid were slowly added so as to form a layer at the bottom of the tube. The tube was immersed in ice-water, the solution was gradually mixed and then set aside for 1 hour. This solution was used as the blank. Similar tubes of solution were prepared in turn in the same manner but with added amounts of different higher alcohols and the colour developed in these tubes was measured on a Beckman spectrophotometer with 1-cm cells at 515 mμ. Results are shown in Table I.

At this stage it was apparent that under these conditions *n*-propyl alcohol and *sec*octyl alcohol play little or no part in the development of the colour. The effect of adding concentrated sulphuric acid rapidly but in separate drops to 10 ml of the sample as 50 per cent.

TABLE I

OPTICAL DENSITIES OF HIGHER ALCOHOLS BY THE OFFICIAL METHOD

Higher alcohol, 0·01 ml, equivalent to 0·2 per cent. v/v in undiluted alcohol	Optical density after 1 hour	Notes
Amyl	0·32, 0·38, 0·38	Triplicate determinations with AnalaR amyl alcohol to check reproducibility. The optical density after half an hour was 0·26 and after two hours was 0·41
*iso*Butyl	0·83	A second peak at 619 mμ was observed. This causes the colour developed by *iso*-butyl alcohol to have a purplish hue instead of the pink developed with amyl alcohol
n-Propyl	0·04	
*sec*Octyl (capryl)	0·05	
Mixture of amyl, *iso*butyl, *n*-propyl and capryl in the ratio of 3:2:1:1	0·59, 0·62	Duplicate determinations with a mixture similar to that used by the Royal Commission. The colour produced was purplish-red

alcohol (all percentages by volume) in a tube immersed in ice-water, with *subsequent* addition of furfural at 20° C, was investigated. The colour was measured both (*a*) after 1 hour at 20° C and (*b*) after heating the tube to 80° C for 6 minutes and cooling quickly to 20° C.

PROPOSED METHOD

PROCEDURE—

Take 10 ml of 50 per cent. alcoholic distillate and immediately afterwards 10 ml of 50 per cent. v/v ethyl alcohol containing added higher alcohols as standards in a 50-ml (7 × 1-inch) stoppered tube and place the tube in a water-bath containing ice-water. Add 10 ml of

TABLE II

OPTICAL DENSITIES OF HIGHER ALCOHOLS BY THE PROPOSED METHOD

Alcohol	Concentration, % v/v	Optical density: Measured after 1 hour at 20° C	Optical density: Measured after 6 minutes at 80° C
Amyl	0·05	<0·01	0·12
"	0·1	<0·01	0·23
"	0·2	0·01	0·45
*iso*Butyl	0·05	0·09	0·61
"	0·1	0·16	1·2
"	0·2	0·3	*
n-Propyl	0·1	—	0·04
"	0·2	—	0·08
*sec*Octyl (capryl)	0·05	—	0·19
"	0·1	0·07	0·34
"	0·2	—	0·68
Mixture of amyl, *iso*butyl, *n*-propyl and capryl in the ratio of 3:2:1:1 ..	0·05	—	0·26
" " "	0·1	—	0·51
" " "	0·2	—	0·91

* Colour too dark for measurement.

concentrated sulphuric acid from a burette in rapid but separate drops taking about 3 minutes in all, whilst shaking the tube continuously. Warm the tube to 20° C, add 0·5 ml of a 1 per cent. aqueous solution of furfural and shake well. For procedure (*a*) set the tube aside for 1 hour. For procedure (*b*) immerse the tube in a water-bath at 80° C for 6 minutes exactly and then

cool quickly to 20° C. Measure the optical density with a spectrophotometer with 1-cm cells 515 mμ. Visual comparison may be made with standards if desired.

Notes on the procedure—(*a*) It is essential to prepare standards simultaneously, as the intensity of the colour is very sensitive to conditions.

(*b*) The furfural solution must be freshly prepared.

(*c*) The first reaction takes place between the alcohols and sulphuric acid only, hence the importance of cooling when mixing.

(*d*) *iso*Butyl alcohol gives a secondary peak at 620 mμ, resulting in a purplish tint instead of the pink from the other alcohols.

(*e*) In all experiments no maximum intensity was reached even after two days. By heating at 100° C for 10 minutes much smaller quantities of the higher alcohols can be detected.

Results on different alcohols by the proposed technique but with the two different procedures are shown in Table II. Procedure (*b*) is recommended for the determination of these higher alcohols.

From Table II it will be seen that with the controlled conditions almost linear graphs can be drawn.

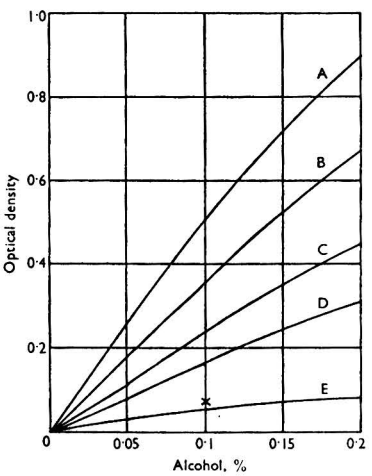

Fig. 1. Optical density curves for higher alcohols. Curve A, mixture by hot method; curve B, capryl alcohol by hot method; curve C, amyl alcohol by hot method; curve D, *iso*butyl alcohol by cold method; curve E, *n*-propyl alcohol by hot method; × = capryl alcohol by cold method

It will be noted that *iso*butyl alcohol gives quite a strong colour in the cold, so this could be determined in presence of the other alcohols if necessary.

The authors thank the Directors of the British Drug Houses Limited for permission to publish these findings.

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The Micro-Determination of Magnesium in Plant Materials with 8-Hydroxyquinoline

By J. DAVIDSON

A micro-method is described for estimating magnesium in plant materials. Magnesium is precipitated as the oxinate, which is then determined in acid solution by measuring the absorption at 358 mμ with a spectrophotometer.

Amounts of magnesium from 20 to 200 μg in 1 to 4 ml of solution can be estimated with an accuracy of ±1 μg. Recovery of magnesium added to various plant materials and ash solutions ranged from 98·8 to 100·4 per cent.

Limits of interference by phosphate, oxalate and manganese have been investigated and methods for eliminating interference have been devised.

Fox[1] described the preparation of insoluble complexes of hydroxyquinoline (oxine) with certain light metals. Hahn[2] used this compound for the gravimetric determination of magnesium. The complex formed was suitable for the determination of small amounts of magnesium because of the high molecular weight of the organic radicle.

