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THE ANALYST

กรมวิทยาศาสตร์

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

Editor: F. L. OKELL, F.R.I.C.
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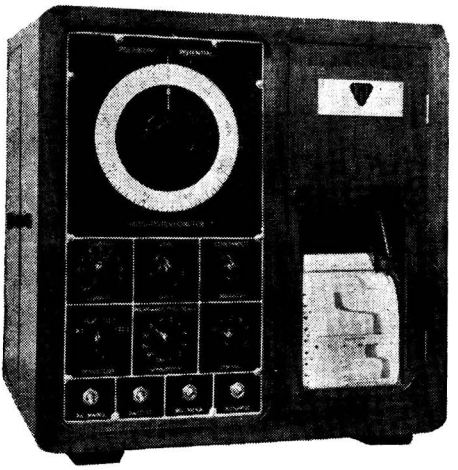

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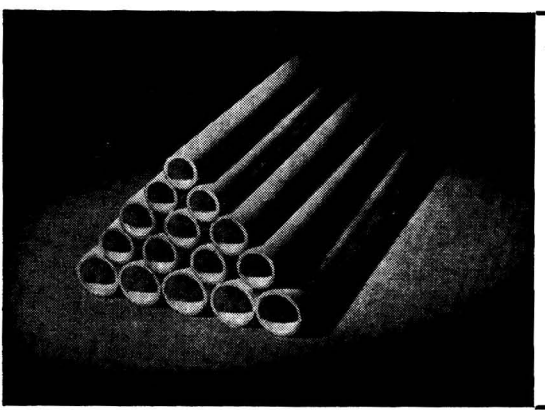

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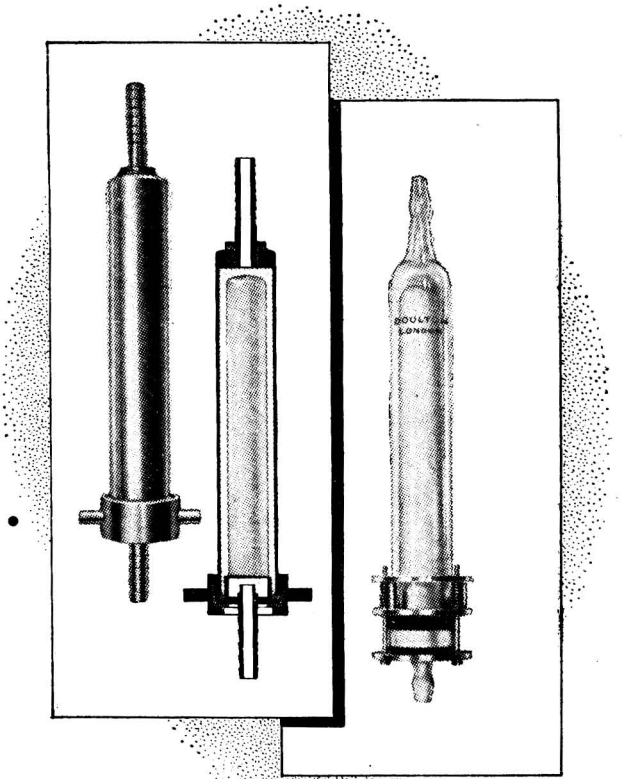

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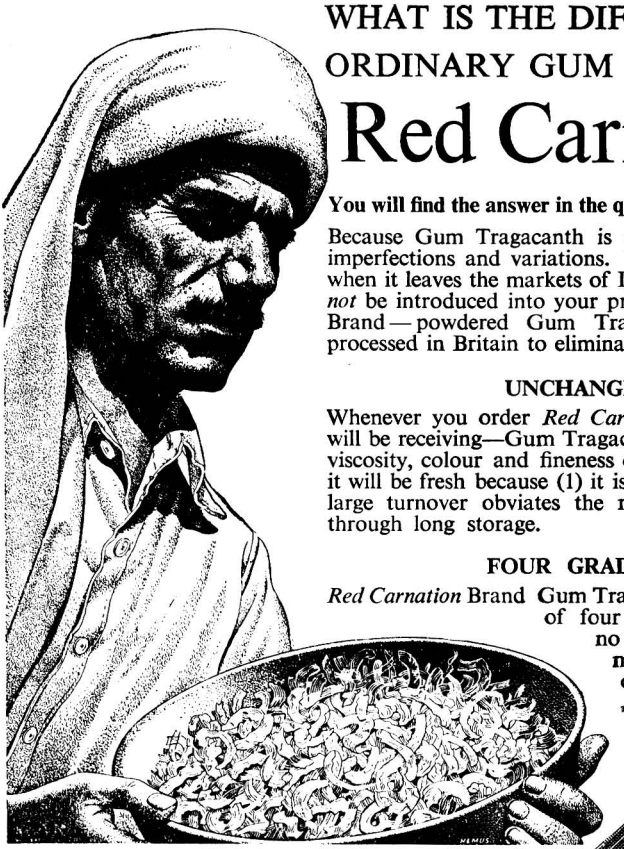

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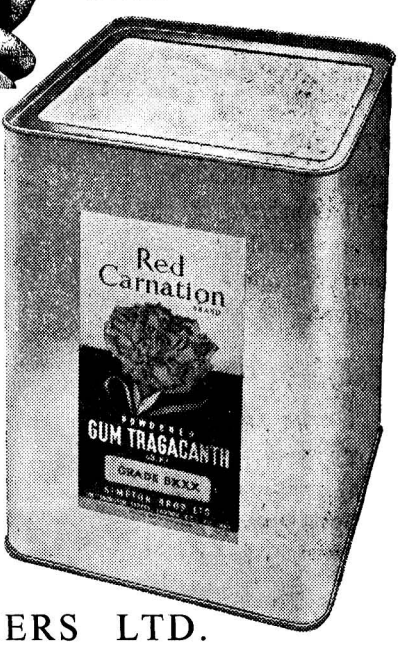

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

ANNUAL GENERAL MEETING

THE seventy-seventh Annual General Meeting of the Society was held at 3.15 p.m. on Friday, March 16th, 1951, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was taken by the President, Mr. George Taylor, O.B.E., F.R.I.C. The financial statement for 1950 was presented by the Honorary Treasurer and approved, and the Auditors for 1951 were appointed. The Report of the Council for the year ending March, 1951 (see pp. 251–260), was presented by the Honorary Secretary and adopted.

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

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

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

Vice-Presidents—R. C. Chirnside, D. C. Garratt and J. G. A. Griffiths.

Honorary Treasurer—J. H. Hamence.

Honorary Secretary—K. A. Williams.

Other Members of Council—The Scrutineers further reported that 406 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—H. E. Cox, 278; T. McLachlan, 200; A. J. Amos, 189; E. C. Wood, 178; D. C. M. Adamson, 165; G. H. Osborn, 159; C. G. Daubney, 149; C. H. Manley, 143; H. E. Monk, 139; G. E. Forstner, 134; R. H. Jones, 129; C. H. R. Gentry, 118; H. Wright Hodgson, 78; S. G. Burgess, 74; R. F. Milton, 60.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—H. E. Cox, T. McLachlan, A. J. Amos, E. C. Wood, D. C. M. Adamson and G. H. Osborn.

