THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE eighty-third Annual General Meeting of the Society was held at 2.45 p.m. on Friday, March 1st, 1957, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was occupied by the President, Dr. K. A. Williams, A.Inst.P., M.Inst.Pet., F.R.I.C. The financial statement for 1956 was presented by the Honorary Treasurer and approved, and the Auditors for 1957 were appointed. The Report of the Council for the year ending March, 1957 (see pp. 300–307), was presented by the Honorary Secretary and adopted.

The Scrutineers, Miss K. P. Dent and Mr. H. E. Brookes, reported that the following had been elected officers for the coming year—

President—J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

Past Presidents serving on the Council—D. W. Kent-Jones, J. R. Nicholls, George Taylor and K. A. Williams.

Vice-Presidents—N. L. Allport, J. Haslam and A. A. Smales.

Honorary Treasurer—A. J. Amos.

Honorary Secretary—R. E. Stuckey.

Honorary Assistant Secretary—S. A. Price.

Other Members of Council—The Scrutineers further reported that 462 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—D. C. Garratt, 373; H. M. N. H. Irving, 312; D. C. M. Adamson, 289; E. Q. Laws, 257; W. Cule Davies, 241; J. G. Sherratt, 228; W. H. Stephenson, 198; F. P. Everett, 191; H. C. Smith, 183; J. R. Leech, 159.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—D. C. M. Adamson, W. Cule Davies, D. C. Garratt, H. M. N. H. Irving, E. Q. Laws and J. G. Sherratt.

S. G. Burgess, R. C. Chirnside, D. D. Moir, F. C. J. Poulton and A. F. Williams, having been elected members of the Council in 1956, will, by the Society's Articles of Association, remain members of the Council for 1957.

A. N. Leather (Chairman of the North of England Section), Magnus A. Pyke (Chairman of the Scottish Section), P. J. C. Haywood (Chairman of the Western Section), R. Belcher (Chairman of the Midlands Section), D. F. Phillips (Chairman of the Microchemistry Group), J. E. Page (Chairman of the Physical Methods Group) and S. K. Kon (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1957.

The retiring President, Dr. Williams, referred to the onerous duties that Dr. Hamence had undertaken so successfully during the past eight years as Honorary Treasurer, and formally installed him in the Chair. Dr. Hamence proposed a vote of thanks, which was carried with acclamation, to Dr. Williams for his work on behalf of the Society, both as President during the previous two years and as Honorary Secretary for the eight years before that.

After the business outlined above had been completed, the meeting was opened to visitors, and the retiring President delivered his Presidential Address (see pp. 320-323).

HONORARY MEMBER

THE Council is pleased to record that—

The Honourable Mr. Justice Lloyd-Jacob

has been elected an Honorary Member of the Society.

ORDINARY MEETING

AN Ordinary Meeting of the Society, organised by the Biological Methods Group, was held at 6.30 p.m. on Wednesday, May 1st, 1957, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. J. H. Hamence, M.Sc., F.R.I.C.

The subject of the meeting was "The Estimation of Antibiotic Residues in Food" and the following papers were presented and discussed: "Antibiotics and the Public Health," by J. M. Ross, M.B., Ch.B., D.P.H., D.Obst.R.C.O.G.; "The Determination of Antibiotics in Milk with Special Reference to Penicillin," by N. J. Berridge, B.Sc., Ph.D.; "The Determination of Antibiotic Residues in the Tissues and Body Fluids of Animals," by J. H. Taylor, Ph.D., M.R.C.V.S.

NEW MEMBERS

ORDINARY MEMBERS

Bernard Michael Allen; Cora Winifred Ayers, B.Sc. (Bristol), A.R.I.C.; Brian Boughton Bach, B.Sc. (Lond.), A.R.I.C.; John Austin Clements, B.Sc. (Lond.), A.R.C.S.; Robert Anthony Close, B.Sc. (Birm.); Graham Evans; William Hewitt, F.P.S.; Robert Andrew Howie, M.A., Ph.D. (Cantab.), F.G.S.; William Hoyle, B.Sc. (Lond.); James Cunningham Jack; Wilfred John Parker, B.Sc. (Lond.), A.R.I.C., A.M.Inst.F., A.M.Inst.Gas E.; Edmund Clarence Potter, B.Sc., Ph.D. (Lond.), D.I.C., F.R.I.C.; Royston Stenhouse Rankin; John Ridlington, B.Sc. (Lond.), A.R.I.C.; Paul Trinder, B.Sc. (Lond.), A.R.I.C.; Fredrick James Wallace.

JUNIOR MEMBERS

Eileen Bedwell, B.Sc. (Dunelm.); Peter Desmond Blundy, B.Sc. (Lond.); Anthony James Bullough.

DEATH

WE record with regret the death of

William Basil Walker.

NORTH OF ENGLAND SECTION

AN Ordinary Meeting of the Section was held at 2.15 p.m. on Saturday, March 16th, 1957, at the City Laboratories, Mount Pleasant, Liverpool, 3. The Chair was taken by the Chairman of the Section, Mr. A. N. Leather, B.Sc., F.R.I.C.

Owing to the indisposition of the intended speaker, a paper entitled "The Composition of Exhaust Gases" was read by A. Fitton, B.Sc., Ph.D., M.I.Chem.E. A discussion on this paper and on the more general aspects of atmospheric pollution followed.

MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 7 p.m. on Thursday, March 28th, 1957, in the Gas Showrooms, Nottingham. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

A discussion on "The Analysis of Complex Sulphur Compounds" was opened by C. E. Kendall, B.Sc., A.R.I.C.

BIOLOGICAL METHODS GROUP

AN Ordinary Meeting of the Group was held at 7 p.m. on Thursday, April 4th, 1957, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Dr. S. K. Kon, F.R.I.C.

The following papers were presented and discussed: "Experience in the Microbiological Assay of Vitamins and Amino-acids by Large-plate Methods," by D. F. Harris and J. S. Simpson, F.I.M.L.T.; "Quantitative Analysis of Immunologically Specific Substances in Agar-gel Plates," by J. G. Feinburg, B.Sc., D.V.M., M.Sc.

Obituary

THOMAS MACARA

THOMAS MACARA was a sturdy example of those Scotsmen who, acquiring a first-rate education and a sound experience in their native land, travel south and place them at the disposal of a wider public. The major part of his life was spent in London, and he died at his home in Stroud Green on January 16th, 1957.

Born in Glasgow in September, 1873, he was educated at Allen Glen's School and the Glasgow and West of Scotland Technical College. His training as an analyst took place in the laboratories of Dr. John Clark, Public Analyst for the City of Glasgow and a number of boroughs and counties. Here he remained for 12 years, gaining a wide general experience, and it will perhaps surprise those who came to know him later that in those years he became an expert in the analysis of such materials as chrome iron ore, in which Glasgow had an important trade. He had many an amusing anecdote about the years spent in Clark's laboratory.

In taking the examinations of the Institute of Chemistry he achieved a "double"—and was the first to do so—by passing the Final examination in two branches, the Chemistry of Food, Drugs and Water, and Biochemistry with Bacteriology and allied subjects. He was elected an Associate in 1901 and a Fellow in 1904, and served on the Council from 1925 to 1928.

Leaving Clark's laboratory, Macara gained his first experience in the food industry as research and factory chemist with James Robertson Ltd. of Paisley and, later, John Buchanan Bros. Ltd. of Glasgow. Migration south came in 1906, when he was appointed chief chemist to Lipton Ltd. in London. His experience here broadened out over the whole field of food manufacture, and his firm adherence to scientific method in the factory was a match for the equally forthright commercial qualities of his brother Scot, Sir Thomas.

In 1920 he was appointed the first Director of Research of the newly formed British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades. He took up this post with nothing but his experience to start from, and in the first few years of the Association's existence it was largely dependent on him personally. He knew the problems of the industries and, indeed, often knew their solution, but was never satisfied until proof had been obtained.

A few years later, in 1925, the British Food Manufacturers' Research Association was formed, to cover fresh sections and to work with the other Association under Macara's directorship. He continued in this dual position for a further 19 years, retiring in September, 1944. Based on a fundamental scientific approach, his abilities and integrity made themselves felt. From small beginnings the Research Associations achieved considerable influence, and Macara became the scientific spokesman of the industry. He played a leading part in the inquiry that led to the Preservatives, etc., in Food Regulations and, later, in 1930, in bringing together Public Analysts and food manufacturers to formulate the agreed standards for jam. This was the first instance of voluntary agreement between the authorities and the manufacturers on standards for a food product. His services to science as applied to food-preservation problems were recognised when he was invited to become a member of the Food Investigation Board.

He was the author of a number of papers in *The Analyst* over a long period on a variety of subjects, and his numerous forewords to the research reports of the Associations were embodiments of great practical experience. Believing as he did in the stimulus of personal contact, particularly through professional societies and institutions, he thought it of great value for younger men to take part in discussions and so gain confidence in imparting ideas verbally.

Macara joined the Society in 1900, and it was always nearest his heart among the various chemical bodies to which he belonged. He was a member of the Council during two periods, 1913 to 1914 and 1925 to 1926, and was a Vice-President during 1928 and 1929. For many

years he served on the Milk Products and the Poisonous Metals in Food Colouring Materials Sub-Committees of the Analytical Methods Committee.

On the outbreak of war in 1939 he offered the Ministry of Food all the help that the two Research Associations could give, and in innumerable ways sought to ensure that the technical side of the industry played a full part in the national effort. Sir Jack Drummond, then scientific adviser to the Ministry, and the Minister himself, Lord Woolton, thanked him handsomely for his work.

In his earlier days Macara was a keen cyclist and on his bicycle was fond of exploring the Highland roads. Later in life he found his main relaxation in golf. He is survived by his second wife and two sons.

C. L. HINTON

Annual Report of the Council: March, 1957

DURING the past year the manifold activities of the Society have been pursued with enthusiasm and success. Again it is a pleasure to report that all the scientific meetings of the Society have been well attended and that many useful papers have been presented and discussed. The four Sections have all been fully active and many more meetings have been promoted by the Groups. The one special meeting held this year was a particularly happy one and took the form of a joint meeting with the Food Group of the Society of Chemical Industry on May 23rd, 1956.

The long awaited move of the Society's headquarters to a suite of newly appointed offices on the top floor of the new house of the Society of Chemical Industry at 14 Belgrave Square, London, S.W.1, was realised in the autumn. Besides offices for the administration of the Society's general business, there is a separate editorial office for *The Analyst* and another for *Analytical Abstracts*, while the Secretariat of the Analytical Methods Committee is also separately accommodated. In addition to all these separate offices there is a spacious Council room, which is now being used by Council and the various committees of the Society.

The detailed activities of the Analytical Methods Committee are discussed under a separate heading, but it is appropriate to emphasise here that good progress has been made in 1956. The original programme has been vigorously pursued and expansions have been implemented; the A.B.C.M. - S.A.C. Joint Committee on Methods for the Analysis of Trade Effluents has published a number of methods; the newly formed Joint Committee with the Pharmaceutical Society on Methods of Assay of Crude Drugs has appointed working panels, and the Sub-Committees of the A.M.C. have continued their investigations, one report having been published. The Analytical Methods Trust has met four times for the purpose of administering the finances of the A.M.C.; all the promised contributions from industry have been received.

As was announced in the last Annual Report of the Council, the subscription of Ordinary Members had to be raised in order to provide against rising costs and the expense involved in extending the activities of the Society. The subscription of Junior Members will remain unchanged. Recently the cost of printing *The Analyst* and *Analytical Abstracts* has been considerably increased and this constitutes a heavy item of expense to the Society. In order to help towards the cost of producing the Society's journals, the price of *The Analyst* with *Analytical Abstracts* to outside subscribers has been raised to 6 guineas. It may be appropriate to mention here that, but for the grants made to us by the Chemical Council, it would have been necessary to increase the subscription of members long ago. These grants were made from funds subscribed by industry for the publication of chemical researches. We can never be too grateful for this assistance, which has enabled us to balance our publication accounts, and it seems no more than right that we should use all our endeavours to make *The Analyst* and *Analytical Abstracts* as nearly self-supporting as possible.

The roll of the Society now numbers 1870, an increase of 28 over the membership of a year ago.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to G. W. Baker and H. C. S. de Whalley, who have completed 40 years of membership.

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

A. W. Armstrong	H. J. Davis	R. K. Matthews
H. Ballantyne	N. T. Foley	W. H. Miles
P. Bilham	D. A. Griffith	O. E. Mott
V. Binns	W. H. Jackson	A. E. J. Vickers
G. H. Butler	M. H. Jenkins	A. S. Whamond
A. Dargie	T. Macara	W. Wilson

ORDINARY MEETINGS—Six ordinary meetings of the Society were held during the year and the following papers were read and discussed—

April, 1956, in London:

"The Determination of 4-Chloro-2-methylphenoxyacetic Acid in MCPA by a Differential Refractometric Method." By R. Hill, B.Sc., A.R.I.C.

"Paper Chromatography with Continuous Change in Solvent Composition. Part I: Separation of Fatty Acids. Part II: Separation of Surface-active Agents." By F. Franks, B.Sc., A.R.I.C.

May, 1956, in London:

"The Composition of Some Deposits and Muds in Estuaries, Rivers and Lakes." By J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

October, 1956, in London, on Chromatography:

"The Determination of Vitamin D and Related Compounds. Part I: Introduction and Preparation of Compounds in the Irradiation Series. Part II: Analysis of Irradiation Products." By W. H. C. Shaw, F.P.S., F.R.I.C., J. P. Jefferies, B.Sc., A.R.I.C., and T. E. Holt, B.Sc., A.R.I.C.

"Some Examples of the Use of Paper Chromatography in Toxicological Analysis." By A. S. Curry, M.A., Ph.D.

November, 1956, in London:

"The Structure of Dithizone and its Metal Complexes." By H. M. N. H. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M.

December, 1956, in London, on Trade Effluents:

Introduction by H. N. Wilson, F.R.I.C.

"The Determination of Metallic Contaminants." By N. T. Wilkinson, F.R.I.C.

"Analytical Problems Concerned with Oil and Grease in Effluents and River Waters." By J. G. Sherratt, B.Sc., F.R.I.C.

"Trade Effluents Analysis: the Oxygen Demand." By C. J. Regan, B.Sc., F.R.I.C.

January, 1957, organised by the Microchemistry Group, on Micro-volumetric Analysis:

"Apparatus and Technique." By D. W. Wilson, M.Sc., F.R.I.C.

"Primary Standards." By R. Belcher, Ph.D., D.Sc., F.R.I.C. (presented on his behalf by J. H. Thompson, B.Sc., Ph.D., A.R.I.C.).

"End-point Location." By E. Bishop, B.Sc., A.R.T.C., A.R.I.C.

JOINT MEETING—As mentioned above, the Society held a Joint Meeting with the Food Group of the Society of Chemical Industry in May, 1956 in London. The following papers were presented and discussed—

"Some New Factors in Pectin Gel Strength." By Mamie Olliver, M.Sc., F.R.I.C., P. Wade, M.Sc., Ph.D., D.I.C., A.R.I.C., and Kathleen P. Dent, A.R.I.C.

"The Binding of Ions and Detergents to Pectin, Protein and Other Colloid Systems." By B. A. Pethica, B.Sc., Ph.D., A.R.I.C.

NORTH OF ENGLAND SECTION—The membership of the Section is 406, compared with 373 last year. During the year, six meetings have been held, including the Summer Meeting and two meetings held jointly with Subject Groups of the Society. The following papers have been read and discussed—

January, 1956, in Manchester:

"Applications of Newer Techniques to the Analysis of Pharmaceutical Products." By D. C. Garratt, B.Sc., Ph.D., F.R.I.C.

March, 1956, in Liverpool:

"New Reagents and New Developments in the Fine Chemical Field." By W. C. Johnson, M.B.E., F.R.I.C.

May, 1956, in Bradford, held jointly with the Microchemistry Group and the Bradford Chemical Society, on Micro-volumetric Analysis:

"Apparatus and Technique." By D. W. Wilson, M.Sc., F.R.I.C.
"Primary Standards." By R. Belcher, Ph.D., D.Sc., F.R.I.C.
"End-point Location." By E. Bishop, B.Sc., A.R.T.C., A.R.I.C.

June, 1956, in Llandudno:

"Memories of the Past Half-century." By F. L. Okell, F.R.I.C.

October, 1956, in Manchester, held jointly with the Physical Methods Group, on Ion Exchange:

"Ion Exchange in the Study of Complexes." By T. V. Arden, B.Sc., Ph.D., F.R.I.C., M.I.M.M.
"Some Recent Applications of Ion Exchange in Biochemistry." By T. S. Work, Ph.D., D.Sc.
"The Selective Elution of Metals Adsorbed on Cation-exchange Resins by Organic Solvents. Part II." By R. A. Wells, B.Sc., A.R.I.C., and Patricia J. Macdonald.

December, 1956, in Liverpool:

"Some Applications of the Weisz Ring-oven." By W. I. Stephen, B.Sc., Ph.D., A.R.I.C.

SCOTTISH SECTION—The membership of the Section, at 108, shows an increase of 5.

The twenty-first Annual General Meeting of the Section, attended by both the President and Honorary Assistant Secretary of the Parent Society, was held in Glasgow in January, 1956, nine of the original twenty-five members being present. The Section was also represented at the annual Ramsay Chemical Dinner. Six scientific meetings have been held, three in Glasgow, including the first joint meeting with the Methods of Analysis Panel (Glasgow), two in Edinburgh and one in Falkirk, jointly with the Stirlingshire and District Sections of the Royal Institute of Chemistry and of the Society of Chemical Industry; the last consisted of an exhibition and demonstration of some modern analytical apparatus, which evoked much interest.

The Section is organising a five-day Congress on Modern Analytical Chemistry in Industry at St. Andrews University from June 24th to June 28th, 1957, and the appointed subcommittee is actively engaged on the project.

The following papers have been presented and discussed—

Glasgow, March, 1956:

"The Determination of Calcium in Plant Material by Flame Photometry." By R. G. Hemmingway, M.Sc.
"The Flame Photometer in Silicate Analysis." By A. J. Shorter, M.Sc., M.S., M.Inst.F., A.R.I.C.
"A New System of Reporting and Recording Analytical Results." By A. O. Pearson, B.Sc., F.R.I.C.

Edinburgh, May, 1956:

"Complexones: Some Recent Developments." By R. E. Stuckey, B.Sc., Ph.D., F.P.S., F.R.I.C.

Glasgow, September, 1956, Joint Meeting:

"The Photometric Determination of Molybdenum as the Thiocyanate." By R. Kerr, B.Sc., A.R.I.C.
"The Determination of Copper in Steel." By L. J. A. Haywood and P. Sutcliffe.
"The Analysis of Titanium and its Alloys." By W. T. Elwell, F.R.I.C.

Falkirk, October, 1956, Joint Meeting. An Exhibition and Demonstration of Some Modern Analytical Apparatus:

"Statistical" Calculating Machine, Monroe Calculating Machine Ltd., demonstrated by R. D. Sutherland and D. K. Liney.
"Electronik" Continuous Balance Potentiometer, Honeywell-Brown Ltd., demonstrated by A. T. Hunter, B.Sc.
Interference Microscope, Scottish Instruments Ltd., demonstrated by A. M. Tennant and J. C. Gentles.
Proximity Meter (Fielden Equipment), A. R. Bolton & Co., demonstrated by J. A. Bolton.
Caravan Mobile Demonstration Unit, Fielden Electronics Ltd.

Edinburgh, November, 1956:

"Colour Chromatography." By J. P. Cunningham, B.Sc., Ph.D., A.R.I.C.

Glasgow, December, 1956:

"Problems and Techniques in Forensic Analysis." By Edgar Rentoul, M.B., Ch.B., LL.B.

WESTERN SECTION—The membership of the Section is 89.

The meetings and visits organised by this Section have been well supported, considering the scattered area, and the younger members continue to give support and to take an active part in the discussions. In the outlying areas of the Section the policy of holding joint meetings with the other chartered bodies has been followed, the results proving very satisfactory, and it is hoped to develop this policy still further. The following papers were presented and discussed—

Bristol, January, 1956:

"Industrial Application of Sequestering Agents." By R. L. Smith, B.Sc., Ph.D., A.R.I.C., and P. Womersley.

Bath, June, 1956:

H. N. Wilson, F.R.I.C., A. Tyler, M.B.E., and C. J. Sears on "Sampling."

Newport, October, 1956:

"Sequestering Agents and Their Analytical Applications." By R. L. Smith, B.Sc., Ph.D., A.R.I.C.

Plymouth, October, 1956:

"Careers in Chemistry," discussed by J. W. Barrett, B.Sc., Ph.D., A.R.C.S., D.I.C., A.M.I.Chem.E., F.R.I.C., Professor H. T. S. Britton, D.Sc., D.I.C., F.R.I.C., J. Idris Jones, M.Sc., D.Sc., F.R.I.C., and A. C. Truman, B.Sc., A.R.I.C.

Coleford, November, 1956:

Visit to the factory of Messrs. H. W. Carter & Co. Ltd.

MIDLANDS SECTION—Membership of the Section is 307, an increase of 25 over last year.

During 1956, 13 ordinary meetings were held, 8 in Birmingham, 3 in Nottingham, 1 in Derby and 1 in Cambridge (jointly with the Microchemistry Group). The following papers were read and discussed—

Birmingham, January, 1956:

"Gas Chromatography." By J. C. Tatlow, Ph.D., D.Sc., A.R.I.C.
"Ionophoresis." By A. B. Foster, B.Sc., Ph.D.

Birmingham, February, 1956:

Discussion on "The Analytical Chemistry of Germanium and Gallium," opened by H. J. Cluley, M.Sc., F.R.I.C., and G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C.

Birmingham, March, 1956:

"Modern Qualitative Analysis and Industrial Practice." By Professor Dr. C. J. van Nieuwenberg.

Nottingham, March, 1956:

"Pharmaceutical Aspects of the Analytical Chemistry of Mercury." By G. J. W. Ferrey, B.Sc., F.R.I.C. (presented on his behalf by D. C. Garratt, B.Sc., Ph.D., F.R.I.C.).
"The Microchemical Estimation of Mercury." By R. F. Milton, B.Sc., Ph.D., F.R.I.C. (presented on his behalf by W. D. Duffield).

Birmingham, April, 1956, jointly with the Biological Methods Group, on The Fundamental Bases of Microbiological Assay:

"The Physiological and Biochemical Background of Microbiological Assay." By R. H. Nimmo-Smith, M.A., D.Phil., M.B., Ch.B.
"The Influence of Physical Factors on the Microbiological Assay of Antibiotics." By J. W. Lightbown, M.Sc., Dip. Bact., F.P.S.
"Practical Considerations of Microbiological Assay." By K. A. Lees, F.P.S., D.B.A.

Birmingham, September, 1956:

"Recent Advances in the Analysis of Cast Iron and Foundry Materials." By W. E. Clarke, A.R.I.C.

Derby, September, 1956:

"High-precision Absorptiometry." By W. T. L. Neal, B.Sc., A.R.I.C.

Birmingham, September, 1956:

"Precipitation from Homogeneous Solution." By Professor L. Gordon.

Cambridge, October, 1956, jointly with the Microchemistry Group, on Sub-micro Methods in Inorganic and Organic Analysis:

Introduction by R. Belcher, Ph.D., D.Sc., F.R.I.C.
"General Review of Sub-micro Methods." By T. S. West, B.Sc., Ph.D., A.R.I.C.
"The Determination of Alkoxyl." By M. K. Bhatty, M.Sc., A.R.I.C.
"The Determination of Nitrogen." By M. Williams, B.Sc., A.R.I.C.
"The Determination of Iodine." By A. R. Shah, M.Sc., A.R.I.C.

Nottingham, October, 1956:

"Recent Advances in Ion-exchange Resins." By D. K. Hale, M.A.

Birmingham, November, 1956:

Discussion on "Laboratory Planning and Organisation," opened by E. W. Dobson and D. Barkaway.

Birmingham, December, 1956:

Discussion on "Qualitative Inorganic Analysis," opened by H. Holness, M.Sc., F.R.I.C., and R. Harrison, M.A., B.Sc., F.R.I.C.

Nottingham, December, 1956:

"Aspects of the Application of Chromatography to the Quantitative Analysis of Inorganic Substances." By F. H. Pollard, B.Sc., Ph.D.

MICROCHEMISTRY GROUP—Forty-eight members have joined the Group during the year and the membership is now 577. During 1956 three ordinary meetings of the Group were held: in London (a meeting of the Society arranged by the Group), in Bradford (together with the North of England Section and the Bradford Chemical Society) and in Cambridge (together with the Midlands Section).

London:

"Microchemical Methods in the Art Gallery and Museum." By A. E. A. Werner, M.A., M.Sc., D.Phil., A.R.I.C.
"The Ring-oven Technique and its Application in Archaeology." By H. Weisz, Dr. techn. Dipl.-Ing.

Bradford: Micro-volumetric Analysis.

The papers presented at this meeting are detailed in the report on the activities of the North of England Section.

Cambridge: Sub-micro Methods in Inorganic and Organic Analysis.

The papers presented at this meeting are detailed in the report on the activities of the Midlands Section.

In addition to the above, four informal discussion meetings have been held in London. The following topics were discussed—

"Small-scale Qualitative Inorganic Analysis," introduced by R. Belcher, Ph.D., D.Sc., F.R.I.C., and H. Holness, M.Sc., F.R.I.C.
"Complexones in Microchemistry," introduced by H. J. Cluley, M.Sc., Ph.D., F.R.I.C., and C. Whalley, B.Sc., F.R.I.C.
"The Kjeldahl Determination of Nitrogen," introduced by R. E. Stuckey, B.Sc., Ph.D., F.P.S., F.R.I.C., and P. R. W. Baker, B.Sc., A.R.I.C.
"The Micro-determination of Sulphur," introduced by S. Bance, B.Sc., A.R.I.C., and G. S. Crouch.

PHYSICAL METHODS GROUP—The membership of the Group is now 627, an increase of 55 since last year.

During the past year the Group has held four ordinary meetings and also organised the Society meeting in November, 1955. Two of the Group meetings were held in London and one each in Oxford and Manchester.

Following the Annual General Meeting on November 30th, 1955, the retiring Chairman, Mr. A. A. Smales, B.Sc., F.R.I.C., addressed the Society on the subject "Atomic Energy and the Analyst." The following papers were read and discussed at other ordinary meetings of the Group—

Polarography—London, February, 1956:

"A Comparison of Three Highly Sensitive Polarographs." By D. J. Ferrett, D.Phil., G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C., H. I. Shalgosky, B.Sc., A.R.I.C., and L. J. Slee, B.Sc.
"Polarography of the Dithionite (Hydrosulphite) Anion and Some Related Oxyacids of Sulphur." By W. Furness, B.Sc., Ph.D., F.R.I.C.
"The Polarographic Determination of Uranium in Ores." By H. I. Shalgosky, B.Sc., A.R.I.C.

Plant Instrumentation—London, April, 1956:

"Progress in Plant Analytical Control Methods." By B. W. Bradford, B.Sc., Ph.D., A.R.C.S., D.I.C., F.Inst.Pet.
"The Sonic Gas Analyser." By A. E. Martin, Ph.D., D.Sc.
"Automation in the Laboratory." By D. A. Patient, B.Sc., A.Inst.P.

Nuclear and Paramagnetic Resonance—Oxford, May, 1956:

"Analytical Applications of Nuclear Resonance Spectroscopy." By R. Richards, M.A., D.Phil.
"Techniques of Magnetic Resonance Spectroscopy." By E. E. Schneider, Dr. Phil. Nat.
"The Detection of Photochemically Formed Radicals by Magnetic Resonance." By D. J. E. Ingram, M.A., D.Phil.

Ion Exchange—Manchester, October, 1956:

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

BIOLOGICAL METHODS GROUP—During the year the membership of the Group increased by 4 and now stands at 272. The Group has held three meetings during the year. In addition, the Group visited Glaxo Laboratories Ltd., Greenford, in May, 1956. The following papers were presented and discussed at the ordinary meetings of the Group—

December 9th, 1955:

"The Microbiological Plate Assay of Penicillin in Compound Feeding Stuffs." By J. S. Simpson and K. A. Lees, F.P.S., D.B.A.
"A Simple Method for the Determination of pA_2 at Two Minutes." By Mary F. Lockett, M.B., B.S., M.D., M.R.C.P., Ph.D.
Demonstration of "An Automatic Apparatus for Isolated Preparations Suitable for the Assay of Oxytocin and Similar Assays," by J. A. Lock, B.Sc., F.P.S.

April 11th, 1956, joint meeting with the Midlands Section, on The Fundamental Bases of Microbiological Assay:

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

ANALYTICAL METHODS COMMITTEE—Considerable activity has been maintained throughout the year, in which about 60 meetings of the Committee, the Joint Committees and their Sub-Committees and Panels have been held.

In April Mr. T. T. Gorsuch, who was awarded a Society for Analytical Chemistry Scholarship provided by the Analytical Methods Trust, began work at the Atomic Energy Research Establishment, Harwell, under the direction of Mr. A. A. Smales. He has made an excellent start and has now submitted three Progress Reports on his investigations by radiochemical methods into losses of trace elements during preliminary preparation of the material under examination.

The Metallic Impurities in Organic Matter Sub-Committee is making progress with collaborative tests on the molybdenum-blue method for arsenic and on a method for lead. Close collaboration is being maintained with Mr. Gorsuch, who attends some of the meetings of the Sub-Committee, and his findings have proved to be of assistance.

The Vitamin-E Panel of the original Vitamin Sub-Committee is continuing its work on the differential analysis of total tocopherols.

The report of the Vitamin-B_{12} Panel of the original Vitamin Sub-Committee has been published (p. 132).

The Direct Micro-determination of Oxygen in Organic Matter Sub-Committee is proceeding with the collaborative investigation of the Unterzaucher method and its modifications.

The Essential Oils Sub-Committee is being reconstituted, under the Chairmanship of Dr. G. W. Ferguson.

Work is in hand on the editing of the Standard Methods recommended by the A.M.C. in their reports since 1927; they are being submitted to referees to bring them up to date and for approval before being passed for publication.

The A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents and its Panels have been very active and made considerable progress; nineteen methods have been published in *The Analyst*, and eleven more are with the printers. One Panel—that dealing with Physical Tests—has now completed its programme.

A Joint Committee on Methods of Assay of Crude Drugs has been set up by the Society and the Pharmaceutical Society to investigate the need for, and, when appropriate, to collect and publish, standard methods of assay of crude drugs of value in commerce but for

which there are no official or accepted methods. The secretarial and editorial work of this Committee and its Panels has been undertaken by the secretariat of the A.M.C. So far, four working Panels have been appointed and have started their investigations into methods of assay for digitalis, capsicum (capsaicin content), anthraquinone drugs and rauwolfia.

A separate Report, giving full details of the work of the A.M.C. during its second year is being prepared and will be circulated to all contributors to the Analytical Methods Trust.*

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

Chemical Council:

Dr. R. E. Stuckey to succeed Dr. J. H. Hamence, whose term of office expired on December 31st, 1956.

B.S.I. Committees:

Dr. K. A. Williams, Chemical Divisional Council.
Dr. K. A. Williams, Chairman, Industry Standards Committee for Oils, Fats and Greases (other than Petroleum and Tar) and Soaps Industry.
Mr. T. E. Rymer, Water for Making Concrete.
Mr. J. T. Yardley, Sulphuric Acid for Use in Lead - Acid Accumulators.
Mr. J. S. Wragg, Volumetric Mouldblown and Lampblown Glassware.

Joint Committee for the Standardisation of Methods for Water Analysis:

Mr. J. G. Sherratt.

Joint Library Committee, Chemical Society:

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

British Iron and Steel Research Association:

Mr. R. C. Chirnside and Dr. J. Haslam represented the Society at the Tenth Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).

Parliamentary and Scientific Committee:

Mr. G. Taylor continued to represent the Society.

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

HONORARY TREASURER'S REPORT—Reference was made in the last Report of the Honorary Treasurer to the substantial increase in the cost of running the Society and also of producing *The Analyst* and *Analytical Abstracts*. With this in mind, early in 1956, the Council decided to increase the subscription to the Society and also the price of *The Analyst* and *Analytical Abstracts* to outside subscribers. Unfortunately, these increases could not be put into operation until January 1st, 1957, and it was therefore realised that 1956 would be a very difficult year from the point of view of finance. The Council realised that unless a considerably increased grant could be obtained from the Chemical Council the Society would be faced with a substantial loss on the year's working.

Unfortunately the response from industry to the appeal by the Chemical Council for funds for publication has not been as good as was hoped for. Consequently the Chemical Council has been unable to meet in full our requests for financial aid for the journals for the year. Nevertheless we are most grateful to the Chemical Council for their generous response to our request in what has undoubtedly been a difficult year for the making of grants. It will be seen from the balance sheet that there was an excess of expenditure over income of just over £1000 for the whole year. This is the first year for some time that the Society's accounts have shown an adverse balance, and in view of the considerable increase in the cost of printing and postage, we must count ourselves lucky that the loss sustained during the year has not been heavier.

It is hoped that the increase in subscription rate and also in the price of *The Analyst* and *Analytical Abstracts* to outside subscribers will go a long way towards balancing our accounts in 1957.

* *Note by Editor*—The text of the Report of the Analytical Methods Committee is reproduced on pp. 307–319 of this issue.