Many methods have been devised to measure the oxine part of magnesium oxinate. Volumetric procedures have included bromination, with iodimetric titration of the excess of bromine,[3,4] and oxidimetry by means of ceric sulphate, the excess of ceric sulphate being

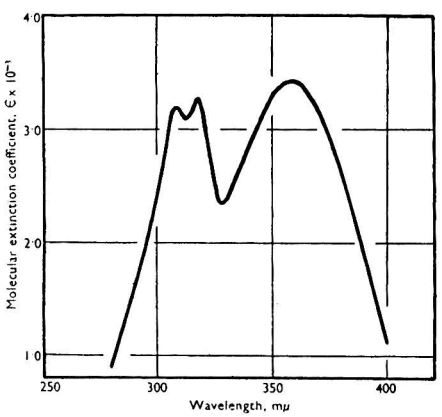

Fig. 1. Absorption curve of magnesium 8-hydroxyquinolinate between 300 and 400 mμ. Determinations were made at 1-mμ intervals in the regions of the peaks and troughs

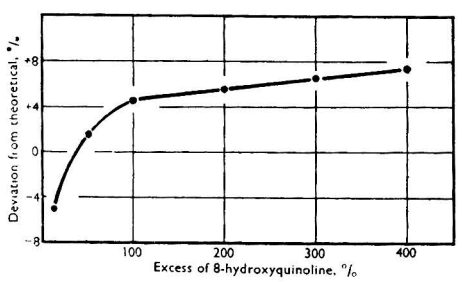

Fig. 2. Effect of excess of 8-hydroxyquinoline

determined with ferrous ammonium sulphate.[5] Colorimetric methods have been based on (*a*) formation of the molybdenum-blue colour with the Folin - Denis reagent,[6,7] (*b*) coupling with diazotised sulphanilic acid to give a red coloured compound[8] and (*c*) formation of a green complex with ferric chloride in acid solution.[9,10,11]

In his original paper, Fox pointed out that oxine absorbs strongly in the ultra-violet part of the spectrum, and recently Ewing and Steck[12] have published the absorption spectrum down to 220 mμ. The absorption peak between 350 and 400 mμ is particularly interesting because spectrophotometric measurements can be made at this wavelength by using a tungsten lamp as the light source; this can be used for wavelengths as short as 320 mμ. Preliminary measurements of the absorption spectrum of magnesium oxinate in dilute hydrochloric acid showed that the peaks between 300 and 400 mμ were, as expected, similar to those of oxine, with maxima at 309, 318 and 358 mμ (Fig. 1). In the proposed method the absorption at 358 mμ is used to enable the amount of magnesium precipitate to be determined.

Examination of precipitates for contamination was carried out by spectrographic analysis.

Experimental

Removal of interfering cations—

In preliminary experiments, calcium, iron and aluminium were removed by the method of Alten, Weiland and Kurmies,[8] as modified by Weeks and Todd[11] for plant and soil analysis. After adjusting the pH of the solution to between 5·0 and 5·2, iron and aluminium were precipitated by oxine, and calcium as oxalate.

In this investigation it was found that the procedure was adequate only for materials having a manganese to magnesium ratio of less than 1:20. Increasing amounts of manganese, above approximately 0·01 per cent. in dried plant material, caused increasing interference. Although normal pasture grass can be expected to contain up to 0·02 per cent. of manganese, figures as high as 0·120 per cent.[13] and 0·132 per cent.[14] have been reported. These high figures made it important to find some method of removing manganese as well as the other interfering cations. The alkaline sulphide precipitation procedure[15] has been suggested for removing manganese before estimating magnesium, but presented many technical difficulties, such as removal of the excess of ammonium salts. A simpler alternative was sought.

Some success was achieved by precipitating and removing manganese as oxinate at pH 6·6 to 6·8 before precipitating iron, aluminium and calcium, but recoveries of added magnesium were irregular and additional centrifuging was necessary.

The procedure finally adopted was that of Duckworth and Godden,[13] in which solutions buffered with sodium acetate were treated with bromine water to precipitate manganese as the hydrated oxide. In ash solutions buffered to approximately pH 5, iron and aluminium were also found to be precipitated.

After removing the metal precipitates by filtration, calcium only has to be removed and this can be done by precipitation with ammonium oxalate without further adjustment of pH value. Spectrographic analysis of the calcium oxalate precipitate showed that less than 0·2 per cent. of the magnesium was co-precipitated with the oxalate when analysing hay ash in which the ratio of calcium to magnesium was 6:1. As an added precaution against traces of interfering cations, alcoholic ammonium hydroxide solution was used to wash the precipitate. According to Javillier and Lavollay[16] the magnesium complex of oxine is insoluble in ammoniacal 96 per cent. alcohol at 16° C, whereas the complexes of iron, aluminium, zinc, manganese and copper have solubilities of 0·010, 0·055, 0·013, 0·021 and 0·010 per cent., respectively.

Effect of phosphate ion—

The maximum quantity of phosphate ion expected in a test sample in the method described is 1 mg. With up to 2·5 mg of phosphate, interference is negligible, but the presence of more than 2·5 mg leads to low results. Results on the average 1, 6 and 9 per cent. lower than the controls were given when 2·5, 5 and 7 mg respectively of phosphate were added to solutions of magnesium sulphate.

Effect of oxalate ion—

In the method described the quantity of oxalate ion added to a test sample for calcium precipitation is 2·2 mg, and the excess with this amount is normally about 1·5 mg. The presence of up to a 3 mg excess of oxalate ion had no appreciable effect, but a 4·4 mg excess of this ion lowered the magnesium figure obtained by 2 to 3 per cent., whilst large excesses of 18, 31 and 44 mg lowered the figures by 16, 29 and 49 per cent., respectively.

Effect of order of addition of reagents and excess of 8-hydroxyquinoline—

In general, two procedures of precipitation are to be found in the literature—

(*i*) An excess of ammonium hydroxide is added to a neutral or slightly acid solution containing magnesium and 8-hydroxyquinoline.[17]

(*ii*) The 8-hydroxyquinoline reagent is added to an ammoniacal solution of magnesium containing ammonium chloride or acetate.[18]

Miller and McLennan[19] have pointed out that determinations of magnesium precipitated as in procedure (*ii*), with less than a 100 per cent. excess of 8-hydroxyquinoline, gave results differing from the theoretical by only 1 per cent., whereas determinations after precipitation as in procedure (*i*) gave positive errors ranging from 1 to 8 per cent. with excesses of oxine from 5 to 100 per cent.

In preliminary experiments with magnesium sulphate solutions, results in agreement with those reported by Miller and McLennan were obtained. Fig. 2 illustrates the adsorption effect of an increasing excess of oxine.

With phosphate present irregular interference occurred with procedure (*ii*) owing to the formation of magnesium ammonium phosphate. Procedure (*i*) was therefore chosen for our purpose because of the presence of phosphates in plant materials. The error due to adsorption was reduced to a minimum by adding a constant volume of reagent to the standard and to the unknown solutions.

TEMPERATURE OF ASHING—

There was no appreciable difference in the magnesium content after ashing grass samples at 430°, 530° and 620° C. At 620° C the furnace was dull red. At 740° C, a bright red heat, there was a 7 per cent. loss of magnesium.

OTHER FACTORS INVESTIGATED—

The results were not affected by variations in the temperature of precipitation between 50° and 80° C, by cooling for as long as 30 minutes in running tap-water before throwing down the magnesium precipitate by centrifugation or by an excess of concentrated ammonium hydroxide.

METHOD

REAGENTS—

Hydrochloric acid—*N* and 0·1 *N* solutions.

Acetic acid, 2 N.

Ammonium hydroxide—Sp.gr. 0·880.

Ammonium oxalate solution, 0·1 N.

Sodium acetate solution—Approximately 50 per cent. w/v (75 g of sodium acetate + 100 ml of water).

Bromine water—A saturated solution of liquid bromine in distilled water.

Wash solution—A 1 per cent. v/v concentrated ammonium hydroxide solution in 96 per cent. v/v ethyl alcohol.

"Teepol" solution—An 0·1 per cent. v/v solution in 50 per cent. v/v ethyl alcohol.

Oxine reagent—A 0·500 per cent. w/v solution of oxine in 2 *N* acetic acid, freshly prepared each day.

Standard magnesium solution—Dissolve 0·1250 g of $MgSO_4.7H_2O$ in water containing 5 ml of *N* hydrochloric acid and make up to 500 ml in a graduated flask.