A. L. Bacharach, H. H. Bagnall, J. Haslam, D. W. Kent-Jones, A. A. Smales and E. Voelcker, having been elected members of the Council in 1950, will, by the Society's Articles of Association, remain Ordinary Members of the Council for 1951.

A. A. D. Comrie (Chairman of the North of England Section), H. C. Moir (Chairman of the Scottish Section), C. L. Wilson (Chairman of the Microchemistry Group), B. S. Cooper (Chairman of the Physical Methods Group) and N. T. Gridgeman (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1951.

After the business outlined above had been completed, the meeting was opened to visitors, and the retiring President, Mr. George Taylor, O.B.E., F.R.I.C., delivered his Presidential Address (see pp. 260–275).

CHANGE OF EDITORSHIP OF *THE ANALYST*

CONSEQUENT on the death of Mr. J. H. Lane, announced briefly last month, the Council has appointed Mr. F. L. Okell as Editor of *The Analyst*.

Mr. Okell has been Assistant Editor since 1946, and has been Acting Editor for some months during Mr. Lane's illness.

SECRETARYSHIP OF THE SOCIETY

ON her return from her recent illness, Miss D. V. Wilson has been re-appointed Secretary by the Council.

NEW MEMBERS

Roger Arnot, B.Sc. (Lond.), A.R.I.C.; David John Barke, B.Sc. (Lond.), A.R.I.C.; Roland Gordon Booth, B.Sc., Ph.D. (Reading); Leonard Frederick Burroughs, B.Sc. (Reading), A.R.I.C.; Wilfred Cassidy, B.Sc., A.M.C.T.; Edward Alfred Clough, B.Sc. (Liv.); David Ian Coutts; Edward Druce, M.Sc. (Manc.), A.R.I.C., A.M.C.T.; Joseph Harold Ewence, B.Sc. (Lond.), A.R.I.C.; Joyce Eleanor Fildes, B.Sc. (Sydney); John Crossfield Hawkes, B.Sc. (Wales); Alfred Grenville Hill, F.R.I.C.; Brian Hulme; John Herbert Humphrey, B.A., M.D. (Cantab.); Ethel Muriel Johnson, M.Sc. (Manc.), A.R.I.C.; John Kay, B.Sc. (Manc.), A.M.C.T., F.R.I.C.; James William Lightbown, M.Sc., Ph.C., Dip.Bact. (Manc.); Barbara Macauley, B.Sc. (Lond.); William Whalley Myddleton, D.Sc. (Belfast), F.R.I.C.; Walter Laing Macdonald Perry, Ch.B., M.D. (St. And.); Winifred Marian Phillips, B.Sc. (Lond.); Cyril Alfred Shacklady, B.Sc. (Liv.); Ronald Sinar, B.Pharm. (Lond.), Ph.C.; Frederick Randall Smith, B.Sc., Ph.D. (Edin.), A.R.I.C.; Pamela Dorothy Waterhouse, B.Sc. (Reading); David Watt, Ph.C. (Edin.); Anthony Arthur Robinson Wood.

DEATH

We regret to record the death of

Harri Heap.

PHYSICAL METHODS GROUP

The Thirtieth Ordinary Meeting of the Group was held at 5.30 p.m. on Friday, March 9th, 1951, in the Chemistry Lecture Theatre of the University of Leeds. This was a joint meeting with the Infra-red Discussion Group, and was preceded by a visit to the Wool Industries Research Association Laboratories. Mr. B. S. Cooper was in the Chair and about 48 members and visitors were present.

The following papers on "Infra-red Spectroscopy" were read and discussed: "The Scope of Infra-red Analysis," by Dr. N. Sheppard; "The Applications of Infra-red Spectroscopy to the Analysis of Polymer Composition," by H. A. Willis, B.Sc.; "Infra-red Spectrometry in the Petroleum Industry," by Dr. H. Powell.

Obituary

JOSEPH HENRY LANE

Joseph Henry Lane died on March 9th, 1951, in his 68th year. He had been in failing health for more than a year and for some weeks before his death it was evident that the end could not be far off.

Lane was educated at Raine's School, Stepney, and at the Finsbury Technical College. After completing the College course he remained as research assistant to Professor Meldola for two or three years and was joint author with Meldola of papers published in the *Journal of the Chemical Society*.

Towards the end of 1904, Lane and the writer became associated in the laboratory of the Beetroot Sugar Association (later the Sugar Association) of London, and in 1910 we began in practice as consulting chemists and analysts, a partnership which continued until Lane's death. The writer has the happiest memories of this long association. Lane's serene and equable temperament made him an ideal companion in the laboratory, and he was ever more considerate for others than for himself and ready to give others more than their due. A very large part of our work consisted in the analysis of sugars and sugar products, and we spent a considerable amount of our spare time, all too abundant in the early days of our practice, in making trial of numerous compounds for use as an internal indicator in the estimation of reducing sugars with Fehling solution—a very long-felt want. Methylene blue was found to be the solution ot this problem. The discovery was Lane's, but with characteristic generosity he insisted on joint publication. Lane also found that such small quantities of calcium salts as are frequently present in tap water are sufficient to affect appreciably the estimation of reducing sugars with Fehling's solution. The error due to the use of tap water instead of distilled water in the volumetric estimation could hardly have been detected prior to the use of methylene blue as internal indicator.

For many years Lane was an abstractor for the *Journal of the Society of Chemical Industry* and for the *Journal of the Institute of Brewing*. For several years he gave a course of lectures on the Sugar Industry at the City of London College, Moorfields.

Lane joined the Society in 1924. He succeeded T. H. Pope as Assistant Editor of *The Analyst* in 1936, C. A. Mitchell as Secretary of the Society in 1937, and Mitchell again, as Editor of *The Analyst* in 1945. To follow Mitchell as Editor was a very formidable task, but Lane was fully equal to it and *The Analyst* is an enduring memorial to both. The work involved increased greatly, however, during Lane's tenure of the Editorship, and additional editorial assistance became necessary.

Lane had a great love and appreciation of music and was very widely read in general literature. In his younger days he had a great liking for walking, a taste which he shared with the writer, who has very pleasant recollections of walking week-ends in Lane's company. It is hardly an exaggeration to say that during the latter half of his life Lane's sole interest was his work, carried on, despite increasing weakness, until nearly the end.

LEWIS EYNON

Annual Report of the Council: March, 1951

THE roll of the Society numbers 1562, an increase of 15 over the membership of a year ago.

HONOURS—During the year Professor R. A. Morton has been elected a Fellow of the Royal Society, and the Council offers him its congratulations.

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

E. E. Billington	G. M. Hills	W. J. Rees
N. P. Booth	E. C. Keeley	T. Rendle
B. S. Evans	J. H. Lane	F. W. Richardson
E. M. Hall	G. Lawson	F. R. Stephens
C. A. Hallas	K. S. MacManus	W. H. Thorns
John Hanley	A. H. Mitchell Muter	H. G. Tribley
J. A. Heald		

Billington graduated with honours in Chemistry and Botany at Liverpool, and then went to McGill University, taking his M.Sc. degree in Engineering. He practised engineering in Canada and the United States of America. On the death of his father he returned to this country and became a director of Edward Billington & Son, of Liverpool. From then he studied chiefly nutrition, especially of animals, and as director of this firm and of Criddle & Co. and Wright, Crossley & Co. he built a reputation as a chemist and scientific adviser of the first rank. He was three times President of the Liverpool Seed, Oil, Cake and General Produce Association, and for some years acted as European representative of McGill University. He was a Fellow of the Royal Institute of Chemistry and a Justice of the Peace. He joined the Society in 1928, and was 61 when he died.