THE ANALYST—The 1956 volume contained 732 pages, compared with 912 in 1955. The numbers of papers and notes published in 1956 were 93 and 30, respectively, against 103 and 49 in 1955. One paper was a Review Paper. The reduced size of the volume, although unplanned, was a necessity; production costs rose by well over 20 per cent. during the year, but no increase of income was available.

When allowance is made for all matter other than papers and notes, and the Review Paper is excluded, the average length of a paper or a note is 4·5 pages. Although this is a drop of half a page from the average for 1955, it only restores the average to the 1954 figure; this average length can still be reduced by more careful presentation of facts by authors. With the cost of production still rising, it is necessary to keep papers to bare essentials unless the publication of analytical knowledge is to suffer.

Besides the usual items, summaries of 18 papers presented at meetings but not being published in full in any journal were printed in the Proceedings of the Society. The Recommended Methods for the Analysis of Trade Effluents prepared by the Joint A.B.C.M. - S.A.C. Committee and published during the year occupied 32½ pages.

Eight issues of the Bulletin were distributed with *The Analyst* during the year, one of them a special issue commemorating the twenty-first anniversary of the founding of the Scottish Section.

During the year Mr. P. W. Shallis joined the editorial staff.

The number printed of each issue has again been raised for 1957, from 6000 to 6400.

ANALYTICAL ABSTRACTS—*Analytical Abstracts* has grown steadily since its initiation, as shown by the following figures—

Year	Pages	Abstracts
1954	392	3190
1955	468	3556
1956	542	3820

The increase is due to the increasing number of published papers on analytical chemistry and to the improved coverage of foreign journals, particularly those from the U.S.S.R.

There has been a marked expansion in circulation and it has been necessary to increase the printing number from 6100 for 1956 to 7000 for 1957.

CHEMICAL COUNCIL—During the year the Chemical Council has again made grants to the Society for the publication of original papers and abstracts. The Council acknowledges with thanks the sums of £1900 for *The Analyst* and of £1000 for *Analytical Abstracts.*

CONFERENCE OF HONORARY SECRETARIES—A meeting of the Honorary Secretaries of the Sections and Groups of the Society was held in June, 1956, on the same lines as those held in previous years. The meeting was highly successful.

K. A. WILLIAMS, *President.*
N. L. ALLPORT, *Honorary Secretary.*

Report of the Analytical Methods Committee 1956

THIS second Report of the Analytical Methods Committee of The Society for Analytical Chemistry indicates that the good progress made in 1955 has been fully maintained. The first Report of the Committee since it was reorganised with a full-time, paid secretariat, supported by the Trust Fund, was issued in May, 1956; it appeared to be well received, both in Great Britain and abroad, and resulted in a number of enquiries and suggestions for future work and collaboration with other organisations.

The Committee was glad to welcome as an additional member Mr. W. H. Simmons, who has given such long and valuable service to the Society and to the Committee in particular; he became Honorary Secretary of the Committee at its inception in 1924 and continued in this office until 1946. In addition, he was Chairman of the Essential Oils Sub-Committee from 1933.

The Secretariat staff of three is now well housed in the Society's new offices at 14 Belgrave Square, London, S.W.1, and the various committees and panels are able to make full use of the Committee Room provided. At the end of February, 1956, Miss A. M. Parry, B.Sc., joined the staff as Assistant Secretary to the Committee.

PROGRESS OF WORK—

There has been steady progress in the work of the various technical committees coming under the aegis of the Analytical Methods Committee. These now number 19, compared with 14 a year ago, and, as is shown in the individual progress reports given later in this Report, methods for a wide variety of substances are under consideration and every effort is being made to give priority to those methods for which there is the most pressing need. Many of the projects now being considered by the sub-committees and panels involve much collaborative research before standard methods can be recommended; hence, it will be appreciated that the number of publications appearing in any one year is only a partial indication of the amount of work done.

The Joint Committee with the Association of British Chemical Manufacturers on Methods for the Analysis of Trade Effluents, which began its work in February, 1954, has completed a very intensive year's work—19 methods were published in *The Analyst* and 11 more are in the press. The Joint Committee hopes to complete its programme during the next year and subsequently to publish all the methods in one volume. Although primarily intended for the analysis of trade effluents, these methods are even now being found to be applicable in other branches of analysis.

The Joint Committee with the Pharmaceutical Society on Methods of Assay of Crude Drugs was formally appointed in March, 1956; four working panels are already actively engaged in collaborative work.

The Analytical Methods Committee itself published the Report on "The Estimation of Vitamin B_{12}," in the March, 1956, issue of *The Analyst*.

The Reports published by the original Committee in *The Analyst* between 1927 and 1954 continue to be reviewed and edited in a standard format with a view to publication in a book of collected standard methods. To ensure that account has been taken of new developments since the Reports were published, each group of edited drafts is being submitted either to an individual referee or to the relevant sub-committee for scrutiny before being approved by the Committee.

Preliminary discussions have taken place between representatives of the Society, the Association of British Insecticide Manufacturers and the Scientific Sub-Committee on Poisonous Substances used in Agriculture and Food Storage of the Ministry of Agriculture, Fisheries and Food. In the event of agreement being reached for collaborative work, the Society's part will be carried out by the Analytical Methods Committee.

RESEARCH SCHOLARSHIP—

The Analytical Methods Committee is indebted to the Director of the Atomic Energy Research Establishment at Harwell for providing facilities for Mr. Gorsuch, the holder of a Society for Analytical Chemistry Scholarship, to work under the direction of Mr. A. A. Smales.

Mr. Gorsuch started work in April, 1956, and has submitted three Progress Reports to the Committee and discussed them with the Metallic Impurities in Organic Matter Sub-Committee. After completing his training in radiochemical techniques and making a thorough survey of the literature on methods of destruction of organic matter prior to the determination of trace elements, he did some preliminary experimental work on the various radiochemical approaches that might be used in detecting the losses of trace elements during the oxidation. A more detailed examination is now being made, using radioactive tracers, of the losses that occur with a number of metals during preliminary preparation of the material under examination. His findings so far have already been of assistance to the Metallic Impurities in Organic Matter Sub-Committee in the problems associated with the determination of traces of arsenic and lead.

TRUST FUND—

Four meetings of the Trustees of the Society for Analytical Chemistry Analytical Methods Trust have been held under the Chairmanship of The Honourable Mr. Justice Lloyd-Jacob. All the donations and subscriptions promised for 1956 have been received

and, in addition to the sums already promised, many of the original subscribers who had not in the first instance committed themselves to making further donations again gave their support. The total income for the year was £6504, and the Trustees are most grateful to the 57 subscribers for their generous contributions.

EXPENDITURE—

The audited statement of accounts (see Appendix I) covers the 12 months from November 1st, 1955, to October 31st, 1956, this period being in line with the Society's financial year.

The expenditure during the year was £3870, the principal items being staff salaries and expenses connected with the Research Scholarship. This sum approximates to the estimated expenditure given in last year's Report.

Expenditure for 1957 is estimated to be a little more, since the move to new premises in November, 1956, has necessitated the furnishing of the Secretariat offices.

REPORTS OF SUB-COMMITTEES OF THE ANALYTICAL METHODS COMMITTEE

METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C. (*Chairman*)	*Public Analyst*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
C. L. Hinton, F.R.I.C.	*British Food Manufacturing Industries Research Association*
E. I. Johnson, M.Sc., A.R.I.C.	*Department of the Government Chemist*
W. C. Johnson, M.B.E., F.R.I.C.	*Hopkin & Williams Ltd.*
I. MacIntyre, M.B., Ch.B.	*University of London (Post-Graduate Medical School)*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
G. Taylor, O.B.E., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
G. E. Willis, B.Sc., Ph.D., A.R.I.C.	*Imperial Chemical Industries Ltd. (Dyestuffs Division)*

TERMS OF REFERENCE—"To investigate the determination of small quantities of metals in organic matter."

PROGRESS OF WORK—

Arsenic—Collaborative work with simple solutions containing arsenic has permitted the Sub-Committee to clarify many of the details of procedure in the method for the determination of arsenic by the molybdenum-blue method, and tests are now being carried out with samples in the presence of organic matter.

Lead—The revised method for the determination of lead is the subject of collaborative tests.

Destruction of organic matter—The Sub-Committee is maintaining close contact with Mr. Gorsuch, whose reports on his work at Harwell have already proved most helpful.

A memorandum on the handling and use of perchloric acid, particularly as applied to the destruction of organic matter, is being prepared for publication.

Standard methods—The recommended methods for the determination of arsenic, lead, copper and zinc that were originally published as Analytical Methods Committee Reports have been referred by the Committee to the Sub-Committee for review and revision where necessary.

VITAMINS

As stated in the Report for 1955, the original Vitamins Sub-Committee was dissolved when the Analytical Methods Committee was reorganised, but the Panel on Vitamin E continues its investigations.

Vitamin-E Panel

CONSTITUTION—

A. L. Bacharach, M.A., F.R.I.C. (*Chairman*)	*Consulting Chemist*
J. Green, B.Sc., Ph.D., A.R.I.C. (*Honorary Technical Secretary*)	*Vitamins Ltd.*

F. Brown, M.Sc., Ph.D.	*Foot-and-Mouth Disease Research Institute*
A. R. Moss, B.Sc., Ph.D.	*Roche Products Ltd.*
H. N. Ridyard, B.Sc., A.K.C., F.R.I.C.	*Research Association of British Flour Millers*
P. W. Russell Eggitt, B.Sc., Ph.D., A.R.I.C.	*Spillers Ltd.*
C. A. Shacklady, B.Sc., A.R.I.C.	*J. Bibby & Sons Ltd.*
P. Stross, B.Sc.	*British Drug Houses Ltd.*
G. Walley, B.Sc., F.R.I.C.	*Unilever Ltd.*
R. J. Ward, B.Sc., A.R.I.C.	*Medical Research Council, Dunn Nutritional Laboratory*
E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.	*Analytical and Consulting Chemist*
P. Harris, Ph.D.*	*Distillation Products Industries, Rochester, New York, U.S.A.*

* Corresponding member.

TERMS OF REFERENCE (OF ADVISORY PANEL)—"To survey the methods already proposed for the estimation of Vitamin E and to recommend to the [Vitamins] Sub-Committee a standard method or methods."

PROGRESS OF WORK—

The vitamin-E activity of any material can be estimated if two conditions are satisfied. First, there must be available means of determining with sufficient accuracy the amounts of the different tocopherols present in the material. Secondly, weighting factors must be available for application to each separately determined tocopherol, so that the total amount present can then be appropriately expressed in terms of the biological activity of one of them, and preferably of α-tocopherol. Of this two-stage process of estimating vitamin-E activity, only the first falls within the scope of the Panel's activities.

When the Panel began its work, four tocopherols had been isolated. Since that time, it has become clear that the three other possible tocopherols also occur in natural products, so that any "reference analytical procedure" should as far as possible be capable of distinguishing between, and individually determining, all of them. The Panel, therefore, set to work to devise a method capable of measuring with reasonable precision and accuracy all seven methylated tocols. A paper-chromatographic method was chosen for collaborative study, because recent advances in this type of separation seemed likely to overcome several difficulties occurring in the classical methods of vitamin-E estimation and to deal successfully with most of the problems raised by the discovery of the new tocopherols. The separated tocopherols are then assayed by a modification of the Emmerie - Engel colorimetric method. In this way, micro-determination is possible far below the range of the older methods.

Analysis of the most complex samples likely to present themselves for tocopherol determinations will frequently involve as many as seven stages—four for purification, one for separation of the tocopherols by paper chromatography and two for measurement of the amounts present.

The Panel has for the most part been occupied with working out details of manipulation; however, it would now be possible to lay down at any rate a provisional method for sufficiently accurate determination of the α-tocopherols in naturally occurring oils and other foodstuffs, but the Panel has decided for the moment to defer doing this, because, for the reasons indicated above, as complete a differential analysis as possible seems essential and, what is perhaps more to the point, because the chances of putting forward such a method seem at last to be within sight.

DIRECT MICRO-DETERMINATION OF OXYGEN IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

D. W. Wilson, M.Sc., F.R.I.C. (*Chairman*)	*Sir John Cass College (Department of Chemistry)*
G. C. Ackroyd, B.Sc., A.R.I.C.	*D.S.I.R., Fuel Research Station*
P. R. W. Baker, B.Sc., A.R.I.C.	*Wellcome Research Laboratories*
Miss B. B. Bauminger, Ph.D., A.R.I.C.	*Dunlop Research Centre*
W. T. Chambers, B.Sc., Ph.D., A.R.I.C.	*British Rubber Producers' Research Association*
A. F. Colson, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Alkali Division)*
Miss M. Corner, B.Sc., F.R.I.C.	*D.S.I.R., Chemical Research Laboratory*
R. R. Gordon, Ph.D.	*National Coal Board, Central Research Establishment*
G. Ingram, A.R.I.C.	*Courtaulds Ltd.*

F. J. McMurray	*Wellcome Chemical Works*
F. H. Oliver	*Parke, Davis & Co. Ltd.*
H. J. Warlow	*D.S.I.R., Fuel Research Station*
C. Whalley, B.Sc., F.R.I.C.	*Paint Research Station*

PROGRAMME OF WORK—To investigate the Unterzaucher method, and its modifications, for the micro-determination of oxygen.

PROGRESS OF WORK—Collaborative experimental work is proceeding on various organic substances. In the first test each member employed his or her own version of the Unterzaucher method, and the results demonstrated clearly the superiority of a carbon - platinum filling in the combustion tube at 900° C over a filling of carbon only at 1100° C. The second series of tests now being carried out has been designed with the object of reducing the "blank" value, and of isolating possible sources of error.

ESSENTIAL OILS SUB-COMMITTEE

The Sub-Committee has been reorganised, under the Chairmanship of Dr. Ferguson, as follows.

CONSTITUTION—

G. W. Ferguson, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
A. J. M. Bailey, B.Sc., F.P.S., F.R.I.C.	*W. J. Bush & Co. Ltd.*
D. Holness, B.A.	*Unilever Ltd., Central Perfumery Department*
H. T. Islip, B.Sc., F.R.I.C.	*Colonial Products Laboratory, Colonial Office*
P. McGregor, B.Sc., A.H.-W.C., F.R.I.C.	*Department of the Government Chemist*
J. H. Seager, M.Sc., F.R.I.C.	*Yardley & Co. Ltd.*
G. E. Smith, B.Sc., F.R.I.C.	*Stafford Allen & Sons Ltd.*
B. D. Sully, B.Sc., Ph.D., A.R.C.S., F.R.I.C.	*A. Boake, Roberts & Co. Ltd.*

MEAT PRODUCTS SUB-COMMITTEE

CONSTITUTION—

S. M. Herschdoerfer, Ph.D., F.R.I.C. (*Chairman*)	*T. Wall & Sons Ltd.*
S. Back, B.Sc., F.R.I.C.	*Crosse & Blackwell Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.	*British Food Manufacturing Industries Research Association*
C. D. Essex, A.R.I.C.	*Oxo Ltd.*
J. R. Fraser, B.Sc., A.C.G.F.C., F.R.I.C.	*Department of the Government Chemist*
H. G. Rees, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C.	*Oxo Ltd.*
H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.	*Public Analyst*

TERMS OF REFERENCE—"(*a*) The determination of the meat content of products containing meat; (*b*) the determination of the constituents of meat and meat products.

NOTE—The term 'meat products' to include hydrolysed protein and, if found necessary, fish pastes."

PROGRESS OF WORK—Owing to pressure of work, Dr. Rees has retired from the Chair and Dr. Herschdoerfer has been appointed to take his place.

TRACE ELEMENTS IN FERTILISERS AND FEEDING-STUFFS SUB-COMMITTEE

CONSTITUTION—

J. H. Hamence, M.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
E. I. Johnson, M.Sc., A.R.I.C.	*Department of the Government Chemist*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
R. L. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Macaulay Institute for Soil Research (Department of Spectrochemistry)*
A. A. Smales, B.Sc., F.R.I.C.	*Atomic Energy Research Establishment, Harwell*
C. Whalley, B.Sc., F.R.I.C.	*Paint Research Station*

TERMS OF REFERENCE—"To devise appropriate methods of analysis (to be recommended for inclusion in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926) for the determination of the trace elements manganese, copper, zinc, cobalt, molybdenum, iodine, selenium and fluorine, and also for boron, magnesium and iron, which can be expected to be present in fertilisers in small quantities as distinct from traces."

PROGRESS OF WORK—Owing to his onerous duties as Honorary Treasurer of the Society and as President Elect, the Chairman has expressed the wish to retire from the Chair.

PESTICIDES RESIDUES IN FOODSTUFFS SUB-COMMITTEE

CONSTITUTION—

G. Taylor, O.B.E., F.R.I.C. (*Chairman*)	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
G. L. Baldit, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
E. D. Chilwell, B.Sc., F.R.I.C.	*Fisons Pest Control Ltd.*
H. Egan, B.Sc., Ph.D., D.I.C., F.R.I.C.	*Department of the Government Chemist (representing Food Group, Society of Chemical Industry)*
B. A. Ellis, M.A., F.R.I.C.	*Department of the Government Chemist*
J. C. Gage, B.Sc., Ph.D., A.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
R. A. E. Galley, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C.	*Colonial Products Laboratory, Colonial Office*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*

TERMS OF REFERENCE—"To examine the present position in respect of methods of analysis of foodstuffs for residual traces of pesticides, as the first action of the Sub-Committee; and, further, if deemed desirable, to recommend for general acceptance methods of analysis now in use, or to develop or assist in the development of new methods of analysis or modifications of methods now in use."

PROGRESS OF WORK—The work of this Sub-Committee is in abeyance, pending the results of discussions between representatives of the Society, the Association of British Insecticide Manufacturers and the Ministry of Agriculture, Fisheries and Food mentioned earlier in this Report (see p. 308).

REPORT OF THE A.B.C.M. - S.A.C. JOINT COMMITTEE ON METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

MAIN COMMITTEE

CONSTITUTION—

Representing the Association of British Chemical Manufacturers—	
H. N. Wilson, F.R.I.C.* (*Chairman*)	*Imperial Chemical Industries Ltd. (Billingham Division)*
J. G. Maltby, B.Sc., F.R.I.C.* (*Secretary*)	*Distillers Co. Ltd.*
F. G. Broughall, B.Sc., F.R.I.C.	*Midland Tar Distillers Ltd.*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
I. S. Wilson, M.Sc., Ph.D., A.R.I.C.	*Monsanto Chemicals Ltd.*
Representing the Society for Analytical Chemistry—	
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.*	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.	*Mersey River Board*
C. J. Regan, B.Sc., F.R.I.C.	*Formerly Chemist-in-Chief, London County Council*
J. G. Sherratt, B.Sc., F.R.I.C.	*Public Analyst and Consulting Analytical Chemist*
K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.	*Analytical and Consulting Chemist*
N. T. Wilkinson, F.R.I.C.	*Imperial Chemical Industries Ltd. (Alkali Division)*

J. S. Evans	*Federation of British Industries*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.*	*Secretary to the Analytical Methods Committee*

* Members of the Publications Sub-Committee, to which J. B. Attrill, M.A., F.R.I.C., Editor of *The Analyst*, has been co-opted.

TERMS OF REFERENCE—"To devise and recommend methods of analysis as applied to trade effluents, specifying in each case their applicability and limitations, but not the interpretation of the results of such tests as would be used to decide on the quality of an effluent. Such methods would be published by the Society as Recommended Methods."

PROGRESS OF WORK—

Remarkable progress can be claimed, considering that a great deal of experimental work has had to be done. Indeed, so good has been this progress that one of the Panels (Panel 4) completed its programme of work in October.

The first intention of the Committee was to make a literature search and to recommend the best methods available for each particular impurity. Unfortunately, the literature on the analysis of trade effluents is scant and it soon became obvious that for a number of methods experimental work would be necessary. The Committee's main task has been to find or devise methods that are not only capable of determining toxic constituents with sufficient accuracy in the very small amounts that have been found to cause damage to the animal and vegetable life of rivers, etc., but are at the same time practical and quick enough to be used in the rapidly changing conditions that may prevail.

Account has been taken of the "Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents" (Second Edition, 1956), published by H.M. Stationery Office for the Ministry of Housing and Local Government; the avoidance of conflict with these methods is particularly important in the determination of oxygen demand and, for this reason, permission has been obtained from H.M. Stationery Office for reproduction in full of the methods for the determination of biochemical oxygen demand and of dissolved oxygen, although it has, of course, been necessary to make modifications to cover special requirements for trade effluents. In addition, a section has been included on the manometric technique and its advantages in the determination of the biochemical oxygen demand of trade effluents.

As far as possible, the methods selected or devised are generally applicable over a wide range of contents, but for some constituents it has been necessary to give modified, or different, methods for application to lower parts of the range. The lack of specificity of reagents for some of the metallic constituents has caused difficulty when very small amounts have to be determined. Some of these difficulties have been surmounted, but mention should be made of silver, which, because of its extreme toxicity to fish, may have to be determined down to 0·01 parts per million; silver is an unlikely contaminant in an effluent in view of its monetary value, but there is always the odd chance of its accidental disposal. A satisfactory method for determination of traces has yet to be found.

Three features of the Committee's work are particularly worthy of note, namely the methods for the determination of immiscible liquids and of chemical oxygen demand (dichromate value test) and the apparatus devised for sampling whereby a truly representative sample can be taken—particularly important when immiscible layers are present.

The method for volatile immiscible liquids deserves special mention because of its ingenuity and its applicability to effluents containing as little as 3 parts per million of contaminant.

The dichromate value test—known in the United States as C.O.D. (chemical oxygen demand)—is a new feature in British practice and is recommended as a standard method, since, for trade effluents, it has considerable advantages over the well known permanganate value test, particularly its reproducibility and its applicability to a wide variety of samples. Experimental work has shown that a larger proportion of carbonaceous matter is oxidised than in the permanganate value test.

Work completed—The following methods were published during the year—

Determination of iron, mercury and nickel (*Analyst*, 1956, **81**, 176);

Sampling, physical examination of the sample (general description, colour, temperature, pH value, transparency), and determination of settleable solids, total suspended solids, residue on evaporation and dissolved solids (*Analyst*, 1956, **81**, 492);

Determination of chromium, lead and selenium (*Analyst*, 1956, **81**, 607);

Determination of organic carbon, chloride (chlorion), acidity, alkalinity and manganese (*Analyst*, 1956, **81**, 721);

Determination of non-volatile matter extractable by light petroleum and of volatile immiscible liquids (*Analyst*, 1957, **82**, 123).

Methods for determining the following have been approved for publication: aluminium, oxygen demand, calcium and magnesium, hardness, the various forms of combined nitrogen, phenols, residual chlorine, sulphide and zinc.

Work in hand—Draft methods for the following are nearing completion: antimony, cyanide, fluoride, phosphorus and synthetic detergents.

PANEL 1: ORGANIC MATTER—GENERAL

CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C. (*Chairman*)	*Formerly Chemist-in-Chief, London County Council*
G. S. Clements, A.R.C.S., F.R.I.C. (*Secretary*)	*Public Health Department, London County Council*
W. M. Cameron, M.Inst.S.P., F.R.I.C.	*Main Drainage Department, Middlesex County Council*
W. T. Lockett, M.Sc.	*Formerly of the Main Drainage Department, Middlesex County Council*
T. B. Moore, B.Sc.	*North Thames Gas Board*
A. E. J. Pettet, B.A.	*D.S.I.R., Water Pollution Research Laboratory*
I. S. Wilson, M.Sc., Ph.D., A.R.I.C.	*Monsanto Chemicals Ltd.*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.	*Secretary to the Analytical Methods Committee*

PROGRAMME OF WORK—

*Methods for determining oxygen demand**—(*a*) general considerations; (*b*) permanganate value (oxygen absorbed from permanganate); (*c*) biochemical oxygen demand; (*d*) dichromate value (oxygen absorbed from boiling dichromate).

*Methods for determining combined nitrogen**—(*a*) free and saline ammonia; (*b*) albuminoid nitrogen; (*c*) organic nitrogen; (*d*) total unoxidised nitrogen; (*e*) nitrogen as nitrite; (*f*) nitrogen as nitrate.

*Methods for determining total organic carbon.**

Methods for determining phosphorus.

*Methods for determining chloride ion (chlorion).**

Methods for determining synthetic detergents.

To list inhibitory substances present in some trade effluents, which may interfere in any of the recommended methods.

PROGRESS OF WORK—

Work completed—Methods for items above marked with an asterisk (*) have been completed (see list under Main Committee, p. 313).

Work in hand—Draft methods for the following are nearing completion: phosphorus; synthetic detergents.

PANEL 2: METALLIC CONTAMINANTS

CONSTITUTION—

N. T. Wilkinson, F.R.I.C. (*Chairman*)	*Imperial Chemical Industries Ltd. (Alkali Division)*
R. Belcher, Ph.D., D.Sc., F.R.I.C.	*University of Birmingham (Department of Chemistry)*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
J. G. Sherratt, B.Sc., F.R.I.C.	*Public Analyst and Consulting Analytical Chemist*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*

PROGRAMME OF WORK—

Preliminary treatment of sample.† Methods for determining aluminium,* antimony, arsenic,† barium, cadmium, chromium,* copper,† iron,* lead,* manganese,* mercury,* molybdenum, nickel,* potassium, selenium,* silicon, silver, sodium, sulphate, titanium and zinc.*

PROGRESS OF WORK—

Work completed—Methods for items marked above with an asterisk (*) have been completed (see list under Main Committee, p. 313); those marked with an obelisk (†) were published in January, 1956.

Work in hand—The final draft for antimony is being prepared; work is proceeding on methods for barium, cadmium and silver.

PANEL 3: NON-METALLIC CONTAMINANTS

CONSTITUTION—

F. G. Broughall, B.Sc., F.R.I.C. (*Chairman*)	*Midland Tar Distillers Ltd.*
W. G. Carey, F.R.I.C.	*Public Analyst and Official Agricultural Analyst; Consultant*
G. U. Houghton, M.Sc., Ph.D., F.R.I.C.	*South Essex Waterworks Co.*
E. A. W. Whitlock, B.Sc., A.R.I.C.	*Wallace & Tiernan Ltd.*

PROGRAMME OF WORK—

Methods for determining free chlorine,* cyanide, fluoride, formaldehyde, phenols,* sulphide,* sulphite, thiocyanate and thiosulphate.

PROGRESS OF WORK—

Work completed—Methods for items marked above with an asterisk (*) have been completed (see list under Main Committee, p. 313).

Work in hand—Work is proceeding on methods for cyanide, thiocyanate and fluoride.

PANEL 4: PHYSICAL TESTS

CONSTITUTION—

J. G. Sherratt, B.Sc., F.R.I.C. (*Chairman*)	*Public Analyst and Consulting Analytical Chemist*
L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.	*Mersey River Board*
G. A. Vaughan, F.R.I.C.	*Coal Tar Research Association*
K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.	*Analytical and Consulting Chemist*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*

PROGRAMME OF WORK—

Method of sampling. Measurement of colour, turbidity, temperature and pH. Determination of suspended solids, settleable solids and dissolved solids. Determination of immiscible liquids, such as oil or tar. Determination of hardness (total hardness; calcium hardness; magnesium hardness). Determination of acidity and alkalinity.

PROGRESS OF WORK—

Work completed—The programme of work has been completed and all the methods have been published or are in the press (see list under Main Committee, p. 313).

REPORT OF THE P.S. - S.A.C. JOINT COMMITTEE ON METHODS OF ASSAY OF CRUDE DRUGS

MAIN COMMITTEE

CONSTITUTION—

Representing the Pharmaceutical Society of Great Britain—

K. R. Capper, Ph.D., B.Pharm., F.P.S., D.I.C. (*Chairman*)	*Pharmaceutical Society of Great Britain*
R. Higson, F.P.S.	*Ministry of Health, Supplies Division*
W. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Stafford Allen & Sons Ltd.*
R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C.	*British Drug Houses Ltd.*

Representing the Society for Analytical Chemistry—

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Boots Pure Drug Co. Ltd.*
H. C. Macfarlane, A.R.T.C.S., F.R.I.C.	*Analytical and Consulting Chemist*
D. Watt, F.P.S.	*T. & H. Smith Ltd.*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C. (*ex officio*)	*Chairman of the Analytical Methods Committee*

Representing the Colonial Products Laboratory—

A. J. Feuell, B.Sc., Ph.D., A.R.I.C.	*Colonial Products Laboratory*

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)

APPOINTED—As a Joint Committee by the Pharmaceutical Society and the Society for Analytical Chemistry, on March 21st, 1956.

TERMS OF REFERENCE—"To prepare standard methods of assay of crude drugs and kindred materials."

PROGRAMME OF WORK—

The Joint Committee was set up, after consultation between the two Societies, because it was felt that there was a need for methods of assay of crude drugs that are in use in commerce but for which there are no standard or official methods at present in force.

The Committee is concerned only with methods of assay and not with specifications. Recommended methods will be published simultaneously by the two Societies; it is hoped eventually to produce a book in which all these methods are collected, together with others which, though recognised as standard, have been deleted from current editions of the British Pharmacopoeia or the British Pharmaceutical Codex.

Active liaison is being maintained with the Secretary of the British Pharmacopoeia Commission, who is being kept regularly informed of the work.

A list of drugs for which chemical methods might be required was examined and an order of priority was decided. It was agreed that each drug or group of drugs should be the concern of a separate working panel, which, after considering the need for a method of assay and assessing the chances of success in devising such a method, would undertake the necessary investigations.

Digitalis, capsicum, anthraquinone drugs and rauwolfia were selected as the subjects of study by the first four panels. These panels, details of which are printed below, are now actively engaged on collaborative tests, and other panels will be appointed from time to time.

The method for the Assay of the Non-phenolic Alkaloids of Ipecacuanha, deleted from editions of the B.P. subsequent to that of 1932 and on which it was not necessary to carry out experimental work, has been accepted by the Main Committee for publication.

PANEL 1: *Digitalis purpurea*—CHEMICAL METHOD

CONSTITUTION—

Professor H. Brindle, M.Sc., F.P.S., F.R.I.C. (*Chairman*)	*Emeritus Professor of Pharmacy, University of Manchester*
G. E. Foster, B.Sc., Ph.D., F.R.I.C.	*Wellcome Chemical Works*
G. J. Rigby, M.Sc., Dip-Bact.	*University of Manchester (Department of Pharmacy)*
J. M. Rowson, M.Sc., Ph.D., F.P.S.	*Pharmaceutical Society of Great Britain*
K. L. Smith, M.P.S.	*Boots Pure Drug Co. Ltd.*
Professor J. P. Todd, Ph.D., F.P.S., F.R.I.C.	*Royal College of Science and Technology, Glasgow (School of Pharmacy)*
Miss A. M. Parry, B.Sc. (*Secretary*)	

FIRST MEETING—December 11th, 1956.

TERMS OF REFERENCE—"To investigate chemical methods for the assay of digitalis and its preparations and to attempt to correlate them with the biological method of assay."

PROGRESS OF WORK—Preliminary collaborative tests on digitalis leaf have already started, and both chemical and biological tests are being carried out simultaneously.

PANEL 2: CAPSICUM—CAPSAICIN CONTENT

CONSTITUTION—

H. B. Heath, M.B.E., B.Pharm., F.P.S. (*Chairman*)	*Stafford Allen & Sons Ltd.*
E. A. Elsbury, F.R.I.C.	*Parke, Davis & Co. Ltd.*
C. A. MacDonald, B.Sc., F.R.I.C.	*Evans Biological Institute*
G. R. A. Short, F.P.S.	*W. J. Bush & Co. Ltd.*
D. O. Singleton, B.Sc.	*Beecham Maclean Ltd.*
Miss A. M. Parry, B.Sc. (*Secretary*)	

FIRST MEETING—July 11th, 1956.

TERMS OF REFERENCE—"To investigate methods of assay of capsicum and capsicum products with particular reference to the determination of the capsaicin content."

PROGRESS OF WORK—After preliminary tests on chillies and the oleoresin, it was decided to concentrate first on establishing a standard absorption curve for pure capsaicin, and good progress in this is now being made. To avoid repeated handling of capsaicin (which has an extremely irritant action) as the reference standard, the Panel is considering substances that could be used as secondary standards.

PANEL 3: ANTHRAQUINONE DRUGS

CONSTITUTION—

J. M. Rowson, M.Sc., Ph.D., F.P.S. (*Chairman*)	*Pharmaceutical Society of Great Britain*
J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S., F.R.I.C.	*University of London, School of Pharmacy*
C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Boots Pure Drug Co. Ltd.*
W. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Stafford Allen & Sons Ltd.*
H. A. Ryan, B.Sc., F.R.I.C.	*Westminster Laboratories Ltd.*
W. Smith, B.Sc., F.R.I.C.	*Allen & Hanburys Ltd.*
Miss A. M. Parry, B.Sc. (*Secretary*)	

FIRST MEETING—October 31st, 1956.

TERMS OF REFERENCE—"To investigate methods for estimating the purgative activity of drugs and preparations of drugs containing anthraquinone derivatives with a view to recommending standard methods of assay."

PROGRESS OF WORK—The drugs (and their galenicals) that the Panel proposes to consider are aloes, cascara sagrada, rhubarb, senna fruit and senna leaf.

Collaborative investigations of methods for assay of Powdered senna leaf (Alexandrian) have already begun.

PANEL 4: RAUWOLFIA

CONSTITUTION—

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C. (*Chairman*)	*Boots Pure Drug Co. Ltd.*
T. Davies, B.Sc., A.R.I.C.	*CIBA Laboratories Ltd.*
J. J. Lewis, M.Sc., F.P.S.	*University of Glasgow (Department of Materia Medica and Therapeutics)*
A. W. Peacock, B.Pharm., F.P.S.	*Riker Laboratories Ltd.*
Miss A. M. Parry, B.Sc. (*Secretary*)	

FIRST MEETING—13th February, 1957.