APPARATUS—

The following are required: 15-ml conical Pyrex centrifuge tubes that taper sharply to the tip; 15-ml and 100-ml graduated flasks; water-baths maintained at 100° and 80° C; a spectrophotometer suitable for measuring optical densities at 358 mμ.

PREPARATION OF ASH SOLUTION AND REMOVAL OF IRON, ALUMINIUM AND MANGANESE—

Reduce a 2-g sample of plant material, or sufficient to contain 1 to 10 mg of magnesium, to ash in a small Vitreosil basin at a temperature of 500° to 540° C (below dull red heat). The ash should be white or of a very light grey colour to ensure avoiding losses by adsorption on carbon particles. Add 10 ml of *N* hydrochloric acid to the ash, cover it with a watch-glass and heat for 30 minutes on the steam-bath. Add 5 ml of sodium acetate solution and 0·5 ml of bromine water. Reduce the volume on the water- or sand-bath to approximately 5 ml to remove traces of bromine. Filter into a 100-ml graduated flask and wash the basin and precipitate thoroughly with hot water. After cooling the filtrate and washings make the volume up to 100 ml.

REMOVAL OF CALCIUM—

Add to 15-ml conical centrifuge tubes, by means of a pipette, up to 4-ml amounts of solution containing 20 to 200 μg of magnesium and make up to 4 ml with distilled water. Prepare reagent blanks with 4 ml of distilled water. Add 0·5 ml of 0·1 *N* ammonium oxalate and rotate the tubes to mix the solution. Place the tubes in a water-bath at 100° C for

30 minutes and then leave them overnight at room temperature to precipitate calcium oxalate. Add one or two drops of "Teepol" solution to sink any floating precipitate. Centrifuge at a relative centrifugal force of 2000 to 2500 (3000 to 3500 r.p.m. and 7½ inches radius) for 5 minutes. Transfer the supernatant liquors to a second set of 15-ml conical centrifuge tubes, wash the precipitates twice with 1-ml portions of water and add the washings to the supernatant liquors.

ISOLATION OF MAGNESIUM AS THE OXINATE—

Add exactly 0·5 ml of oxine reagent to the combined supernatant liquors and washings and mix by rotation. Add 2 ml of ammonium hydroxide, sp.gr. 0·880, stir and wash the rod. The volume will now be approximately 11 ml. Fix rubber stoppers fitted with pieces of 1-mm capillary glass tubing to each tube to prevent excessive loss of ammonia. Place the tubes in a water-bath at 80° ± 2° C for 30 minutes. Remove the stoppers, add 0·5 ml of

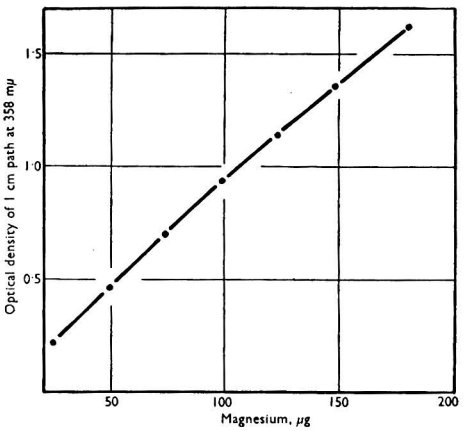

Fig. 3. Standard calibration curve

"Teepol" solution to sink any floating precipitate and centrifuge for 10 minutes at a relative centrifugal force of 2500. Withdraw the supernatant liquor to within 1 mm of the surface of the precipitate by means of a suction bottle and tube with its tip drawn out and bent. Add two drops of the ammoniacal wash solution. Re-suspend the precipitate by sharply tapping the end of the tube with the left hand while holding the rim of the tube in the right hand. Add a further 10 ml of wash solution and rotate the tube to ensure mixing. Add 0·5 ml of "Teepol" solution and centrifuge again at a relative centrifugal force of 2500 for 15 minutes. Withdraw the wash liquor, taking care that the tip of the suction tube is kept as near the central axis of the tube as possible, to avoid disturbing any fine precipitate that may have adhered to the walls of the tube. If the conical centrifuge tube is sufficiently narrow at the bottom, one washing is sufficient to remove the excess of reagent.

Add one drop of 0·1 *N* hydrochloric acid and re-suspend the precipitate. Add a further 1 ml of 0·1 *N* hydrochloric acid and rotate the tube to dissolve the precipitate. Transfer the solution with water through a small filter funnel into a 15-ml graduated flask and make up to the mark with water. The final acidity is not critical.

MEASUREMENT OF OPTICAL DENSITY—

With distilled water in the reference cell, measure the optical density of each solution at 358 mμ in 1-cm cells. The slit width used with a Beckman DUV spectrophotometer was 0·2 mm.

CALCULATION OF RESULTS—

Subtract from each optical density reading, the reading of the reagent blank and read the value of the magnesium content of each solution from a calibration curve (Fig. 3) prepared with 1, 2, 3, 4, 5, 6, 7 and 8 ml of the standard magnesium solution treated as described from the isolation procedure onwards.

ALTERNATIVE PROCEDURE WITH AN ABSORPTIOMETER—

During the course of this work other procedures for measuring the hydroxyquinoline part of the precipitate were examined. The blue colour that develops when ferric chloride is added to oxinate[10,11] is suitable for visual and absorptiometric measurement. The colour is relatively stable and easy to measure with a filter with maximum transmission close to 650 mμ.

RECOVERY EXPERIMENTS—

The method was checked in two ways—

(*a*) Ash extracts were prepared as described from several samples of dried plant material. Eight 2-ml aliquots were taken from each extract, magnesium being added as sulphate solution in quadruplicate determinations. The magnesium was then determined. The results in Table I show that mean recoveries ranged from 99·8 to 100·4 per cent.

TABLE I

RECOVERY OF MAGNESIUM ADDED TO PLANT ASH EXTRACTS

Material	Average amount found in control 2 ml, μg	Average amount found in 2 ml + magnesium, μg	Difference, μg	Magnesium added, μg	Recovery, %
Clover 112	81·3	130·2	48·9	48·7	100·4
Bracken 118	51·4	100·0	48·6	48·7	99·8
Grass 111	67·5	116·4	48·9	48·7	100·4
Hay 353	78·2	126·9	48·7	48·7	100·0

(*b*) Duplicate 2-g samples of hay and grass, with and without magnesium sulphate, were reduced to ash and the magnesium was determined on 2-ml aliquots of the 100-ml extract as described. The results shown in Table II indicate that replication is good and that mean recoveries ranged from 98·8 to 100·4 per cent.

TABLE II

RECOVERY OF MAGNESIUM ADDED TO HAY AND GRASS

Sample No.	Magnesium added to 2 g of sample, mg	Magnesium found in 2 g of sample, mg	Average amount of magnesium found, mg	Recovery, %
Hay 353	0·00	3·90, 3·91 3·91, 3·86	3·90	
	0·00	3·94, 3·90 3·89, 3·89	3·90	
	2·50	6·42, 6·30 6·38, 6·36	6·37	98·8
	2·50	6·43, 6·37 6·37, 6·40	6·39	99·6
Grass 108	0·00	3·52, 3·53 3·54, 3·52	3·53	
	0·00	3·57, 3·57 3·54, 3·61	3·57	
	2·47	5·98, 5·97 6·03, 6·02	6·00	99·2
	2·47	6·06, 6·06 5·96, 6·03	6·03	100·4

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The Separation of Silver from Copper by Electro-Deposition from Ammoniacal Solution

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The method of controlled cathode potential electro-deposition can be used to separate silver from copper rapidly and quantitatively. Deposition is made from an ammoniacal solution. Passage of oxygen through the solution during the electrolysis of silver prevents the formation of metallic silver throughout the solution itself and renders unnecessary the addition of hydrogen peroxide suggested earlier. The method has been applied with success to the analysis of silver solder.