Booth was educated at King Edward VI Grammar School, Camp Hill, and Mason College, Birmingham. He worked in the laboratories of the Worshipful Society of Apothecaries of London from 1898 to 1901, when he became the first qualified chemist to be employed by Cadbury Brothers Ltd. In 1911 he set up the research laboratory for that company, and he was appointed managing director and chairman of Cadbury - Fry - Pascall Ltd., at Hobart, Tasmania, in 1923, holding these posts until his retirement in 1938. He became an Associate of the Institute of Chemistry in 1901 and a Fellow in 1903. He joined the Society in 1900.

Evans received his early education at the Grammar School, Faversham, Kent. He worked in the laboratories of L. Taylor, Public Analyst for Hackney, and Briant and Harmon, Consultants. In the 1914–18 war he was awarded the Military Cross for gallantry and was severely wounded at Arras. He was invalided from the Army and undertook research in the Ministry of Munitions, Chemical Warfare Department, for which he was awarded the M.B.E. In 1919 he was appointed to the Analytical Section, Metallurgical Branch, Armament Research Department, Woolwich, where he remained until his retirement on account of ill-health in 1948. He became a member of the Society in 1917, served as Vice-President from 1937 to 1939 and was an active member of the Publication Committee from 1929 until his death in his 70th year, in December, 1950. (Obituary, *Analyst*, 1951, **76**, 188.)

Hall died at Hull on February 6th, 1951, aged 58. He was educated at Lucton School, Herefordshire, and Birmingham University. His first appointment was science master at Blundells School, and he later became assistant chemist in the Department of the Government Chemist. In 1919 he joined the laboratory staff of the Olympia Oil and Cake Co., Selby, and shortly afterwards was appointed chief chemist. In 1941 he transferred to the British Oil and Cake Mills Ltd., Hull, to take charge of the Hull laboratory, and also became chief chemist to the Oil Mills Executive, Lever Brothers and Unilever Limited. He was elected an Associate of the Institute of Chemistry in 1917, and joined the Society in 1950.

Hallas obtained the fellowship of the Royal Institute of Chemistry in Branch E; he joined the Society in 1947. He had been chemist at the Royal Institute of Public Health and later became chemist to James Pascall Ltd. Since 1929 he was chemist at the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades.

Hanley died in his 80th year. He was educated privately and at University College, Liverpool, and became a student in the laboratory of Norman Tate under Watson Gray. He joined J. Bibby & Sons Ltd. as a chemical engineer in 1896. He did much pioneer work for the firm and was their chief chemist for many years, retiring from that post in 1936. He carried on a consulting practice from his retirement until during the war. For many years he was Honorary Treasurer of the Committee of Learned Societies of Liverpool. He became an Associate of the Institute of Chemistry in 1894 and a Fellow in 1901. He was a member of the Institution of Chemical Engineers; he joined the Society in 1925.

Heald was educated at Sedgebrook Grammar School, Grantham, and University College, Nottingham, where he graduated under the late Professor S. S. Kipping. He enlisted in the Royal Engineers, and served in "E" Special Company in France, being mentioned in despatches and awarded the Military Cross. He joined Levinstein Ltd. in 1919 and in 1922 was appointed a chemist in the Department of the Government Chemist. He obtained the Fellowship of the Institute in Branch E in 1925 and was called to the Bar in 1933. At the time of his death, in his 57th year, he was a Principal Scientific Officer and was seconded for special advisory duties to the War Department, where he was head of the Laboratory Services dealing with the Royal Army Service Corps supplies. He joined the Society in 1934.

Hills was drowned in his 38th year while bathing. He was educated at the Central Secondary School, Sheffield, and Corpus Christi College, Oxford, where he obtained second class honours in Chemistry and was awarded the degrees of B.Sc. in 1934 and of M.A. in 1937. After working for a short time in the Medical Chemistry Department of the University of Edinburgh he went, in 1934, as personal assistant to Professor E. C. Dodds at the Courtauld Institute of Biochemistry. He held a Mackenzie - McKinnon Fellowship of the Royal College of Physicians from 1936 to 1939, and then joined the Medical Research Council Unit for Bacterial Chemistry under Sir Paul Fildes. He later worked in the Department of Bacteriology in the University of Sheffield and in the Microbiological Research Department at the Experimental Station (Ministry of Supply), Porton. He was a Principal Scientific Officer at Porton up to the time of his death. He became an Associate of the Institute of Chemistry in 1934 and a Fellow in 1947. He joined the Society in 1948, and was a member of all the three Groups of the Society.

Keeley died in his 48th year. He was educated at Maidstone Grammar School and King's School, Canterbury. He was a pupil of the late P. A. Ellis Richards from 1921 to 1923, and then entered King's College, London, where he graduated B.Sc. in 1926. The following year he obtained an appointment with Bovril Ltd. as analyst, and in later years was on the research side. He became an Associate of the Institute of Chemistry in 1927, and joined the Society in 1925.

Lane died on March 9th, 1951, at the age of 68. He was educated at Raine's School, Stepney, and at the Finsbury Technical College. He subsequently obtained the degree of B.Sc. (Lond.), with first class honours in Chemistry. In 1910 he went into partnership with Lewis Eynon as Consulting Chemist and Analyst. He became a Fellow of the Institute of Chemistry in 1910. He joined the Society in 1924, became Assistant Editor of *The Analyst* in 1936, Secretary of the Society in 1937 and Editor of *The Analyst* in 1945. (Obituary, *Analyst*, 1951, **76**, 250.)

Lawson was in his 41st year when he died. He was educated at Newmilns Public School, Galston Higher Grade School and Kilmarnock Academy. In 1930 he entered the Royal Technical College, Glasgow, qualifying as a pharmaceutical chemist. He was later demonstrator in botany and in organic chemistry at this college. In 1936 he became chief

chemist to Cumming, Parsons Ltd., and was later general manager and director of the company. He was elected an Associate of the Institute of Chemistry in 1937, and joined the Society in 1944.

McManus worked for many years in the Powell Duffryn Laboratories at Ystrad Mynach, and was later appointed chief analyst for the South-West Regional Coal Board. He joined Bowmans Chemicals Ltd. in 1947 as head of the Chemical Research Department.

Muter was educated in Germany and at King's College, London. He became assistant to his father, Dr. J. Muter, an early Editor of *The Analyst*, and on his father's death in 1912, was made Public Analyst for the Metropolitan Boroughs of Lambeth and Wandsworth and for the Parts of Lindsey, Lincolnshire. In 1936 he became Public Analyst and Official Agricultural Analyst for the Parts of Holland and Kesteven, Lincolnshire. He was made a Fellow of the Institute of Chemistry in 1899, obtaining the certificate in Branch E in 1903. He joined the Society in 1893. (An obituary notice will appear later.)