TERMS OF REFERENCE—"To investigate methods of assay for rauwolfia and its preparations with particular regard to the content of reserpine and related alkaloids."

PROGRESS OF WORK—At its inaugural meeting the Panel agreed that a chemical method of assay of the reserpine content of rauwolfia and its preparations should be sought, since the existing bio-assay is not considered satisfactory for assessing the hypotensive activity. Preliminary collaborative work on establishing a standard absorption curve for reserpine and the investigation of colorimetric assays for reserpine has started.

APPENDIX I

THE SOCIETY FOR ANALYTICAL CHEMISTRY ANALYTICAL METHODS TRUST ACCOUNTS FOR THE YEAR ENDED OCTOBER 31ST, 1956

Income and Expenditure Account for the Year Ended October 31st, 1956

"A.M.C." 1955					"A.M.C." 1955			
£	£		£	£	£		£	£
49		Rent, Light, Heat and Telephone	630			Subscriptions from Industry as result of Appeal ..		
1198		Salaries	2274			Received in 1955 for 1956	150	
232		Office Equipment ..	81		8794	Received during 1956 ..	6344	
67		Printing and Stationery	168					6494
50		Travelling Expenses ..	62			Interest from Investments (representing former Analytical Chemistry Research Fund):		
27		Expenses of Meetings ..	26					
—		Audit Fee	21			Received gross	7	
92		Postage and Petty Expenses	83			Received net	2	
1715				3345		Income Tax recoverable	1	
—		Scholarship Grant (7 months)		525	—			10
7079		Excess of Income over Expenditure for the year ended October 31st, 1956, transferred to Accumulated Fund		2634				
£8794				£6504	£8794			£6504

Accumulated Fund

1955				1955			
£			£	£		£	£
—		Legal Expenses in connection with formation of the Trust	93		Balance at October 31st, 1955	7079	
7079		Balance carried to Balance Sheet ..	9690		*Less:* Subscriptions received in 1955:		
					For 1956 150		
					For 1957 150		
						300	
				—			6779
					Cost Price of Investments (representing the former Analytical Chemistry Research Fund) transferred by Resolution of the Society for Analytical Chemistry ..	244	
					Accumulated Income therefrom to October 31st, 1955 ..	126	
				—			370
				7079	Excess of Income over Expenditure for the year ended October 31st, 1956		2634
£7079			£9783	£7079			£9783

Balance Sheet at October 31st, 1956

1955				1955			
£		£	£	£		£	£
	Accumulated Fund:				*Investments (at Cost):*		
7079	Balance at 31st October, 1956		9690		£100 3¼% Ceylon Government Stock, 1934–59 ..	61	
—	*Sundry Creditors*	21			£100 3½% Conversion Stock	83	
—	*Subscriptions in Advance* ..	150			£100 3½% War Stock ..	100	
			171				244
					Income Tax recoverable ..		1
					Cash:		
				—	At Bank	9474	
					In the Hands of the Society		
				7079	for Analytical Chemistry	142	
							9616
£7079			£9861	£7079			£9861

Report of the Auditors to the Trustees of The Society for Analytical Chemistry Analytical Methods Trust Fund

We have examined the above Balance Sheet which in our opinion gives a true and fair view of the state of affairs of the Trust at 31st October, 1956.

10 New Court,
Lincoln's Inn,
LONDON, W.C.2.
14th March, 1957.

(Signed) RIDLEY, HESLOP & SAINER,
Chartered Accountants,
Auditors.

Schedule of Investments at October 31st, 1956

	Nominal Amount	Cost	Market Value 31.10.56	Income Received
Ceylon Government 3¼% Stock, 1959 ..	100	61	90	3
3½% Conversion Stock	100	83	69	2
3½% War Stock	100	100	72	4
		£244	£231	£9

APPENDIX II

SUBSCRIBERS TO THE TRUST FUND

Albright & Wilson Ltd.
James Anderson & Co. (Colours) Ltd.
The Associated Ethyl Company Ltd.
Bakelite Ltd.
Baker Perkins Ltd.
Baker Platinum Ltd.
J. Bibby & Sons Ltd.
A. Boake, Roberts & Co. Ltd.
Boots Pure Drug Co. Ltd.
Borax Consolidated Ltd.
The British Aluminium Co. Ltd.
The British Arkady Co. Ltd.
British Celanese Ltd.
The British Drug Houses Ltd.
British Electricity Authority
British Glues & Chemicals Ltd.
The British Oxygen Co. Ltd.
Brotherton & Co. Ltd.
Cadbury Brothers Ltd.
Cooper, McDougall & Robertson Ltd.
The Distillers Company Ltd.
Dunlop Research Centre
Esso Development Co. Ltd.
Ferranti Ltd.
Fisons Ltd.
Glaxo Laboratories Ltd.
Thomas Hedley & Co. Ltd.
Hopkin & Williams Ltd.
Horlicks Ltd.
Huntley & Palmers Ltd.
Imperial Chemical Industries Ltd.
Laporte Chemicals Ltd.
Levy West Laboratories Ltd.
J. Lyons & Co. Ltd.
Macfarlane, Lang & Co. Ltd.
John Mackintosh & Sons Ltd.
The Marmite Food Extract Co. Ltd.
May & Baker Ltd.
The Metal Box Company Ltd.
The Millers' Mutual Association
Monsanto Chemicals Ltd.
National Coal Board
Oxo Ltd.
Peek, Frean & Co. Ltd.
Pilkington Brothers Ltd.
Procea Products Ltd.
Reckitt & Colman Ltd.
Roche Products Ltd.
Rowntree & Co. Ltd.
"Shell" Research Ltd.
John & E. Sturge Ltd.
Tate & Lyle Ltd.
Thorium Ltd.
Unilever Ltd.
Virol Ltd.
Vitamins Ltd.
The Wellcome Foundation Ltd.
Weston Research Laboratories Ltd. (formerly Allied Bakeries Research Laboratories Ltd.)

Address of the Retiring President

K. A. WILLIAMS, B.Sc., PH.D., A.INST.P., M.INST.PET., F.R.I.C.

(Delivered after the Annual General Meeting, March 1st, 1957)

FROM the earliest days of our Society it has been the pleasant duty of its President to report each year on what has happened during the year to the Society, how it has progressed in its relations with the outside world, and how it has served the needs of its members.

For at least half the Society's life-time the President's annual addresses were mainly concerned with those matters that were our primary interest at the inception of the Society, namely means whereby adulteration of food might be suppressed and the moves that had to be taken to that end. It was not until the period of the First World War that a President turned his attention to other matters, and it is not surprising for those who knew him to realise that it was Chaston Chapman who took this revolutionary step, and that his subject was the training of the analytical chemist. It must not, however, be assumed that our first interest of the early years was our only one. From the very beginning *The Analyst* has included in its pages papers ranging over the whole subject of analytical chemistry as known at the time, and the abstracts in the journal have always been designed to cover as far as possible a similarly wide field.

With the opening up of fresh fields for a President to address his Society upon, we find that while some continued to speak on conventional lines others spoke on matters not directly connected with the Society's progress, and still others set out to advise their fellow members and those attracted to the profession on how to advance its credit in the eyes of the world. In particular, addresses by Chaston Chapman and Bolton on this aspect of the subject, though they brought some criticism at the time, did much to increase the respect of others for our members.

After the First World War it was felt, too, that too big a burden was placed on each President by requiring him to speak formally at the end of each of his two years of office, and for many years now it has been the custom for the address to be given at the end of the term, and for a lecture to be given in the intermediate years by a distinguished guest. At about the same time, the formal report on the work of the year was removed from the President's address and presented to the Annual General Meeting of the Society by the Honorary Secretary on behalf of the President and the Council.

It is a little difficult to assign a date from which analytical chemistry may be said to have developed, but there are some reasons for choosing February 1st, in the year 1769, as it was then that Lavoisier completed his first quantitative experiments with the balance and so led the way to establish the foundations of modern chemistry. The next seventy years saw the rise of many new chemical industries and the establishment of special schools and laboratories for training chemists and investigators; and with them came the growing development of the technical and industrial chemist and the new profession of practical chemistry.

The new profession, as was to be expected, found many sources of difficulty. Not only were there no industrial schools in which training could be obtained, but the employment of pure science as a source of profit was looked on by many, especially those of an academic turn of mind, with disfavour. The practitioners of pure science regarded applied science as impure science. As has been said by Schiller, "Science to one is the mother revered by the gods; to another only a cow whence to squeeze profits in butter and cheese."

In those days there were circumstances that tended to justify this conception of an impure science, for the growth of knowledge led to the appearance of a multitude who put their learning to base uses. The adulteration of food began to be practised to an almost unlimited degree, and in ways so subtle as to escape detection. A new type of scientist had to appear, so that the problem of adulteration might be coped with. It may well be that this is why analytical chemistry developed first and most powerfully through work on foods rather than in other directions.

Tribute must be paid to Frederick Accum for his handling of the situation, for it was he who took the first steps to suppress sophistication and to popularise analytical chemistry. In the first twenty years of the nineteenth century he published books dealing with methods for discovering the purity of drugs and medicinal preparations, a system of chemistry, a

practical essay on the analysis of minerals, a course of lectures on experimental chemistry and mineralogy, a descriptive catalogue of apparatus and instruments employed in experimental and operative chemistry and in analytical chemistry, a treatise on gaslight, a practical essay on chemical reagents and tests, a book of chemical amusements and, most famous of all, a treatise on the adulterations of food and culinary poisons, with methods for detecting them: "Death in the Pot."

His work was taken up a few years later in a more official manner by Hassall and Lethaby, who, in 1850, conducted their Analytical Sanitary Commission to investigate food adulteration in London and the neighbourhood at the instigation of the Editor of *The Lancet*. They reported in 1855, a Select Parliamentary Committee was set up to investigate further, and as a result the first Adulteration Act was passed in 1860. It proved of little practical use, but paved the way for the new Act of 1872.

Surprising as it may seem, the operations of Hassall and his colleagues did not meet with universal approval, for I find these strictures on their helpful advice in an early adition of "Enquire Within upon Everything." In the twenty-first edition, of 1864, it is remarked: "Someone has written a little book to inform people 'How to detect Adulterations in our Daily Food and Drink," and there is room for someone else to write a key to the said little book entitled 'How to understand the instructions in How to Detect Adulteration in our Daily Food and Drink,' for although the advertisement of the book says that it gives instructions for the employment of 'simple Means' of detection, the means suggested are highly impracticable and in some instances dangerous. Thus the housewife who sets about the discovery of some supposed evil may, by an error or accident—the upsetting of a bottle of sulphuric acid, or the explosion of a receiver of gas—do herself more injury in an hour than she would suffer from adulteration in a lifetime." After satirically exposing the difficultites and dangers of chemical analysis, the writer goes on to give his methods for ensuring the cleanliness and purity of foods. It must be recorded that they are relatively simple and ineffective, and where adulteration cannot be found by simple observations of a water extract, or similarly, the advice is usually "buy the best" or "prepare the material yourself."

It was in this atmosphere, with the Act of 1872 in mind, that our Society was formed. We have the history of its formation and its development preserved for us in the pages of the minute books of the Council, which are complete, and in the pages of *The Analyst*, and, of course, I need hardly mention, in Dr. Bernard Dyer's account published after we had been in existence for fifty years.

Whether one reads the early accounts of the Council meetings or the early pages of *The Analyst*, one cannot fail to be impressed by the earnestness of the Society's members. At all times they were ready to find ways and means of catching out the adulterator of food or drugs, at all times they were ready to pass strictures on any fellow member who, in their view, failed to carry out his duties with sufficient care or with zeal equivalent to their own. Indeed, the pursuit of one member for his supposed lack of care so roused the feelings of other members in reaction that dissension appeared in the ranks of the Council itself, and the President and Honorary Treasurer resigned in protest. Such dissension was, however, unique and soon yielded to mediation; the officers rejoined the Society, largely at the instance of Bernard Dyer.

I do not remember ever to have heard of another such instance of disagreement within the Society, certainly never of one that led to such drastic action. Even in the negotiations that led to the great changes of recent years—the alteration of our name and the abandonment of professional objects—the greatest goodwill prevailed. We have always appeared the most united of scientific societies in this country and the most renowned for the friendship existing between its members.

It was to a Society with this reputation for kindliness and goodwill that I was introduced at the outset of my own practical experience of chemistry.

We were then throwing off the worst effects of the first great war to have engaged this country's attention for a number of generations; we looked forward to a period when war should be no more, when the good things of the earth could once again be at our service freely; and with the knowledge gained in the last few years at our disposal, we saw in front of us a period of peace and unlimited prosperity. That this was not to be enjoyed in the manner we hoped became apparent only later. But it was in the atmosphere of hope and progress that I entered the laboratory of E. R. Bolton, then Honorary Secretary of the Society. I can claim therefore, as few others can, that from the outset of my practical

experience of chemistry, as applied to natural products, I have been under the wing of the Society. Years before I became a member I was being instructed in its ways, and I think that many of the ideas of progress that were floating around in the Council, and many of the schemes that offered themselves for improving the lot of analytical chemists, came to my ears far earlier in the nineteen twenties than could have been expected. This is not, of course, to suggest that Bolton or any of his colleagues ever disclosed matters to a very junior analyst that should have remained in the Council room; very much to the contrary. But there was a kindliness about that I shall never forget; an interest taken by the senior members of the Society in the new recruits, and indeed in those who might be recruits, that speaks volumes in praise of the great men of the period. I believe we still have this interest to-day; it is true that it is not so easy to show it, with our so greatly increased membership. But I still find plenty of evidence that help is there for all who want it, and a sympathetic and helpful outlook to young chemists remains among our chief characteristics.

There is no doubt that we were then emerging as a Society with a future as well as a past. Gone were the days of the eighties when we nearly amalgamated with the Institute of Chemistry on the grounds of similarity of objects. Now it was clear that our function lay in the furtherance of analytical chemistry, and not in qualifying men to practice it, though for many more years we were to look after the professional status of public analysts with a very jealous eye. In this period your Presidents added, as I have said, to their addresses some ideas for helping the progress of our branch of the profession of chemistry. We widened our outlook on Analytical Chemistry, and thereby strengthened our standing in the world. But let us not forget the activities of our early forebears. Had the need not arisen for them and for the thrust they used in advancing the analytical chemistry of food and drugs, we should not have seen so quick an advance in analytical chemistry generally or in the welfare of our Society.

The days since 1940 have been, I suppose, even more difficult from the point of view of carrying out any practical policy than those that followed the First World War. Our viewpoint certainly seemed more rational. We had the great fillip derived from the impact of science on the community to help our expansion; and this we organised to our advantage by the setting up of subject groups. I have always thought that this practical idea, introduced as it was in the dark days of the war, to have been one of the finest that we have ever had, and its implementation to have been one of the most practical. But expansion was not limited to the starting up of groups: the Society itself and its Sections, soon to number four in all, were pushing ahead. Meetings, perhaps rather sparsely attended during the war, found themselves with a greater audience than even the Chemical Society's room could hold. We had succeeded in popularising them. How did this come about? I think many of you know the answer; it lay in the deliberate adoption by those then responsible for choosing the programmes of meetings of a settled policy designed to exactly the end that was achieved.

It is of course arguable whether it is better to interest a large number of people at a given meeting by the choice of a popular subject, or to concentrate on a subject of limited appeal and gather only a small audience. Good will come from either type of meeting; but it has been felt very strongly that it is the larger meetings that redound most to the Society's credit and help it best to advance the knowledge of its members. Perhaps there is room for both kinds of meeting; we have had both in recent years. We have, too, tried the experiment of holding meetings addressed by distinguished foreign chemists, and these have proved most successful. There is no doubt whatever that such meetings should be continued. With the right lecturer we can continue to fill the lecture room of the Royal Institution, and provide what is perhaps one of the largest audiences in this country for a chemical lecture to-day.

It seems only right to me that I should in relinquishing the Presidential Chair of this Society, which nurtured me and through which I have learnt almost all I know about analytical chemistry, bring before you some thoughts such as these on the means which we have adopted for furthering our objects; and I feel that if I speak of our meetings I should also speak of our journals as well. I am sure that you will all agree with me that from the scientific point of view both *The Analyst* and *Analytical Abstracts* are highly successful. It is part of your Council's declared policy to make them as nearly self-supporting as possible in the next year or so. The cost of the journals is mounting rapidly. It now costs about £100 to print a paper of average length in *The Analyst*, and nearly fifty shillings for each abstract.

It is believed that after the next year or two it may prove very difficult for the Chemical Council to make grants even for the publication of original work in pure chemistry, let alone for the publication of abstracts. We are therefore faced with the prospect of having to cut our coat according to our supply of cloth; in other words, of making quite sure in the immediate future that the cost of producing our journals does not exceed the funds we can raise ourselves. It is true that there might be a possibility of persuading industry to help us, but success in such a direction would certainly depend on outstanding quality in the publications. Now, therefore, is the time for us to take stock and to see what we can do.

One's first reaction is that some form of curtailment of printed matter is wanted. I believe that we could well compress most of the chemical papers that are published in this country to-day into a fraction of the space they occupy. I do not for a moment advocate the suppression of anything that is useful in analysis or to analysts, and I am sure this is not necessary. But most writers use many more words in describing their work than are needed, either unwittingly or even in some instances from a desire to impress. To some length is synonymous with importance; to many of us it can be pretentious and boring; and I am sure that to most the short paper, streamlined and precise in its statements, is the most acceptable and of the greatest interest. When, therefore, an author has written a paper, I would counsel him to dissect it critically and prune it remorselessly. He will be surprised how much it improves. And at the same time not only will the reputation of the author grow, but so will that of the journal.

With abstracts the same principles apply. I yield to none in appreciation of what we have done in the last few years in providing an acceptable abstracts journal of our own, and I believe that a similar high opinion of it is held in industry. Certainly sales of *Analytical Abstracts* are rising satisfactorily. Nevertheless, in the changing world in which we find ourselves to-day we need to streamline the journal. I believe this can be done by making a judicious selection of papers, recording all in title, and adding abstracts where they are justified, of length depending on the importance of the contents of the paper. It can be objected that any form of selection is bad and that all analytical papers should be abstracted. We can no longer do this. And I am sure that we shall gain immensely by boldly adopting a policy such as I have outlined, not only in our finances, but also in increased services to our readers.

Anniversary Dinner

In the evening following the Annual General Meeting, a Dinner to celebrate the eighty-third anniversary of the Society was held, by kind permission of the Master and Wardens of the Vintners' Company, at Vintners' Hall, Upper Thames Street, London, E.C.4. The members and guests, numbering 102, were received by the President, Dr. K. A. Williams, B.Sc., A.Inst.P., M.Inst.Pet., F.R.I.C., and Miss Mamie Olliver, M.Sc., F.R.I.C. The President afterwards took the Chair at the Dinner.

The guests of the Society and of the President included The Honourable Mr. Justice Lloyd-Jacob, M.A., D.C.L., and Lady Lloyd-Jacob; Professor F. Bergel, D.F.C., D.Phil., Ph.D., F.R.I.C. (representing the Chemical Society), and Mrs. Bergel; D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C. (President of the Royal Institute of Chemistry), and Mrs. Kent-Jones; Julian M. Leonard, M.I.Chem.E. (President of the Society of Chemical Industry), and Mrs. Leonard; Frank Hartley, B.Sc., Ph.D., F.P.S., F.R.I.C. (representing the Chemical Council), and Mrs. Hartley; Eric Voelcker, A.R.C.S., F.R.I.C. (President of the Association of Public Analysts), and Mrs. Voelcker; and Lindsay R. Ring and Mrs. Ring.

The Loyal Toast was proposed by the President.

The Honourable Mr. Justice Lloyd-Jacob proposed the Toast of The Society. He said that it had been a great honour and a great pleasure to be associated with the Society. He had assisted in the foundation of one of its more important institutions, the Analytical Methods Trust. As time had passed, the interests he and the Society had in common had steadily increased. It was a pleasure to be proposing this Toast, particularly because this year saw the Golden Jubilee of the Society's registration as a Company limited by guarantee. The Toast of The Society was coupled with the name of the President.

The President, Dr. Williams, in replying, said that Council had asked Mr. Justice Lloyd-Jacob to become an Honorary Member of the Society. He had Sir George's permission to say that he would be pleased to accept. This announcement was greeted with applause.

The President continued that he had asked Sir George to propose this Toast for many reasons, not the least being that he had first been introduced to the Society by the late H. E. Cox just before he died. Sir George, at the invitation of Dr. Cox, had accepted the duty of giving a Bernard Dyer Memorial Lecture and had since dined twice with the Society. He was the Chairman of the Analytical Methods Trust. The President added that all members would want to thank him for doing the Society the honour of accepting Honorary Membership.

In conclusion, the President recalled that earlier in the afternoon he had produced at the Annual General Meeting the Society's first Minute Book. In it was described how, after the first or second annual meeting of the Society, 26 people had sat down to such a good dinner that they had voted to continue the custom "every year." In spite of a lapse of 30 years at the beginning of the century, this anniversary dinner had again become a regular institution. Once more members of the Society had enjoyed themselves, and he wanted to return most hearty thanks to the Master and Wardens of the Vintners' Company for their permission to hold the dinner in their fine hall.

Dr. A. J. Amos proposed the Toast of The Guests. He said that he had often had occasion to present a case before a High Court Judge, but although he felt free from judicial interruption if he should stray in his remarks, the Society had provided a curb by inviting his partner to reply for the Guests. He was pleased that the guest of honour should be Sir George Lloyd-Jacob, Chairman of the Analytical Methods Trust and the Second Bernard Dyer Memorial Lecturer. Among the other guests was Mr. Eric Voelcker, president of the Association of Public Analysts. Our Society was inextricably linked with the Association: the Society's new President had been chosen from the ranks of the Association; and Mr. Voelcker's father and uncle had both been Presidents of the Society. He welcomed the representatives of the three chartered bodies. The Chemical Society was represented by an Honorary Secretary, Professor Bergel, whose interests in chemistry had ranged from life-giving vitamins to death-dealing carcinogenic compounds. The Society of Chemical Industry was represented by its President, Mr. Julian Leonard, who, he was pleased to see, was now recovering from his operation, although he was still encased in plaster. The Royal Institute of Chemistry was represented by its President, Dr. Kent-Jones; a particularly welcome guest not only because he had been President of our Society for two years, but also because in this year they were celebrating the Silver Jubilee of their business partnership, and he could not have had, nor would he have wished for, a better partner. Dr. Hartley represented the Chemical Council, a body that did much for the Society in helping to keep the accounts in black rather than in the red—and as the Society's new Treasurer he was glad to know he had a "friend at court." Finally, and by no means least, he welcomed the ladies. They brought gaiety, charm and colour to these gatherings: they cause the conversation to turn from test-tubes to Terylene; from lipids to lipsticks. It might be that the ladies had to be told that reducing substances were not for slimming and that spectroscopy had nothing to do with the H line; but they appeared to know the value to the analyst of standard curves! The Toast of The Guests was coupled with the name of Dr. Kent-Jones.

Dr. Kent-Jones replied for the guests. He was glad that the Society had elected Dr. Amos as Honorary Treasurer: he was undoubtedly one of those who would lead the Society when many who were present would be incapable of doing so. He had been in chemistry for well over 30 years, and whenever he was asked what had been his greatest discovery, he always replied: Bill Amos.

The President, Dr. Williams, drew attention to the fact that the Society had just experienced bigger changes in direction than had happened for a long time. He thanked Mr. Allport, the retiring Honorary Secretary, and the other retiring officers, for their services to the Society, and welcomed the new officers. He then invested Dr. J. H. Hamence with the Presidential Badge and wished him success during his tenure of the office. Dr. Hamence replied by thanking Dr. Williams on behalf of the new officers, and at the same time thanked him on behalf of the Society for the work he had done, not only in the past two years as President, but over the last decade during which he had guided the Society as well. He presented him with a replica of the Society's badge to wear as Past President.

Dr. Williams led a round of applause for Miss Mamie Olliver, who had so ably supported him during the reception and dinner.

Analytical Methods Committee

REPORT PREPARED BY THE ESSENTIAL OIL SUB-COMMITTEE

The Determination of Linalol in Essential Oils

THE Analytical Methods Committee has received the following report from its Essential Oil Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

INTRODUCTION—

The investigation was undertaken by the Sub-Committee on Essential Oils under the Chairmanship of Mr. W. H. Simmons, the other members of the Sub-Committee being: Mr. A. J. M. Bailey (Honorary Secretary), Mr. J. F. Charpy, Mr. C. W. Cornwell, Dr. G. W. Ferguson, Dr. D. C. Garratt, Mr. H. T. Islip, Mr. P. McGregor, Mr. W. M. Seaber, Mr. J. H. Seager and Mr. G. E. Smith.

EXPERIMENTAL WORK—

Several methods of determining linalol were investigated and, as a result, two were found worthy of more exhaustive consideration—the method of Glichitch[1] and that adopted by the Essential Oil Association of the U.S.A.[2] and originally described by Fiore.[3]

Collaborative work was first carried out on the Glichitch method. This method proved satisfactory provided that strict attention was paid to the purity of the reagents used; however, the chief disadvantage of the method lies in the length of time taken for the determination, which is at least four days.

TABLE I

DETERMINATION OF TOTAL LINALOL AND OIL OF BOIS DE ROSE BY THE METHOD OF THE ESSENTIAL OIL ASSOCIATION OF THE U.S.A. (FIORE METHOD)

	Total linalol in					
	Linalol			Oil of bois de rose		
Laboratory	Variation,* %		Average, %	Variation,* %		Average, %
1	96·9 96·0	0·9	96·4	89·6 88·9	0·7	89·4
2	93·9 93·8	0·1	93·8	87·3 87·0	0·3	87·2
3	95·7 93·4	2·3	94·2	90·8 86·5	4·3	88·9
4	95·5 95·0	0·5	95·2	88·5 87·0	1·5	87·9
5	96·5 95·9	0·6	96·2	88·7 88·3	0·4	88·5
6	92·1 87·7	4·4	89·7	85·3 83·6	1·7	84·3
7	93·5 92·8	0·7	93·1	88·1 87·2	0·9	87·8
8	96·4 93·6	2·8	95·3	89·5 85·6	3·9	87·1
9	96·2 94·4	1·8	95·5	90·3 87·5	2·8	88·8
10	89·0 81·5	7·5	84·9	—		—

* Maximum and minimum results only are given.

COMMENTS—

Laboratory 10—"Our results seem curious, and we suggest our acetyl chloride must have deteriorated."

Attention was then turned to the Fiore method and the considerable amount of collaborative experimental work done yielded encouraging results, although certain members of the Sub-Committee obtained results that were erratic, largely owing to the use of impure reagents. The collated results of the final collaborative test are shown in Table I.

TABLE II

DETERMINATION OF LINALOL IN LINALOL AND BOIS DE ROSE BY THE ORIGINAL GLICHITCH METHOD

Laboratory	Total linalol in Linalol, %	Total linalol in Oil of bois de rose, %
1	89·53, 89·70	83·84, 84·27
2	93·9, 93·9	87·5, 87·6
3	89·9, 90·6	86·6, 86·2
4	94·70, 94·86	87·47, 88·54
5 (Analyst A)	92·8, 92·6	85·6, 85·0
6	92·4, 91·7	87·9, 87·2
7	83·8, 83·5	84·4, 84·5
8	94·1, 94·1	86·9, 86·8
9	87·8, 87·8	81·1, 81·9
Additional results—		
1 (Fiore method)	92·93, 93·12	85·68, 85·38
1 (Glichitch method; kept at 20° C)		
5 (Glichitch method; Analyst B)		
5 (Fiore method)	94·8, 94·3	87·4, 87·3
9 (Glichitch method; kept at 20° C)		

COMMENTS—

Laboratory 1—"I consider that the results of the Glichitch method are far too low, but the material was left at room temperature over the week-end and this temperature must have been very low, as there was no heat in the factory. I am having a fresh lot started next week, keeping the temperature at 20° C by means of a thermostat."

Laboratory 9—"The mixture stood for exactly 72 hours at a room temperature of probably not more than 10° C for almost all this period (due to a cold week-end in an unheated laboratory). The determinations were repeated, keeping the temperature of formylation at 20° C."

TABLE III

DETERMINATION OF LINALOL IN OIL OF BOIS DE ROSE BY THE REDRAFTED GLICHITCH METHOD

Laboratory	Formylation	Total linalol %
1	1st	89·7, 89·5
	2nd	89·4, 89·4
2	1st	88·2, 88·2
	2nd	88·3, 88·3
3	1st	89·7, 90·8
	2nd	89·6, 89·3
4	1st	89·2, 88·9
	2nd	89·4, 89·4
5	1st	86·3, 86·7
	2nd	86·6, 86·7
6	1st	88·3, 88·0
	2nd	87·8, 87·9
7	1st	86·9, 86·8
	2nd	87·4, 87·1
8	1st	LOST, 87·6
	2nd	87·0, 87·0
9	1st	89·6, 89·5
	2nd	88·8, 88·7
10	1st	88·9, 88·7
	2nd	88·9, 88·6

The Glichitch method was then reconsidered and a fresh series of collaborative experiments was undertaken. Table II shows the results of this collaborative work, together

with members' comments, on samples of (*a*) linalol and (*b*) oil of bois de rose. In view of these results the method was redrafted and another series of experiments was carried out on a further sample of oil; the results of this work are shown in Table III. These collated results fell into two groups, three of the laboratories (numbers 5, 7 and 8) recording lower results than the other seven, and subsequent work (see Table IV) by two of the laboratories —one from each group—showed that this discrepancy was due to variations in the saponification stage of the method; this discrepancy, however, was not greater than had occurred with ester determinations.[4]

TABLE IV

TOTAL ALCOHOLS AS LINALOL

	Formylations			
	Laboratory 9		Laboratory 7	
Saponifications	1	2	1	2
Laboratory 9	89·2%	88·8%	88·4%	88·2%
Laboratory 7	87·9%	86·6%	87·3%	87·4%

The data in Tables III and IV were analysed statistically, the results being shown in Tables V and VI.

Analysis of the data in Table III—After the insertion of a calculated value of 87·6 to supply that missing from the results from Laboratory 8, the data were analysed by standard methods; the results of this are summarised in Table V. From this analysis it is estimated that the standard deviation of a single determination (one formylation, one saponification) in a laboratory chosen at random would be $(V_s + V_f + V_l)^{\frac{1}{2}} = 1{\cdot}1515$, when levels are of the order of 88·4 per cent., *i.e.*, the grand mean of the experiment. The coefficient of variation is 1·3 per cent. Using the value of t appropriate for 9 degrees of freedom, it can be calculated that a series of single determinations made by a number of laboratories would show a total range of rather more than 5·2 per cent. at P = 0·95 level.

Since both V_s and V_f are small compared with V_l, the magnitude of the estimated error is not appreciably reduced by making replicate determinations within laboratories.

TABLE V

SUMMARISED RESULTS OF STATISTICAL ANALYSIS OF DATA IN TABLE III

Source of variation (1)	Degrees of freedom (2)	Mean squares (3)	Variance ratio (4)	Component (5)
Between laboratories (L)	9	4·99169	L/F = 23·9***	$V_s + 2V_f + 4V_l$
Formylations within laboratories (F) ..	10	0·20875	F/S = 4·06**	$V_s + 2V_f$
Saponifications within formylations (S)	19	0·051316	—	V_s

*** = Significant at 0·1 per cent. level. ** = Significant at 1·0 per cent. level.

On equating columns (3) and (5), the components of variance were calculated to be—

Saponifications	(V_s)	0·051316
Formylations	(V_f)	0·078717
Laboratories	(V_l)	1·19574

Analysis of the data in Table IV—The results of this analysis are summarised in Table VI, and it is concluded that the difference between the determinations by the two laboratories arises wholly in the saponification stage.

TABLE VI

SUMMARISED RESULTS OF STATISTICAL ANALYSIS OF DATA IN TABLE IV

Source of variation	Degrees of freedom	Mean squares	Variance ratio
Saponifications between laboratories	1	3·645	20·0*
Formylations between laboratories ..	1	0·180	0·99 N.S.
Formylations within laboratories ..	2	0·362	1·99 N.S.
Residual	3	0·182	—

* = Significant at 5 per cent. level. N.S. = Not significant.

CONCLUSIONS—

It is the opinion of the Sub-Committee that the Glichitch method should be used in view of its greater dependability. Details of the quicker Fiore method are also given, but it must be stressed that anomalous results may be obtained from time to time.

The two methods are described in the Appendix.

APPENDIX

RECOMMENDED GLICHITCH METHOD

REAGENTS—

Acetic anhydride—Analytical-reagent quality.

Formic acid, 98 to 100 per cent. w/v—Analytical-reagent quality.

Sodium bicarbonate solution, 5 per cent. w/v.

Sodium sulphate, anhydrous.

Aceto-formic acid reagent—To two volumes of acetic anhydride, previously cooled to at least 0° C, add slowly one volume of formic acid similarly cooled. Mix thoroughly and then heat the mixture slowly to 50° C, taking a total time of 15 minutes, and then immediately cool in an ice-bath. The reagent should be freshly prepared. (See Note 1.)

PROCEDURE—

Introduce 15 ml of aceto-formic acid reagent into a 125-ml glass-stoppered Erlenmeyer flask. Cool the contents to 0° C in an ice-bath and slowly add 10 ml of the oil, previously dried over anhydrous sodium sulphate and cooled to the same temperature.