THE determination of silver by cathodic deposition from an ammoniacal solution was first reported by Schoch and Crawford,[1] who found that only 99·8 per cent. of the silver could be so deposited and that complete deposition could only be secured by acidifying the solution and adding oxalic acid as a reducing agent. The total electrolysis time was 45 to 50 minutes as the maximum allowable current was 0·35 amperes. Miller[2] effected the separation of silver from copper by deposition from an ammoniacal solution, arbitrarily limiting the current to 0·4 amperes throughout the electrolysis. Miller found that some metallic silver appeared in the solution itself and that the addition of hydrogen peroxide towards the end of electrolysis effected the re-solution of this metallic silver and insured its ultimate deposition on the cathode.

Although Miller states that with adequate stirring the current can safely be doubled, the permissible current will depend on the size of electrodes used and the manner of stirring. The Miller procedure has been improved by avoiding the necessity of adding hydrogen peroxide and by increasing the rate of electrolysis; this is accomplished by bubbling oxygen through the solution and by controlling the cathode potential. An auxiliary reference electrode is used to give a direct indication of the cathode potential, which is the factor that governs the nature of the reaction that occurs at the cathode. With a knowledge of the highest value of the cathode potential that will insure a separation of silver from copper, it is possible to increase the current used and shorten the time required for deposition.

THEORETICAL ELECTROCHEMICAL CONSIDERATIONS—

The complex ions of silver and copper in ammoniacal solution and their respective instability constants according to Bjerrum[3] are—

$$Ag(NH_3)_2^{\cdot} \rightleftharpoons Ag^{\cdot} + 2NH_3,\ k = 6{\cdot}0 \times 10^{-8},$$
$$Cu(NH_3)_4^{\cdot\cdot} \rightleftharpoons Cu^{\cdot\cdot} + 4NH_3,\ k = 4{\cdot}56 \times 10^{-14}$$
and $$Cu(NH_3)_2^{\cdot} \rightleftharpoons Cu^{\cdot} + 2NH_3,\ k = 1{\cdot}35 \times 10^{-11}.$$

The reduction potentials of these ions were calculated from these constants; the standard reduction potentials for the silver, cupric and cuprous ions are—

$$E_o\ (Ag^{\cdot}\ \text{to}\ Ag) = 0{\cdot}7995\ \text{volt},$$
$$E_o\ (Cu^{\cdot\cdot}\ \text{to}\ Cu) = 0{\cdot}3448\ \text{volt}$$
$$\text{and}\ E_o\ (Cu^{\cdot}\ \text{to}\ Cu) = 0{\cdot}522\ \text{volt}.$$

The values obtained were—

$$Ag(NH_3)_2^{\cdot} + e^- \rightleftharpoons Ag + 2NH_3 \qquad E_o = 0{\cdot}371\ \text{volt},$$
$$Cu(NH_3)_4^{\cdot\cdot} + e^- \rightleftharpoons Cu(NH_3)_2^{\cdot} + 2NH_3 \qquad E_o = 0{\cdot}02\ \text{volt},$$
$$Cu(NH_3)_4^{\cdot\cdot} + 2e^- \rightleftharpoons Cu + 4NH_3 \qquad E_o = -0{\cdot}05\ \text{volt}$$
$$\text{and}\ Cu(NH_3)_2^{\cdot} + e^- \rightleftharpoons Cu + 2NH_3 \qquad E_o = -0{\cdot}12\ \text{volt}.$$

It is apparent that from an ammoniacal solution containing silver and copper the silver will be deposited first and that at a more negative cathode potential the tetra-amminocupric ion will be reduced to the diamminocuprous ion in preference to the deposition of metallic copper. Moreover, a calculation indicates that the electrode potentials are sufficiently apart to permit a reduction in concentration of silver to about 10^{-6} molar prior to the deposition of copper. In this calculation it was assumed that the diamminocuprous ion concentration is molar; in practice it would be much less, so favouring the separation even more. It was also assumed that the ammonia concentration is molar and that the polarisation potential of silver on silver is negligible. The first assumption is valid since the amount of excess ammonia present in both the Miller and the proposed procedures approximates to 1·0 *M*. The polarisation term, however, was found to be of the order of 0·1 volt towards the end of electrolysis. This means that the separation will be less effective by a factor of twenty or so.

The calculated reduction potentials indicate that the cathode potential should be maintained in the neighbourhood of zero on the hydrogen scale. This was confirmed experimentally, for it was found that complete deposition of silver could be effected without deposition of copper at a cathode potential —0·24 volt against the saturated calomel electrode.

As reported by Miller, a precipitate of silver, or possibly a sub-salt of silver, appeared in the solution shortly after the electrolysis was begun; sometimes this appeared as a black mirror on the walls of the beaker. This precipitate was readily dissolved by hydrogen peroxide although occasionally further treatment was necessary. Inasmuch as the precipitate did not appear when copper was absent, it seemed likely that this reduction was caused by the amminocuprous ion formed by cathodic reduction. A search for a mild oxidising agent that could keep the copper oxidised without interrupting the silver deposition showed that oxygen should be suitable. Tests confirmed this and showed that pure oxygen was more effective than air, as the gas stream could be made much smaller and the danger of carrying away solution in the spray was lessened. The loss of silver and copper by diffusion into the fritted glass dispersion disc was avoided by starting the gas stream before immersing the tube in the solution.

In the electro-deposition of copper following the deposition of silver from the solutions, two separate procedures were found necessary. Where copper was the only readily reducible metallic constituent remaining in solution electro-deposition was effected from an ammoniacal solution. Hydroxylammonium chloride was added to reduce the tetra-amminocupric ion to the diamminocuprous complex, a reaction accompanied by the disappearance of the blue colour of the amminocupric ion. The copper then was deposited more rapidly and the quality of the copper deposit was excellent. At the end of the electrolysis and before removing the electrode, the solution was neutralised with hydrochloric acid to minimise the loss of copper by re-solution during washing.

The separation of copper from such metals as cadmium and zinc cannot be effected by electro-deposition from an ammoniacal solution, so the copper must be deposited from an acid solution in the analysis of an alloy containing cadmium and zinc. Following the removal of silver, the solution was acidified with nitric acid, hydroxylammonium sulphate was added as an anodic depolariser and the copper deposited.

Experimental

The electro-depositions were made by the controlled cathode potential method with the automatic apparatus of Diehl.[4] The electrodes used consisted of two concentric platinum-gauze cylinders with the shaft of the stirrer passing down the axis and the arms of the stirrer doubled back up between the gauze electrodes in the form of a double U; the set-up is pictured on page 16 of Diehl's book.[4]

The silver used was prepared by electro-deposition of highly purified silver from a nitrate solution; the silver crystals obtained were fused to buttons in depressions in a block of calcium oxide by a gas-oxygen flame. The buttons were allowed to solidify and cool in the cold reducing part of the gas flame. The buttons were leached with dilute nitric acid, washed, and dried. The copper used was ordinary copper wire, sand-papered to remove the oxide film, washed, and dried. The results shown in Table I were obtained for synthetic mixtures containing only silver and copper by procedure A, page 271.