Rees joined the Society in 1934. He became an assistant in the Physics Laboratory at Mason College, Birmingham, in 1896; he studied chemistry at the Royal College of Science, London, in 1899–1900 and resumed part-time study in Birmingham in 1901. In that year he became senior assistant in the laboratory of Chance Brothers & Co., Ltd., Smethwick, and in 1907 he was made chief chemist to the company. He was appointed lecturer on refractory materials in the Department of Applied Science, University of Sheffield, about 1918, graduated B.Sc.Tech. of the University, and later proceeded to M.Sc.Tech. and D.Sc.Tech. He received a Sir George Beilby award in 1932 and after his retirement from the University practised as a consultant. He was awarded an O.B.E. in 1944. He was elected a Fellow of the Institute of Chemistry in 1917 and acted as a special examiner in Branch G, Industrial Chemistry. He died in his 71st year.

Rendle was educated at the Carpenter Company's Institute. He spent two years in the laboratories of A. Boake Roberts & Co., Ltd., and a year as assistant to B. E. R. Newlands, and he was then chief assistant to A. R. Ling for eight years. He was appointed chief chemist to Hargreaves Brothers & Co. in 1911, but returned to A. Boake Roberts & Co., Ltd. in 1916 as chief chemist and works manager. He went back to Hargreaves & Co. in 1921, and in 1924 went to Chivers & Co., Ltd., Histon, as chief chemist and senior technician. He was senior technical manager of the company at the time of his death. He became a Fellow of the Institute of Chemistry in 1940. He joined the Society in 1925, and was a member of the Council from 1940 to 1941, and a Vice-President from 1942 to 1943.

Richardson attended the Hull Grammar School and, at the age of 18, became pupil-assistant to Rimmington, Public Analyst to the City of Bradford. Subsequently, in partnership with Adolf Jaffé, he founded an important consulting practice and held several appointments under the Food and Drugs Acts as Public Analyst. He joined the Society in 1888 and died in December, 1950, at the age of 90. (Obituary, *Analyst*, 1951, **76**, 190.)

Stephens died on December 7th, 1950, in his 81st year. He received his early education at the Bristol Grammar School and Sidcot School. His scientific training was obtained in the laboratories of the Pharmaceutical Society, King's College, Finsbury Technical College and the Birkbeck Institution. He gained the Ph.C. Diploma in 1893, and F.R.I.C. in 1918. On completion of his scientific training, he joined Idris Ltd., of Camden Town, London, as assistant to the late Dr. W. H. Symons, whom he succeeded as chief chemist. He remained with Idris throughout his career, and latterly became a director. He joined the Society in 1897.

Thorns was educated at the Clapham School, London, and he became an apprenticed pupil to the late Dr. F. W. Passmore in 1894 and attended classes at the School of the Pharmaceutical Society. In 1898 he became assistant to Dr. Passmore and was from 1907 to 1918 his chief assistant. He then entered into partnership with Dr. Passmore, and after the latter's death he carried on the analytical and consulting practice. He was elected a Fellow of the Institute of Chemistry in 1928.

Tribley was educated at Boyle's School, Yetminster, Dorset, and Foster's Grammar School, Sherborne, and at the Finsbury Technical College, obtaining the diploma of the latter in 1919. He served in the chemical section of the R.N.A.S. from 1915 to 1919. After being assistant for a short time to the County Analyst for Worcestershire, he became chemist to the United Chemists Association Ltd., at Cheltenham. He later became chief chemist to this company and remained so until his death. He became an Associate of the Institute of Chemistry in 1920 and a Fellow in 1943; he joined the Society in 1944.

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

"The Determination of Bromine in Brine." By J. Haslam, M.Sc., F.R.I.C., and G. Moses, A.M.C.T., F.R.I.C.

"The Bromine Content of the Cheshire Salt Deposit and of Some Borehole and Other Brines." By E. C. Allberry, B.A., J. Haslam, M.Sc., F.R.I.C., and G. Moses, A.M.C.T., F.R.I.C.

"Survey of the In-shore Waters Round the Coasts of Great Britain, with particular reference to the Bromine Content." By R. O. Gibson, D.Sc., F.R.I.C., and J. Haslam, M.Sc., F.R.I.C.

"The Analysis of Bromine and Compounds containing Bromine." By J. Haslam, M.Sc., F.R.I.C.

"The Testing of Atmospheric Conditions in Theatres and Cinemas." By J. F. Clark, M.Sc., A.R.C.S., D.I.C., F.R.I.C., F.A.C.I.

"Determination of Fluoride by Etching." By H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.

"Observations on the Spectrophotometric Estimation of Vitamin D." By H. E. Cox, Ph.D., D.Sc., F.R.I.C.

"The Analysis of Petrol - Kerosine Mixtures, with Special Reference to the Boiling-Point." By C. H. Manley, M.A., F.R.I.C.

"The Evaluation of Liming Materials for Agricultural Purposes." By A. M. Smith, Ph.D., D.Sc., A.H.-W.C., F.R.I.C., A. Comrie, B.Sc., A.R.I.C., and K. Simpson, B.Sc., A.R.I.C.

"The Accurate Determination of 'Phosphoric Anhydride' by Means of Quinoline Phosphomolybdate." By H. N. Wilson, F.R.I.C.

"The Determination of Potassium in Fertilisers by Flame Photometry." By L. Brealey, B.Sc.

"Chemical Determination of Magnesium in Cast Iron." By W. Westwood, B.Sc, A.I.M., and R. Presser.

"The Determination of Sodium in Aluminium and its Alloys by Vacuum Distillation." By W. McCamley, B.Sc., T. E. L. Scott, and R. Smart, B.Sc., A.R.I.C.

"The Determination of Lead Oxide in the Presence of Lead." By R. M. Black, M.Sc., A.R.I.C.

"Inorganic Chromatography on Cellulose, Part IV. Determination of Inorganic Compounds by Paper Strip Separation and Polarography." By J. A. Lewis, A.R.I.C., and Mrs J. M. Griffiths.

"Inorganic Chromatography on Cellulose, Part V. The Use of Columns of Cellulose in Combination with Organic Solvent Extraction for the Separation of Uranium from Other Metals." By F. H. Burstall, M.Sc., F.R.I.C., and R. A. Wells, B.Sc., A.R.I.C.

"Microphotometric Determination of Carboxyhaemoglobin in Blood." By H. B. Salt, M.Sc., F.R.I.C.

JOINT MEETING—A Joint Meeting was held on December 6th, 1950, with the Food Group of the Society of Chemical Industry, at which Mr. A. L. Bacharach, Chairman of the Food Group, took the Chair. At this meeting the following paper was presented—

"Applications of Paper Chromatographic Methods in the Sugar Industry." By H. C. S. de Whalley, F.R.I.C., M.I.Chem.E., N. Albon, B.Sc., A.R.I.C., and D. Gross, Dip.Eng., Ph.D.

NORTH OF ENGLAND SECTION—Four meetings have been held during the year at which the following contributions have been made—

"The Estimation of Small Amounts of Zinc." By R. W. Sutton, B.Sc., F.R.I.C., and J. Markland, B.Sc., F.R.I.C.

"Seeing the Invisible." By H. Baines, D.Sc., Hon.F.R.P.S., F.R.I.C.

"Food Standards and Kindred Topics." By C. A. Adams, C.B.E., B.Sc., F.R.I.C.

In addition to the above, a number of matters of professional and scientific interest have been discussed.

SCOTTISH SECTION—In addition to the Annual General Meeting, three ordinary meetings were held during the year, one in Edinburgh and two in Glasgow.