Mix well and allow the mixture to stand for 72 to 96 hours at a temperature of 20° to 22° C. (See Note 2.) At the end of this time pour the contents of the flask into a separating funnel. Add 50 ml of ice-cold water, shake the mixture well and allow it to stand for 2 hours. Separate the oil and wash it successively with 50 ml of cold water, 50 ml of sodium bicarbonate solution and then with two 50-ml portions of water. Separate the oil, dry it with anhydrous sodium sulphate and then filter. Determine the ester value by the method described in Report No. 13 of the Essential Oil Sub-Committee to the Analytical Methods Committee.[4] (See Note 3). Calculate the percentage of linalol from the formula: $\frac{A \times 154{\cdot}2}{561 - 0{\cdot}28A}$, where A = ester value of the formylated oil.

NOTES—1. The reagent must be prepared precisely as described.

2. The temperature of formylation is critical and, if it is allowed to drop below 20° C, results may be low.

3. The dried formylated oil should be almost neutral and, in the determination of the ester value, not more than one drop of 0·1 *N* potassium hydroxide should be required to give a pink colour. The first pink colour is taken as the neutral point, since linalyl formate is readily hydrolysed.

FIORE METHOD

REAGENTS—

Dimethylaniline—Reagent quality, free from monomethylaniline and aniline. (See Note 1.)

Acetyl chloride—Analytical-reagent quality. (See Note 1.)

Acetic anhydride—Analytical-reagent quality.

Sodium sulphate, anhydrous.

Sodium sulphate solution—A 10 per cent. w/v solution of anhydrous sodium sulphate.

Sulphuric acid solution—A 2·5 per cent. w/v solution in sodium sulphate solution.

Sodium bicarbonate - sulphate solution—A 5 per cent. w/v solution of sodium bicarbonate in sodium sulphate solution.

PROCEDURE—

Introduce 10 ml of the oil, previously dried with anhydrous sodium sulphate, into a 125-ml glass-stoppered Erlenmeyer flask and cool in an ice - water mixture. Add 20 ml of dimethylaniline to the cooled oil and mix thoroughly; then add 8 ml of acetyl chloride and 5 ml of acetic anhydride. (The anhydride serves as a solvent to prevent crystallisation of the reaction mass.)

Cool the mixture for a few minutes and allow it to stand at room temperature for 30 minutes, after which immerse the flask in a water bath maintained at 40° ± 1° C for 3 hours. At the end of this time wash the acetylated oil as follows (it is important that each washing should be shaken vigorously for 30 seconds and the oil then allowed to separate)—

(*i*) twice with 75 ml of the sodium sulphate solution;

(*ii*) with 50-ml portions of the sulphuric acid solution until the washings are free from dimethylaniline (usually five washings are necessary);

(*iii*) twice with 25 ml of the sodium bicarbonate - sulphate solution; and

(*iv*) twice with 25 ml of the sodium sulphate solution.

Determine the ester value of the acetylated oil by the method described in Report No. 13 of the Essential Oil Sub-Committee to the Analytical Methods Committee.[4] (See Note 2.)

Calculate the total linalol from the formula: $\frac{A \times 154{\cdot}2}{561 - 0{\cdot}42\,A}$, where A = ester value of the acetylated oil.

NOTES—1. The dimethylaniline and acetyl chloride should be fully up to analytical-reagent quality standards at the time the test is carried out.

2. The dried acetylated oil should be almost neutral and, in the determination of the ester value, not more than one drop of 0·1 *N* potassium hydroxide should be required to give a pink colour. The first pink colour is taken as the neutral point, since linalyl acetate is readily hydrolysed.

REFERENCES

1. Glichitch, M. L. S., *Bull. Soc. Chim. France*, 1923, **33**, 1284.
2. "Determination of Linalool," General Test C, from the Specifications and Standards of the Essential Oil Association of the U.S.A.
3. Fiore, A. T., *News Capsule* (Essential Oil Association of the U.S.A.), 1943, **1**, No. 15.
4. Analytical Methods Committee, "The Determination of Esters," Report No. 13 of the Essential Oil Sub-Committee, *Analyst*, 1937, **62**, 541; and Addendum to Report No. 13, *Ibid.*, 1951, **76**, 387.

A Recording Spectrophotometric Titrimeter*

BY ROBERT A. CHALMERS† AND C. A. WALLEY

An apparatus is described for the determination of titrimetric end-points from an automatic recording of the rate of change of optical density of the solution being titrated. The apparatus is useful for the titration of very dilute solutions and of small amounts of more concentrated solutions.

SPECTROPHOTOMETRIC detection of the end-point in titrimetry has been described many times and has been reviewed by Goddu and Hume.[1] Usually the titration has been conducted manually and the results have been plotted on a graph. Marple and Hume[2] have pointed out that curiously little attempt has been made to adapt the technique for automatic detection of the end-point. The apparatus that has been described[2,3,4,5,6,7,8] has been of two main types; that in which a large change in optical density at the end-point has been recorded or used to operate a trigger mechanism, and that in which the optical density is recorded during the course of the titration. The second type of apparatus has the wider field of application, but it suffers from the disadvantage that the end-point is sometimes located at the intersection of two lines that cross at a very obtuse angle and so is difficult to determine exactly. In the present work the location of the end-point is made easier by recording the rate of change of optical density, *i.e.*, the first derivative with respect to volume of titrant added. The apparatus has been designed for the titration of microgram quantities, and gives results with a good degree of precision.

* Presented at the XVth International Congress on Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 8th to 16th, 1956.

† Present address: Chemistry Department, University of Aberdeen, Old Aberdeen.

Experimental

Apparatus—

A block diagram of the apparatus is shown in Fig. 1. A spectrophotometer, in this equipment a Unicam SP600, is fitted with a cell-compartment cover arranged to support rigidly a Pyrex-glass boiling-tube of diameter 1 inch, reduced in length so that the curved base of the tube is only just below the light-path of the spectrophotometer. Titrant is added from a micrometer-syringe burette driven by a synchronous electric motor through a gear train so that the burette discharges completely in about 40 seconds. The solution in the cell is stirred at about 5000 r.p.m. by a glass stirrer, which ends in a hollow bell with four holes in its wall and is driven by a universal electric motor controlled by a Variac. The stirrer and burette mechanism are mounted together with the tip of the burette just above the bell of the stirrer (see Fig. 2); the mounting is clamped to a heavy retort-stand placed on sponge rubber to prevent transmission of vibration to the rest of the apparatus. The burette has a spring-loaded plunger and its driving mechanism is fitted with a reversing switch, making it easy to reload the burette. The jet of the burette should be cemented or sealed to the barrel.

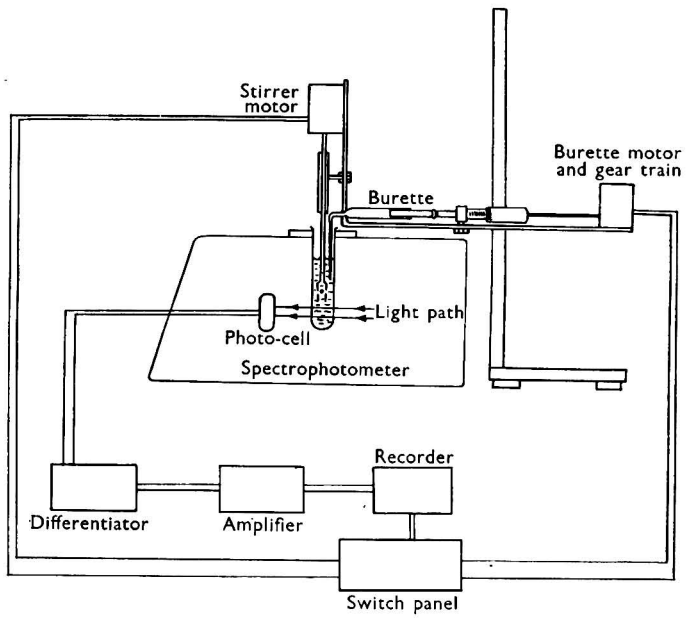


Fig. 1. Block diagram of recording spectrophotometric titrimeter

The output from the amplifying valve of the spectrophotometer is fed into a differentiating and amplyfing circuit, which has its output recorded by a Kelvin - Hughes Teledeltos high-speed recorder. The spectrophotometer output is connected to the differentiator through a jack-plug mounted on the spectrophotometer instrument panel. The amplifier is fitted with a gain control so that the recorded signal may be as large as possible without saturating the recorder. The maximum gain of the complete unit is such that a 1-cm deflection of the recorder pen occurs when the cathode of the spectrophotometer valve changes in potential at a rate of 15 mV per second. The spectrophotometer output contains a large signal at the frequency of the a.c. mains. The differentiator is therefore fed through a low-pass filter. In addition, the amplifier gain is arranged to fall rapidly for frequencies above 5 cycles per second. Switches are arranged so that the burette drive and the recorder can be switched off and on independently. Two switches, coupled by a connecting bar, are arranged so that, simultaneously, they switch off the burette drive, apply a magnetic brake to the drive motor and feed an a.c. signal into the recorder to mark the switching operation. The electronics circuit and the switching circuit are shown in Figs. 3 and 4. No steps are taken to exclude extraneous light.

PROCEDURE—

Two procedures are possible, one being an adaptation of the other. In the first, "Procedure A," a very dilute solution is titrated, the aliquot taken being large enough to fill the titration cell to the required depth. In the second, "Procedure B," a small aliquot of a more concentrated solution is used and must be diluted with water; the volume of water used is itself sufficient to fill the cell to the necessary depth and a blank titration must be performed upon it before the addition of the aliquot to be titrated.

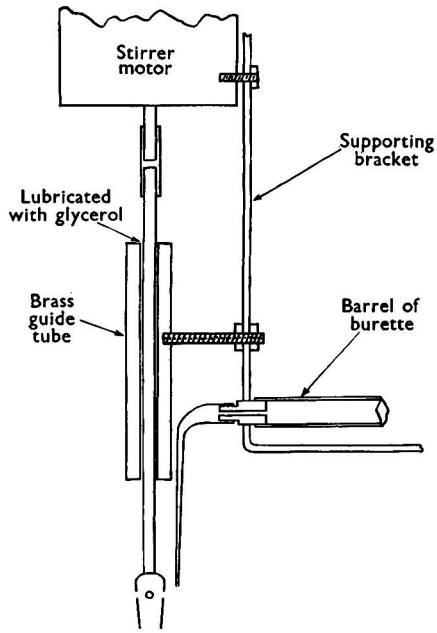


Fig. 2. Diagram of the stirrer assembly

Procedure A—Switch on the spectrophotometer, power unit, amplifier and recorder, and allow them to warm up for at least 10 minutes. Remove the barrel of the burette, fill in the usual way and replace it in the micrometer assembly in such a way that no air bubbles enter the jet or barrel, and then fill the burette completely. To do this, switch on the burette drive in the forward direction and collect the ejected titrant; switch off the burette, reverse the drive, immerse the burette jet in titrant contained in a suitable storage vessel, *e.g.*, a weighing bottle with a ground-over cap, and start the burette drive. When the micrometer head has gone just past the end of the graduations, stop the drive and remove the store of titrant. Switch to forward drive, switch on the burette drive and, as soon as liquid emerges from the jet, switch on the magnetic brake. Switch off the burette drive and then the magnetic brake. Wipe the surplus liquid from the jet with a piece of absorbent tissue. The burette is now ready for use, and any backlash has been taken up in the direction of drive. The sequence of switching operations is soon learnt, and is made obvious by study of the circuit.

Place in the cell a 25 or 30-ml aliquot of the solution to be titrated; its normality should not be greater than 1/80 that of the titrant. Lower the stirrer and burette assembly so that it does not project into the light-path, and does not touch the titration cell or spectrophotometer but is immersed with at least 1 inch of liquid above the bell of the stirrer. If the stirrer is too high in the solution, air bubbles will be stirred in from the vortex and will vitiate the results. Add any indicator necessary, and set the prism for a wavelength at which there is maximum difference in optical density between the fully titrated and untitrated solutions. Start the stirrer slowly from rest and increase its speed steadily to about 5000 r.p.m. If the stirrer is started too rapidly, there is a greater risk of loss by splashing. In titrations conducted in an ammoniacal medium, such as the determination of magnesium by means of

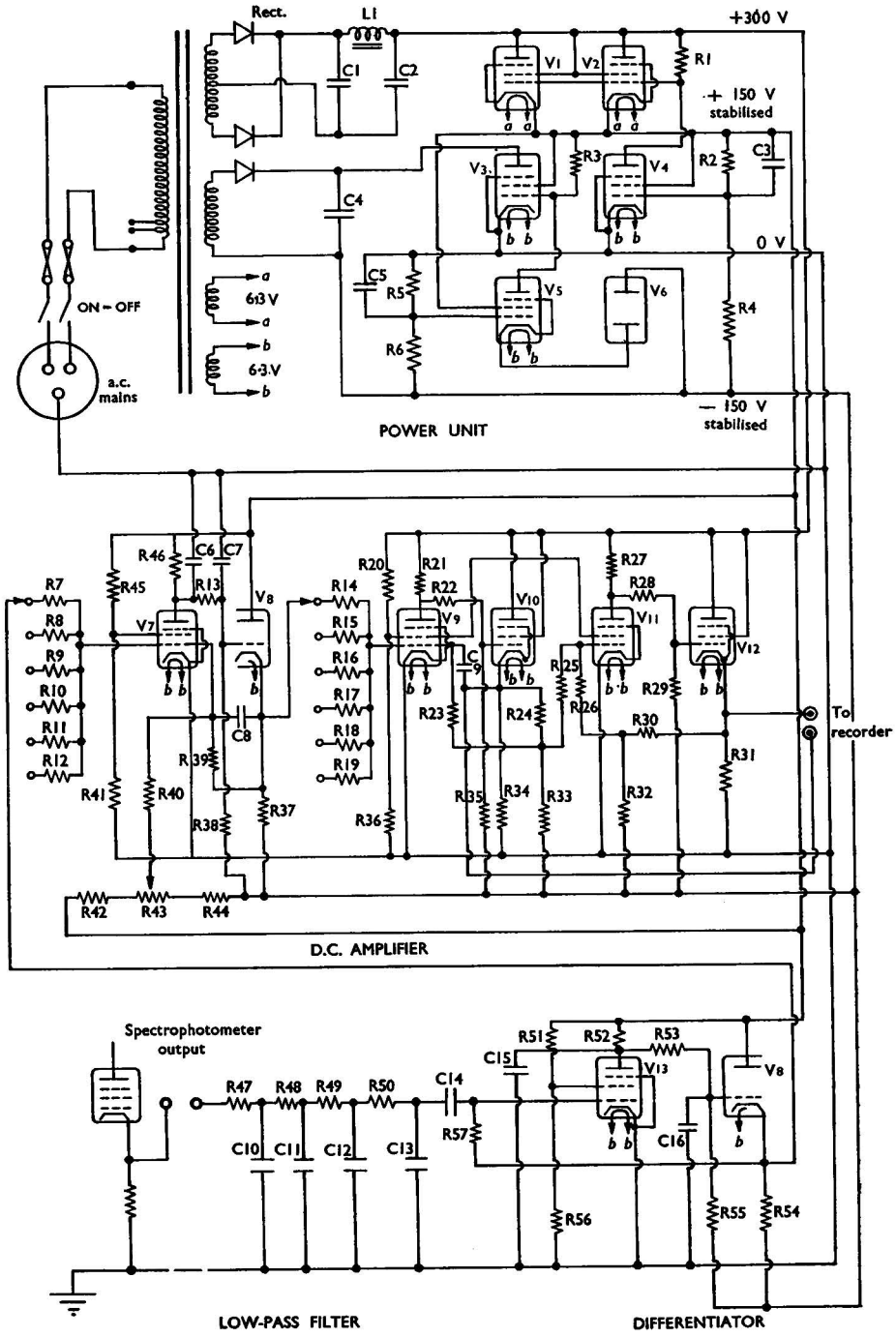


Fig. 3. Circuit diagram

C_1, C_2	= 8 μF	R_1	= 47,000 ohms
C_3, C_5	= 0·1 μF	R_2, R_4, R_{20}, R_{21}, R_{24}, R_{27}, R_{30}, R_{42}, R_{44}, R_{45}	
C_4	= 32 μF	R_{46}, R_{51}, R_{52}	= 220,000 ohms
C_6, C_{15}	= 0·02 μF	R_3	= 120,000 ohms
C_7, C_{16}	= 0·005 μF	R_5, R_6, R_{32}, R_{33}	= 470,000 ohms
C_8, C_9	= 0·002 μF	R_7, R_{14}, R_{37}, R_{54}	= 100,000 ohms
C_{10}, C_{11}, C_{12}, C_{13}	= 4 μF	R_8, R_{15}	= 180,000 ohms
C_{14}	= 0·5 μF	R_9, R_{16}	= 330,000 ohms
		R_{10}, R_{17}	= 560,000 ohms
		R_{11}, R_{18}, R_{22}, R_{28}, R_{53}	= 1 megohm
		R_{12}, R_{19}	= 2·2 megohms
		R_{13}	= 680,000 ohms
		R_{23}, R_{25}, R_{26}, R_{39}, R_{40}, R_{57}	= 6·8 megohms
L_1	= 10-henry choke	R_{29}, R_{35}, R_{55}	= 3·3 megohms
Rect.	= D55 rectifier	R_{31}, R_{34}	= 22,000 ohms
V_1, V_2, V_3, V_4, V_5	= EF91	R_{36}, R_{41}, R_{56}	= 390,000 ohms
V_6	= 85 A2	R_{38}	= 1·5 megohms
V_7, V_9, V_{11}, V_{13}	= EF86	R_{43}	= 100,000 ohms (SET ZERO)
V_8	= ECC83		
V_{10}, V_{12}	= EL90	R_{47}, R_{48}, R_{49}, R_{50}	= 8200 ohms

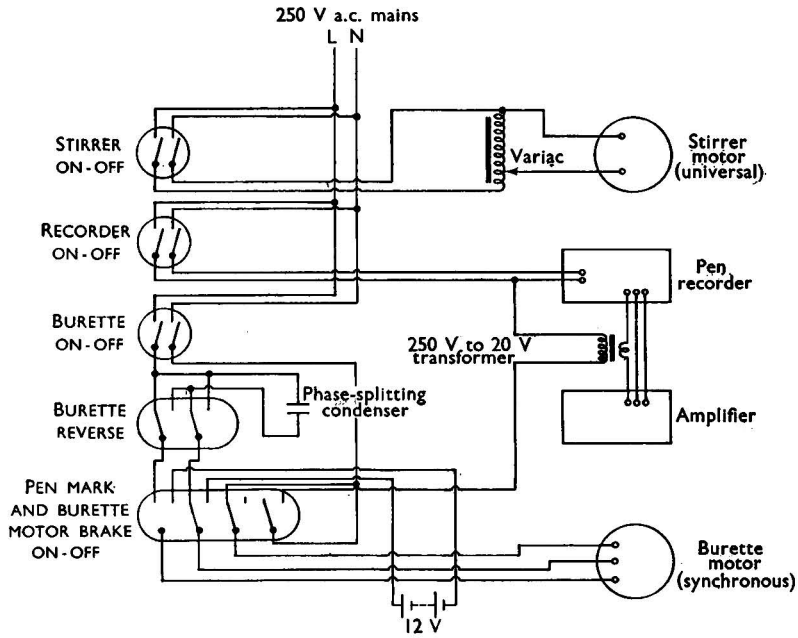


Fig. 4. Switching circuit

ethylenediaminetetra-acetic acid (EDTA) the stirring speed must be reduced to avoid stirring out bubbles of ammonia. The solution must be free from specks of dust or fibre (which would cause fluctuation in the output from the photo-cell as they are stirred through the light beam).

Adjust the dark-current, switch to the CHECK position on the spectrophotometer, and balance the meter needle by means of the slit control. Set the transmission dial at 5 per cent. transmission, and adjust the amplifier gain to give a large peak without saturating the recorder (this adjustment is first made by trial and error, but once found it remains valid for a particular type of titration). Take the burette reading, set the spectrophotometer to TEST and switch on the burette drive and the recorder. When the differential peak has appeared on the trace (see Fig. 5 (*b*)), switch on the magnetic brake - pen mark (this simultaneously stops the burette drive), stop the recorder, and switch off first the burette drive and then the magnetic brake - pen mark. Switch the spectrophotometer back to

DARK-CURRENT and take the burette reading. Raise the burette assembly from the cell, refill the burette, and remove, empty and wash the cell. The unit is now ready for the next sample. Interpret the record as described below.

Procedure B—Prepare the burette as described under "Procedure A." Place about 25 ml of water in the cell, add any indicator and reagents required, and titrate as in Procedure A, but record only the second burette reading. If necessary, add to the water a small amount of the solution to be titrated to ensure that titrant is consumed to reach the end-point. Add a 1 to 5-ml aliquot of the solution to be titrated (the normality of the diluted solution must not exceed 1/80 that of the titrant) and continue the titration as in Procedure A. Interpret the results as described below.

INTERPRETATION OF THE RECORD—

The ratio of distance on the paper to rate of delivery of titrant is first determined. The burette is filled and the backlash taken up as usual by means of the magnetic brake. The burette reading is taken, and the magnetic brake - pen mark, the burette drive and the recorder are switched on in that order. The magnetic brake - pen mark is switched off and is again switched on when about 50 to 60 cm of paper have run through the recorder; this starts and stops the burette. The recorder, burette drive and magnetic brake - pen mark are switched off in that order, and the burette reading is taken. This is repeated several times. Once the ratio has been determined it need be checked only at intervals. The record will appear as in Fig. 5 (*a*), from which it is seen that the distance AB corresponds to volume of titrant delivered.

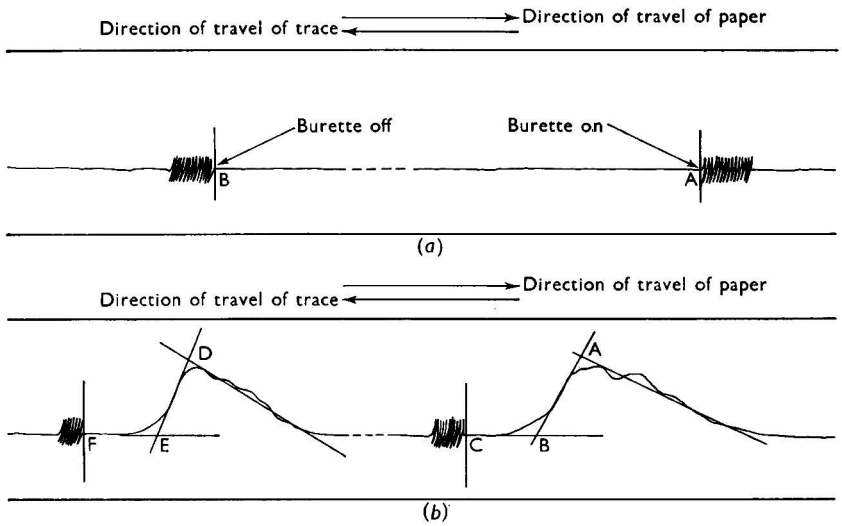


Fig. 5 (*a*) and (*b*). Trace recordings

The record of a titration made by Procedure B is shown in Fig. 5 (*b*). The right-hand peak represents the blank and the left-hand one the titration end-point. In Procedure A only one peak is recorded. The end-point is located by the construction yielding points B and E, which correspond to the same stage in the blank and actual titrations. Because the ratio of distance on the paper to volume of titrant varies slightly from experiment to experiment (the error observed was about 5 parts per 1000), it is better to measure not the distance from B to E (which would eliminate the need to take burette readings) but the amount of over-run from the end-point to the point of switch-off of the burette (BC or EF) and to subtract this from the volume of titrant added. In Procedure A the titre is the total volume delivered *minus* the volume of over-run. In Procedure B the titre is the total volume delivered after the blank run *plus* the volume of over-run on the blank and *minus* the volume of over-run on the titration. As the distances measured are usually only a few centimetres, the error from variation in paper speed is negligible.

This construction is preferred to the alternative one yielding points A and D as end-points. Usually the slope leading to D is irregular, probably because the stirring is not efficient enough to prevent local concentrations of titrant and rapid fluctuations in optical density just before the end-point. Further, because of the arc described by the pen of the recorder, it is necessary to use a cursor with this radius of curvature when measuring the over-run from A to C.

In both procedures a considerable amount of paper can be saved if the recorder is switched on just before the end-point. With a little practice the time to switch on can easily be judged by watching for the first appreciable deflection of the pen.

Results

The apparatus was used to perform various titrations by Procedure B, as follows—

(*a*) 0·200 to 0·600-ml portions of approximately 0·1 *N* hydrochloric acid were titrated with approximately 0·1 *N* sodium hydroxide; 0·3 ml of bromocresol purple indicator solution (obtained from The British Drug Houses Ltd.) was added as indicator;

(*b*) 0·200 to 0·600-ml portions of approximately 0·1 *N* calcium chloride were titrated with approximately 0·1 *N* disodium ethylenediaminetetra-acetate; the solution to be titrated was made alkaline, *i.e.*, pH greater than 10, by means of 2 *N* sodium hydroxide, and 0·15 to 0·20 ml of 0·1 per cent. w/v aqueous murexide solution (freshly prepared) was added as indicator,

(*c*) 0·200 to 0·600-ml portions of approximately 0·1 *N* magnesium chloride were titrated with approximately 0·1 *N* disodium ethylenediaminetetra-acetate; the solution to be titrated was originally slightly acid, and its pH was adjusted to about 10 by addition of 1 ml of a buffer solution composed of 7 g of ammonium chloride dissolved in 60 ml of concentrated ammonia solution and diluted to 100 ml with distilled water; 0·4 to 0·5 ml of a 0·1 per cent. w/v freshly prepared solution of Solochrome black WDFA in ethanol was added as indicator.

The paper speed throughout these experiments was 2·5 cm per second. The amount of indicator required is not critical, but the quantities mentioned should be taken as a guide. The results are presented in Table I and show good reproducibility and a linear relationship between the volumes of titrant and of solution titrated. The relatively large standard deviation of the titre in the EDTA titrations is a consequence of the bias introduced by the titrations with small volumes.

Table I

Results of various titrations

All solutions were approximately 0·1 *N*

Solution *A*	Solution *B*	Volume of solution *A* taken, ml	Volume of solution *B* required, ml	Number of determinations	Ratio *B*/*A*
HCl	NaOH	0·2000	0·1293 ± 0·0008	7	0·6464 ± 0·0040
		0·4000	0·2576 ± 0·0010	6	0·6442 ± 0·0026
		0·6000	0·3873 ± 0·0015	9	0·6454 ± 0·0024
					Mean 0·6453
					Standard deviation 0·0027
$CaCl_2$	EDTA	0·1000	0·0836 ± 0·0013	8	0·8360 ± 0·0130
		0·2500	0·2073 ± 0·0014	6	0·8291 ± 0·0057
			− 0·0010		− 0·0039
		0·4000	0·3337 ± 0·0006	4	0·8343 ± 0·0015
					Mean 0·8335
					Standard deviation 0·0070
$MgCl_2$	EDTA	0·1000	0·0732 + 0·0005	6	0·7320 + 0·0050
			− 0·0009		− 0·0090
		0·3000	0·2171 + 0·0018	5	0·7237 + 0·0060
			− 0·0010		− 0·0034
		0·5000	0·3613 ± 0·0011	4	0·7219 ± 0·0017
					Mean 0·7261
					Standard deviation 0·0056

Discussion

The errors likely to arise are those from measurements made on the burette and on the paper trace, and those from splashing of the liquid in the cell. The last-named error is probably negligible, since the volume of liquid in the cell is about 25 to 30 ml and any drops of spray will be of the order of 0·01 ml or less. Reading errors associated with reproducibility of burette discharge volumes have been found to be of the order of 0·0002 ml. The lengths are measured on the trace to the nearest 0·5 mm; the error in measurement together with the error from variation of paper speed gives an error of about 0·0004 ml. When account is taken of the error associated with the micrometer-syringe used to add the aliquots to the titration cell, the total observational error expected is about 0·0005 ml and this error will be independent of the volumes of titration liquid and titrant. That is to say, the relative error will decrease with increasing volume of titrant. In general, it is possible to perform titrations with not more than 0·5 ml of titrant with a reproducibility to 0·0015 ml or better. The difference between the observed and calculated errors may be associated with the method of locating the end-point or with loss by spray during stirring. The end-point could be more sharply defined by running the paper at a lower speed, but there would be a corresponding loss of precision in relating distance on the paper to rate of delivery of titrant. Loss by spray can be avoided only by designing a better method of stirring. The electrical parts of the apparatus could be improved by running the spectrophotometer lamp on direct current, so that the frequency response of the amplifier might be improved. The operation of the controls could be simplified, at the expense of additional complication, so that most of the switching sequence is done automatically.

One of us (R.A.C.) wishes to acknowledge the receipt of a Grant-in-aid from the Royal Society and a grant from the Research Fund of Durham Colleges, University of Durham.

References

1. Goddu, R. F., and Hume, D. N., *Anal. Chem.*, 1954, **26**, 1740.
2. Marple, T. L., and Hume, D. N., *Ibid.*, 1956, **28**, 1116.
3. Barredo, J. M. G., and Taylor, S. K., *Trans. Electrochem. Soc.*, 1947, **92**, 437.
4. Hickman, K., and Sanford, C. R., *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 65.
5. Juliard, A., Van Cakenberghe, J., and Heitner, C., *Ind. Chim. Belge*, 1952, **17**, 25.
6. Müller, R. H., and Partridge, H. M., *Ind. Eng. Chem.*, 1928, **20**, 423.
7. Malmstadt, H. V., and Gohrbandt, E. C., *Anal. Chem.*, 1954, **26**, 442.
8. Malmstadt, H. V., and Roberts, C. B., *Ibid.*, 1955, **27**, 741.

Department of Geology
Durham Colleges
Durham

Department of Electrical Engineering
King's College
Newcastle upon Tyne

August 27th, 1956

The Colorimetric Determination of Cadmium, Chromium, Copper, Iron, Lead, Manganese, Nickel and Zinc in Sewage and Industrial Wastes

By A. A. Christie, J. R. W. Kerr, G. Knowles and G. F. Lowden

Methods for the determination of small amounts of metals in sewage and industrial wastes have been examined. Published procedures for cadmium, lead and nickel were found to be satisfactory, but some modifications were required in the methods for chromium, copper, iron, manganese and zinc, and descriptions of the recommended procedures for these metals are given.

Investigations into the effect of the discharge of wastes containing metallic salts on sewage purification and on fish life necessitate agreed and simple methods of analysis, and the work described in this paper was carried out at the request of the Committee engaged in revising "Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents."[1]

The more commonly occurring metallic salts in industrial effluents are those of cadmium, chromium, copper, iron, lead, manganese, nickel and zinc, and their determination in concentrations as low as 0·1 p.p.m. is necessary. Various simple colorimetric procedures were tested, and the amount of interference caused by other metal ions was noted and, if possible, eliminated. As well as being suitable for measurement in photo-electric absorptiometers, the colours can be measured in visual colorimeters or by visual comparison with a row of standards in Nessler tubes.

The method finally recommended is given in full only if it differs from published procedures; if a simple amendment suffices or if the published method is completely satisfactory, the reference to the original publication is considered sufficient. Methods published for cadmium,[2] lead by the mono-colour dithizone procedure[3] and nickel by dimethylglyoxime[3] were found to be satisfactory for the types of sample concerned, and are not dealt with further in this paper.

Procedures are recommended for chromium, copper, iron, manganese and zinc and, although the methods are not original, they are set out in some detail, as no one reference could be found to incorporate all the modifications required.

Preliminary Treatment of Sample

Preliminary treatment of sewage effluents and trade wastes is necessary to destroy organic matter and bring metals into solution. Butts, Gahler, and Mellon[4] give wet-oxidation methods for this, but tests in the present work showed that organic matter is more easily destroyed by ignition at 300° C after wet-oxidation with a mixture of nitric and perchloric acids; the residue after the ignition is soluble in hydrochloric acid. Tests showed that cadmium and zinc are not lost at 300° C, and that the perchlorate ion, which may be present in the solution obtained for analysis, does not affect determinations with dithizone.

Method

All reagents should be of recognised analytical quality.

Procedure—

Place a known amount of the sample (about 500 ml) in a beaker, add 5 ml of concentrated nitric acid and evaporate to small volume. Transfer to a porcelain or silica basin and further reduce the volume to about 15 ml by placing the basin on a water bath. Add 2 ml of 60 per cent. perchloric acid and gently evaporate to dryness with a stronger heat, for example, with a bunsen burner, removing the source of heat immediately the sample becomes dry. Ignite at not more than 300° C for about 40 minutes. Dissolve the residue by adding 2 ml of 5 *N* hydrochloric acid and a small amount of distilled water and heating gently. The residue after ignition may have a brown-black colour or the dish or solution may have such a colour, indicating that the organic material has not been completely oxidised. In this event, after adding the hydrochloric acid and water, add 2 ml of 60 per cent. perchloric acid and 2 ml of concentrated nitric acid and repeat the procedure of evaporation to dryness followed by ignition and solution. If a clear solution is obtained without production of a precipitate or a turbidity, proceed with the determination of the metals.

A white turbidity or white precipitate at this stage may be silica or lead sulphate. If such a precipitate is obtained, remove it by filtration, using a sintered-glass crucible of porosity 4, washing it with a few millilitres of distilled water. Proceed with the determinations of the metals, except lead, in the filtrate and washings.