Table I

Determination of silver and copper in synthetic mixtures
Consecutive analyses

Silver taken, g	Silver found, g	Error, mg	Maximum current, amp.	Copper taken, g	Copper found, g	Error. mg
0·5793	0·5797	0·4	1·2	0·3000	0·2995	−0·5
0·7802	0·7781	−2·1	1·5	0·4458	0·4457	−0·1
0·5366	0·5355	−1·1	1·4	0·5459	0·5467	0·8
0·8880	0·8880	0·0	2·0	0·1698	0·1700	0·2
0·4579	0·4575	−0·4	1·4	0·3410	0·3413	0·3
0·5408	0·5412	0·4	1·5	0·4265	0·4265	0·0
0·2088	0·2086	−0·2	0·9	0·6794	0·6795	0·1
0·6551	0·6546	−0·5	1·4	0·4782	0·4779	−0·3
0·3860	0·3861	0·1	1·4	0·8118	0·8117	−0·1
0·3591	0·3590	−0·1	1·4	0·4039	0·4042	0·3
0·1327	0·1328	0·1	0·9	0·8529	0·8531	0·2
0·2147	0·2127*	−2·0	1·0	0·6400	0·6410	1·0
0·2553	0·2554	0·1	1·0	0·4933	0·4941	0·8
0·3965	0·3973	0·8	1·6	0·1779	0·1779	0·0
0·4451	0·4454	0·3	1·7	0·9001	0·9004	0·3
0·4357	0·4357	0·0	1·6	0·5918	0·5915	−0·3
0·7212	0·7211	−0·1	2·0	0·0931	0·0931	0·0
0·0623	0·0623	0·0	0·8	0·7222	0·7220	−0·2
0·1289	0·1287	−0·2	1·0	0·8677	0·8673	−0·4
0·2754	0·2752	−0·2	1·4	0·6967	0·6965	−0·2
0·3069	0·3067	−0·2	1·2	0·3104	0·3099	−0·5
0·0167	0·0165	−0·2	0·6	1·0238	1·0235	−0·3
0·0148	0·0148	0·0	0·6	0·7820	0·7820	0·0
0·0277	0·0268	−0·9	0·6	0·8956	0·8954	−0·2
0·3856	0·3858	0·2	1·5	0·0174	0·0175	0·1
0·4887	0·4886	−0·1	1·4	0·0219	0·0220	0·1
0·5935	0·5936	0·1	1·5	0·0082	0·0082	0·0

* Electrolysis deliberately discontinued after 16 minutes. Good deposit; would probably have been complete in 25 minutes.

A representative commercial silver solder (Type KH–7) was procured in the form of a wire from the General Plate Division, Metals and Controls Corporation, Attleboro, Massachusetts. This wire was cut into small pieces, washed with organic solvents and water, dried and the pieces thoroughly mixed. The silver solder sample was analysed according to the A.S.T.M. procedure[5] except as noted below. Weighed samples were dissolved in nitric acid, the solution diluted, and silver chloride precipitated by the addition of dilute hydrochloric acid. The precipitate was filtered, washed and dried at 110°. The hydrochloric

acid in the filtrate was eliminated by evaporation with sulphuric acid and the copper was deposited electrolytically. The separation of cadmium from zinc was effected by precipitating cadmium sulphide with hydrogen sulphide in sulphuric acid solution. The cadmium sulphide was filtered off, dissolved in warm hydrochloric acid, and re-precipitated. Cadmium sulphide was then re-dissolved and cadmium precipitated as cadmium ammonium phosphate. The latter was re-precipitated and the cadmium finally weighed as the pyrophosphate. Zinc was determined in the combined filtrate from the sulphide separation by precipitating it as zinc ammonium phosphate and ignition to the pyrophosphate.

Table II compares the results obtained by gravimetric analysis with those obtained by electro-deposition methods according to Procedure B, below.

TABLE II

ANALYSIS OF SILVER SOLDER

Composition as determined gravimetrically—Silver, 50·92 per cent.; copper, 15·74 per cent.; cadmium, 17·0 per cent.; zinc, 15·9 per cent.

Sample weight taken, g	Electro-deposition by proposed method	
	Silver, %	Copper, %
0·5437	50·91	15·71
0·6050	50·96	15·69
0·5414	50·94	15·74
0·6522	50·97	15·70
0·5300	50·92	15·81
0·5933	50·98	15·69
Mean	50·95	15·72

METHOD

PROCEDURE—

Silver—Dissolve a sample of 0·4 to 0·7 g in 6 ml of diluted nitric acid (1 + 1) in a 300-ml tall-form beaker. Heat the solution gently to expel oxides of nitrogen. Dilute the solution to about 150 ml with water and add 8 ml of concentrated ammonium hydroxide. With a flow of oxygen of about 8 to 10 ml per minute already passing through a glass tube bearing a fritted glass dispersion disc, bring the solution up around the electrodes and gas tube. The gas dispersion disc should be centred beneath the anode to obtain maximum dispersion of the oxygen. Start the stirring at a moderate rate. Electrolyse and increase the current until the cathode reaches a potential of −0·24 volt against the saturated calomel electrode. Adjust the apparatus to limit the cathode potential automatically to this value. Continue to electrolyse for 25 minutes. Remove the platinum gauze cathode from solution with continuous washing, dry at 110° and weigh. Rinse the solution adhering to the gas dispersion disc into the main body of the solution with dilute nitric acid.

Copper, A (copper alone present)—Remove the oxygen dispersion tube from the solution. Add about 2 g of hydroxylammonium chloride to the solution and deposit copper on a clean platinum gauze electrode. Start the stirring and electrolyse at 3·0 amperes without automatic cathode potential control. Maintain the current at 3·0 amperes by periodic adjustment and continue to electrolyse for 20 to 25 minutes, depending on the amount of copper present. Neutralise the solution to a pH of about 8 by adding 2 to 3 ml of concentrated hydrochloric acid, taking care not to let the acid come into contact with the cathode. Remove the electrode with continuous washing, dry it at 110° and weigh it.

Copper, B (copper in the presence of such metals as cadmium and zinc)—Remove the oxygen dispersion tube from the solution. Add 7 ml of concentrated nitric acid and about 1 g of hydroxylammonium sulphate to the solution. Start the stirring and deposit copper on a clean platinum gauze electrode at a current of 2·0 amperes without automatic cathode potential control. Maintain the current at this value and continue the electrolysis for 25 minutes. Remove the electrode with continuous washing, dry at 110° and weigh it.

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DEPARTMENT OF CHEMISTRY
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First submitted *May*, 1951
Amended *February*, 1952

Notes

IODOMETRIC DETERMINATION OF SELENIUM BY ARSENIOUS OXIDE

SELENIUM in selenious acid is usually determined by permanganate or thiosulphate.[1] In the thiosulphate procedure, iodine liberated by selenious acid in an acid medium is determined with standard sodium thiosulphate.

$$H_2SeO_3 + 4HI \rightarrow Se + 2I_2 + 3H_2O \quad .. \quad .. \quad .. \quad .. \quad .. \quad (i)$$
$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \quad .. \quad .. \quad .. \quad .. \quad .. \quad (ii)$$

Alternatively, a slight excess of standard thiosulphate is added to a known volume of selenious acid and the excess of thiosulphate is determined with standard iodine solution.[2]

$$H_2SeO_3 + 4Na_2S_2O_3 + 4HCl \rightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O \quad .. \quad (iii)$$

A large excess of sodium thiosulphate, however, leads to high results.[3] For an accurate determination according to equation (*iii*) it is necessary to determine beforehand, by trial experiments, the appropriate quantity of thiosulphate required to react with the selenious acid solution.