The Edinburgh meeting took the form of a display of Scientific Films shown by Dr. H. Dryerre. The selection of films included the following: "The Discovery of a New Pigment," "War Under the Microscope," "Pattern of Chemistry," "A Ship Comes from Texas," "Cracking" and "Ammonia."

At the other two meetings the following papers were presented and discussed—

"Microbiological Assay as an Analytical Technique." By R. F. Looney, A.R.I.C.

"The Polarograph, its Uses and Applications." By J. C. Speakman, M.Sc., Ph.D., and J. C. James, B.Sc., Ph.D.

Mr. R. S. Watson who has been Honorary Secretary of the Section for the last eight years has retired, and the Council thank him for his services.

There has been a slight increase in membership of the Section during the year, the total membership now being 91.

MICROCHEMISTRY GROUP—Three meetings have been held during 1950; in London, Teddington and Birmingham respectively. The Teddington meeting was held jointly with the London and South-Eastern Counties Section of the Royal Institute of Chemistry, and the Birmingham meeting with the Birmingham and Midlands Section of the Royal Institute of Chemistry.

The following twenty papers have been read—

"Split-Type Micro Furnace." By G. Ingram.

"One-millilitre Syringe Burette and Stirrer Outfit." By G. Ingram.

"Heating Blocks for Micro-electrolytic Apparatus." By A. J. Lindsey, M.Sc., Ph.D., F.R.I.C.

"Combustion and Absorption Tube for the Micro-determination of Sulphur and Halogens." By W. T. Chambers, B.Sc., Ph.D., A.R.I.C.

"Simple Pressure Regulator for Micro-combustion Trains." By W. T. Chambers, B.Sc., Ph.D., A.R.I.C.

"Semi-automatic Micro-combustion Furnace." By F. J. McMurray.

"A Photo-electric Micro-nephelometer." By A. C. Mason, B.Sc., F.R.I.C.

"Micro-magnetic Bar Stirrer." By M. A. Fill, A.R.I.C., and J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Vacuum Operated Stirring Devices." By M. A. Fill, A.R.I.C., and J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Clamps and Stands for Micro-apparatus." By M. A. Fill, A.R.I.C., and J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Improvised Micro-burette." By M. A. Fill, A.R.I.C., and J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Hydrogen Sulphide Delivery Systems in Semi-micro Qualitative Apparatus." By P. Heath, W. Marshment, and J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Apparatus for Conductiometric Micro-titration." By J. T. Stock, M.Sc., Ph.D., F.R.I.C.

"Paper Chromatography." By R. A. Wells, B.Sc., A.R.I.C.

"The Micro-gravimetric Determination of Sodium as Sodium Zinc Uranyl Acetate and its Application to the Analysis of Refractories." By A. F. Colson, B.Sc., Ph.D., F.R.I.C.

"Micro-analysis in the Oil and Colour Industries." By C. Whalley, B.Sc., A.R.I.C.

"Analysis of Organic Fluoro-compounds." By F. P. Johnson, B.Sc.

"Micro-determination of Carbon and Hydrogen in Fluoro-compounds." By W. T. Chambers, B.Sc., Ph.D., A.R.I.C.

"A Study of the Potentiometric Titration of Fluoride with Lead." By F. R. Cropper, B.Sc., Ph.D., F.R.I.C.

"Demonstration of a Multiple Apparatus for the Determination of Micro Quantities of Fluorine." By R. F. Milton, B.Sc., F.R.I.C.

An exhibition of microchemical apparatus was held in London in January, and the Committee hope that this may become an annual event in connection with the Annual General Meeting in London.

Three meetings will be held during 1951; the Annual General Meeting in London in January, the Spring Meeting in Edinburgh in April, and the Autumn Meeting at Liverpool.

Work has continued on the compiling of a card index showing the special interests of each member of the Group.

The papers given at the Nottingham meeting in 1949 are due to appear as a Royal Institute of Chemistry monograph on Micro-balances, the three authors concerned having rewritten their papers in expanded form.

In response to a request from Messrs. British Drug Houses Ltd., a Sub-Committee on Micro-analytical Reagents has co-operated with that company in evolving specifications for purity of reagents and to recommend what substances should be standardised.

The 1st International Microchemical Congress in Graz was held in July, and 18 Group members participated, including 7 Group officers and members of Committee. The Chairman, Ronald Belcher—who also represented the Parent Society at the Congress—was one of the six microchemists on whom was conferred the distinction of Honorary Membership of the Osterreichische Gesellschaft für Mikrochemie. An illuminated translation in German of the message of greeting from the Microchemistry Group to the Congress was presented to the Osterreichische Gesellschaft für Mikrochemie. A total of 623 delegates was present, representing no less than 28 different nations, and upwards of 130 papers were read. These papers are to be published in Vol. XXXVI of *Mikrochemie*.

The Congress was most inspiring to all who took part and marks a definite milestone in the progress of microchemistry.

The number of Group members is now 341, an increase of 32 since the last report.

PHYSICAL METHODS GROUP—The Group has held three meetings in London and one each in Cambridge and Poole during the past year. The Cambridge meeting was organised by the Polarographic Discussion Panel. The Poole meeting was held jointly with the Mid-Southern Counties Section of the Royal Institute of Chemistry. All the meetings were well attended.

The Group also organised the meeting of the Parent Society on the subject of "Modern Methods of Moisture Determination." This was held on February 1st, 1950.

The Polarographic Discussion Panel, which now has 71 members, organised one Group meeting. Mr. J. Haslam is the Chairman of the Panel and Mr. G. A. Wood is Honorary Secretary.

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

Annual General Meeting, London, November 29th, 1949.

"The Mass Spectrometer, a Survey of its Applications in Analysis." By J. G. A. Griffiths, B.A., Ph.D., F.R.I.C.

Spectroscopy Meeting, London, January 3rd, 1950.

"The Determination of Strontium in Sea Water by a Combination of Flame Photometry and Radiochemistry." By A. A. Smales, B.Sc., A.R.I.C.

"A Photo-electric Spectrophotometer for the Visible and Ultra-violet Regions." By R. A. C. Isbell, A.Inst.P.

"The Application of the Uvispek Spectrophotometer to Biochemical Problems." By D. C. M. Adamson, F.R.I.C.

Polarography Meeting, Cambridge, April 21st, 1950.

"The Indirect Determination of Aluminium." By G. Jessop, M.Sc., Ph.D.

"The Ilkovic Equation—its Present Status." By W. Cule Davies, D.Sc., Ph.D., A.R.I.C.

"An Electronic Polarometer for Metallurgical Purposes." By C. H. R. Gentry, B.Sc., A.R.I.C.

Radiochemistry Meeting, London, May 23rd, 1950.

"Radiometric Assay in Tracer Research." By F. P. W. Winteringham, A.R.I.C.

"The Determination of Potash (in Fertiliser) by Measurement of its Radioactivity." By D. S. Lees, B.A., A.Inst.P., W. Broomfield and H. N. Wilson, F.R.I.C.

"Radio-activation Analysis—Some Glimpses of its Scope." By A. A. Smales, B.Sc., A.R.I.C.

Flame Photometry Meeting, Poole, October 6th, 1950.

"Flame Photometers—A Description of Two Instruments." By L. Brealey, B.Sc., and R. E. Ross.

"Notes on the Internal Standard Technique (in Flame Photometry), with Special Reference to Liquid Filters." By T. C. J. Ovenston, B.Sc., Ph.D., F.R.I.C.