Chromium

Diphenylcarbazide produces a red-violet colour with dichromate, and this reaction is used for the determination of small amounts of chromium, which is first converted to dichromate by oxidation with ammonium persulphate, with silver nitrate as catalyst.

Comparisons were made of two versions of the method, in which use was made of different procedures for countering the difficulty arising from the presence of chloride, which gives an opalescence or precipitate with the silver nitrate. Both versions were critically examined.

Investigation of procedures for removing chloride

Procedure A—

The first stage is to remove chloride by evaporation to fuming with sulphuric acid, and this is followed by neutralisation. Unfortunately, all alkalis tried for the neutralisation,

including analytical-reagent grade sodium carbonate, contained sufficient chloride to make visual determinations of about 0·1 p.p.m. of chromium very difficult. Accordingly, it was decided to modify the method by omitting the neutralisation of the acid, and to this end tests made showed that full colour development occurred in less than 1 minute for concentrations of sulphuric acid of between 1 and 20 per cent., and that the colour was stable for at least 1 hour for 1 and for 5 per cent. of sulphuric acid.

Tests on interference by iron showed that with iron to chromium ratios of 20 to 1 and 100 to 1 (with both 0·1 and 1·0 p.p.m. of chromium) interfering yellow and orange colours made visual determination impossible. However, further tests showed that addition of phosphoric acid eliminated interference by iron up to an iron to chromium ratio of 200 to 1, for the range 0·1 to 1·0 p.p.m. of chromium, whereas use of either sodium fluoride, sodium citrate or sodium tartrate was less satisfactory.

Manganese can also interfere, being oxidised to the coloured permanganate ion by persulphate. An unsuccessful attempt was made to find a more convenient reducing agent than sodium nitrite to reduce the permanganate, and at the same time leave dichromate and silver ions unaffected; among the reducing agents tried were oxalic acid, hydrogen peroxide, sodium arsenite, ethanol and sodium azide. Accordingly, reduction with sodium nitrite was chosen, although care must be taken to avoid an excess, since it causes a slight reduction of dichromate also.

PROCEDURE B—

Snell and Snell[5] avoid the difficulty arising from the presence of chloride in the reagents by adding hydrochloric acid and filtering off the silver chloride, and so leaving no silver in solution, but tests showed that chromium was retained on the filter. This was significant when a sintered-glass filter of porosity 4 was used, and greater still when Whatman No. 42 filter-papers were used, typical results being as follows—

Chromium initially present, p.p.m. ..	0·1	0·5	1·0
Chromium finally present, p.p.m. ..	0·0	0·3	0·6

In these experiments the precipitate was washed with three 5-ml portions of dilute hydrochloric acid (1 + 99) and the washings were added to the filtrate.

For these reasons procedure A, with some modification from the published procedure to eliminate interference from iron and chloride, is recommended.

METHOD

REAGENTS—

All reagents should be of recognised analytical quality.

Diphenylcarbazide solution—Dissolve 0·2 g of diphenylcarbazide in 100 ml of ethanol. Keep the solution in a refrigerator if possible; discard it when it becomes brown in colour.

Sulphuric acid, diluted (1 + 1)—Add 1 volume of concentrated sulphuric acid to 1 volume of distilled water.

Silver nitrate solution—Dissolve 5 g of silver nitrate in 100 ml of distilled water.

Sodium nitrite solution—Dissolve 1 g of sodium nitrite in 100 ml of distilled water.

Ammonium persulphate.

Phosphoric acid, sp.gr. 1·75.

Standard chromium solution—Dissolve 0·283 g of dried potassium dichromate in water and dilute to 1 litre. Dilute 10 ml of this stock solution to 200 ml with distilled water so that—

$$1 \text{ ml} \equiv 0{\cdot}005 \text{ mg of chromium.}$$

PROCEDURE WHEN CHROMIUM IS PRESENT AS CHROMATE—

To an aliquot of the original sample, filtered if necessary through sintered glass and containing not more than 0·05 mg of chromium, add 5 ml of diluted sulphuric acid (1 + 1) and dilute to 50 ml with distilled water. Add 1 ml of phosphoric acid, mix and then add 2 ml of diphenylcarbazide solution. Mix again and set aside for 5 minutes. Compare with standards similarly prepared, either in Nessler tubes or a visual colorimeter. Alternatively, determine the absorption of light at about 540 mμ in a photo-electric absorptiometer, when a calibration curve should be prepared by using standard chromium solutions treated as for the sample.

PROCEDURE FOR TOTAL CHROMIUM—

To an aliquot of the prepared solution containing not more than 0·05 mg of chromium and diluted to about 30 ml with distilled water, add 5 ml of diluted sulphuric acid (1 + 1). Remove any chloride by evaporation to fuming. Cool the solution, dilute it to 30 ml with distilled water, heat it nearly to boiling and add 1 ml of silver nitrate solution and then about 1 g of ammonium persulphate. Boil for at least 10 minutes until the total volume is less than 50 ml and then cool. If a pink colour due to manganese is present at this stage, add sodium nitrite solution drop by drop until the pink colour is just discharged. This addition must be made with care, since excess of nitrite will reduce dichromate and give low results. Transfer the solution to a Nessler tube and dilute to 50 ml with distilled water. Add 1 ml of phosphoric acid, mix and add 2 ml of diphenylcarbazide solution. Mix again and set aside for 5 minutes. A blank determination on all reagents, including those used in the preliminary treatment, must be made in exactly the same way as for the sample. Compare with standards similarly prepared, either in Nessler tubes or a visual colorimeter. Alternatively, determine the optical density at about 540 mμ in a photo-electric absorptiometer, and read the amount present from a calibration curve prepared by treating known amounts of chromium in the same way as the sample.

Copper

Dithio-oxamide is a sensitive and highly selective reagent for the determination of copper; an alternative reagent, sodium diethyldithiocarbamate, reacts with lead or zinc and its use involves a separation by extraction. However, the dithio-oxamide method, as usually specified with acetate buffer, is seriously affected for visual determinations by iron, which with the acetate gives an interfering orange colour. As recommended by West and Compere,[6] malonate was used in place of acetate. The results with this method in the presence of comparatively high concentrations of other metal ions are shown in Table I.

TABLE I

EFFECT OF METAL IONS ON THE RESULTS GIVEN BY THE METHOD OF DETERMINATION OF COPPER WITH DITHIO-OXAMIDE

Copper present, p.p.m.	Interfering metals							Copper found by absorptiometer, p.p.m.	Degree of visual interference
	Fe^{III}, p.p.m.	Ni^{II}, p.p.m.	Pb^{II}, p.p.m.	Zn^{II}, p.p.m.	Co^{II}, p.p.m.	Sb^{III}, p.p.m.	Sn^{II}, p.p.m.		
0·40	—	10	—	—	20	—	—	0·45	Very slight
0·40	—	10	50	50	20	—	—	0·45	Very slight
0·40	50	—	—	—	—	50	50	0·42	None
0·40	50	10	100	100	—	30	30	0·42	None
0·40	50	10	100	100	10	30	30	0·45	Slight
0·40	50	10	100	200	20	—	—	0·45	Slight
0·40	100	10	—	—	20	—	—	0·45	Slight
0·40	100	20	100	100	—	—	—	0·42	None
0·40	150	10	50	50	—	30	50	0·45	None
0·40	200	10	—	—	30	—	—	0·42	Slight
0·40	200	10	50	50	10	50	50	0·47	Slight
0·40	200	30	100	200	70	30	30	0·47	Great
0·40	300	10	—	—	20	—	—	0·52	Great
0·40	300	50	100	200	100	—	—	0·52	Great

METHOD

REAGENTS—

All reagents should be of recognised analytical quality.

Ammonium acetate solution—Dissolve 20 g of ammonium acetate in distilled water and dilute to 100 ml.

Malonic acid solution—Dissolve 20 g of malonic acid in distilled water and dilute to 100 ml.

Gum acacia solution—Dissolve 1 g of gum acacia in distilled water and dilute to 100 ml. Stabilise the solution by boiling it and adding thymol.

Dithio-oxamide solution—Dissolve 0·2 g of dithio-oxamide in 100 ml of 90 per cent. ethanol.

Standard copper solution—Dissolve 0·1964 g of clear crystals of copper sulphate, showing no signs of efflorescence, in water, add sufficient hydrochloric acid to make the final acidity about 0·1 *N*, and dilute to 500 ml. Dilute 10 ml of this stock solution with 0·1 *N* hydrochloric acid to 100 ml, so that—

1 ml ≡ 0·010 mg of copper.

PROCEDURE—

From the prepared solution take an aliquot containing between 0·01 and 0·2 mg of copper, and reduce the acidity by adding ammonia solution. As care should be taken not to precipitate any iron, it is best to leave the solution slightly acid. Add 1 ml of malonic acid solution and 5 ml of ammonium acetate solution; this should bring the pH value to approximately 5·2. Add 1 ml of gum acacia solution and finally 0·5 ml of dithio-oxamide solution, mixing well after each addition. Dilute to 50 ml, mix, and set aside for 20 minutes. A blank determination on all reagents used, including those in the preliminary treatment, should be made in the same way as for the sample.

Compare with standards similarly prepared, in Nessler tubes or a visual colorimeter; a commercial comparator is available, in which permanent glass colour discs are used, but these must be re-calibrated, since the procedure described above is a modified one that permits a greater tolerance to iron. Alternatively, determine the optical density at about 650 mμ in a photo-electric absorptiometer, and read the amount present from a calibration curve prepared by treating known amounts of copper in the same way as the sample.

Iron

Thioglycollic acid reacts quantitatively with both ferrous and ferric iron. This method is said to be affected by the presence of zinc, but it was found that 1 p.p.m. of iron could be determined accurately in the presence of 100 p.p.m. of zinc. The presence of cadmium, copper and lead, singly or in a mixture also containing zinc had no effect, but when nickel was present in excess marked interference occurred. This is shown by the following results—

Iron present, p.p.m.	0·1	1·0
Nickel present, p.p.m.	10	100
Iron found, p.p.m.	0·4	3·0

Further work showed that at lower concentrations of nickel when the ratio of nickel to iron was less than 5, interference was negligible. The recommended method[7] follows.

METHOD

REAGENTS—

All reagents should be of recognised analytical quality.

Ammonia solution—Dilute 37 ml of ammonia solution, sp.gr. 0·880, to 100 ml with distilled water.

Citric acid solution—Dissolve 20 g of citric acid in 100 ml of distilled water.

Thioglycollic acid.

Standard iron solution—Dissolve 0·1000 g of electrolytic iron in 50 ml of diluted nitric acid (1 + 3), boil to expel oxides of nitrogen and dilute to 1 litre with iron-free water. Dilute 10 ml of this solution to 100 ml with 0·2 *N* nitric acid, so that—

1 ml ≡ 0·010 mg of iron.

PROCEDURE—

To an aliquot of the prepared solution containing not more than 0·05 mg of iron, diluted to 50 ml with distilled water, add 2 ml of citric acid solution, 0·1 ml of thioglycollic acid and sufficient ammonia solution to make the mixture ammoniacal (usually about 2 ml are required). Mix and set aside for 5 minutes. A blank determination, using all reagents, including those in the preliminary treatment, must be made in the same way as for the sample.

Compare with standards similarly prepared, in Nessler tubes or a visual colorimeter. Alternatively, determine the optical density at about 535 mμ in a photo-electric absorptiometer and read the amount present from a calibration curve prepared by treating known amounts of iron in the same way as the sample. For this determination permanent glass colour discs are obtainable for use with a visual colorimeter, but if these are used they should first be re-calibrated against standard iron solutions.

Manganese

Manganese is quantitatively oxidised to permanganate by ammonium persulphate, with silver nitrate as catalyst. Measurement of the red colour produced gives a sensitive method for the determination of manganese.

Chloride interferes through its reaction with silver nitrate, but can be removed by preliminary evaporation to fuming with sulphuric acid. The effect of metals producing coloured solutions was tested, but chromium at low concentrations was the only one found to give serious trouble in the visual procedure; if a photo-electric absorptiometer is used, this trouble is avoided. The following results show that in the visual procedure chromium causes results to be low when its concentration rises to about twice that of the manganese—

Manganese present, p.p.m.	0·2	0·2	0·2	0·5	0·5	0·5	1·0	1·0	1·0	1·0	1·0
Chromium present, p.p.m.	0·2	0·4	0·6	1·0	1·5	2·0	1·5	2·0	3·0	4·0	5·0
Manganese found, p.p.m.	0·2	0·1	0·1	0·5	0·4	0·3	1·0	0·9	0·7	0·6	0·5

Interference by other metals with the visual determination was as follows for both 0·2 and 0·5 p.p.m. of manganese. Iron did not affect the determination when the iron to manganese ratio was 100 to 1, but caused results to be about 10 per cent. low when the ratio was 200 to 1. Nickel did not affect the determination when the nickel to manganese ratio was 200 to 1, but caused the results to be about 10 per cent. low when the ratio was 400 to 1. Copper did not affect the determination when the copper to manganese ratio was 400 to 1.

Method

Reagents—

All reagents should be of recognised analytical quality.

Silver nitrate solution—Dissolve 5 g of silver nitrate in 100 ml of distilled water.

Sulphuric acid, diluted (1 + 1)—Add 1 volume of concentrated sulphuric acid to 1 volume of distilled water.

Ammonium persulphate.

Sodium nitrite solution—Dissolve 1 g of sodium nitrite in 100 ml of distilled water.

Standard manganese solution—Dissolve 0·2877 g of potassium permanganate in about 100 ml of water. Add 10 ml of diluted sulphuric acid (1 + 1) and heat to boiling. Add sodium bisulphite solution until the permanganate colour is discharged. Boil to expel the sulphur dioxide. Cool and dilute to 1 litre with distilled water. Dilute 10 ml of this solution to 100 ml, so that—

$$1 \text{ ml} \equiv 0{\cdot}010 \text{ mg of manganese.}$$

Procedure—

Transfer an aliquot of the prepared solution containing not more than 0·2 mg of manganese to a beaker. Add 5 ml of diluted sulphuric acid (1 + 1) and remove chloride by evaporation to fuming. Adjust the volume of the solution to about 30 ml. Add 1 ml of silver nitrate solution and heat to boiling. Add approximately 0·5 g of ammonium persulphate and simmer gently for about 10 minutes. Cool and transfer to a Nessler glass and dilute to 50 ml with distilled water. A blank determination on all reagents used, including those in the preliminary treatment, must be made in the same way as for the sample.

Compare with standards similarly prepared, in Nessler tubes or a visual colorimeter. Alternatively, determine the optical density at 525 mμ in a photo-electric absorptiometer, when the liquid in the reference cell should consist of an aliquot treated as described above, to which has been added sufficient nitrite solution to discharge the permanganate colour; read the amount present from a calibration curve prepared by treating known amounts of manganese in the same way as the sample.

Zinc

The method adopted is largely the mono-colour dithizone procedure described by Sandell,[8] in which interference by other metals that form coloured dithizonates is prevented by adjustment of pH value to between 4·6 and 5·5 and addition of sodium thiosulphate. The function of the thiosulphate is to complex copper and lead, and Sandell recommends addition of 500 to 600 mg of the crystals, $Na_2S_2O_3.5H_2O$, for every milligram of copper present. However, the results of tests showed that it was necessary to add more thiosulphate for amounts of

copper below 5 mg. Determinations were carried out with a Spekker absorptiometer; the volume of test solution was 25 ml, and the results were as follows—

Amount of copper	mg	0·25	2·5	5·0	10·0
	p.p.m.	10	100	200	400
Amount of sodium thiosulphate required to prevent interference, mg of $Na_2S_2O_3.5H_2O$ per mg of Cu		6000	1000	500	400

Method

The method recommended is that described by Sandell,[3] but modified as follows. The amount of sodium thiosulphate to be used for a volume of 10 to 25 ml of original sample should be 5 ml of a solution containing 50 g of the analytical-reagent grade solid, $Na_2S_2O_3.5H_2O$, dissolved in 100 ml of distilled water when less than 5 mg of copper are present, but when more than 5 mg of copper are present the amount should be 1 ml of the sodium thiosulphate solution for every milligram of copper present.

With this procedure the results were good in the presence of large amounts of copper and iron. Although figures are not given, quite large amounts of lead may be present without interference. The results for 0·50 p.p.m. of zinc were as follows—

Interfering metals	Cu^{II}, p.p.m.	40	—	50
	Fe^{II}, p.p.m.	—	100	100
Zinc found, p.p.m...		0·52	0·54	0·54

This paper is published by permission of the Government Chemist and the Department of Scientific and Industrial Research.

References

1. Ministry of Health, "Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents," H.M. Stationery Office, London, 1929.
2. Saltzmann, B. E., *Anal. Chem.*, 1953, **25**, 493.
3. Sandell, E. B., "Colorimetric Determinations of Traces of Metals," Second Edition, Interscience Publishers Inc., New York, 1950.
4. Butts, P. G., Gahler, A. R., and Mellon, M. G., *Sewage Ind. Wastes*, 1950, **22**, 1543.
5. Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," Third Edition, D. Van Nostrand Co. Inc., New York, 1949, Volume II, p. 272.
6. West, P. W., and Compere, M., *Anal. Chem.*, 1949, **21**, 628.
7. "A Handbook of Colorimetric Chemical Analytical Methods," The Tintometer Ltd., Salisbury, England.

Government Laboratory
Dudley House
Endell Street
London, W.C.2

Water Pollution Research Laboratory
Elder Way, Stevenage, Herts.

July 13th, 1955

The Use of Elution Chromatography from Cellulose Columns for the Systematic Analysis of Special Steels

BY G. VENTURELLO AND A. M. GHE

A chromatographic method is described for the systematic separation and determination of the most important elements in special steels, namely molybdenum, cobalt, manganese, vanadium, nickel and chromium. The method involves a microchemical colorimetric determination of the elements, which are fractionally separated by elution from cellulose columns. The method is widely applicable and highly sensitive; it makes possible the determination of the elements in quantities of the order of 1 μg in the eluate.

The difference between the theoretical and experimental results is $\pm$ 0·05 per cent. for cobalt, chromium and nickel, and $\pm$ 0·02 per cent. for manganese, molybdenum and vanadium, when the results are expressed as a percentage of the steel being analysed.

IN a previous study,[1] we pointed out the possibility of analysing some steels by means of radial-paper chromatography in order to determine the most important elements. The procedure was recommended for qualitative and sometimes quantitative determinations. We have now studied a method of chromatographic separation of the elements of special steels by elution from cellulose columns.

Elution chromatography can advantageously be substituted for the more difficult and longer methods involving precipitation, electrolysis, extraction procedures and so on, used in routine analysis in order to separate interfering elements contemporaneously present in steels.

Easy systematic separation is achieved for molybdenum, cobalt, manganese, vanadium, nickel and chromium. The scheme is also suitable for their quantitative determination. The selective separation of the elements into many fractions is also possible, even when they are present in very small amounts, by varying either the volume or the kind of solvent, and the diameter or the length of the column.

Until now, in the inorganic field, the method has been used mainly for the separation of some of the rarer metals from minerals, for instance, the determination of uranium by Burstall and Wells[2] and by Ryan and Williams,[3] of thorium and of thorium and uranium by Kember[4] and by Williams,[5] of gold and metals of the platinum group by Kember and Wells,[6] and of tantalum and niobium by Williams[7] and by Mercer and Williams.[8]

Chromatographic applications in the field of steel analysis have been very few and all of them have been directed to the determination of single elements, not to a systematic analysis. Nevertheless, the cobalt - nickel and cobalt - copper separations made by Burstall, Davies and Wells[9] in steels and iron pyrites, and the quantitative determination of molybdenum in several special steels, which one of us described in a previous paper,[10] are noteworthy.

EXPERIMENTAL

BEHAVIOUR ON ELUTION FROM CELLULOSE COLUMNS, WITH DIFFERENT SOLVENTS, OF THE MOST IMPORTANT ELEMENTS OF SPECIAL STEELS—

Preparation of solvents—All solvents were freshly prepared before use. The methyl *n*-propyl ketone - hydrochloric acid solvent was prepared by mixing 95 ml of methyl *n*-propyl ketone with 5 ml of hydrochloric acid, sp.gr. 1·19. After use the methyl *n*-propyl ketone was recovered by distillation and purified for further use by neutralisation with sodium hydroxide, treatment with alkaline potassium permanganate, redistillation, drying over sodium hydroxide and a final fractionation.

Preparation of the column—The column consisted of a glass tube having a diameter of about 0·5 cm and 20 cm long. The lower end was tapered and was closed with a plug of cotton-wool. Whatman ashless cellulose powder, standard grade for chromatography, which did not require any preliminary activation, was used in the column.

Small quantities of the cellulose powder were put into the clean and dry column, each portion being gently pushed down with a glass rod flattened at one end to form a plunger having a diameter slightly smaller than that of the column. Under standardised conditions

the cellulose powder filled 11·5 cm of the column (0·9 g of cellulose powder was generally sufficient). The column was then thoroughly moistened with acetylacetone.

Preparation of solutions and extraction procedure—For preliminary determinations of the most common elements of special steels and their separation from iron, solutions containing, respectively, 1 per cent. of molybdenum, cobalt, manganese, vanadium, nickel or chromium and 99 per cent. of iron were used. These solutions were prepared by dissolving the metal chlorides in diluted hydrochloric acid (1 + 1) and adding a few drops of concentrated nitric acid. For molybdenum and vanadium a molybdate and vanadyl sulphate, respectively, were used.

It is particularly important to control carefully the acidity of the initial solution, because in elution, as in other chromatographic techniques, the pH of the medium plays a fundamental role in the separations. Hence the absolute necessity of adhering to the same experimental conditions, which should approximate as closely as possible to those existing in an actual steel analysis. For single determinations 0·1-ml portions and for binary determinations 0·2-ml portions of solution, added from a microburette, were placed on the top of the cellulose column, which had been previously moistened with the solvent to be used for the elution. The separation was carried out without the use of suction so as to allow slow stratification and consequently a clear separation of the zones.

Extraction of iron and molybdenum with acetylacetone—We studied the behaviour of the elements of special steels on elution with (*a*) acetylacetone, (*b*) ethyl acetoacetate, (*c*) a mixture of methyl *n*-propyl ketone, acetone, water and concentrated hydrochloric acid in the proportions of 100 to 30 to 4 to 1 by volume, and (*d*) a mixture of methyl *n*-propyl ketone, acetone and water in the proportions of 100 to 30 to 4 by volume.

With 7 ml of solvent (*a*), iron and molybdenum passed into the eluate and cobalt, manganese, vanadium, nickel and chromium remained on the column. This was also true with 12 ml of solvent (*b*), 10 ml of solvent (*c*) and 7 ml of solvent (*d*). With solvents (*b*) and (*d*), however, cobalt and molybdenum gave mixed zones of collection.

Removal of iron and molybdenum from the column by elution with acetylacetone was confirmed by investigation of prepared steel solutions containing 1 per cent. of each of the elements present in special steels, when, apart from iron and molybdenum, all other elements remained on the column.

Fractional elution of the various elements of special steels and their identification—On elution with 7 ml of acetylacetone, iron and molybdenum passed into the eluate, iron as the dark red ferric acetylacetonate and molybdenum as an orange-yellow complex; cobalt, manganese, vanadium, nickel and chromium remained on the column.

Several solvents, mainly ketones containing various amounts of hydrochloric acid, were tried in order to obtain a selective and fractional separation of the elements remaining on the column. The best solvent was found to be methyl *n*-propyl ketone containing 5 per cent. of concentrated hydrochloric acid. With 7 ml of this solvent, cobalt and manganese passed into the eluate, cobalt as a light green-blue complex and manganese as a colourless complex; vanadium, nickel and chromium remained on the column.

TABLE I

CHROMATOGRAPHIC ELUTION OF THE ELEMENTS PRESENT IN SPECIAL STEELS

Solvent	Metals remaining on column	Eluate
7 ml of acetylacetone	Co, Mn, V, Ni and Cr	Fe and Mo
7 ml of methyl *n*-propyl ketone containing 5 per cent. of concentrated hydrochloric acid	V, Ni and Cr	Co and Mn*
A further 13 ml of methyl *n*-propyl ketone - hydrochloric acid mixture	Ni and Cr	V
A mixture of 8 ml of water and 2 ml of dilute sulphuric acid (1 + 20)	—	Ni and Cr†

* For steels containing less than 0·3 per cent. of manganese two columns should be used, manganese being determined on one and cobalt on the other.

† Eluate evaporated to 0·5 ml and made up to 10 ml in a calibrated flask; 2 ml of this solution were taken for determining between 0·5 and 5 per cent. of nickel and 1 ml for more than 5 per cent. For less than 0·5 per cent. of chromium 2 ml were taken and for more than 0·5 per cent. 1 ml was taken.

Further elution with 13 ml of the same methyl *n*-propyl ketone - hydrochloric acid mixture gave another fractional separation of the elements remaining on the column. Vanadium passed into the eluate as a green-blue complex; nickel and chromium remained on the column.

Nickel and chromium passed into the eluate when the column was eluted with 10 ml of acidified water, *i.e.*, 8 ml of water and 2 ml of dilute sulphuric acid (1 + 20).

The order and method of elution of the various elements are shown in Table I.

Qualitative analysis of steels

To prepare the solution 0·25 g of the steel, carefully weighed, was treated with 2 ml of diluted hydrochloric acid (1 + 1) and digested on a sand-bath, more diluted hydrochloric acid being added drop by drop to replace any lost by evaporation, up to a total volume of 8 ml. After concentration to a small volume, 3 ml of diluted hydrochloric acid (1 + 1) were added and successively, drop by drop, another 3 ml; the heated solution was oxidised with 6 drops of concentrated nitric acid. The solution was again evaporated nearly to dryness and the residue was dissolved in 2 ml of diluted hydrochloric acid (1 + 1); the solution was put into a 5-ml calibrated flask and finally diluted to the mark with the same acid.

For the analysis of each sample 0·2 ml of the steel solution was put on the column and eluted in the order and with the solvents shown in Table I. Several British Chemical Standard and National Bureau of Standards special steels were analysed; each separate eluate corresponded to the results obtained with prepared steel solutions. The compositions of the steels are given in Table II.

Table II

Composition of some standard steels

Steel sample	Present in the steel					
	Manganese, %	Nickel, %	Chromium, %	Vanadium, %	Molybdenum, %	Cobalt, %
B.C.S. No. 246 ..	—	12	18·8	—	2·89	—
B.C.S. No. 252 ..	0·016	4·100	0·200	0·460	0·007	—
B.C.S. No. 253 ..	0·355	2·920	0·355	0·220	0·950	—
B.C.S. No. 255 ..	1·110	0·560	0·960	0·265	1·410	—
B.C.S. No. 256 ..	1·210	0·185	2·340	0·360	0·535	—
B.C.S. No. 257 ..	1·420	0·840	1·720	0·115	0·320	—
B.C.S. No. 258 ..	0·790	0·048	3·070	0·645	0·425	—
N.B.S. No. 153 ..	0·219	0·107	4·140	2·04	8·380	8·450
N.B.S. No. 106A ..	0·546	0·277	1·150	0·002	0·203	—
N.B.S. No. 50B ..	0·325	0·089	4·080	1·020	0·401	—
N.B.S. No. 121b ..	1·52	11·14	17·68	0·042	0·075	—

Visual stages in the chromatographic elution of N.B.S. steel No. 153—

The various visual stages during the elution of N.B.S. steel No. 153 were—

First stage—When 0·5 ml of acetylacetone had been added, a green zone had separated at the top of the column (cobalt, manganese, vanadium, nickel and chromium) and below it a brown-red zone (iron and molybdenum).

Second stage—When 1 ml of acetylacetone had been added, the distance between the two zones had increased. In the lower part of the upper zone the formation of a green-blue zone of cobalt and manganese was just visible.

Third stage—When 4 ml of acetylacetone had been added, the brown-red zone was about to pass out of the column in the eluate. The greenish zone of nickel, vanadium and chromium was still at the top of the column and beneath it the green-blue zone of cobalt and manganese was more clearly defined.

Fourth stage—After the iron and molybdenum had been completely removed by elution with acetylacetone and 4 ml of the methyl *n*-propyl ketone - hydrochloric acid solvent had been added, the green-blue zone of cobalt and manganese had reached the middle of the column and the greenish zone was still at the top of the column.

Fifth stage—When 6 ml of the methyl *n*-propyl ketone - hydrochloric acid solvent had been added, a blue zone of cobalt and manganese was passing into the eluate. A light green zone of nickel and chromium was still at the top of the column and a green-blue zone of vanadium was visible at the middle of the column.

Sixth stage—When 7 ml of the methyl *n*-propyl ketone - hydrochloric acid solvent had been added, all the cobalt and manganese had been eluted from the column. A grey-green zone of nickel and chromium was now visible about 2 cm from the top of the column and at the middle of the column a greenish zone of vanadium could be seen. The vanadium zone was then eluted by further addition of 13 ml of the same solvent and the nickel and chromium zone by elution with water acidified with dilute sulphuric acid (1 + 20).

It was found that the colours of the zones and eluates depended on the composition of the steel analysed.

Quantitative analysis of steels

After separation of the elements into the different eluates it was found that their determination could be carried out most conveniently by absorptiometric methods. We used a Langede double photo-electric cell apparatus, model V, which had a cell volume of 100 ml and an absorbing layer thickness of 34·4 mm.

Determination of molybdenum—

Some different colorimetric reactions have been proposed for the quantitative determination of molybdenum. In steel analysis the method most used is based on the reaction with potassium thiocyanate in presence of stannous chloride. We chose this reaction, because it can be applied in the presence of the organic solvent and iron, which does not interfere when reduced with stannous chloride. All the elements that interfere with the molybdenum reaction had been removed by the chromatographic elution.

Calibration graph for molybdenum—A standard molybdenum solution was prepared by dissolving 1·83 g of pure ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (obtained from Merck & Co. Inc.), in 1 litre of water. From this standard solution containing 0·001 g of molybdenum per ml a series of solutions containing 200, 166, 100, 83, 50, 25 and 10 μg per ml was prepared.

To 1 ml of each solution in separating funnels 7 ml of acetylacetone, 9 ml of diluted sulphuric acid (1 + 4), 35 ml of diethyl ether, 5 ml of 10 per cent. w/v potassium thiocyanate solution and 25 ml of stannous chloride solution (62·5 g of the dihydrate dissolved in 50 ml of concentrated hydrochloric acid and 200 ml of water) were added successively. After the funnel had been shaken and the solution allowed to separate the ethereal layer containing the orange coloured molybdenum complex was run into the glass cell and made up to 100 ml with diethyl ether. The scale of the instrument was set to zero against diethyl ether and then the optical densities of the solutions were read at a wavelength corresponding to the absorption maximum at 625 mμ, a green VG9 filter being used. All measurements were made 15 minutes after the addition of the stannous chloride. A graph was drawn of all the values obtained and was applicable to between 5 and 300 μg of molybdenum.

Determination of molybdenum in steel—The eluate containing the iron and molybdenum eluted from the column was prepared in the same manner as the solutions used for the preparation of the calibration graph and its optical density was measured. By reference to the calibration graph the concentration of molybdenum (μg per 0·2 ml of steel solution) was obtained and the percentage of molybdenum in the analysed steel was calculated. The theoretical and experimental values of molybdenum in the steels are given in Table III. The average error in determining molybdenum contents between 0·05 and 3 per cent. was not more than $\pm$ 0·02 per cent.

Table III

Determination of molybdenum in standard steels

Steel sample	Molybdenum found,		Molybdenum present,		Error,
	μg	%	μg	%	%
N.B.S. No. 121b	5	0·062	6	0·075	−0·013
N.B.S. No. 106A	18	0·182	20	0·203	−0·021
B.C.S. No. 257	32	0·320	32	0·320	0·000
B.C.S. No. 256	50	0·514	52	0·535	−0·021
B.C.S. No. 253	92	0·950	92	0·950	0·000
B.C.S. No. 255	142	1·430	140	1·410	+0·020
B.C.S. No. 246	290	2·910	288	2·890	+0·020

DETERMINATION OF COBALT—

Among the methods proposed for determining cobalt in steels, the colorimetric methods give the best results. The reaction with nitroso-R salt (disodium 1-nitroso-2-naphthol-3:6-disulphonate) and the ammonium thiocyanate reaction, with its modifications, are the most useful. The ammonium thiocyanate method was used, as it is suitable for use in the presence of a ketone, as organic solvent, and of manganese, which does not interfere. Iron, molybdenum and vanadium have been removed by elution and therefore they cannot affect the determination.

Calibration graph for cobalt—A standard cobalt solution was prepared by dissolving 4·03 g of pure cobalt chloride, $CoCl_2.6H_2O$ (obtained from Merck & Co. Inc.), in 1 litre of water. From this standard solution containing 0·001 g of cobalt per ml a series of solutions containing 666, 500, 400, 333, 250, 200, 100 and 50 μg per ml was prepared.

To 1 ml of each solution, 7 ml of methyl *n*-propyl ketone containing 5 per cent. of concentrated hydrochloric acid and 1 ml of acetylacetone in separating funnels, 30 ml of ammonium thiocyanate in acetone (3 g of ammonium thiocyanate dissolved in 5 ml of water and 25 ml of acetone) were added. The layer containing the blue cobalt complex was run into ethanol and its optical density was measured against ethanol at a wavelength corresponding to the absorption maximum at 644 to 700 mμ, an orange OG2 filter being used. All measurements were made 10 minutes after the addition of the ammonium thiocyanate solution. A graph was drawn of all the values obtained and was applicable to between 10 and 700 μg of cobalt.