The reversible reaction between arsenious oxide and iodine

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (iv)$$

proceeds quantitatively from left to right, if the hydrogen iodide is removed as soon as it is formed. Washburn,[4] from studies of the equilibrium constant of this reaction, calculated that the pH should be between 4 and 9. Recent observations by McAlpine,[5] however, show that the determination of iodine by arsenious oxide can be carried out even in an alkaline medium of pH 11. As hydrochloric acid is necessary for the quantitative liberation of iodine by selenious acid, the pH of the medium is usually much below 4. This renders direct titration with arsenious oxide impracticable. According to Evans,[6] the determination of selenium by arsenious oxide should be possible if, after the liberation of iodine by an initially acidified selenious acid, the major portion of the acid is neutralised by 20 per cent. sodium hydroxide solution and an excess of barium carbonate cream. Experience has shown that this procedure leads to uncertain results, the effect presumably, of unspecific experimental conditions. The quantity of sodium hydroxide solution necessary for partial neutralisation or almost complete neutralisation of the acidity has not been defined. This and the presence of excess of barium carbonate cream prevents a sharp and accurate end-point. In the present series of experiments (Table I), an excess of the boric acid - borax buffer was used prior to the commencement of the titration (see Method), because neutralisation by sodium bicarbonate is usually accompanied by a brisk evolution of carbon dioxide and a partial loss of iodine.[4]

The present note reports in some detail a modified and accurate procedure for the iodometric determination of selenium by arsenious oxide.

METHOD

REAGENTS—

All reagents should be of recognised analytical purity.

Selenious acid solution—Make an approximately 0·1 *N* aqueous solution from selenious acid recrystallised several times from absolute alcohol. Determine the selenium content by the standard thiosulphate method.[1]

Arsenious oxide solution, 0·1 N—Dissolve 4·946 g of arsenious oxide in 20 per cent. sodium hydroxide solution. Neutralise to litmus paper with hydrochloric acid, add about 2 g of sodium bicarbonate and make up to 1 litre with water.[7]

Boric acid - borax buffer solution[8]—Dissolve 40 g of borax and 20 g of boric acid in water and make up to 500 ml.

Hydrochloric acid—4 *N*.

Potassium iodide—A 20 per cent. solution.

PROCEDURE—

Add 5 to 10 ml of carbon tetrachloride or carbon disulphide and 10 ml of 4 *N* hydrochloric acid to an aliquot portion of the selenious acid solution and then 10 to 15 ml of potassium iodide in a fine stream with continuous swirling. Cool in an ice-salt mixture for about 10 minutes and add 80 to 90 ml of the buffer solution, equivalent to 10 ml of 4 *N* hydrochloric acid as determined by titration with bromo-thymol blue as indicator. Titrate with arsenious oxide, add 2 ml of starch solution near the end-point and continue until the blue colour just disappears. The volume of arsenious oxide added corresponds to the quantity of free iodine and hence to the amount of selenious acid.

Table I shows a typical set of results.

TABLE I

DETERMINATION OF SELENIUM IN SELENIOUS ACID

By thiosulphate method, g	By arsenious oxide method, g	Difference, g
0·01274	0·01275	+0·00001
0·01782	0·01780	−0·00002
0·02547	0·02546	−0·00001
0·02802	0·028005	−0·000015
0·03056	0·03054	−0·00002
0·03311	0·03309	−0·00002
0·03820	0·03818	−0·00002
0·04329	0·04326	−0·00003
0·04840	0·04835	−0·00005
0·05093	0·05083	−0·00010

The agreement between the values for selenium in selenious acid found by thiosulphate and by arsenious oxide shown in Table I emphasises the importance of this new analytical procedure with arsenious oxide as a primary standard.

Further work on the analysis and estimation of various metal selenites is in progress.

We wish to express our grateful thanks to Professor S. S. Joshi for facilities and keen interest in the work and to the National Institute of Sciences of India for award of a research fellowship to one of us (G. S. D.).

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DEPARTMENT OF CHEMISTRY
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G. S. DESHMUKH
B. R. SANT

October, 1951

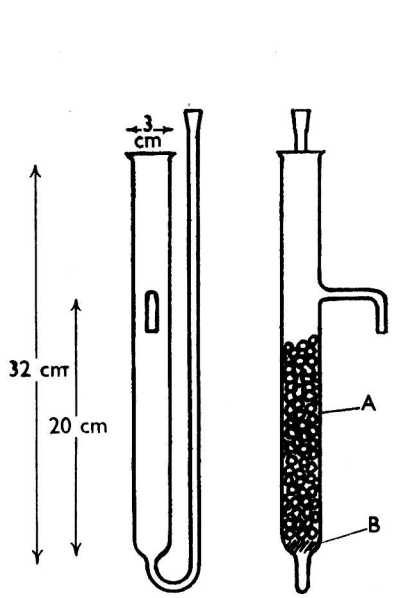
AN EXTRACTOR AND DISTILLATION HEAD SUITABLE FOR USE IN THE DETERMINATION OF URINARY CORTIN

URINARY corticoids are generally determined by extracting acidified urine with an organic solvent, usually chloroform, and estimating the reducing material present in the dried extract.

When acidified urine is shaken vigorously with chloroform, persistent emulsions that cannot be dispersed completely in a centrifuge frequently occur. This difficulty can be avoided by passing a thin stream of one liquid through the other; previous papers by Robinson and Warren,[1] Craig,[2] Cohen,[3] and Robinson and Norton[4] have described apparatus designed for this purpose. The single-piece extractor described here, reduces the total time of extraction to 25 minutes and requires only 40 ml of chloroform for 100 ml of urine. A simple apparatus for evaporating the washed extract *in vacuo* is also described.

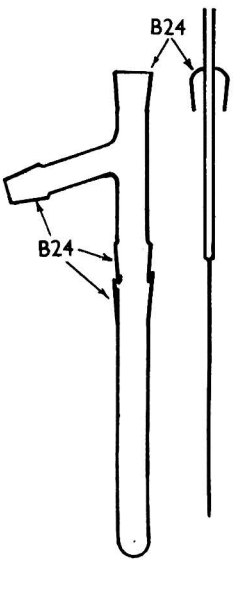
APPARATUS

The extractor—The improved extractor shown in Fig. 1 (*a*) consists of a large hard-glass tube with a delivery arm and an inlet at the lower end. The apparatus is easily made or repaired and is therefore preferable to more complicated two-piece extractors. Before use, the inlet is covered with a small pad of glass wool and the tube partly filled with glass balls, preferably



(*a*)

Fig. 1 (*a*). Details of the extractor
A, glass balls of 6–8mm diameter
B, glass wool



(*b*)

Fig. 1 (*b*). The distillation head

6 to 8 mm in diameter. These balls are covered with chloroform and distribute the up-flowing urine into many thin streams, so ensuring an intimate mixture of urine and chloroform and preventing channelling.

The distillation head—The distillation head, attached to an 8 × 1-inch tube with a B24 neck, is shown in Fig. 1 (*b*). The head consists of a T-shaped tube with B24 joints on the side-arm, upper and lower ends. A fine glass capillary that acts as an air leak in the distillation is fitted to the upper end of the T-piece by a B24 joint and reaches to the bottom of the distillation tube.