"The Rapid Determination of Sodium and Potassium in Rocks and Minerals." By G. H. Osborn, F.R.I.C., A.M.Inst.M.M., and H. Johns, B.Sc.

The number of Group members is now 356. This represents an increase of 30 since the last Annual Report.

BIOLOGICAL METHODS GROUP—During the period under review the Group has held four meetings, during the course of which a total of 18 papers have been read and discussed.

The Annual General Meeting on December 13th, 1949, was followed by an Ordinary Meeting, at which the following papers were presented—

"The Microbiological Assay of Riboflavine in Yeast and Yeast Products, using *Lactobacillus helveticus* in a 17-hour Titrimetric Method." By A. Jones and S. Morris, D.Sc.

"A 24-hour Plate Assay Technique for the Vitamin B_6 Complex of Yeast, with a Note on the Possible Presence in Certain Yeasts of a Fourth Member of the B_6 Complex." By A. Jones and S. Morris, D.Sc.

"The Assay of Serum Gonadotrophin by the Ovary Weight Method." By G. L. M. Harmer.

On March 14th, 1950, the Group held a symposium jointly with the Biometric Society (British Region), under the title "The Design and Evaluation of Biological Assays." Dr. Trevan, F.R.S., was in the Chair for the afternoon session, when the following papers were presented—

"The Graphical Calculation of the Results of Biological Assays with Graded Responses." By N. T. Gridgeman, B.Sc., A.R.I.C.

"The Estimation of Error in Certain Types of Biological Assays." By E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.

"The Problem of Combining the Results of Independent Assays." By E. C. Fieller, M.A.

The evening session was something of an innovation, and was devoted to a discussion of problems related to the subject of the symposium that had been submitted by members and announced prior to the meeting. The occasion provided a unique opportunity for practical bio-assayists and statisticians to get together and discuss, quite informally, questions of common interest. The good attendance at the meeting and the favourable comments it provoked were evidence of its success.

Dr. S. K. Kon took the Chair for a meeting on May 23rd, 1950, when the subject under discussion was "The Assay of Vitamin B_{12}." The papers read were—

"Assays of Vitamin B_{12} in Man." By C. C. Ungley, M.D., F.R.C.P.

"Chick Assays." By M. E. Coates, Ph.C.

"The Cup-Plate Assay of Vitamin B_{12}." By W. F. J. Cuthbertson, B.Sc., Ph.D., F.R.I.C., J. T. Lloyd, B.Sc., and H. F. Pegler.

"Some Observations on Cup-Plate Assay for Vitamin B_{12}, using *Lactobacillus lactis* Dorner 10697." By F. E. Larkin and R. E. Stuckey, B.Sc., Ph.D., F.R.I.C., Ph.C.

"The Assay of Vitamin B_{12} by the Turbidimetric Method, using *Lactobacillus leichmanii* 313." By W. B. Emery, B.Sc., F.R.I.C., K. A. Lees and J. P. R. Tootill.

"A Comparison of *Lactobacillus lactis* Dorner and *Lactobacillus leichmanii* for the Assay of Vitamin B_{12} by a Test-tube Method." By G. E. Shaw, B.Sc., Dip.Bact.

"Experience with Microbiological Assay of Vitamin B_{12} in an Analytical and Consulting Laboratory." By H. Pritchard, M.Sc., F.R.I.C.

Finally, on October 24th, 1950, attention was focussed on another subject of topical interest, "The Assay of Adrenocorticotrophic and Cortical Hormones." The following papers were presented and discussed—

"Technique for Hypophysectomy and Adrenalectomy in Mammals." By M. Pickford, M.Sc., M.R.C.S., L.R.C.P.

"The Adrenal Ascorbic Acid Depletion and Adrenal Repair Methods for the Bio-Assay of the Adrenocorticotrophic Hormone." By C. J. O. R. Morris, M.Sc., Ph.D., F.R.I.C.

"Adrenocorticotrophic Hormone Assay. Experiences with the Ascorbic Acid Depletion Method and Comparison with Preliminary Observations on the Use of the Inhibition of Tissue Repair." By B. E. Clayton, M.B., Ch.B., Ph.D., and F. T. G. Prunty, M.A., M.D., B.Ch.

"Assay of Cortical Hormones on Small Laboratory Animals." By M. Vogt, M.D., Ph.D.

"Methods in the Evaluation of Adrenocorticotrophic and Cortical Hormones in Man." By E. G. L. Bywaters, M.B., B.S., M.R.C.P., M.R.C.S., L.R.C.P.

The growing interest of members of the Society in biological and microbiological methods of assay is apparent from the continued increase in membership of the Group, which has more than doubled in the last four years. Nineteen new members have joined during the year and there have been three resignations and one death; membership now stands at 179.

ANALYTICAL METHODS COMMITTEE—A report from the Carotene Panel of the Sub-Committee on Vitamin Estimations on the Determination of Carotene in Green-Leaf Material, Part 1: Fresh Grass (*Analyst*, **1950, 75**, 568) has been published, and reports from the Aneurine Panel, Chemical Panel, Soapless Detergents Sub-Committee and Meat Extract Sub-Committee have been passed and are to be published in the near future.

The compilation of the Bibliography of Standard Methods of Analysis has been completed and the Bibliography has now been published. It is believed to be the first complete guide to the literature of analytical methods and consists of annotated references to a very wide range of subjects. The text is divided into 33 subject groups, classification being based on that used in "British Abstracts."

The activities of the Sub-Committees will produce more work for publication shortly; methods for traces of lead in foodstuffs, for Linalool in certain essential oils and examination of the Hortvet freezing-point test are among the Sub-Committee work showing good progress.

PUBLIC ANALYSTS AND OFFICIAL AGRICULTURAL ANALYSTS COMMITTEE—The Committee has met formally twice and informally on several occasions.

Negotiations with the County Councils Association, the Association of Municipal Corporations, the Urban District Councils Association and the Metropolitan Boroughs Standing Joint Committee regarding the remuneration and service conditions of Public Analysts have been carried on by correspondence throughout the year. On November 2nd, Messrs. Cox, Taylor, Monk and Sutton met representatives of the various bodies for the first time. It is anticipated that a further meeting will take place in the near future.

A letter has been received from the Ministry of Fuel and Power thanking members of the Committee for the assistance they gave regarding the testing of commercial (red) petrol.

Bulletins No. 7 and 8 have been published and Public Analysts have been kept informed of current matters.

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

B.S.I. Committees—

Dr. H. E. Cox, Glycerine Committee.
Mr. D. D. Moir, Distillation Apparatus Committee.
Dr. K. A. Williams, Sampling of Oils and Fats Committee.
Dr. H. J. Stern, Tests for Cellular Rubber Committee.
Mr. R. F. Milton, Granular Soda Asbestos Committee.
Dr. J. T. Stock, Laboratory Ovens Committee.
Dr. R. C. Hoather, Laboratory Autoclaves Committee.
Mr. Noel L. Allport, Ampoules Committee.

Other Committees—

Mr. W. M. Seaber and Mr. A. H. Ward, Dried Grass Marketing Standards Advisory Committee of the Ministry of Agriculture and Fisheries.

A number of interesting reports have been received from representatives of the Society, and the Council takes this opportunity of thanking all its representatives for the work that they have carried out on the various Committees during the year on behalf of the Society.