Determination of cobalt in prepared steel solutions—By adding cobalt chloride to solutions of N.B.S. steel No. 50B, solutions containing 1, 3, 4, 5, 7, 10, 12 and 14 per cent. of cobalt were prepared. Because of the high cobalt content of the solutions, only 0·1 ml of each was taken for the chromatographic elution procedure.

The eluate containing the cobalt and the manganese, which does not interfere, was prepared in the same manner as the solutions used for the preparation of the calibration graph, except that it was unnecessary to add acetylacetone or methyl *n*-propyl ketone. The optical density of the eluate was then measured and by reference to the calibration graph the concentration of cobalt (μg per 0·1 ml of steel solution) was obtained and the percentage of cobalt in the proposed steel solution was calculated. The theoretical and experimental values of cobalt in the steels are given in Table IV. The average error in determining between 1 and 14 per cent. of cobalt in steels was of the order of $\pm$ 0·05 per cent.

TABLE IV

DETERMINATION OF COBALT ADDED TO A SOLUTION OF N.B.S. STEEL NO. 50B

Cobalt found,		Cobalt added,		Error,
μg	%	μg	%	%
48	0·96	50	1	−0·04
147	2·94	150	3	−0·06
198	3·96	200	4	−0·04
248	4·96	250	5	−0·04
350	7·00	350	7	0·00
505	10·10	500	10	+0·10
602	12·04	600	12	+0·04
705	14·10	700	14	+0·10

It is possible to determine cobalt and manganese separately in two different portions of the same eluate.

DETERMINATION OF MANGANESE—

The standard colorimetric reaction for the determination of manganese is the oxidation of Mn^{2+} ions to MnO_4^- ions. This oxidation can be achieved by using many different reagents, for example, lead peroxide, sodium bismuthate, potassium periodate, silver peroxide[11,12] and ammonium persulphate in the presence of silver nitrate. The ammonium persulphate method was adopted.

Other elements giving coloured ions (iron, chromium, titanium, molybdenum, vanadium and nickel) had been removed by elution in a different fraction.

When the cobalt content is greater than 6 per cent., interference can be suppressed by operating at a wavelength of about 570 mμ (in this region its absorption is negligible) and by employing differential colorimetric methods.

Calibration graph for manganese—Solutions containing various amounts of manganese were prepared by diluting different volumes of 0·01 *N* potassium permanganate, measured from a microburette, to 100 ml with water. The optical densities of the solutions were measured against water at a wavelength corresponding to the absorption maximum at 530 mμ, a green VG9 filter being used. A graph was drawn of all the values obtained and was applicable to between 5 and 200 μg of manganese.

Determination of manganese in steel—The eluate containing the cobalt and manganese (or a known fraction of the eluate if cobalt is also to be determined) was put into a glass beaker having a diameter of 5 cm and was slowly evaporated to 0·5 ml. The solution was again evaporated to 0·5 ml after 2 ml of concentrated nitric acid had been added and finally 2 ml of water were added. This treatment ensured the elimination of organic solvents from the eluate. The resulting solution and the water washings from the beaker (2 ml) were put into a test-tube and then 0·2 ml of concentrated nitric acid, 0·2 ml of dilute sulphuric acid (1 + 50), 0·2 ml of concentrated phosphoric acid, 4 drops of 0·1 *N* silver nitrate solution and 0·5 g of ammonium persulphate were added. The test-tube was heated in a steam-bath at 70° to 80° C for about 20 minutes and then the solution was put into the glass cell of the absorptiometer and made up to 100 ml with water and its optical density was measured. The manganese concentration (μg per 0·2 ml of steel solution) was obtained from the calibration graph and the percentage of manganese in the steel was calculated. The theoretical and experimental values for manganese in the steels are given in Table V. The average error in determining between 0·3 and 1·5 per cent. of manganese was not more than ±0·02 per cent.

TABLE V

DETERMINATION OF MANGANESE IN STANDARD STEELS

Steel sample	Manganese found,		Manganese present,		Error,
	μg	%	μg	%	%
B.C.S. No. 253	32	0·35	32	0·35	0·00
N.B.S. No. 106A	55	0·55	54	0·54	+0·01
B.C.S. No. 255	108	1·09	110	1·11	−0·02
B.C.S. No. 257	142	1·44	140	1·42	+0·02

Up to 6 per cent. of cobalt does not affect the results, but for higher concentrations a differential procedure is to be preferred. Potassium permanganate could be reduced by sodium nitrite and the difference in the optical densities determined. With a manganese content higher than 0·3 per cent., it is possible to determine both cobalt and managanese on two fractions of the eluate. When there is no more than 0·3 per cent. of manganese, it is useful to work on two columns, in order to determine manganese in the eluate from one, and cobalt in the eluate from the other.

DETERMINATION OF VANADIUM—

The most commonly used procedures for the colorimetric determination of vanadium are based on the formation of brown-red coloured pervanadic complexes with hydrogen peroxide and of tungstovanadophosphate. The first reaction is unsatisfactory for less than 0·15 per cent. of vanadium and some elements, particularly iron, molybdenum and titanium, interfere. We have adapted the latter method to the determination of small amounts of vanadium in steels. Titanium, zirconium, bismuth and antimony interfere by forming insoluble phosphates and cobalt, nickel, manganese, chromium and molybdenum by forming coloured ions. All interfering elements have been removed by chromatographic elution.

Calibration graph for vanadium—A standard vanadium solution was prepared by dissolving 0·390 g of vanadyl sulphate, $VOSO_4.2H_2O$ (obtained from Merck & Co. Inc.), in 1 litre of water. A series of solutions containing various amounts of vanadium was prepared by measuring different volumes of the standard solution from a microburette and adding to them, in a glass beaker having a diameter of 5 cm, 13 ml of the methyl *n*-propyl ketone - hydrochloric acid solvent so as to resemble the conditions of an actual steel analysis.

The solution in the beaker was evaporated to about 0·5 ml, 1 ml of concentrated nitric acid was added and the solution was again evaporated to 0·5 ml and the volume was adjusted

to 2 ml with water. This ensured that all organic solvent had been eliminated from the solution.

The resulting solution was oxidised with sodium peroxide (about 0·05 g) until an alkaline reaction was obtained and was then boiled gently for 20 minutes, water being added to keep the volume at about 10 ml. The solution was then cooled and 5 ml of 0·5 *N* sulphuric acid, 1 ml of diluted phosphoric acid (1 + 2) and 0·5 ml of a 0·5 *M* solution of sodium tungstate were added and the solution was boiled for 10 minutes, the volume being kept at about 10 ml by adding water.

After cooling, the solution was made up to 100 ml with water and put into the glass cell of the absorptiometer and its optical density was measured against water at a wavelength corresponding to the absorption maximum at 405 mμ, a blue BG12 filter being used. A graph was drawn of all the values obtained and was applicable to between 10 and 200 μg of vanadium.

Determination of vanadium in steel—The vanadium eluate was treated in the same manner as the solutions used for the preparation of the calibration graph. The optical density of the treated eluate was measured and the concentration of vanadium (μg per 0·2 ml of steel solution) was obtained and from this the percentage of vanadium in the steel was calculated. The results are given in Table VI. The average error in determining between 0·1 and 2 per cent. of vanadium was not more than ± 0·02 per cent.

TABLE VI

DETERMINATION OF VANADIUM IN STANDARD STEELS

Steel sample	Vanadium found,		Vanadium present,		Error,
	μg	%	μg	%	%
B.C.S. No. 257	10	0·13	8	0·11	+0·02
B.C.S. No. 253	20	0·22	20	0·22	0·00
B.C.S. No. 258	92	0·67	88	0·64	+0·03
N.B.S. No. 50B	102	1·02	102	1·02	0·00
N.B.S. No. 153	202	2·02	204	2·04	−0·02

DETERMINATION OF NICKEL—

The best colorimetric methods for determining nickel are based on the red colour produced with oxidising reagents (lead peroxide, iodine, persulphates and bromine) in the presence of dimethylglyoxime and ammonia solution. Vanadium, chromium, iron, manganese and titanium, which form precipitates, and cobalt and chromium (as chromate), which form coloured compounds, interfere.

In the classical methods the interfering elements are removed chemically. However, after chromatographic elution only chromium is present with the nickel. Interference caused by chromium is easily eliminated by the presence of citrate ions. Further, the chromatographic method solves what has previously been a very complex problem, namely, the determination of traces of nickel in the presence of large amounts of cobalt.

Calibration graph for nickel—A standard nickel solution was prepared by dissolving 0·478 g of pure nickel sulphate, $NiSO_4.7H_2O$ (obtained from Merck & Co. Inc.), in 1 litre of water. A series of solutions containing various amounts of nickel was prepared by measuring from a microburette the required volume of the standard solution. The standard solution contained 0·0001 g of nickel per ml.

To each solution in a glass beaker having a diameter of 5 cm, 4 or 5 drops of methyl *n*-propyl ketone and 10 ml of acidified water, *i.e.*, 8 ml of water and 2 ml of dilute sulphuric acid (1 + 20), were added and the solution was evaporated nearly to dryness, and a further 2 ml of water were added. Then, successively, 1 ml of dilute sulphuric acid (1 + 20), 1 ml of a solution of 2 g of ammonium citrate dissolved in 10 ml of water and 10 ml of diluted ammonia solution (1 + 1), 1 ml of bromine water (1·5 ml of bromine in 100 ml of water at 60° C), about 6 ml of dilute ammonia solution (1 + 10) (to discharge the yellow bromine colour), 0·3 ml of concentrated ammonia solution and 1 ml of dimethylglyoxime solution (1 per cent. in ethanol and water (4 + 1) mixture) were added. The solution was transferred to the glass cell of the absorptiometer and made up to 100 ml with water. The optical density of the solution was measured against water at a wavelength corresponding to the absorption maximum at 530 mμ, a green VG9 filter being used. All measurements were made between 2 and 10 minutes after the dimethylglyoxime had been added. A graph was drawn of all the values obtained and was applicable to between 5 and 100 μg of nickel.

Determination of nickel in steel—The acidified water eluate, which contained the nickel and chromium, was evaporated to 0·5 ml and transferred with washings to a 10-ml calibrated flask and made up to the mark. The procedure for the preparation of each of the solutions used in preparing the calibration graph, except that it was unnecessary to add the drops of methyl *n*-propyl ketone and the acidified water, was carried out on 2 ml (for between 0·5 and 5 per cent. of nickel) or 1 ml (for more than 5 per cent. of nickel) of this solution. The optical density was then measured and from the calibration graph the concentration of nickel (μg per 0·2 ml of steel solution) was obtained and the percentage of nickel in the steel was calculated. The results are shown in Table VII. The average error in determining nickel was not more than $\pm$ 0·05 per cent.

TABLE VII

DETERMINATION OF NICKEL IN STANDARD STEELS

Steel sample	Nickel found in 2 ml of eluate, μg	Nickel in 0·2 ml of steel solution*, μg	Nickel found in steel*, %	Nickel present in 0·2 ml of steel solution, μg	Nickel present in steel %	Error, %
N.B.S. No. 106A	5	25	0·26	26	0·27	−0·01
B.C.S. No. 255	11	55	0·55	56	0·56	−0·01
B.C.S. No. 257	17	85	0·85	84	0·84	+0·01
B.C.S. No. 253	57	285	2·88	288	2·92	−0·04
B.C.S. No. 252	83	415	4·15	410	4·10	+0·05
B.C.S. No. 246	119†	1190	11·90	1200	12·00	−0·10

* Calculated from the result of the determination on 2 ml of eluate.

† Determined on 1 ml of eluate (see p. 344).

DETERMINATION OF CHROMIUM—

The most useful colorimetric method for determining chromium in steels is based on the reaction with diphenylcarbazide and this method was adopted. The reagent reacts with chromium in the form of CrO_4^{2-} ions.

The oxidation is achieved by many oxidising agents, *e.g.*, persulphate or sodium peroxide. Excess of oxidising agent destroys the violet complex of chromium and must be removed. Some elements interfere in the reaction, *e.g.*, vanadium, molybdenum, iron and cobalt, but in the chromatographic analysis these elements, if present, are separated in a different fraction of the eluate and therefore present no difficulties. The determination of chromium is made in the presence of nickel only, which does not interfere.

Calibration graph for chromium—A 0·01 *N* solution of chromic potassium sulphate was used to prepare a series of solutions containing various amounts of chromium. For each solution the required volume was measured into a glass beaker having a diameter of 5 cm from a microburette and 8 ml of water and about 0·5 g of sodium peroxide were added, and the solution was boiled slowly to oxidise Cr^{3+} ions to CrO_4^{2-} ions. (The solution was alkaline and had a yellow colour.)

The excess of sodium peroxide was removed by boiling, the volume of solution being kept at about 10 ml by the addition of water. The solution was evaporated to small volume and set aside for 6 or 7 hours, and then 0·2 ml of 6 *N* sulphuric acid (to adjust the pH to between 2 and 3) and 2 ml of diphenylcarbazide reagent (1 ml of 6 *N* sulphuric acid and 1 ml of a 0·5 per cent. solution of diphenylcarbazide in acetone) were added. The resulting solution was transferred to the glass cell of the absorptiometer and made up to 100 ml with water. The optical density of the solution was measured against water at a wavelength corresponding to the absorption maximum at 644 to 700 mμ. All measurements were made 15 to 20 minutes after addition of the diphenylcarbazide reagent. A graph was drawn of all the values obtained and was applicable to between 5 and 70 μg of chromium.

Determination of chromium in steel—The acidified water eluate was evaporated to 0·5 ml, transferred to a 10-ml calibrated flask and diluted to the mark with water. The procedure for the preparation of each of the solutions used in preparing the calibration graph was carried out on 2 ml (for less than 0·5 per cent. of chromium) or 1 ml (for more than 0·5 per cent.

of chromium) of this solution. The optical density was then measured and from the calibration graph the concentration of chromium (μg per 0·2 ml of steel solution) was obtained and the percentage of chromium in the steel was calculated. The results are given in Table VIII. The average error in determining between 0·3 and 2 per cent. of chromium was not more than $\pm$ 0·05 per cent.

Table VIII

Determination of chromium in standard steels

Steel sample	Chromium found in 1 ml of eluate, μg	Chromium in 0·2 ml of steel solution*, μg	Chromium found in steel*, %	Chromium present in 0·2 ml of steel solution, μg	Chromium present in steel, %	Error, %
B.C.S. No. 255	10	100	1·00	96	0·96	+0·04
N.B.S. No. 106A	11	110	1·11	114	1·15	−0·04
B.C.S. No. 257	17	170	1·70	172	1·72	−0·02
B.C.S. No. 253	—	32†	0·35†	32	0·35	0·00

* Calculated from the result of the determination on 1 ml of eluate.

† Calculated from the result of the determination on 2 ml of eluate.

Analysis of steels of unknown composition

By way of comparison, a steel of unknown composition was analysed by both the chromatographic method and a more usual chemical method. The results of the analyses, expressed as a percentage of the steel being analysed, differed by not more than $\pm$ 0·04 per cent. for all the elements present. The results are shown in Table IX.

Table IX

Comparison of the chromatographic and a more usual chemical method of steel analysis

Metal present	Found after chromatographic separation— per 0·2 ml of solution, μg	Found after chromatographic separation— in the steel, %	Found by chemical method— per 0·2 ml of solution, μg	Found by chemical method— in the steel, %	Difference, %
Molybdenum ..	127	1·28	128	1·29	−0·01
Cobalt	72	1·44	71	1·42	+0·02
Manganese	53	0·53	52	0·52	+0·01
Vanadium	56	0·56	52	0·52	+0·04
Nickel	205	2·05	208	2·08	−0·03
Chromium	53	0·54	52	0·53	+0·01

Discussion of results

The experimental results indicate that the proposed method is successful for the determination of molybdenum, cobalt, manganese, vanadium, nickel and chromium in special steels. The method allows detection of the elements with good sensitivity even if present in small amounts, *i.e.*, 0·1 per cent. to 0·01 per cent. in some cases (*e.g.*, molybdenum). Sensitivity may be increased without any alteration of the method itself, as there is the possibility of using twice to three times the amount of the original solution.

By elution from cellulose columns it is possible to eliminate the complex procedures used in the chemical separation of interfering elements. For many elements it is possible to operate directly on the eluate even in presence of the organic solvent and without too many manipulations, which might affect the quantitative results. The maximum error in the single determination is $\pm$ 0·05 per cent. for cobalt, nickel and chromium and $\pm$ 0·02 per cent. for manganese, molybdenum and vanadium, when the results are expressed as a percentage of the steel being analysed.

REFERENCES

1. Venturello, G., and Ghe, A. M., *Ann. Chim. Appl., Roma*, 1954, **44**, 960.
2. Burstall, F. H., and Wells, R. A., *Analyst*, 1951, **76**, 396.
3. Ryan, W., and Williams, A. F., *Ibid.*, 1952, **77**, 293.
4. Kember, N. F., *Ibid.*, 1952, **77**, 78.
5. Williams, A. F., *Ibid.*, 1952, **77**, 297.
6. Kember, N. F., and Wells, R. A., *Ibid.*, 1951, **76**, 579.
7. Williams, A. F., *J. Chem. Soc.*, 1952, 3155.
8. Mercer, R. A., and Williams, A. F., *Ibid.*, 1952, 3399.
9. Burstall, F. H., Davies, G. R., and Wells, R. A., *Disc. Faraday Soc.*, 1949, **7**, 179.
10. Ghe, A. M., and Fiorentini, A. R., *Ann. Chim. Appl., Roma*, 1955, **45**, 400.
11. Rosi, D., and Mendola, I., *Metallurgia Italiana*, 1951, **43**, 443.
12. Tanaka, M., *Bull. Chem. Soc. Japan*, 1953, **26**, 299.

INSTITUTE OF CHEMISTRY "G. CIAMICIAN"
UNIVERSITY OF BOLOGNA
ITALY

December 14th, 1955

Microchemical Determination of Sulphur in Organic Compounds

BY W. H. S. MASSIE

A titrimetric finish for the micro-determination of sulphur in organic compounds containing nitrogen is described. The method is based on the conductimetric titration with barium acetate of the sulphuric acid produced during combustion and makes use of readily available apparatus. The method is rapid and is proposed mainly for application to routine work; it gives an accuracy of approximately ± 0·2 per cent. on 5 mg of starting material.

THE classical Carius method for the micro-determination of sulphur, which involves heating with nitric acid in a bomb and precipitation and weighing as barium sulphate, is a time-consuming procedure and one that makes demands on the analyst. The discovery a number of years ago that derivatives of trithioformaldehyde are extraordinarily resistant to decomposition in the Carius method, and the necessity for a more simple and rapid technique led to the study of Pregl's method of combustion in a stream of oxygen over platinum and titration of the sulphuric acid produced. This was not only entirely satisfactory with carbon - hydrogen - oxygen - sulphur compounds, but admitted of ready extension to compounds containing halogen also. The real difficulty arises with compounds in which nitrogen is also present, for, on combustion in oxygen over platinum, nitrogen is always partly and never quantitatively converted to nitrous and nitric acids. Consequently, although sulphur may still be determined gravimetrically in the products of combustion, the much more rapid volumetric determination can only be effected after more or less complicated modification.

Gibson and Caulfield's[1] procedure of precipitating the sulphate with a known excess of barium chloride, removing the excess of barium with a known excess of chromate and finally determining the excess of chromate by the iodine - thiosulphate method was, according to two American authors, the least unsatisfactory method they had seen described. More recently, Wilson, Pearson and Fitzgerald[2] have proposed a method in which a measured excess of barium chloride is titrated with disodium ethylenediaminetetra-acetate (EDTA). This method is claimed to take only 30 minutes and have an accuracy of within ± 1 per cent. Sijderius,[3] however, states that, for solutions containing less than 30 mg of sulphur per litre, a period of 24 hours is required for complete precipitation of the sulphate before the excess of barium is titrated with EDTA. He quotes errors of 10·6 and 2·2 per cent. for the determination of sulphate by this method after 1 and 6 hours, respectively, had been allowed for precipitation.

Another method with a volumetric end-point is Zimmermann's modification[4] of Bürger's method of fusion with potassium in a sealed tube. A total time of 30 minutes for a determination with an accuracy of ± 0·2 per cent. on a 5-mg sample is claimed, but the apparatus and technique are somewhat complicated.

Conductimetric methods have also been suggested, but for various reasons none has been universally acceptable. The conductivity of a solution depends primarily on the number of ions present and on their velocities and mobilities, and so it is often possible to detect the removal of an ion or the exchange of one for another by measuring the change in conductivity that occurs on the progressive addition of a suitable reagent to the original solution. Hence, if barium chloride is added to sulphuric acid, barium sulphate is precipitated; SO_4^{2-} is replaced by $2Cl^-$, and there is little alteration in conductivity until all the sulphate is precipitated. When this occurs, the addition of excess of barium chloride causes an increase in conductivity, which continues with further addition of the titrant. Provided that there is no appreciable change in volume of the solution, a conductivity - volume graph should consist of two straight lines intersecting at the equivalence point, as shown in Fig. 1.

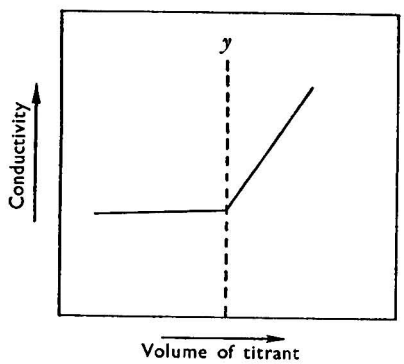


Fig. 1. Typical graph of conductimetric titration; line *y* passes through the equivalence point

In practice the shape of the graph is affected by various factors, such as dilution, variation in temperature and nature of titrant ions. Precipitation itself is, moreover, a time process and depends on the solubility of the precipitate, temperature, presence of foreign ions, local excesses of reagent, adsorption effects and so on, and the slopes of the lines depend on these factors. The essential feature for a conductimetric titration, however, is that the change in slope of the conductivity - volume curve should be sufficiently well defined for a sharp intersection to be possible at the equivalence point.

One of the factors militating against the adoption of conductivity methods is the belief that the apparatus is complicated and the taking of measurements is tedious. This may be true when absolute conductivity measurements of high accuracy are required, but for many purposes satisfactory titrations can be performed with easily operated apparatus that is readily available at moderate cost and, as will be shown in this paper, can be adapted to use in micro-determinations.

Experimental

In preliminary experiments sulphuric acid solutions of known concentration with and without admixed nitric acid were titrated conductimetrically with various titrants of approximate concentration 0·02 *N* added from a 10-ml burette. The acid solutions were chosen so as to represent in concentration and volume the conditions likely to be produced by a micro-scale combustion in which normally not more than 5 mg of compound are oxidised, *i.e.*, 0·3 to 1 mg of sulphur in a volume of 50 ml.

Titrants tested in this way included barium chloride, nitrate, hydroxide and acetate. All except the acetate, for various reasons, gave unsuitable graphs. For example, with barium chloride or nitrate the similarity between the mobilities of Cl^- or NO_3^- and $\frac{1}{2}SO_4^{2-}$ made the pre-equivalence section of the graph almost parallel to the *x*-axis, and the post-equivalence section was then not steep enough to give an angle sufficiently acute for accurate intersection at the equivalence point.

Again, with barium hydroxide both the H^+ and SO_4^{2-} from the sulphuric acid were immobilised, resulting in a greatly enhanced pre-equivalence decrease in conductivity.

When nitric acid was present, however, additional hydrogen ions were introduced and their removal gave a continued decrease in conductivity at the point (the sulphate equivalence point) where an increase was required. The equivalence point for sulphate was therefore obscured.

Further, the acetate ion, which has a mobility much lower than that of most inorganic ions, was also found to give a pre-equivalence decrease in conductivity, but, owing to the formation of slightly ionised acetic acid and consequent removal of the H^+ from the nitric acid, the expected post-equivalence increase in conductivity was again obscured.

It was eventually found to be more satisfactory first to neutralise the sulphuric - nitric acid mixture with ammonium hydroxide and then to titrate the ammonium salts produced with barium acetate.

Greater accuracy was obtained by—

(*a*) the use of 0·1 *N* barium acetate added from a 2-ml microburette instead of the use of 0·02 *N* solution, in order to keep the change in volume of the test solution to a minimum;

(*b*) the addition of ethanol to the test solution in order to accelerate precipitation and to reduce the solubility of the barium sulphate; and

(*c*) the inclusion in the circuit of a separate comparison solution of such concentration that, when it was connected to the conductivity bridge through separate electrodes, the potentiometer readings during titration indicated the changing ratio of the conductivities of the test and comparison solutions. By varying the initial concentrations of this comparison solution, it was possible to obtain readings from the lower and most accurate section of the logarithmic scale of the bridge, whatever the original concentration of the test solution.

It was found that for some of the combustions with the Pregl spiral tube[5] efficient washing of the products from the tube was possible with only 15 ml of distilled water (three 5-ml portions). This made it possible, by also reducing the volume of ethanol to 5 ml (20 per cent. by volume), to keep the total volume of the washings to about 25 ml. This is desirable, as it is possible that at high dilution, owing to less complete precipitation, the intersection of the straight-line graphs will coincide less exactly with the equivalence point.

Method

Apparatus—

Conductivity bridge—A Mullard type E 7566 was used. It is basically a modified Wheatstone bridge operating at a test frequency of 2·9 kilocycles per second. Balance is obtained by means of a precision potentiometer that forms the two ratio arms of the bridge, the circuit being designed so that full movement of the potentiometer corresponds to a ratio change of 100 to 1. Balance is indicated by an electron-beam indicator or Magic Eye.

The bridge may be used with the test solution in conjunction with a comparison solution, as described in (*c*) above.

Test cell—A beaker-type cell of Pyrex glass with an internal diameter of 4·5 cm, 11 cm deep and having a capacity of approximately 150 ml with polished 9-mm × 15-mm platinum electrodes set internally on opposite sides about 6 mm from the base. Connecting wires to the electrodes are sealed into the glass of the cell through wax-filled glass tubes lying vertically along the external wall of the cell (see Fig. 2).

Comparison cell—A 100-ml Pyrex-glass beaker containing the comparison solution into which suitable electrodes are inserted; Mullard Dip Electrodes type E 7591 (polished platinum) were used.

Microburette—A self-filling burette of capacity 2 ml, having an accuracy of ± 0·001 ml.

Thermostatically controlled oil-bath—A 10-litre glass tank filled with transformer oil. This is constant to within ± 0·05° C of initial room temperature during a determination.

The arrangement of the apparatus is shown diagrammatically in Fig. 3.

Reagents—

Barium acetate, 0·1 N—Prepared from analytical-reagent grade material and standardised gravimetrically.

Ammonium hydroxide, approximately 0·04 N.

Methyl red indicator solution—A saturated solution in *N*/60 sodium hydroxide.

Comparison solution—Prepared by diluting 3 ml of 0·02 *N* nitric or sulphuric acid with distilled water to 50 ml.

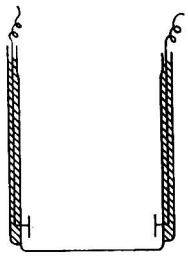


Fig. 2. Test cell for conductimetric titration

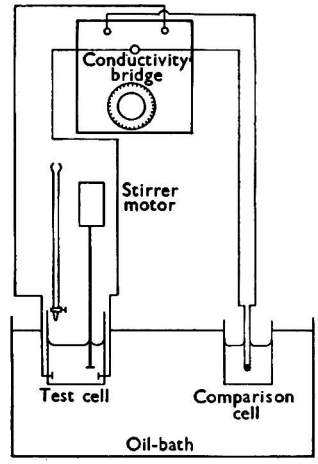


Fig. 3. Conductimetric titration assembly

PROCEDURE—

The organic compound may be oxidised by any standard method giving sulphuric acid, provided that the volume of the combustion products is not excessive. If a Pregl spiral tube is used, wash it out when cool with three 5-ml portions of water, collect the washings in the test cell and boil them to destroy hydrogen peroxide. Then add 5 ml of ethanol and one drop of methyl red indicator solution and titrate with 0·04 *N* ammonium hydroxide to the neutral point. Place the test cell in the thermostatically controlled oil-bath and connect the electrodes to the conductivity bridge. Connect the electrodes in the comparison solution to the bridge also, and adjust the solution by adding either more acid or water until the potentiometer reading, with the test cell in the circuit, is about 0·2 to 0·3. Start the stirrer and, when thermal equilibrium is established, titrate with 0·1 *N* barium acetate, added from the 2-ml microburette. When the potentiometer scale is steady, take readings, initially after each 0·05 or 0·1-ml addition of the barium acetate, and later in the experiment after each 0·1 or 0·2-ml addition.

Plot the potentiometer reading against the volume of titrant; the end-point is indicated by the point of intersection of the straight lines.

1 ml of 0·1 *N* barium acetate = 1·603 mg of sulphur.

RESULTS

Preliminary conductimetric titrations were carried out on prepared sulphuric - nitric acid mixtures; the volume of each solution titrated was about 50 ml and contained about 10 per cent. of ethanol by volume. Usually 2 or 3 ml of approximately 0·02 *N* sulphuric acid that had been standardised gravimetrically by Pregl's method[5] were taken (the acid used was 0·02266 *N*). The results are given in Table I and show a satisfactory degree of accuracy (error not greater than ± 1 per cent.), but, owing to the waiting period required after each addition of titrant for the precipitation of barium sulphate to reach equilibrium, the total time was excessive, being about 2 hours for each titration. Fig. 4 shows how the end-points of the titrations were determined.

Further experiments were carried out on prepared sulphuric - nitric acid mixtures containing 15 ml (approximately 30 per cent. by volume) of ethanol in an attempt to reduce the length of the waiting periods. The total time required for each titration was reduced to 30 minutes and the desired accuracy was maintained, as shown by the results given in Table II; Fig. 5 shows typical titration curves.

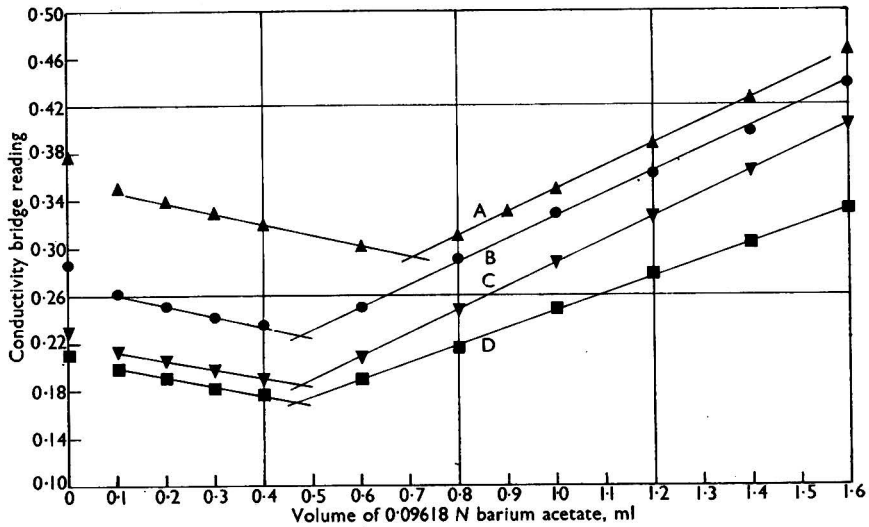


Fig. 4. Conductimetric titration curves: curve A, test No. 2; curve B, test No. 4; curve C, test No. 3; curve D, test No. 5

TABLE I

CONDUCTIMETRIC TITRATIONS OF PREPARED SULPHURIC - NITRIC ACID MIXTURES HAVING A VOLUME OF ABOUT 50 ml AND CONTAINING APPROXIMATELY 10 PER CENT. OF ETHANOL BY VOLUME

Test No.	Volume of 0·02266*N* sulphuric acid present, ml	Volume of 0·02*N* nitric acid present, ml	Volume of 0·09618*N* barium acetate required, ml	Sulphur added, mg	Sulphur found, mg	Error, %
2	3·000	2·0	0·707	1·0899	1·0901	—
3	2·000	1·0	0·474	0·7266	0·7309	+0·6
4	2·000	2·0	0·473	0·7266	0·7294	+0·4
5	2·000	2·0	0·468	0·7266	0·7217	−0·7

TABLE II

CONDUCTIMETRIC TITRATIONS OF PREPARED SULPHURIC - NITRIC ACID MIXTURES HAVING A VOLUME OF ABOUT 50 ml AND CONTAINING APPROXIMATELY 30 PER CENT. OF ETHANOL BY VOLUME

Test No.	Volume of 0·02266*N* sulphuric acid present, ml	Volume of 0·02*N* nitric acid present, ml	Volume of 0·09618*N* barium acetate required, ml	Sulphur added, mg	Sulphur found, mg	Error, %
11	1·000	2·0	0·240	0·3633	0·3701	+1·6
12	1·000	2·0	0·232	0·3633	0·3578	−1·5
14	2·000	2·0	0·466	0·7266	0·7186	−1·1
15	2·000	2·0	0·470	0·7266	0·7248	−0·3
18	3·000	1·0	0·700	1·0899	1·0794	−1·0
19	3·000	1·0	0·706	1·0899	1·0887	−0·1
20	2·000	2·0	0·475	0·7266	0·7325	+0·8
22*	2·000	1·0	0·468	0·7266	0·7217	−0·7
23*	1·000	1·0	0·238	0·3633	0·3670	+1·1

* Total volume of 25 ml, containing 20 per cent. of ethanol by volume.