METHOD

PROCEDURE—

Cover the glass balls in the extractor with 40 ml of chloroform and pour 100 ml of urine, acidified to a pH of 1·0 with 10 *N* sulphuric acid, into a separating funnel. Adjust the rate

of flow from it into the inlet arm so that the urine percolates through the solvent without sweeping it out through the exit arm. Collect the out-flowing urine and return it to the separating funnel; repeat the process 20 times. Each extraction takes from 60 to 70 seconds. Wash the chloroform extract *in situ* by passing 100 ml of distilled water through the extractor and then pour the mixture of chloroform, glass balls and supernatant water into the separating funnel through a 3½-inch glass filter funnel fitted with a small plug of glass wool. Wash the balls twice with 30 ml of water and allow to drain. Discard the water layer and wash the chloroform in the usual way with three 15-ml portions of chilled 0·1 *N* sodium hydroxide solution and three 15-ml portions of cold water. Dry the extract for 1 hour over anhydrous sodium sulphate, filter through sintered glass into an 8 × 1-inch tube and attach the distillation head. Distil the chloroform under vacuum from the apparatus on a water-bath maintained at 45° to 50° C, with a moderate stream of air passing through the capillary. Under these conditions 40 to 50 ml of chloroform can be removed in less than 15 minutes.

The cortin in the dried extract can be estimated by any of the established methods of Talbot, Saltzman, Wixom and Wolfe,[5] Heard and Sobel,[6] Daughaday, Jaffe and Williams,[7] or Sprechler.[8]

Extracts obtained by this procedure give results that compare favourably with those obtained by the normal shaking method and by the extraction apparatus of Robinson and Warren.[1]

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Biochemical and Endocrinological Research Department
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E. R. Cook
M. E. Rooks

January, 1952

Ministry of Food

STATUTORY INSTRUMENTS*

1952—No. 507. The Meat Products Order, 1952. Price 9d.

This Order, which came into operation on March 16th, 1952, replaces the Meat Products and Canned Meat (Control and Maximum Prices) Order, 1948 (S.I., 1948, No. 1509; Analyst, 1948, 73, 341), as amended (S.I., 1949, Nos. 782, 1303 and 2045; S.I., 1950, No. 1764; S.I., 1951, Nos. 314, 1029 and 1317).

It removes the restriction on the use of soya, and increases the maximum meat content for a number of meat products.

British Standards Institution

NEW SPECIFICATIONS†

B.S. 658:1952. Apparatus for the Determination of Distillation Range. Price 2s. 6d.
B.S. 914:1952. Quality of Laboratory Porcelain. Price 2s.
B.S. 1428:1952. Microchemical Apparatus. Price 2s. each part.
Part A2—Nitrogen Combustion Train (Micro-Dumas).
Part H1—Weighing Vessels for Microchemical Analysis.
Group A of the series comprises combustion trains for the determination of elements.
Group H of the series covers weighing accessories.
For details of some other Specifications of this series see Analyst, 1951, **76**, 54.
B.S. 1752:1952. Sintered Disk Filters for Laboratory Use. Price 2s.
B.S. 1797:1952. Tables for Use in the Calibration of Volumetric Glassware. Price 10s. 6d.
B.S. 1820:1952. Vegetable Parchment for Wrapping Dairy and Other Food Products. Price 4s.
B.S. 1834:1952. *iso*Propyl Acetate. Price 2s.
B.S. 1835:1952. 2-Ethylhexyl Alcohol (2-Ethylhexanol). Price 2s.

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.
† Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

AMENDMENT SLIPS*

Printed slips bearing Amendments to British Standards have been issued by the Institution as follows—

PD 1268—Amendment No. 2 (September, 1951) to B.S. 684:1950. Methods of Analysis of Oils and Fats.

PD 1291—Amendment No. 1 (December, 1951) to B.S. 1428 Part D.3:1950. Micro-nitrometers (Pregl type).

PD 1319—Amendment No. 1 (December, 1951) to B.S. 655:1950. Refined Cottonseed Oil.

PD 1336—Amendment No. 1 (January, 1952) to B.S. 692:1951. Meteorological Thermometers.

PD 1351—Amendment No. 2 (February, 1952) to B.S. 632:1950. Raw Linseed Oil for General Purposes.

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and can be obtained on application to the Secretary, Society of Public Analysts and Other Analytical Chemists, 7–8, Idol Lane, London, E.C.3.

Draft Specifications prepared by Technical Committee LBC/1—Volumetric, Mouldblown and Lamp-blown Glassware.

CN(LBC)9637—Draft B.S. for Separating Funnels.

CN(LBC)9638—Draft B.S. for Glass Filter Funnels.

Draft Specification prepared by Technical Committee LBC/5—Hydrometers.

CN(LBC)9474—Draft B.S. for Density Hydrometers and Specific Gravity Hydrometers.

Draft Specification prepared by Technical Committee LBC/6—Standard Distillation Flasks.

CN(LBC)9248—Draft B.S. for Distillation Flasks (Revision of B.S. 571).

Draft Specifications prepared by Technical Committee FCC/4—Solvents and Allied Products.

CO(FCC)406—Draft B.S. for Triphenyl Phosphate.

CO(FCC)407—Draft B.S. for Glycerol Triacetate (Triacetin).

Publications Received

SUPPLEMENT 1952 TO THE BRITISH PHARMACEUTICAL CODEX 1949. Pp. xii + 148. London: The Pharmaceutical Press. 1952. Price 25s.

MILK TESTING. By J. G. DAVIS, D.Sc., Ph.D., F.R.I.C. Pp. 260. London: Dairy Industries Ltd. 1951. Price 15s.

THE CHEMISTRY OF LIGNIN. By FRIEDRICH EMIL BRAUNS. Pp. xv + 808. New York: Academic Press Inc. 1952. Price $14.50.

THE CHEMISTRY OF SYNTHETIC DYES. Volume I. By K. VENKATARAMAN. Pp. xvi + 704. New York: Academic Press Inc. 1952. Price $14.50.

ELEKTROCHEMIE. THEORETISCHE GRUNDLAGEN UND ANWENDUNGEN. By GIULIO MILAZZO. Translated into German from Italian by W. SCHWABL. Pp. xiii + 419. Vienna: Springer-Verlag. 1952. Price 61s. 6d.

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LES THÉORIES ÉLECTRONIQUES DE LA CHIMIE ORGANIQUE. By BERNARD PULLMAN, D. ès Sc., and ALBERTE PULLMAN, D. ès Sc. Pp. x + 665. Paris: Masson et Cie. 1952. Price 5800 fr.

MANIPULATIONS DE CHIMIE. By CLÉMENT DUVAL. Second Edition. Pp. 382. Paris: Masson et Cie. 1951. Price 2500 fr.

DOSAGES COLORIMÉTRIQUES. PRINCIPES ET MÉTHODES. By G. CHARLOT and R. GAUGUIN. Pp. 244. Paris: Masson et Cie. 1952. Price 1500 fr.

THE NATIONAL FORMULARY 1952. Pp. 196. London: The British Medical Association and The Pharmaceutical Press. 1952. Price 4s. 6d.; interleaved, 7s. 6d.

NORTH OF ENGLAND SECTION

THE Summer Meeting of the North of England Section will be held at the Imperial Hotel, Llandudno, N. Wales, from Friday, June 13th, to Monday, June 16th, 1952.

A paper entitled "The Analyst in the Plastics Industry" will be given at 10.30 a.m. on Saturday, June 14th, by Dr. J. Haslam, F.R.I.C.

Further particulars can be obtained from the Honorary Secretary of the Section, Mr. Arnold Lees, F.R.I.C., 87, Marshside Road, Southport, Lancs.

* Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

HER MAJESTY'S COLONIAL SERVICE

APPLICATIONS are invited for the following post:—

CHEMIST, 27106/56/52, EAST AFRICA

A vacancy exists for a Chemist in the East African Hides, Tanning and Allied Industries Bureau. Appointment is on probation to the pensionable establishment. Salary, according to qualifications and experience in the scale £585 to £1,320 per annum (with a promotion bar at £1,140). In addition a variable cost of living allowance of between £100 and £200 per annum is also payable and outfit allowance of £30 if initial salary is less than £810 per annum. Free return passages on first appointment and on leave for officer, wife and children up to the cost of one adult fare. (Permission must be obtained for wife and children to travel); Government Quarters when available, at a rent of 10 per cent. of salary subject to a maximum of £150 per annum; leave at the rate of 4–5 days for each completed month of resident service. Officers must contribute to Widows and Orphans Pension Scheme. Local Income Tax at low rates. Applications are invited from men and women, preferably under 35, who hold a B.Sc. or equivalent degree in Chemistry and if possible a diploma or the City of London Guild Examination in leather technology. Selected candidate may be required to undergo a course in leather chemistry at an approved Institute. Duties include the carrying out of routine leather analyses, research into tanning processes and the preparation of hides and skins.

Intending candidates should apply in writing to the Director of Recruitment (Colonial Service), Colonial Office, Sanctuary Buildings, Great Smith Street, London, S.W.1, giving brief details of their age, qualifications and experience. They should mention this paper and quote the reference number (27106/56/52).

TANGANYIKA SISAL GROWERS ASSOCIATION

APPLICATIONS are invited for the post of Scientific Assistant at the Sisal Research Station, Ngomeni, Tanganyika. The commencing basic salary will be in the scale £550–£750 per annum and will be determined by qualifications and experience. The appointment will be on a three years contract which is subject to renewal. Other emoluments include free housing, medical attention, participation in a Provident Fund Scheme, Leave and Free Passages.

The duties of the Scientific Assistant will be chiefly in connection with spectrographic work on soils and plant materials with special reference to sisal cultivation. Some experience of modern spectrographic methods is desirable but not essential since the appointee would work and be given special training in the spectrographic laboratory at the East African Agriculture and Forestry Research Organisation, Kenya, for a period of not less than six months.

The minimum qualifications required are a higher certificate in chemistry or physics but qualifications to a degree standard would be an advantage. Experience in analytical chemistry is desirable.

Further details may be obtained from:—
The Sisal Growers' Association, Ltd.,
Room 101, Grand Buildings,
Trafalgar Square, London, W.C.2
to whom applications should be addressed.

SUDAN GOVERNMENT

APPLICATIONS are invited for the post of Analytical Chemist in the Government Analyst's Laboratory, Khartoum. The work of this Laboratory includes the analysis of waters, foods and drugs, dairy produce, and certain clinical specimens; toxicology; forensic chemistry and general miscellaneous analysis including minerals and metals. Some opportunities for research are open to the keen worker. Applicants should be aged 26–32, should possess a good Honours Degree in Chemistry or A.R.I.C., and should have had several years' post-graduate experience, preferably of general analytical work. Appointment will be on probation for Short Term Contract (with bonus) up to six years. Salary scale ranges from LE. 950 to LE. 1675. Starting rate of pay is fixed according to age, qualifications and experience of selected candidate. Cost of Living Allowance which is reviewed quarterly is payable. An Outfit Allowance of LE. 50 is payable when the contract is signed. No Income Tax is at present payable in the Sudan. Free passage on appointment and annual leave after the first tour. Full particulars and application forms will be sent on receipt of postcard only addressed to the Sudan Agent in London, Wellington House, Buckingham Gate, London, S.W.1, quoting "Analytical Chemist, 1210" and name and address in BLOCK LETTERS.

ANALYST required, male, preferably with experience in the analysis of Metallurgical materials. Successful applicant may be required to do shift work. Five-day week. Staff pensions scheme. State age, training, experience and salary required. Box 3813, THE ANALYST, 47, Gresham Street, London, E.C.2, or local Employment Exchange.

CHEMIST, recently graduated, wanted for work in connection with the control and development of works' processes, by manufacturers of aluminium sheet, extrusions and paste (paint pigment). The Chemist's work would be largely practical, but would include laboratory work in both organic and inorganic chemistry. Box No. 3805, THE ANALYST, 47, Gresham Street, London, E.C.2.

ROCHE PRODUCTS LIMITED have an opening for a man of Inter. B.Sc. or B.Sc. standard with experience in analytical work. Letter stating qualifications, experience and salary required to the Secretary, Roche Products Ltd., Welwyn Garden City, Herts.

YOUNG LADY, aged approximately 22–30 years, required for the Chemical Laboratory of a large electrical engineering company in the West London area. Applicants should have studied Chemistry up to H.S.C. or Inter. B.Sc. standard and should be experienced in chemical analysis. Five-day week, good conditions and pay. Write giving details of age and previous experience to Box 3814, THE ANALYST, 47, Gresham Street, London, E.C.2.

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Candidates must have a relevant University degree, or equivalent, and be between 26 and 32 years of age. Salary will range between £700–£1,100, depending on qualifications and experience. Successful applicants will be given 6 months training in this country. Apply: Staff Manager, Distillers Co., Ltd., 21, St. James' Square, London, S.W.1.

ANALYTICAL CHEMIST. Senior Analytical Chemist required in the Central Laboratories of the Nuffield Organization. A University Graduate is preferred with a minimum of ten years varied industrial experience of the Chemistry and Analysis of engineering materials, both organic and inorganic. The position is pensionable and salary will be between £500 and £750 per annum, dependent upon qualifications and experience. Applications to be sent to the Chief Chemist and Metallurgist, Nuffield Central Research Laboratories, Morris Motors Limited, Courthouse Green, Coventry.

GLAXO LABORATORIES, LTD., require for their Stoke Poges Fermentation Research Division a Graduate with experience of radio active Isotopes as biochemical tracers or as an analytical tool. Salary according to experience together with participation in the Company's Pension and Incentive Schemes. Applications, which will be treated in strict confidence, should be addressed to the Senior Personnel Officer, Glaxo Laboratories, Ltd., Greenford, Middlesex.

ANALYTICAL CHEMIST. Capper Pass & Son, Limited, Smelters and Refiners of Non-ferrous Metals require an experienced analytical chemist for their Works in Yorkshire. The post will carry an initial salary of from £900 per annum upwards according to qualifications and experience and offers good prospects of advancement. Apply in writing to the Secretary, Capper Pass & Son, Limited, Bedminster Smelting Works, Bristol, 3.

METALLURGIST required by Marconi's Wireless Telegraph Company Limited, Chelmsford, to lead a section of the Works Laboratory. Sound background in ferrous and non-ferrous metallurgy with several years experience in engineering industry. Technical education should not be less than Higher National certificate standard. Commencing salary £450–£550 according to qualifications. Superannuation, five-day week, etc. Please apply in confidence quoting reference 814B to Central Personnel Services, English Electric Company Ltd., 24/30, Gillingham Street, London, S.W.1.

DR. V. E. YARSLEY (Research Laboratories) Limited, require the following staff:—

(1) One recently qualified chemist for organic preparations.
(2) One recently qualified chemist for plastics development.
(3) One qualified chemist for analytical work on high polymers.

Applicants who are about to qualify at the forthcoming B.Sc. examinations will be considered for posts (1) and (2).

Applications should be addressed for the attention of the Managing Director of Oaklands, Clayton Road, Hook, Surrey.

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THE ANALYST

THE JOURNAL OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

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