HONORARY TREASURER'S REPORT—This is the first year for which the increased subscription to the Society has been in operation, and it is pleasing to report that this increase has not affected the membership of the Society. Furthermore, although the cost of *The Analyst* to outside subscribers was also increased at the same time as the subscription to the Society, this has not resulted in a drop in the sales of *The Analyst*. The increase in subscription rates has now put the Society on a satisfactory financial basis, and although from a financial point of view this has been a bad year for the Society owing to unexpected expenditure as a result of illness, we were able to show a satisfactory balance. As a result of this improved financial position, it has been possible to increase the grants to the Groups of the Society in order to assist them in extending their activities.

This year has also seen an extension of the Society's office accommodation, which it is hoped will enable the office staff to keep pace with the considerable increase in the Society's activities.

THE ANALYST—The publication date of *The Analyst* is now restored to the 16th of each month. It is to be regretted that a dispute in the London printing trade prevented the simultaneous appearance of "Abstracts C" for several months.

The volume for 1950 contained 694 pages, compared with 662 pages in 1949, and carried 103 original papers and 38 Notes against 75 papers and 35 Notes in 1949. This increase in the amount of original work published in 1950 has absorbed the space formerly occupied by abstracts of papers from other journals. Nearly 40 per cent. of the total circulation of *The Analyst* is sent abroad and distributed to 53 different countries.

The decennial index for the years 1936 to 1945 is ready for printing as soon as paper, deliveries of which to the printers are still delayed, is available.

JUNIOR MEMBERSHIP OF THE SOCIETY—The Council has discussed at length the recommendation of a Sub-Committee appointed to consider the matter that a grade of Junior Membership should be established. The principle of forming such a grade has been agreed upon, and a recommendation will be made to the Society that the Articles of Association should be altered accordingly.

ORGANISATION—We very much regret that Mr. Lane's health did not permit him to resume full-time work as Editor of *The Analyst*, but he nevertheless attended at the Society's office whenever it was possible, and the Society was very grateful for the efforts he made on its behalf in trying circumstances. Mr. Lane died just before the Annual General Meeting; his loss will be felt by the Society very much indeed. (Obituary, *Analyst*, 1951, **76**, 250.)

Mr. Okell has continued as Acting Editor during the year with the assistance of Mr. Attrill. Miss Wilson fell ill soon after she had been appointed Secretary of the Society early last year and was granted sick leave. We are very pleased to record that she has made a very good recovery from a serious illness, and that she resumed work in the office at the beginning of February.

MISS ELLIOTT FUND—The Society has purchased a bookcase with a sum left by the late Miss Elliott to act as a memorial to her, and this is now in the Society's office.

INTERNATIONAL CONGRESS OF ANALYTICAL CHEMISTRY, 1952—The President of the Society has continued to act as Chairman of the Executive Committee. The date and place of the Congress have now been fixed and it will be held at Oxford in September, 1952. The Council of the Society has agreed to place *The Analyst* at the disposal of the organisers for the publication of the proceedings of the Congress.

CENTRAL RIVERS PROTECTION COUNCIL—The Society is a constituent body of this Council, which has recently become active in connection with the new Bill on River Pollution. The Council's objects include the prevention of pollution in rivers and the drawing of the Government's attention to such pollution whenever it becomes necessary. The Society has agreed, through its representatives on this Council, to act as its technical adviser.

BUREAU OF ABSTRACTS—The Society is a constituent body of the Bureau of Abstracts and during the year has distributed Abstracts C of the Bureau to all members and subscribers to *The Analyst*. We have had the benefit of nominating Dr. J. R. Nicholls to sit on the Board of Directors of the Bureau, and Dr. D. C. Garratt and Mr. H. S. Rooke to sit on the Committee of Abstracts C. Mr. Rooke has resigned from this Committee on taking an appointment with the Bureau.

BRITISH STANDARDS INSTITUTION—As is noted above, the Society has nominated a number of representatives to sit on technical Committees of the British Standards Institution.

The Council has resolved during the year to continue its support of the B.S.I. on the lines of the agreement negotiated between the two bodies a number of years ago, and means are now being worked out to ensure a proper liaison between the B.S.I. and the Society.

FERTILISERS AND FEEDING STUFFS ACT—The Minister of Agriculture and Fisheries and the Secretary of State for Scotland have appointed a reconstituted Advisory Committee to advise and assist them with respect to the making of Regulations under the Act of 1926, and the members of this Committee include Mr. George Taylor, O.B.E., F.R.I.C., and Mr. Eric Voelcker, A.R.C.S., F.R.I.C., both nominated by the Council of the Society.

PRESERVATIVE REGULATIONS—At the instance of the Society and the Food Group of the Society of Chemical Industry, the Ministry of Food has set up a Sub-Committee of the Food Standards Committee to review the Public Health (Preservative etc. in Food) Regulation and to make any recommendations considered desirable for their amendment. Dr. H. E. Cox has been appointed to represent the Society on this Sub-Committee.

GEORGE TAYLOR, *President.*
K. A. WILLIAMS, *Honorary Secretary.*

Address of the Retiring President

GEORGE TAYLOR, O.B.E., F.R.I.C.

(*Delivered after the Annual General Meeting, March 16th,* 1951)

IN our Society it is the practice that the Presidential Address shall be given at the end of the presidential two years of office. Accordingly, it must be regarded as conventional that the retiring President will refer to the Society's activities during the preceding two years and will further, with suitable humility, express his personal views on the spirit that has animated the Society—the spirit that must animate any living Society such as ours—and which in its trend has in fact directed either the general or any special activities. With regard to the first matter I am greatly indebted to Dr. Williams, our Honorary Secretary, for his last two Annual Reports, in which he gives a much better résumé of our activities than I can give, and which I therefore regard as permitting me to turn immediately to my second matter. I would, however, take this opportunity of referring to our excellent position with regard to membership and financial status, and paying my personal tribute to the hard and devoted work of our Honorary Secretary, Dr. K. A. Williams, and our Honorary Treasurer, Dr. J. H. Hamence, to whom this very satisfactory position is largely due.

Coming now to the second matter, I find that over the last two years I have become aware on every side of an increasing consciousness of the fundamental purpose of our Society.

You will remember that the first object of our Society as declared in our Memorandum of Association, is as follows—

> "To encourage, assist and extend the knowledge and study of analytical chemistry, whether by the holding of periodical meetings, by the establishment and promotion of lectures, demonstrations, experiments, discussions, conferences or correspondence, by the formation of reading rooms and libraries (whether of reference or lending), or by the publication of newspapers, periodicals, journals, pamphlets, reports or books."

This is the rock on which our Society was founded.

The objectives of the Society were at first of course somewhat fluid, and could be regarded as applying only to one branch of analytical chemistry and as being limited in scope. But with the publication of the journal of the Society, *The Analyst,* the objectives became sharply crystallised. It is interesting to refer to the title page of volume one (1877), where the following is recorded—"*The Analyst,* including the proceedings of the Society of Public Analysts—a monthly journal of analytical chemistry." This, however, was altered in the second volume, and then read—"*The Analyst*—including the proceedings of the Society of Public Analysts, a monthly journal for the information of those interested in the purity of food and drugs and in general analytical microscopical research."