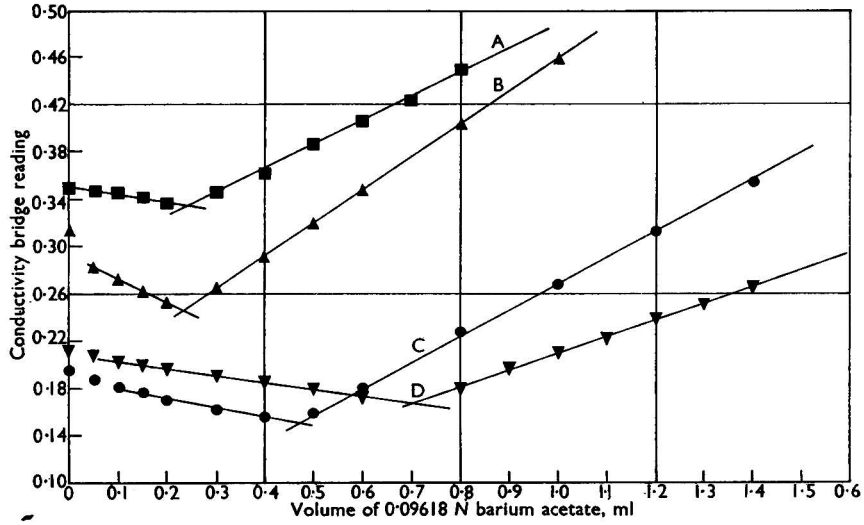


Fig. 5. Conductimetric titration curves: curve A, test No. 23; curve B, test No. 12; curve C, test No. 15; curve D, test No. 18

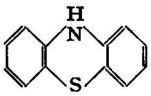
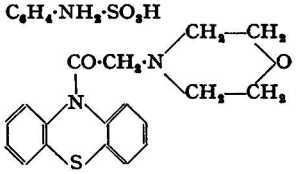
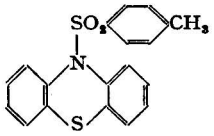
The results of titrations additional to and including those reported in Tables I and II show that the precision with which the equivalence point may be determined graphically is usually of the order of ± 0·005 ml of 0·09618 *N* barium acetate, *i.e.*, approximately ±0·008 mg of sulphur. Errors as milligrams of sulphur in tests Nos. 2 to 5 and 11 to 20 are as follows—

Test No.	2	3	4	5	11	12	14	15	18	19	20
Sulphur, mg	0·000	+0·004	+0·003	−0·005	+0·007	−0·006	−0·008	−0·002	−0·011	−0·001	+0·006

Results for the determination of sulphur in a number of organic compounds are shown in Table III; for the first three compounds the volume of the washings was about 50 ml, containing 30 per cent. of ethanol by volume, and for the other two compounds it was about 25 ml, containing 20 per cent. of ethanol by volume.

TABLE III

DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS BY CONDUCTIMETRIC TITRATION OF THE WASHINGS FROM THE PREGL SPIRAL TUBE

Compound	Weight of compound taken, mg	Theoretical sulphur content of compound, %	Determined sulphur content of compound, %
$C_6H_4{\cdot}NH_2{\cdot}SO_2NH_2$	3·930	18·65	18·82
	4·188	16·11	16·29
$C_6H_4{\cdot}NH_2{\cdot}SO_2H$	4·038	18·55	18·41
	6·934	9·85	9·94
	5·220	18·18	18·20

I acknowledge with thanks the assistance of Dr. D. T. Gibson, The University, Glasgow.

This paper extends work that was reported at the meeting of the Society held in Glasgow on Wednesday, May 6th, 1953.

REFERENCES

1. Gibson, D. T., and Caulfield, T. H., *Analyst*, 1935, **60**, 522.
2. Wilson, H. N., Pearson, R. M., and Fitzgerald, D. M., *J. Appl. Chem.*, 1945, **4**, 490.
3. Sijderius, R., *Anal. Chim. Acta.*, 1954, **11**, 28.
4. Pregl, F., "Quantitative Organic Micro-Analysis," Fifth English Edition, J. & A. Churchill Ltd., London, p. 132.
5. ——, *op. cit.*, Third English Edition, p. 117.

CHEMISTRY DEPARTMENT
HERIOT-WATT COLLEGE
EDINBURGH, 1

September 18th, 1956

The Micro-determination of Active Hydrogen in Organic Compounds by Reaction with Lithium Aluminium Hydride

BY A. F. COLSON

A procedure is described for the accurate micro-determination of active hydrogen in solid or liquid organic compounds by reaction with lithium aluminium hydride. A suitable weight (3 to 10 mg) of the sample is added in a closed system to an organic solvent containing lithium aluminium hydride, and the mixture is shaken in a constant-temperature cabinet until evolution of hydrogen ceases. The active-hydrogen content of the sample is then calculated from the volume of gas liberated in accordance with the equation—

$$4RH + LiAlH_4 = LiAlR_4 + 4H_2.$$

The determination is carried out in an apparatus originally designed for the micro-determination of unsaturation by catalytic hydrogenation. This apparatus is described in detail elsewhere. The method is suitable for routine or occasional use and under the specified conditions will give results accurate to 3·0 per cent. and reproducible to 2·5 per cent., expressed as standard deviations in each case.

The results obtained with various types of compound including acids, alcohols, phenols and amines are given.

UNDER suitable conditions one or more of the hydrogen atoms in many types of organic compound will react with a Grignard reagent, such as methyl magnesium halide, in accordance with the following equation—

$$RH + CH_3MgX = RMgX + CH_4.$$

From the volume of methane evolved the amount of this so called active hydrogen present in the organic compound can be accurately determined, as in the well known Zerewitinoff method.

In recent years a new substance, lithium aluminium hydride, first prepared by Finholt, Schlesinger and Bond[1] in 1947, has been proposed as an alternative reagent for this determination, and various procedures have been described.[2,3,4,5]

This metal hydride reacts with active hydrogen in accordance with the equation—

$$4RH + LiAlH_4 = LiAlR_4 + 4H_2$$

and the volume of hydrogen liberated provides a measure of the active-hydrogen content of the sample.

The relative merits of these two reagents have been examined by several investigators,[2,3,4] who find that lithium aluminium hydride is in general as satisfactory as the Grignard reagents. For routine or occasional determinations of active hydrogen, we required a simple micro-scale method accurate to 5 per cent. or better, and suitable for use with an apparatus designed originally for the micro-determination of unsaturation by hydrogenation.[6] As

the Grignard reagents were unsuitable for use in this apparatus, attention was directed to the development of a method based on the use of lithium aluminium hydride, and the procedure described in this paper was finally adopted.

METHOD

APPARATUS—

An apparatus designed for the micro-determination of unsaturation by hydrogenation and fully described elsewhere[6] can be used without modification.

For convenience of reference a sufficiently detailed diagram of the assembled apparatus is shown in Fig. 1.

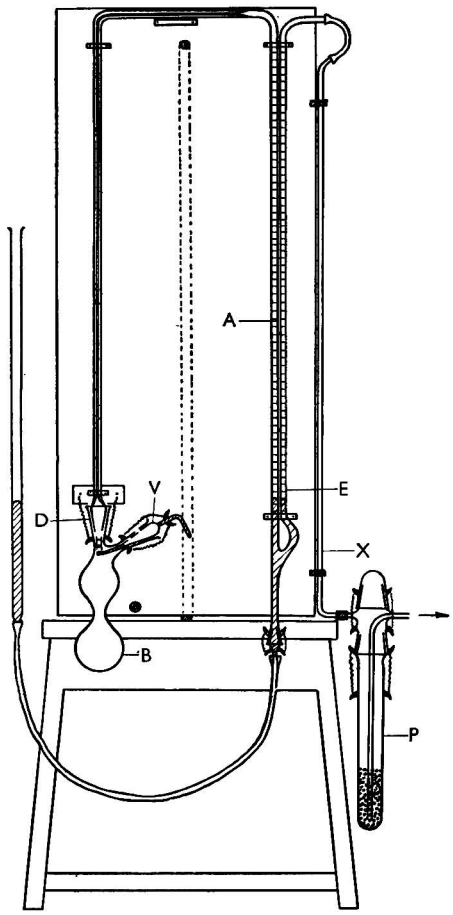


Fig. 1. Assembled apparatus for micro-determination of active hydrogen

REAGENTS—

Solvents—The solvents used were di-*n*-butyl ether and N-ethylmorpholine. They were purified before use by being dried over calcium hydride, heated for 1 hour at 90° C with lithium aluminium hydride (1 g per litre) and distilled *in vacuo*. The distilled solvents were stored over calcium hydride in glass bottles fitted with the dispensing device illustrated in Fig. 2.

Additional solvents that have been used by other workers include diethyl ether, di-*n*-propyl ether, di*iso*propyl ether, dioxan, tetrahydrofuran and anethole, of which dioxan and di*iso*propyl ether possess the disadvantage of low solvent power for lithium aluminium hydride.

Lithium aluminium hydride—The reagent used throughout was a commercial product supplied in powder form. The material as received was found to be unsuitable for use and was purified in the following manner. About 10 g of the powder were heated under reflux with about 200 ml of dry ether for several hours, and the cold solution was filtered through an immersion filter into a dry distillation flask. The filtrate was concentrated by distillation and the resulting syrup heated *in vacuo* at 70° C to remove residual ether. The dry solid residue was broken up, sieved through platinum gauze and transferred in portions of about 30 mg each to a series of glass tubes (12 cm long and having an internal diameter of 8 mm) previously dried and filled with dry nitrogen. Each tube was quickly drawn out to a long narrow neck and sealed off as shown in Fig. 3. In all operations special care was taken to protect the reagent from moisture. Although not completely soluble in the solvents employed, the purified reagent proved to be entirely satisfactory in use. It is probable that lithium aluminium hydride can now be purchased in a form suitable for use without further treatment, but the storage of suitable quantities of the reagent in sealed tubes should not be omitted, since it provides a very convenient method of dispensing the required amount of reagent, and eliminates the difficulties associated with the manipulation and storage of solutions of this material.

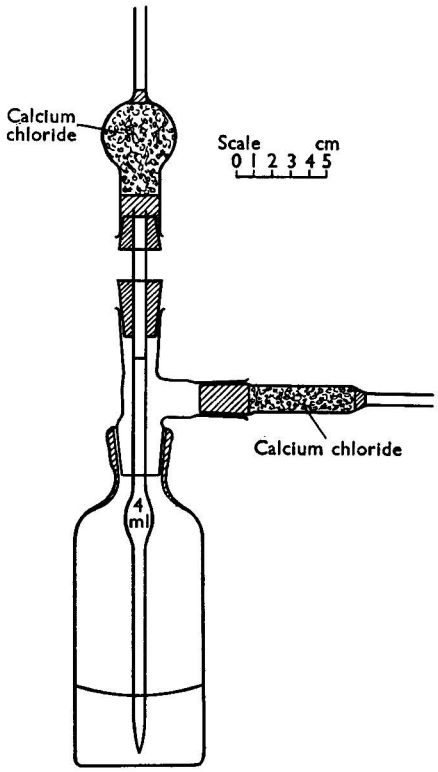


Fig. 2. Apparatus for storing and dispensing solvents

Fig. 3. Ampoule for storing lithium aluminium hydride

PROCEDURE FOR SOLID OR NON-VOLATILE LIQUID SAMPLES—

Clean the reaction vessel, B (Fig. 1), dry it in an oven and cool it in a stream of dry air.

Using the dispenser shown in Fig. 2, put 4·0 ml of the selected solvent into the reaction vessel and add the contents of one tube of lithium aluminium hydride.

Insert the lubricated plug, V, into the side-arm of vessel B, and introduce the weighed sample and its container so that they are supported on the glass platform at the lower end of the plug. Attach the reaction vessel to the lubricated joint, D (Fig. 1), turn the plug, V,

to the open position and lower the mercury in the burette, A, until it falls below the junction with the branch tube, E.

Connect the tube, X, to the saturator, P (containing about 2·0 ml of the same solvent as that in the reaction vessel), attach the saturator to a supply of hydrogen free from oxygen and sweep out the apparatus for about 20 minutes. Detach the tube, X, from the saturator, raise the mercury in the burette, A, until it reaches the 5·0-ml graduation, and then turn the plug, V, until the exit orifice on the reaction vessel is just closed and the sample container remains securely on its support.

Switch on the shaking mechanism and, when no further increase in volume is observed, record the reading on the gas burette, A, after levelling the mercury in A and E.

TABLE I

DETERMINATION OF ACTIVE HYDROGEN IN BENZOIC ACID (0·82 PER CENT. OF ACTIVE HYDROGEN), BY REACTION WITH LITHIUM ALUMINIUM HYDRIDE IN DI-*n*-BUTYL ETHER

Weight taken, mg	Active hydrogen found, %	Deviation from true value (0·82%), %	Deviation from mean value (0·83%), %
8·017	0·80	0·02	0·03
7·747	0·86	0·04	0·03
7·173	0·85	0·03	0·02
8·444	0·84	0·02	0·01
8·082	0·83	0·01	0·00
7·948	0·84	0·02	0·01
6·520	0·79	0·03	0·04
8·141	0·85	0·03	0·02
7·625	0·83	0·01	0·00
8·113	0·81	0·01	0·02
	Mean value = 0·83	Standard deviation = 3·0%	Standard deviation = 2·5%

TABLE II

DETERMINATION OF ACTIVE HYDROGEN BY REACTION WITH LITHIUM ALUMINIUM HYDRIDE, WITH DI-*n*-BUTYL ETHER AS SOLVENT

Compound	Weight taken, mg	Active hydrogen present, %	Active hydrogen found, %	Error,† %
p-Toluic acid	8·442	0·74	0·75	+1·5
	8·244	0·74	0·76	+3·0
	7·939	0·74	0·75	+1·5
Acetanilide	8·885	0·75	0·73	−3·0
	8·931	0·75	0·77	−3·0
	9·183	0·75	0·74	+1·5
Aniline	4·176	2·16	2·24	+3·5
	3·418	2·16	2·25	+4·0
	3·334	2·16	2·23	+3.0
Ethanol	3·201	2·19	2·26	+3·0
	3·564	2·19	2·23	+2·0
	3·321	2·19	2·17	−1·0
tert.-Amyl alcohol	5·234	1·14	1·17	+2·5
	5·434	1·14	1·19	+4·5
	6·070	1·14	1·16	+2·0
Cholesterol	16·114	0·26	0·27	+4·0
	20·660	0·26	0·27	+4·0
Resorcinol	5·342	1·83	1·86	+1·5
	5·453	1·83	1·85	+1·0
	5·579	1·83	1·85	+1·0
2-Naphthol	9·601	0·70	0·72	+3·0
	9·470	0·70	0·73	+4·5
	9·466	0·70	0·68	−3·0
	9·262	0·70	0·72	+3·0
Phloroglucinol*	3·120	2·39	2·30	−4·0
	3·422	2·39	2·32	−3·0
	3·316	2·39	2·44	+2·0

* In N-ethylmorpholine as solvent.

† Figures in this column have been "rounded off" to the nearest 0·5.

Turn the plug, V, until the sample container drops from its platform into the solvent, shake the reaction vessel until evolution of hydrogen is complete, and again record the reading on the gas burette to obtain the volume of hydrogen evolved.

Calculate the percentage of active hydrogen in the sample from the expression—

$$\text{Active hydrogen, per cent.} = \frac{V \times 4{\cdot}5}{W},$$

where V = volume of hydrogen evolved in ml, corrected to S.T.P.,
W = weight of sample in mg, and
4·5 = factor for conversion of volume to weight of hydrogen.

PROCEDURE FOR VOLATILE LIQUID SAMPLES—

Proceed as described for solids, but use the modified reaction vessel in conjunction with a glass capillary sample tube as directed in the method for the determination of unsaturation by catalytic hydrogenation.[6]

RESULTS

With di-*n*-butyl ether as the solvent and pure benzoic acid as the test substance, the accuracy and precision of the method have been determined from a series of ten experiments. The results obtained and the relevant standard deviations are given in Table I.

The results for a few determinations carried out on each of several different types of compound are presented in Table II.

REFERENCES

1. Finholt, A. E., Schlesinger, H. I., and Bond, A. C., *J. Amer. Chem. Soc.*, 1947, **69**, 1199.
2. Krynitsky, J. A., Johnson, J. E., and Carhart, H. W., *Ibid.*, 1948, **70**, 486.
3. Zaugg, H. E., and Horrom, B. W., *Anal. Chem.*, 1948, **20**, 1026.
4. Hochstein, F. A., *J. Amer. Chem. Soc.*, 1949, **71**, 305.
5. Lieb, H., and Schöniger, W., *Mikrochemie*, 1950, **35**, 404.
6. Colson, A. F., *Analyst*, 1954, **79**, 298.

IMPERIAL CHEMICAL INDUSTRIES LIMITED
RESEARCH DEPARTMENT, ALKALI DIVISION
WINNINGTON, NORTHWICH, CHESHIRE

October 23rd, 1956

The Quantitative Determination of the Antioxidants Propyl, Octyl and Dodecyl Gallate in Oils and Fats

BY H. J. VOS, H. WESSELS AND C. W. TH. SIX

Propyl, octyl and dodecyl gallates are determined absorptiometrically in a sodium acetate buffer solution with ferrous tartrate, which is specific for the gallates. After solution of the fat in light petroleum, propyl gallate is extracted with water and the higher gallates with absolute methanol. The conditions governing the reaction were studied. With the extraction methods described a 95 to 97 per cent. recovery of antioxidant from oils and fats was possible.

GALLIC acid esters of certain primary aliphatic alcohols, *viz.*, propyl, octyl and dodecyl gallates, are permitted as antioxidants for use in foods in a number of European countries. As the statutory regulations in force limit the permissible amounts, there is need for a simple and accurate method of assessing the amounts of these esters present.

Colorimetric,[1,2] spectrophotometric,[3] potentiometric,[4] polarographic[5] and paper-chromatographic[6] methods for the determination of one or more of the antioxidants are described in the literature.

In order to develop for the quantitative determination of propyl and the higher gallates in fats and oils a simple method by which at least 95 per cent. of the added gallate can be recovered, we modified the colorimetric method of Mahon and Chapman[1] for propyl gallate. This method is based on the colour reaction with ferrous tartrate, specific for polyphenolic compounds, used by Mattil and Filer[7] for the determination of gallic acid in oils and fats.

METHOD

REAGENTS—

Methanol—Boil 1 litre of absolute methanol under reflux for 1 hour with 8 g of solid potassium hydroxide and 5 g of aluminium powder and then distil.

Ferrous tartrate solution—Dissolve 100 mg of analytical-reagent grade ferrous sulphate and 500 mg of analytical-reagent grade potassium sodium tartrate (Rochelle salt) in 100 ml of distilled water. This reagent should be freshly prepared for each series of determinations.

Sodium acetate solution, 1 per cent.—Dissolve 10 g of analytical-reagent grade sodium acetate, $CH_3COONa.3H_2O$, in 1 litre of distilled water.

iso*Amyl alcohol*—Analytical-reagent grade.

Light petroleum, boiling range 40° to 60° C—Shake 1 litre of the light petroleum with small amounts of concentrated sulphuric acid until colourless and then wash it several times with 1 per cent. sodium hydroxide solution and finally with distilled water until it is free from acid. Dry the solvent with anhydrous sodium sulphate, filter and distil.

EXTRACTION PROCEDURE—

Dissolve 50 g of oil or fat in 200 ml of light petroleum, with gentle heating when necessary to effect solution. If the investigation involves coconut fat, palm-kernel fat, beef fat or lard, take 25 g of the fat together with 25 g of gallate-free arachis oil.

Extract the solution 5 times successively with 20-ml portions of distilled water at 30° C, taking 2 minutes over each extraction. Separate the phases and filter the aqueous layer into a 110-ml calibrated flask; then wash the filter with water and add the washing to the filtrate in the flask until the mark is reached.

Shake the fat - light petroleum layer, from which the water has as far as possible been separated and removed, first with a 55-ml portion and then with four 15-ml portions of methanol, taking 2 minutes over each extraction. With some fats partial crystallisation of the glycerides may occur owing to cooling. If so, the extraction should be carried out at 25° C, *e.g.*, by gentle heating of the separating funnel. It is essential to wait at least 5 minutes after each extraction in order to obtain good separation of the layers, which can be assisted by swirling the separating funnel. At least 30 minutes must be allowed after the last extraction before running off the lower layer.

Transfer each extract as completely as possible to a 150-ml separating funnel. Add 3 ml of distilled water to the combined extracts and shake well. After 30 minutes have elapsed, add the final residue of methanol that has separated from the fat - light petroleum layer and shake the separating funnel again. Run off the clear lower layer into a 110-ml calibrated flask and add sufficient methanol to make up to the mark. When necessary, a 125-ml calibrated flask may be used instead.

PROCEDURE FOR DETERMINING PROPYL GALLATE—

Place by pipette 10 ml of the water extract in a 50-ml calibrated flask. Add 1 ml of ferrous tartrate solution, fill up to the mark with sodium acetate solution and mix well. After 10 minutes measure the optical density of the solution at 530 mμ relative to that of water, using an absorptiometer and a 2-cm cell. To determine the optical density of the blank, dilute 10 ml of water extract, without ferrous tartrate solution, to 50 ml with sodium acetate solution and measure the optical density after 10 minutes.

Determine the reference value for propyl gallate by treating 10-ml portions of a solution containing 5 mg of propyl gallate per 100 ml of methanol in a similar manner.

The percentage of propyl gallate present in the oil or fat is given by—

$$\frac{E_1 - E_2}{E_3 - E_4} \times \frac{1}{2p} \times \frac{110}{100},$$

where E_1 = the optical density of the water extract with ferrous tartrate solution,
E_2 = the optical density of the water extract without ferrous tartrate solution,
E_3 = the optical density of standard propyl gallate solution (500 μg) with ferrous tartrate solution,
E_4 = the optical density of standard propyl gallate solution without ferrous tartrate solution, and
p = the weight of fat taken in grams.

PROCEDURE FOR DETERMINING OCTYL AND DODECYL GALLATE—

Place by pipette 10 ml of the methanol extract in a 150-ml separating funnel; with coconut fat, palm-kernel fat, lard or beef fat, 20 ml should be taken. Add 1 ml of ferrous tartrate solution and 40 ml of sodium acetate solution, and mix well. After 10 minutes add 20 ml of a mixture of equal parts of *iso*amyl alcohol and light petroleum, and shake vigorously for 2 minutes. Extract the lower layer, after separation, again for 2 minutes with another 20-ml portion of the mixture of equal parts of *iso*amyl alcohol and light petroleum. Run off the remaining water from the combined extracts as completely as possible, and transfer to a 50-ml flask. Add 3 ml of methanol to obtain a clear solution, dilute to volume with *iso*amyl alcohol and mix well. Measure the optical density of the solution at 550 mμ relative to that of *iso*amyl alcohol, using an absorptiometer and a 2-cm cell. Determine the optical density of the fat extract alone by treating 10 ml of the methanol extract (20 ml for coconut fat, palm-kernel fat, lard or beef fat) in the same way, omitting the ferrous tartrate solution.

Determine the reference value for either octyl or dodecyl gallate by treating 10-ml portions of a solution containing 5 mg of the gallic acid ester in 100 ml of methanol in the same way. If it is not known which gallate is present, octyl and dodecyl gallate can be distinguished from each other by adding 1·5 ml of ferrous tartrate reagent solution to 5 ml of the methanol extract. After 5 minutes add 1 ml of a mixture of equal parts of *iso*amyl alcohol and light petroleum. Shake the mixture carefully (shaking too violently considerably delays the separation of the phases). If the upper layer becomes a violet-blue colour, dodecyl gallate is indicated, since no colour is formed with octyl gallate.

Note that, if the optical density of the methanol extract is more than 1½ times that of the reference solution, the procedure should be repeated with 2 ml instead of 1 ml of ferrous tartrate solution.

The percentage of gallate present in the oil or fat is given by—

$$\frac{E_1 - E_2}{E_3 - E_4} \times \frac{1}{2p} \times \frac{V_1}{100} \times \frac{10}{V_2},$$

where E_1 = the optical density of the methanol extract with ferrous tartrate solution,
E_2 = the optical density of the methanol extract without ferrous tartrate solution,
E_3 = the optical density of standard gallate solution (500 μg) with ferrous tartrate solution,
E_4 = the optical density of standard gallate solution without ferrous tartrate solution,
p = the weight of fat taken in grams,
V_1 = the final volume of the methanol extract (110 or 125 ml), and
V_2 = the volume of the methanol extract taken for the determination (10 or 20 ml).

INVESTIGATION OF THE METHOD

DETERMINATION OF PROPYL GALLATE—

Some of the factors liable to interfere with the determination were investigated.

Influence of the acetate buffer—The pH of the gallate - ferrous tartrate mixture is an important factor governing the intensity and character of the colour formed, as the maximum optical density is attained at pH 7·0 to 7·6. Glasstone[8] recommends ammonium acetate as a buffer for this pH.

Mahon and Chapman[1] also used ammonium acetate; they extracted a solution of fat in light petroleum with an ammonium acetate solution, the propyl gallate passing into the aqueous phase. However, ammonium acetate has several disadvantages, namely (*i*) the extraction of the light petroleum solution is handicapped by emulsification, which is not reduced by the addition of octanol and ethanol, (*ii*) the optical density of the colour formed proves to be dependent upon the concentration of ammonium acetate and (*iii*) ammonium acetate is highly hygroscopic.

We found that extraction of the fat solution with distilled water only was adequate for the quantitative isolation of propyl gallate, no emulsion being formed. On using non-hygroscopic sodium acetate instead of the ammonium salt in the colour development, it appeared that the colour intensity was independent of the amount added. For this reason the addition of a 1 per cent. sodium acetate solution to the water extract is sufficient to ensure maximum intensity, which is measured at 530 mμ.

Effect of extraction—The way in which propyl gallate was extracted by water from a fat - light petroleum solution was investigated by determining the amount of propyl gallate

present in each 20-ml extract, calculated as a percentage of the total amount added. The results are shown in Table I.

TABLE I

RECOVERY OF PROPYL GALLATE FROM SOME OILS AND FATS BY EXTRACTION WITH WATER

	Propyl gallate present in					Total propyl gallate recovered, %
	first extract, %	second extract, %	third extract, %	fourth extract, %	fifth extract, %	
Arachis oil	58·6	24·8	10·0	4·6	—	98·0
Hardened cotton-seed oil ..	58·6	23·8	10·0	5·2	—	97·6
Lard	42·5	22·1	13·0	8·9	—	86·5
Lard (25 g) + arachis oil (25 g)	46·5	24·9	12·9	8·1	4·4	96·8

Approximately 58·5 per cent. (for the two vegetable oils) and 42·5 per cent. (for lard) of propyl gallate present in the fat phase was isolated during each extraction, indicating a rather unfavourable distribution of the gallate between lard and the aqueous phase. If, however, a mixture of equal parts of lard and arachis oil, instead of lard alone, is extracted, the distribution of propyl gallate is more favourable, five extractions being sufficient to recover at least 95 per cent. of the gallate.

We also found that mixing the lard with oil resulted in a considerable reduction of the partial crystallisation that frequently accompanies the aqueous extraction of pure lard - light petroleum solutions. If, in addition, the temperature of the water was maintained at 30° C, crystallisation did not occur at all.

The results with beef fat were similar. Four extractions of pure beef fat led to the recovery of 85 per cent. of gallate. When a mixture of equal parts of beef fat and arachis oil was extracted 5 times, the recovery was 96 per cent.

Influence of synergists—In addition to antioxidants, synergists, *e.g.*, citric acid, ascorbic acid and phosphoric acid, are sometimes used in food. Being highly soluble in water, these compounds pass into the water phase together with the propyl gallate. Ascorbic acid at a concentration of 0·3 per cent. and citric acid at a concentration of 0·01 per cent., calculated on the basis of the fat, do not interfere. If the fat contains 0·02 per cent. of citric acid, however, the optical density will be lower.

Even at a concentration of 0·01 per cent. phosphoric acid reduces the colour intensity noticeably, and at higher concentrations an opalescent solution results, yielding an unreliable optical density. The addition of more ferrous tartrate did not counteract this adverse effect.

DETERMINATION OF OCTYL AND DODECYL GALLATE—

The solubility of the higher gallic acid esters in a fat - light petroleum solution is such that they cannot be extracted by distilled water or by 72 per cent. ethanol, as is recommended for the extraction of several other antioxidants.[1] Our experience confirms that of others.[2,9] Higher concentrations of ethanol proved no more successful, and the use of 96 per cent. ethanol led to a homogeneous mixture. It was found that absolute methanol was suitable as an extraction solvent for the higher gallates. The methanol extract, however, still contained so much fat and light petroleum that the addition of the ferrous tartrate solution and sodium acetate solution produced a milky liquid that, although coloured when gallates were present, could not be measured in the absorptiometer. *iso*Amyl alcohol was the only solvent that proved satisfactory for extracting the colour complex quantitatively from the turbid reaction mixture.

The presence of light petroleum in the methanol extract induced us to investigate the effect of this solvent on colour extraction with *iso*amyl alcohol. The best results were obtained when the reaction mixture was extracted twice for 2 minutes each time with mixtures of *iso*amyl alcohol and light petroleum, the ratio of alcohol to light petroleum being between 3 to 2 and 2 to 3. Within these limits the presence of light petroleum in the methanol extract had no influence on the colour intensity. The maximum colour intensity of the *iso*amyl alcohol - light petroleum extract, which was measured at 550 mμ, was achieved at pH 6·8 to 7·1. This pH can be obtained by using a 1 per cent. sodium acetate solution.

The extraction of oils and fats with methanol—Refined soya-bean oil was chosen as the test material; 50 g dissolved in 200 ml of light petroleum were mixed with 10 ml of methanolic

gallate solution, containing 5 mg of gallate. This mixture was extracted first with a 45-ml portion and then with three 15-ml portions of methanol. A fairly large amount of fat and light petroleum was dissolved in the methanol. This could be separated by the addition of 3 ml of water, the lower methanolic layer still containing the total amount of the extracted gallate.

The blank extract was prepared by extracting 50 g of the oil dissolved in 200 ml of light petroleum first with a 55-ml portion and then with three 15-ml portions of methanol and adding 3 ml of water to the combined extracts. Both extracts were made up to 100 ml and the optical density of each was determined on 10-ml aliquots.

The way in which the gallate was extracted by methanol was investigated in a second experiment by measuring the optical density of each extract separately. After deduction of the corresponding blank value, the percentage of gallate present in all the extracts could be calculated relative to the reference value of 1 ml of the standard gallate solution.

In an investigation of the extraction of octyl gallate with methanol, it was found that the recovery from the combined extracts, after 3 ml of water had been added, was 93·7 per cent. The recoveries from a 55-ml extract and three 15-ml extracts were 69·0, 11·9, 7·5 and 4·7 per cent., respectively, the recovery from the extracts together being 93·1 per cent.

During four extractions, 69, 39, 39·3 and 40 per cent. of the gallate still present in the fat phase were isolated. This indicated a constant degree of distribution of the gallate when the fat phase was shaken with 15 ml of methanol. It was therefore impossible, even when absolute methanol was used, to isolate the higher gallates quantitatively from the fat fraction. A fifth extraction with 10 ml of methanol was necessary to recover at least 95 per cent. of the gallate originally added to the fat.

When the extraction method was applied to coconut fat or palm-kernel fat, the gallate recovered proved to be considerably less than 95 per cent., the end volume of the extract (without the addition of water) being less than normal. When, however, a mixture of 25 g of coconut fat or palm-kernel fat and 25 g of arachis oil was extracted, the final volume of the extract was found to be normal, and the percentage of recovered gallate no longer deviated.

Effect of other antioxidants and synergists—If other antioxidants, such as butylated hydroxyanisole or butylated hydroxytoluene were also present in the fat, they passed into the methanol phase together with the gallates on being shaken with methanol. Both antioxidants, however, at the customary concentration of 0·02 per cent., had no adverse effect on determinations of the gallic acid esters.

The influence of the synergists citric acid, ascorbic acid and phosphoric acid on the determination of the higher gallates was completely identical with their effects on the determination of propyl gallate and will only be apparent if the fat is extracted directly with methanol. Normally these materials will be removed in the water extract with the propyl gallate.

Application of the method to determining propyl and dodecyl gallates in the presence of each other

Finally we have tried by combining the two extraction procedures to separate and determine quantitatively a mixture of propyl and of dodecyl gallate in arachis oil. To 50 g of the oil dissolved in 200 ml of light petroleum, 5 mg of propyl gallate and 5 mg of dodecyl gallate were added, each dissolved in 1 ml of methanol. The solution was extracted with five 20-ml portions of water and then with a 55-ml portion, three 15-ml portions and finally a 10-ml portion of methanol. The aqueous treatment results in the light petroleum solution becoming saturated with water. This permits the fifth extraction with methanol to be performed with 15 ml instead of 10 ml, without any noticeable change in the final volume of the methanol extract after the addition of 3 ml of water. The recovery figures for the propyl and dodecyl gallates were 98·0 and 97·1 per cent., respectively.

Results

The extraction method developed for soya-bean oil was used on various other fats and oils.

The results shown in Table II for oils and fats to which either octyl gallate or dodecyl gallate dissolved in 10 ml of methanol had been added were obtained by extraction with a 45-ml portion, three 15-ml portions and finally a 10-ml portion of methanol.

TABLE II

RECOVERY OF OCTYL AND DODECYL GALLATES FROM VARIOUS OILS AND FATS BY EXTRACTION WITH METHANOL

	Octyl gallate recovered, %	Dodecyl gallate recovered, %
Hardened train oil	97·5	97·0
Lard	96·8	95·5
Beef fat	98·0	96·2
Margarine fat	96·4	96·7
Arachis oil	95·0	96·0
Soya-bean oil	96·0	93·9
Coconut fat (25 g) + arachis oil (25 g)	96·0	96·5
Palm-kernel fat (25 g) + arachis oil (25 g)	96·5	96·0

These results show that for both gallic acid esters five extractions with methanol are satisfactory.

The method was applied to various fats and oils to which a mixture of propyl and dodecyl gallate had been added, and the results are shown in Table III.

TABLE III

RECOVERY OF PROPYL AND DODECYL GALLATE IN THE PRESENCE OF EACH OTHER FROM VARIOUS OILS AND FATS

	Propyl gallate recovered, %	Dodecyl gallate recovered, %
Arachis oil	97·7	97·0
Hardened cotton-seed oil	98·0	96·0
Lard (25 g) + arachis oil (25 g)	96·7	97·5
Beef fat (25 g) + arachis oil (25 g)	97·3	98·0
Coconut fat (25 g) + arachis oil (25 g)	98·0	97·0

REFERENCES

1. Mahon, J. H., and Chapman, R. A., *Anal. Chem.*, 1951, **23**, 1116.
2. Kahan, S., *J. Ass. Off. Agric. Chem.*, 1952, **35**, 186.
3. Whetsel, K. B., Roberson, W. E., and Johnson, F. E., *J. Amer. Oil Chem. Soc.*, 1955, **32**, 493.
4. Wenger, F., *Mitt. Lebensmitt. Untersuch. Hyg., Bern*, 1954, **45**, 185.
5. Baltes, J., *Fette, Seif., Anstrichmitt.*, 1954, **56**, 483.
6. Gander, K. F., *Ibid.*, 1955, **57**, 423.
7. Mattil, K. F., and Filer, L. J., *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 427.
8. Glasstone, S., *Analyst*, 1925, **50**, 49.
9. Janecke, H., *Dtsch. LebensmittRdsch.*, 1955, **51**, 121.

CENTRAL INSTITUTE FOR NUTRITION RESEARCH, T.N.O.
UTRECHT, THE NETHERLANDS

June 19th, 1956

The Use of Oxycellulose in the Assay of Aqueous Alkaloidal Solutions for Injection

BY D. A. ELVIDGE, K. A. PROCTOR AND C. B. BAINES

Oxycellulose can be used as a carboxylic cation-exchange medium for the separation of the active ingredient and bacteriostatic agent in aqueous solutions for injection. The two constituents are separated quantitatively and in a pure form so that spectrophotometric determinations are possible. The method, which is simple and rapid, has been applied to seventeen different solutions containing phenol or chlorocresol.

MANY of the aqueous solutions for injection listed in the British Pharmacopoeia and the British Pharmaceutical Codex contain only an active ingredient and a bacteriostatic agent. When the active ingredient exhibits characteristic ultra-violet absorption, the obvious approach to its determination would seem to be by spectrophotometric measurement. Such measurements can be carried out simply and rapidly, and the necessary equipment is now

a common feature of analytical and control laboratories. The spectrophotometric determination of the active ingredient becomes more difficult, however, when the bacteriostatic agent also exhibits ultra-violet absorption, and it is often impossible without some preliminary separation. Unless this is rapid and straightforward the advantages gained by the use of spectrophotometry are nullified.

Of the bacteriostatic agents at present in common use, only phenol and chlorocresol absorb in the ultra-violet region, and in 1955 Brealey and Proctor[1] described three fundamentally different methods of assay for eight preparations containing chlorocresol. When the absorption of the active ingredient was so high in comparison with that of the chlorocresol that the latter could be ignored, a "direct spectrophotometric method" was used. For those samples in which the absorption characteristics of the two components were so different as to allow both to be determined by making measurements at two wavelengths, a "simultaneous determination method," such as is used for many two-component mixtures, was applied. "Separation methods" involving solvent extraction or partition chromatography were used when the absorption curves of the two ingredients were so similar as to render simultaneous determination inaccurate or when the absorption of the active ingredient was much less than that of the chlorocresol.

Although the spectrophotometric assays were accurate and more rapid than chemical determinations, it was realised that they were of only limited application and that the ideal method would be one by which any injection solution containing an interfering bacteriostatic agent could be determined. We believe that we have gone a considerable way towards the solution of this problem in the method described below, which has been applied to injection solutions of the following containing phenol or chlorocresol—

adrenaline acid tartrate,
apomorphine hydrochloride (with and without sodium metabisulphite),
atropine sulphate,
diamorphine hydrochloride (with sodium metabisulphite),
emetine hydrochloride,
hyoscine hydrobromide,
lobeline hydrochloride,
methylamphetamine hydrochloride (with and without sodium chloride),
morphine sulphate (with and without sodium metabisulphite and with atropine sulphate),
neostigmine methylsulphate,
pethidine hydrochloride,
procaine and adrenaline,
quinine hydrochloride.

In these injection solutions we have determined both the active ingredient and bacteriostatic agent.

Although it might often have proved possible to develop a two-point method for the simultaneous determination of the two absorbing components, there is no doubt that fundamentally it is much more satisfactory from the point of view of accuracy to separate the components quantitatively and determine them individually. The use of ion-exchange resins for the separation of alkaloids has been investigated fairly extensively, but it has usually been found difficult to retain the alkaloid and almost impossible to elute it quantitatively once retention had been achieved. These difficulties are believed to be due to the comparatively large size of the alkaloidal molecules. Early in 1956, however, Freeman[2] described the use of oxidised cellulose as an ion-exchange medium in alkaloidal analysis and we have investigated its application to injection solutions.

Oxidised cellulose is expensive (£28 per lb) and is only obtainable, at present, in limited quantities. This is not inimical, however, to its use as described below, since only 1 g is used per column and, once prepared, a column can be used for about twenty determinations, so that the cost is only ¾d. per determination. It is obtained by the action of oxides of nitrogen on cellulose, which preferentially oxidise a large portion of the primary hydroxyl groups to carboxyl groups, although the physical properties and appearance of the cellulose remain substantially unaltered. The theoretical maximum carboxyl content is 25·6 per cent., but the practical limit to oxidation is about 22 per cent. Oxidised cellulose with a carboxyl content of more than 15 per cent. is insoluble in water, mineral acids and the common organic solvents, but is readily soluble in aqueous alkaline solutions. It slowly degrades at room temperature, but can be kept indefinitely without deterioration if stored dry in a refrigerator. We have demonstrated its function as a carboxylic cation-exchange medium for the separation of the active principle and bacteriostatic agent in seventeen different

injection solutions containing chlorocresol or phenol and these comprise almost all the official injection solutions containing a bacteriostatic agent that can be assayed spectrophotometrically. The method failed to work with aminophylline and nicotinamide.

METHOD

REAGENTS—

Oxidised cellulose powder—Carboxyl content preferably from 16 to 22 per cent.
Sulphuric acid, N.

APPARATUS—

Unicam SP500 or similar spectrophotometer.
Columns of the type shown in Fig. 1, made of Pyrex glass.

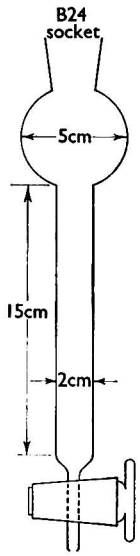


Fig. 1. Apparatus for the cellulose column

PROCEDURE FOR PREPARING COLUMNS—

One gram of oxidised cellulose was slurried with 50 ml of *N* sulphuric acid and transferred to a column, shown in Fig. 1, plugged with glass-wool. After the cellulose had settled, a small plug of glass-wool was placed on top to avoid disturbance of its upper surface. The column was then washed with water (about 200 ml) until the eluate was free from acid, slight air pressure being applied to give a flow rate of about 3 ml per minute. The final few millilitres of eluate were checked on the spectrophotometer to ensure that they were free from impurities absorbing between 220 and 280 mμ.

PROCEDURE FOR DETERMINING THE BACTERIOSTATIC AGENT—

A volume of injection solution was transferred to the column so that the amount of active ingredient when eluted with a minimum volume of 25 ml of *N* sulphuric acid could be determined spectrophotometrically. As shown in Table I, the volume varied from 1 to 50 ml, depending on the concentration and extinction of the active ingredient. The column was then washed with at least 50 ml of water (two 25-ml portions) under pressure, and the eluate containing the bacteriostatic agent was diluted to a suitable volume so as to permit determination of the bacteriostatic agent by measuring the maximum extinction at about 269 mμ for phenol or 279 mμ for chlorocresol. When 0·5 per cent. of phenol was used as the bacteriostatic agent, it was necessary to dilute the initial aliquot 100 to 200 times to obtain a suitable concentration in the eluate. With an injection containing 0·3 per cent. of chlorocresol as bacteriostatic agent the dilution necessary was 50 to 100 times.

In calculating the amount of bacteriostatic agent, the $E^{1\%}_{1\,cm}$ value at 269 mμ of phenol was taken as 164 and the $E^{1\%}_{1\,cm}$ value at 279 mμ of chlorocresol as 105.

PROCEDURE FOR DETERMINING THE ACTIVE INGREDIENT—

After elution of the bacteriostatic agent as described above, the active ingredient was eluted under pressure with *N* sulphuric acid, a minimum volume of 25 ml being used. The eluate was adjusted to a suitable volume and the active ingredient was determined spectrophotometrically. The volumes of eluate, wavelengths and $E^{1\%}_{1\,cm}$ values used in these determinations are listed in Table I.

TABLE I

EXPERIMENTAL CONDITIONS

Active ingredient	Concentration, mg per ml	Aliquot on column, ml	Dilution of sulphuric acid eluate	Wavelength for determination, mμ	$E^{1\%}_{1\,cm}$ of pure material
Adrenaline acid tartrate ..	0·5	10	→100	279	84·4
Apomorphine hydrochloride	3·0	1	→250	272	550
Atropine sulphate	0·648	30	→25	257	5·94
Diamorphine hydrochloride	10·0	1	→100	279	41·2
Emetine hydrochloride	60·0	1	→100, then 10→100	282	102
Hyoscine hydrobromide ..	0·4	50	→25	257	4·45
Lobeline hydrochloride ..	3·0	1	→200	249	363
Methylamphetamine hydrochloride	20·0	1	→50	257	9·96
Morphine sulphate	10·0	1	→100	285	40·1
Neostigmine methylsulphate	1·0	5	→25	260	14·7
Pethidine hydrochloride ..	25·0	1	→25	257	7·60
Procaine hydrochloride ..	20·0	1	→100, then 5→100	228	485
Quinine hydrochloride	3·0	1	→250	250	757
			→50	347	141

RESULTS

Sometimes the complete absorption spectra of both the bacteriostatic agent and active ingredient were examined and showed that both components were separated in a pure form. The recoveries given in Table II show also that the separation and elution were quantitative, the average recovery of active ingredient being 99·0 per cent., with a coefficient of variation of ± 2 per cent. For the bacteriostatic agent the corresponding figures were 99·6 per cent. and ± 1·7 per cent.

As a check on the degree of reproducibility of the method, an injection solution of atropine sulphate (1/100 grain per ml) with 0·3 per cent. of chlorocresol was examined four times by the method described above and the results were as follows—

Atropine sulphate found: 0·630, 0·644, 0·640, 0·640 mg per ml.
Average = 0·639 = 98·5 per cent. recovery.
Coefficient of variation = ± 1·0 per cent.

Chlorocresol found: 3·02, 3·00, 3·00, 3·04 mg per ml.
Average = 3·02 = 100·7 per cent. recovery.
Coefficient of variation = ± 0·75 per cent.

This good degree of reproducibility can be seen further in Table II, in which the results for the percentage recovery of active ingredient can be regarded as duplicates, since the phenol or chlorocresol was added to the same solution of active ingredient. For the seventeen sets of results listed the average variation is 0·7 per cent. from the average result.

Freeman[2] studied the effect of the presence of other salts and showed that for a given length of column the adsorption of alkaloid was dependant both on the total salt concentration of the solution and on the alkaloid to salt ratio. It was therefore necessary to consider

the effect of various concentrations of sodium chloride and sodium metabisulphite in several of the injection solutions examined. Under the conditions of the experiments and at the concentrations used their effect was negligible.

TABLE II

EXPERIMENTAL RESULTS

Active ingredient	Amount taken, mg per ml	Amount found, mg per ml	Recovery, %	With 5·0 mg of phenol per ml present: Amount found, mg per ml	With 5·0 mg of phenol per ml present: Recovery, %	With 3·0 mg of chlorocresol per ml present: Amount found, mg per ml	With 3·0 mg of chlorocresol per ml present: Recovery, %
Adrenaline acid tartrate	0·50	0·495	99·0	5·08	102·0		
	0·50	0·504	101·0			2·98	99·3
Apomorphine hydrochloride	3·0	2·92	97·4	4·82	96·4		
	3·0	2·96	98·7			3·0	100·0
Apomorphine hydrochloride*	3·0	2·95	98·5	5·0	100·0		
	3·0	2·97	99·0			3·0	100·0
Atropine sulphate	0·648	0·643	99·4	4·99	99·8		
	0·648	0·622	96·0			3·03	101·0
Diamorphine hydrochloride†	10·0	9·96	99·6	5·0	100·0		
	10·0	9·72	97·2			3·17	106·0
Emetine hydrochloride	60·0	60·8	101·0	4·94	98·8		
	60·0	61·0	102·0			2·99	99·7
Hyoscine hydrobromide	0·40	0·399	99·8	5·0	100·0		
	0·40	0·392	98·0			3·02	100·6
Lobeline hydrochloride	3·0	2·93	97·7	4·97	99·4		
	3·0	2·90	96·7			2·92	97·4
Methylamphetamine hydrochloride	20·0	19·4	97·0	4·98	99·6		
	20·0	19·6	98·0			2·94	98·0
Methylamphetamine hydrochloride‡	20·0	20·6	103·0	5·05	101·0		
	20·0	20·4	102·0			2·96	98·7
Morphine sulphate	10·0	10·0	100·0	5·06	101·0		
	10·0	10·0	100·0			3·03	101·0
Morphine sulphate*	10·0	10·1	101·0	4·90	98·0		
	10·0	9·90	99·0			3·01	100·0
Morphine sulphate§	10·0	9·70	97·0	5·0	100·0		
	10·0	9·65	96·5			2·96	98·7
Neostigmine methylsulphate	1·0	1·02	102·0	4·97	99·4		
	1·0	0·989	98·9			3·06	102·0
Pethidine hydrochloride	25·0	24·4	97·6	5·0	100·0		
	25·0	24·6	98·4			3·02	101·0
Procaine hydrochloride‖	20·0	20·0	100·0	5·05	101·0		
	20·0	20·0	100·0			2·95	98·3
Quinine hydrochloride	3·0	2·94	98·0	4·94	98·8		
	3·0	2·96	98·7			2·98	99·3

* Contained 0·1 per cent. of sodium metabisulphite.
† Contained 0·25 per cent. of sodium metabisulphite.
‡ Contained 0·03 per cent. of sodium chloride.
§ Contained 0·06 per cent. of atropine sulphate and 0·1 per cent. of sodium metabisulphite.
‖ Contained 0·002 per cent. of adrenaline.

In two instances the injection solutions contained two active ingredients, *i.e.*, morphine and atropine, and procaine and adrenaline. The concentration and extinction values of the atropine and adrenaline were such that they could not be determined spectrophotometrically, but they did not interfere with the determinations of the morphine and procaine.

In view of the increasing use of benzyl alcohol as a bacteriostatic agent, its behaviour was studied and found to correspond to that of chlorocresol and phenol. The method as described should therefore also be applicable to injection solutions containing this bacteriostatic agent.

CONCLUSIONS

The use of oxidised cellulose as a cation-exchange medium for the determination of the active ingredient and the bacteriostatic agent in injection solutions has been examined

and shown to be of fairly general application by its utilisation in assaying seventeen different injection solutions containing chlorocresol or phenol. Both the active ingredient and bacteriostatic agent are quantitatively separated in a pure form, which allows them to be determined spectrophotometrically.

A single determination takes about 1 hour, but four samples could easily be examined simultaneously. The separation could not therefore be regarded as increasing disproportionately the amount of time taken for a direct two-point determination, particularly in view of the increased accuracy obtained. The cost of the oxidised cellulose as used in these determinations is negligible.

We thank Mr. B. Peutrell for assistance with some of the determinations.

REFERENCES

1. Brealey, L., and Proctor, K. A., *J. Pharm. Pharmacol.*, 1955, **7**, 830.
2. Freeman, F. M., *Ibid.*, 1956, **8**, 42.

BOOTS PURE DRUG CO. LTD.
STANDARDS DEPARTMENT
NOTTINGHAM

October 24th, 1956

Notes

THE SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM

OF the several methods that have been proposed for the colorimetric determination of rhenium (see, for example, Sandell[1] and Ryabchikov and Lazarev[2]), that based upon the treatment of an acid solution of perrhenate with thiocyanate and stannous chloride[3] has found the widest application. Tungsten and molybdenum both interfere with this method and in their presence it is necessary to make a preliminary separation of the rhenium by volatilisation of the heptoxide,[4] precipitation of the sulphide with a suitable collector,[5] extraction of the tetraphenylarsonium perrhenate by chloroform[6] or removal of molybdenum as quinquivalent molybdenum thiocyanate in ether.[4]

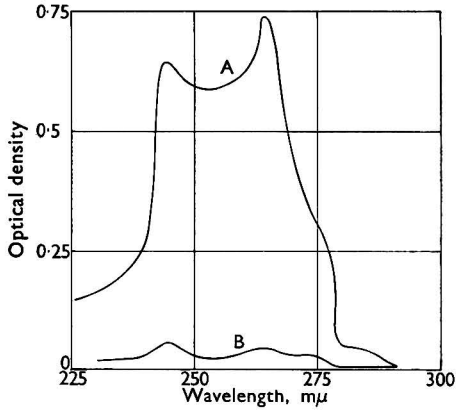


Fig. 1. Absorption spectrum of a solution of tetraphenylarsonium perrhenate in chloroform: curve A, 0·3 mg of rhenium per 10 ml of chloroform; curve B, blank solution. A 1-cm cell and a slit width of 0·15 mm were used for all measurements

Recently we have had occasion to analyse a number of alloys containing 0·1 to 10 per cent. of rhenium. In the course of this work, the ultra-violet absorption spectrum of the chloroform extraction of the tetraphenylarsonium perrhenate was recorded on a Unicam SP500 spectrophotometer. This spectrum is shown in Fig. 1. The existence of the absorption band permitted a marked simplification over the methods previously proposed for the determination of rhenium in the presence of molybdenum or tungsten; the optical density of the chloroform extract was simply measured directly at the appropriate wavelength, which eliminated the need for evaporation and subsequent determinations with thiocyanate.

In view of the thorough theoretical and practical work of Tribalat,[6] the extraction conditions have not been studied by us and the conditions recommended by Tribalat for quantitative recovery have been adopted. As the reagent, tetraphenylarsonium chloride, could not be obtained in the United Kingdom, it was prepared by the method of Shriner and Wolf,[7] a method that presented no difficulties and gave a good yield of the pure product. The only modification made to the published instructions was in the purification of the final crude product, which we preferred to dissolve in the minimum amount of absolute ethanol and then re-precipitate by the addition of five times the volume of dry ether. After filtration with suction, the purified material was washed with dry ether.

Method

Reagents—

Tetraphenylarsonium chloride solution—A 0·1 per cent. w/v solution in water.
Citric acid solution, 20 per cent. w/v.
Sodium hydroxide solution, 5 per cent. w/v.
Sodium sulphate, anhydrous.

Procedure—

To a solution of the sample containing 0·5 to 7 mg of rhenium, add 10 ml of citric acid solution and dilute to 100 ml in a calibrated flask. By pipette transfer 5 ml to a small extraction funnel and adjust the pH to between 8 and 9 with sodium hydroxide solution. Add 2·0 ml of tetraphenylarsonium chloride solution and dilute to 10·0 ml. Add 10·0 ml of chloroform and extract by shaking for 3 minutes. Allow to settle and run off most of the chloroform layer into a dry flask containing about 1 g of anhydrous sodium sulphate. Read the optical density at 255 mμ in a 1-cm quartz cell, using a spectrophotometer, with chloroform as the reference liquid.

Procedure for tungsten - rhenium and molybdenum - rhenium alloys—

Weigh 0·2 g of finely divided sample into a silver crucible. Add 1·0 g of sodium hydroxide. Fuse carefully until solution is complete. Extract with water and continue as described under "Procedure."

Discussion

Calibration graphs were prepared in accordance with the Procedure and optical densities were measured at 245, 255 and 265 mμ. All the graphs were of the same general shape, a straight line for amounts of rhenium up to 0·32 mg in the aliquot and curving over for larger amounts of rhenium. When allowance was made for the blank, by carrying out the procedure with a solution containing no rhenium, the calibration graphs passed through the origin. For analytical purposes, the wavelength of 255 mμ was preferred, because, as can be seen from Fig. 1, this wavelength was less critical than those corresponding to the two peaks and because the relative value of the blank was less at this wavelength. After correction had been made for the blank, 0·2 mg of rhenium in the aliquot gave an optical density of 0·325.

Amounts of tungsten or molybdenum of up to 20 mg in the aliquot did not perceptibly interfere with the determination. Interferences have not been thoroughly studied, but tin, permanganate, perchlorate, bromide and fluoride have been shown to interfere.

We thank Dr. J. A. M. van Moll and the Directors of the Mullard Radio Valve Company Limited for permission to publish this Note.

References

1. Sandell, E. B., "Colorimetric Determination of Metals," Second Edition, Interscience Publishers Inc., New York, 1950, p. 511.
2. Ryabchikov, D. I., and Lazarev, A. I., *Zhur. Anal. Khim.*, 1955, **10**, 228.
3. Geilmann, W., and Bode, H., *Z. anal. Chem.*, 1948, **128**, 489; **128**, 495.
4. Hoffmann, J. I., and Lundell, G. E. F., *J. Res. Nat. Bur. Stand.*, 1939, **23**, 497.
5. Poluektov, N. S., *Zhur. Prikl. Khim.*, 1938, **11**, 534.
6. Tribalat, S., *Anal. Chim. Acta*, 1949, **3**, 113.
7. Shriner, R. L., and Wolf, C. N., *in* Cope, A. C., *Editor*, "Organic Syntheses," Volume 30, J. Wiley & Sons Inc., New York, and Chapman & Hall Ltd., London, 1950, p. 53.

Material Research Laboratory
Mullard Radio Valve Co. Ltd.
Mitcham Junction, Surrey

T. R. Andrew
C. H. R. Gentry
January 14th, 1957

DETERMINATION OF THIOCYANATE OR CYANIDE IN THE PRESENCE OF GLYCINE

ACCORDING to the method devised by Aldridge,[1,2] either thiocyanate or cyanide may be determined after conversion into cyanogen bromide by reaction with bromine water in neutral or acid solution. The cyanogen bromide is then allowed to react with pyridine in the presence of benzidine and the red colour due to the condensation product of benzidine with glutacondialdehyde is related to the original concentration of thiocyanate or cyanide. It is known that interference sometimes results from the presence of protein and that this can be avoided by deproteinisation, for instance by means of trichloroacetic acid.[1] The present observations arose in attempting to apply Aldridge's method to aqueous extracts of barley or malt, in which the amount of protein present is small and its removal is therefore unnecessary. The characteristic red colour formed when thiocyanate or cyanide are present was observed, and moreover the absorption spectrum of the solution was identical with that produced from authentic thiocyanate. It was, therefore, at first concluded that substantial amounts of thiocyanate were present.

Two anomalies were, however, observed. First, the optical density of the final solution was not proportional to the amount of the sample, even though other factors were unchanged. Secondly, it was found that, although the red colour was produced in the reaction with pyridine and benzidine after bromine water had been added to the sample at pH 5, it failed to appear when the solutions were acidified with hydrochloric acid before the addition of bromine. For these reasons it was suspected that the observed colour was due to some constituent other than thiocyanate or cyanide. Attention was therefore directed to constituents of malt that might interfere under the conditions of the Aldridge test.

In strongly oxidising conditions several amino acids have been shown to yield traces of cyanide.[3] It was therefore of interest to investigate whether the amino acids found in malt would yield cyanogen bromide, either directly or through the intervention of cyanide, under the less vigorous oxidising conditions appertaining to the Aldridge test. Several natural amino acids were subjected to the conditions laid down by Aldridge, the bromine being added to nearly neutral solutions of the test substances. It was found that of these only glycine gave a significant coloration and that the absorption spectrum of the final solution was the same as that produced from authentic thiocyanate. Moreover, the intensity of the colour produced from solutions containing authentic glycine at concentrations comparable with those known to be present in the malt extracts used was similar to that found when samples of malt extract were subjected to the Aldridge test. Again, the reaction with glycine does not take place in the presence of free hydrochloric acid, and the intensity of colour produced from glycine is not proportional to the concentration of the latter substance. Thus, 0·1 mg of glycine gave a colour equal in intensity to that produced by 0·5 μg of thiocyanate ion, whereas 1 mg of glycine was equivalent in this respect to 0·8 μg of thiocyanate ion.

It is clear therefore that, in neutral solution, glycine can react with bromine to produce small amounts of cyanogen bromide. This presumably is the reason for the interference of glycine with the determination of cyanide ion by Aldridge's method, as noted by Ludzack, Moore and Ruchhoft.[4] These authors recommend that when glycine is present the cyanide ion should be removed as hydrogen cyanide by aeration of the acidified solution and determined after absorption in alkali. However, the present results show that the use of this procedure, or of other more complicated methods that might be used to separate glycine from cyanide or especially from thiocyanate, is unnecessary, as glycine does not provide cyanogen bromide when treated with bromine in strongly acid solution. Accurate results can therefore be obtained if the solution containing cyanide or thiocyanate and glycine is acidified before the bromine water is added.

REFERENCES

1. Aldridge, W. N., *Analyst*, 1944, **69**, 262.
2. ——, *Ibid.*, 1945, **70**, 474.
3. Plimmer, R. H. A., *J. Physiol.*, 1904, **31**, 65.
4. Ludzack, F. J., Moore, W. A., and Ruchhoft, C. C., *Anal. Chem.*, 1954, **26**, 1784.

BREWING INDUSTRY RESEARCH FOUNDATION
LYTTEL HALL
NUTFIELD
NR. REDHILL
SURREY

J. R. HUDSON
J. R. A. POLLOCK
February 18th, 1957

A DETECTOR-PAPER FOR PHOSGENE

THE reagent at present widely used for the detection of phosgene is a mixture of diphenylamine and *p*-dimethylaminobenzaldehyde.[1,2] It suffers from the disadvantage that the colour change from white to yellow is not easy to see, especially in artificial light; it is very sensitive to mineral-acid vapours and these give the same colour as does phosgene.

Some other combinations of aldehydes and amines were examined, and the most satisfactory was found to be a mixture of *p*-dimethylaminobenzaldehyde and N-ethyl-N-2-hydroxyethyl-aniline. It gives a colour change with phosgene from white to bright blue and this is neither retarded nor brought about by any reasonable concentration of mineral-acid vapour.

A detector paper suitable for use in the pump mentioned in the D.S.I.R. publication or a similar pump is prepared by dipping Whatman No. 1 filter-paper in a solution of 1·68 g of N-ethyl-N-2-hydroxyethylaniline (crystallising point 37·2° C), 0·75 g of *p*-dimethylaminobenzaldehyde and 2·5 ml of diethyl phthalate in 25 ml of ethanol. Other solvents such as acetone or chloroform are also satisfactory. The solvent should be allowed to evaporate before use, as the wet paper is quite insensitive. Papers should be prepared as required, but the reagent solution will keep for many months in the dark.

The sensitivity of the reagent is such that, when 500 ml of air containing phosgene at a concentration of 1 μg per litre are drawn through a circular detector-paper of diameter 0·110 inch, an identifiable blue colour is produced. A good blue colour is obtained with 75 ml of air containing 5 μg of phosgene per litre under the same conditions.

I thank the Chief Scientist, Ministry of Supply, for permission to publish this Note.

REFERENCES

1. Ball, W. C., Unpublished report, January 1917.
2. D.S.I.R., "Methods for the Detection of Toxic Gases in Industry. *Leaflet No.* 8: Phosgene," H.M. Stationery Office, London 1939.

MINISTRY OF SUPPLY
CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT
PORTON, WILTS.

H. F. LIDDELL
February 28th, 1957

British Standards Institution

NEW SPECIFICATIONS*

B.S. 509:1957. Acetone. Price 3s.
B.S. 549:1957. Diacetone Alcohol. Price 2s. 6d.
B.S. 552:1957. Amyl Acetate. Price 3s.
B.S. 574:1957. Diethyl Phthalate. Price 2s. 6d.
B.S. 577:1957. Hexachloroethane. Price 3s.
B.S. 663:1957. Ethyl Lactate. Price 3s.
B.S. 1595:1957. *iso*Propyl Alcohol. Price 3s.

AMENDMENT SLIP*

A PRINTED slip bearing an amendment to a British Standard has been issued by the Institution, as follows—

PD 2736—Amendment No. 2 (March, 1957) to B.S. 1997:1953. Glycerol Triacetate.

* Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

Book Review

TRAITÉ DE MICRO-ANALYSE MINÉRALE: QUALITATIVE ET QUANTITATIVE. Volume III. By CLÉMENT DUVAL. Pp. 548. Paris: Presses Scientifiques Internationales. 1956. Price 3200 fr.

Professor Duval, with the assistance of his colleagues, has now gone a stage further in the completion of this extensive and valuable reference work. The present volume follows the pattern of those reviewed earlier (*Analyst*, **1955**, **80**, 79; **1956**, **81**, 504) and is a worthy successor to them.

The elements dealt with comprise the remainder of the transition group not already covered in Volume II; that is, iron to zinc, ruthenium to cadmium and osmium to mercury. There is therefore once more a balance of more and less familiar elements, and every analyst, before long, is bound to find something of value to him in an immediate problem within the covers of the present volume.

The reviewer's pleasure at the regular and (in view of the vast field covered) speedy appearance of each of these volumes in turn will be shared by all those who have the good fortune to have the earlier volumes already on their shelves. The books are likely, as in the reviewer's laboratories, to be in constant use for reference purposes, and it is good to know that now information is available for a further fifteen elements. CECIL L. WILSON

Publications Received

ELEMENTARY PRACTICAL ORGANIC CHEMISTRY. Part I: SMALL SCALE PREPARATIONS. By A. I. VOGEL, D.Sc., D.I.C., F.R.I.C. Pp. xvi + 347 + Appendix and Index xiv. London, New York and Toronto: Longmans, Green & Co. Ltd. 1957. Price 21s.

BIOCHEMICAL INDIVIDUALITY. THE BASIS FOR THE GENETOTROPHIC CONCEPT. By ROGER J. WILLIAMS. Pp. xiv + 214. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1956. Price $5.75; 46s.

ENCYCLOPEDIA OF CHEMICAL REACTIONS. Compiled by C. A. JACOBSON. Edited by CLIFFORD A. HAMPEL. Volume VI: Samarium, Scandium, Selenium, Silicon, Silver, Sodium. Pp. viii + 438. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1956. Price $12.50; 100s.

HETEROCYCLIC COMPOUNDS. Volume 5: FIVE-MEMBERED HETEROCYCLES CONTAINING TWO HETERO ATOMS AND THEIR BENZO DERIVATIVES. Edited by ROBERT C. ELDERFIELD. Pp. viii + 744. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price $20.00; 160s.

THE ENCYCLOPEDIA OF CHEMISTRY. Editor-in-Chief GEORGE L. CLARK. Pp. xvi + 1037. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1957. Price $19.50; 156s.

SOLVENTS. By THOMAS H. DURRANS, D.Sc., F.R.I.C. Seventh Edition. Pp. xvi + 244. London: Chapman & Hall Ltd. 1957. Price 30s.

STATISTICAL METHODS IN RESEARCH AND PRODUCTION WITH SPECIAL REFERENCE TO THE CHEMICAL INDUSTRY. Edited by OWEN L. DAVIES, M.Sc., Ph.D. Third Edition. Pp. x + 396. Edinburgh and London: Oliver & Boyd, *for* Imperial Chemical Industries Ltd. 1957. Price 45s.

RECOMMENDED METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

REPRINTS of the Recommended Methods prepared by the Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents are now available from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1; price to members 1s. 6d., or to non-members 2s. 6d., each. Remittances made out to The Society for Analytical Chemistry must accompany orders, and these reprints are not available through Trade Agents.

Reprints Nos. 1 to 7 were listed last month. The following additional reprint is now available—

Reprint No. 8. Determination of Combined Nitrogen (April, 1957).

Erratum

MESSRS. M. W. Hardy & Co. Ltd., who supplied the Eulan NK used in the work described by H. Holness and W. R. Stone in their paper "A Systematic Scheme of Semi-micro Qualitative Analysis for Anionic Surface-active Agents" (*Analyst*, 1957, **82**, 166), have informed us that this material, made by Farbenfabriken Bayer A.G., Leverkusen, Germany, is now distributed in Great Britain by Messrs. Industrial Dyestuffs Ltd. We regret the inconvenience caused to these firms.

The following correction should be made to the text of the paper—

MARCH (1957) ISSUE, p. 168, 13th line. *For* "M. W. Hardy & Co." *read* "Industrial Dyestuffs Ltd."