But in 1891 there appears a significant change, for now we find the journal described as "the organ of the Society of Public Analysts, a monthly journal devoted to the advancement of Analytical Chemistry." Observe the change! From being a periodical with a purpose, which incidentally included the proceedings of a Society, it now proclaims itself as the voice of a Society devoted to that purpose. And, in effect, the title page has so remained since.

During the two years of my office I have had the opportunity of observing very closely the trend of our Society and I have noted the following.

The three Groups dealing with the specialised branches of analytical chemistry, Biological Methods, Microchemistry and Physical Methods, have continued to develop, and have published the results of much original investigational work, so much so that *The Analyst* now claims many new subscribers on this account alone. Some eighteen members of the Microchemistry Group attended the First International Microchemical Congress in Graz, and our Society was there honoured by the conferment on Mr. Ronald Belcher of the distinction of Honorary Membership of the Austrian Microchemical Society. In my view, much of the continued progress of our Society is directly due to the work of these three Groups.

The Analytical Methods Committee steadily continues its work of publishing standard methods of analysis. Perhaps most important, because it marks a new departure in this country, is the publication of the first edition of a Bibliography of Standard Methods of Analysis. The work of compiling and editing this Bibliography has been very hard and tedious and has covered some four years; and the thanks of the Society must be given to Dr. Kent-Jones, upon whom fell practically the whole of this work, and who was the originator of the idea and the main-spring of the responsible Sub-Committee.

Our Society is concerning itself very intimately with the Second International Congress of Analytical Chemistry to be held in England, at Oxford, in 1952. We contributed the money necessary for the initial expenses of the preliminary arrangements, we are well represented on both the Central and the Executive Committees, and *The Analyst* has been accepted as the organ in which the proceedings of the Congress will be published.

Also during the last two years our Society has, through its nominated members, concerned itself with Government legislation in connection with the Fertilisers and Feeding Stuffs Act, the Rivers (Pollution of Effluents) Bill and the Preservative Regulations.

One other matter in this connection is the continued increase in circulation of *The Analyst*—and this despite the increased price to outside subscribers, that is, persons, firms or institutions not members of our Society. It is interesting to mention here that of a total of 2350 of these outside subscribers, no less than about 1600 are scattered throughout the world outside the United Kingdom, in no less than 57 different countries.

While dealing with *The Analyst* I would wish to acknowledge the invaluable work of the Assistant Editors, F. L. Okell and J. B. Attrill, during the many months of illness of our late Editor.

Now this is a two years' record and I have dealt with it at some considerable length as a background to a matter that has caused me very much concern and one that I regard it as my duty now to deal with to the best of my ability.

When I first took office there was a movement among members to alter the name of the Society to one more indicative of its fundamental purpose for the advancement of analytical chemistry, and also to remove from our Memorandum of Association two sections dealing with professional objects. Early in my period of office a resolution to this end was submitted to members at a general meeting but failed to get the necessary majority for its purpose. Since then, however, a new factor has emerged which may well have a great influence on this question, namely, an announcement of the Government's intention to found a Science Centre. In May, 1950, Mr. Phillips Price, M.P., the Chairman of the Parliamentary and Scientific Committee, a body on which our representative, Dr. H. E. Cox, takes an active part, was fortunate in the House of Commons (to quote the Rt. Hon. Viscount Samuel) "in the fact that his devoted work for this Committee was recognised by Providence in giving him the first place in the ballot for Private Members Motions. He seized that opportunity by putting down a resolution on the utilisation of Britain's scientific resources. Seventeen members of the House of Commons spoke, of whom thirteen were members of this Committee. In November, Mr. Morrison announced, on behalf of H.M. Government, the acceptance of a proposal long advocated for the creation of a new British Science Centre in London." Subsequently, the Rt. Hon. Herbert Morrison, M.P., stated that the actual building of such a

Centre was a long-term policy; the planning of the Centre and the preliminary arrangements were to proceed immediately, and the Royal Society would take a great part in the negotiations.

In December, Sir Robert Robinson, in his presidential address at the anniversary meeting of the Royal Society, said that it was possible that the scientific societies would be housed in a worthy and impressive building, and that the quarters of the various societies would be separate, each retaining its individual library. He enumerated the various societies which had agreed to participate, a list of some sixteen. He further stated that it was understood that many of the smaller scientific clubs and societies would receive hospitality as they did at the present and had done in the past.

But our Society is not included in that list, although I believe that at least one of the societies included has a membership no larger than ours. There is, of course, no official reason given for our non-inclusion. It is to be observed, however, that all the societies included in the list fall into the general category of "pure" scientific bodies, that is to say, they have no professional interests. It is probable, therefore, that it is because we have professional objects in our Memorandum and our name suggests a professional angle that we are not considered to be eligible. I doubt whether the name carries much weight from this point of view, but certainly the fact as regards our Memorandum is another matter. It may be also that the position of analytical chemistry as a branch of the science of chemistry is not considered of sufficient separate importance to justify a position among the chosen scientific societies; this point, however, I will deal with later.

I have referred to the fundamental purpose of our Society, and to the background of our activities during my years of office. I hold the view that as our Society represents analytical chemistry in the United Kingdom, and that as analytical chemistry, a branch of the science of chemistry, has now attained a status of national importance, the Royal Society could and should be persuaded, even now at this somewhat late stage, to consider favourably any application that we may make for inclusion in the bodies to constitute the Science Centre. I know that the movement among some members of our Society to remove the particular sections of our Memorandum is again reviving. I think that we are now at a turning point in our Society's existence. We have to make a decision that will vitally affect our future. We can remain constituted as at present and hope that we shall continue our present excellent progress, or we can reconstitute ourselves with the hope that thereby we shall be admitted into the Science Centre, with the prospect of a permanent home, and of being universally accepted as the Society representing the science of analytical chemistry. I believe that we cannot possibly evade this issue. Personally, I am convinced that we should be a body devoted only to the advancement of the science of analytical chemistry without any professional interests; and as a professional analyst I am now also convinced that my professional interests would best be served by a separate but closely connected association devoted to that special purpose. This is not the time or place to go into the question of how such reconstitution could be brought about, but I am aware of suggestions, which have been put forward after grave consideration, that offer a course of action that might well be acceptable to all members of our Society.

Coming now to the question of the status of analytical chemistry in the chemical world, it has repeatedly been urged that this is not properly recognised. It is said that analysis is regarded as the handmaiden but not as an essential branch of chemistry. L. Eynon, my predecessor in the presidential chair, laid emphasis in his presidential address[1] on the desirability of recognition by the Universities by the institution of Chairs of Analytical Chemistry. The President of the Royal Institute of Chemistry, Professor J. W. Cook, in his presidential address in Glasgow,[2] in 1950, referred to the need to publicise the work of chemists and their real achievements as opposed to the popular conception of men engaged in the development of the destructive forces of atomic energy; and although not specifically referred to, his address quoted instances of analytical achievements. C. L. Wilson[3] has also recently dealt with this subject in considerable detail in an article on "The Future of Analytical Chemistry."

These are all typical of many earnest endeavours in many places towards the same end. Where, however, they fail to some extent is in their direction and their aim; and in the method of attaining publicity. To a large extent they consist of claims and statements made in wide and general terms. These I fear do not have sufficient weight; they constitute the advertisement, but there is I think much to be said for the old adage, as forceful to-day as it was in the yesterdays, that the proof of the pudding is in the eating. We should, I believe,

progress much more rapidly in general acceptance if we would talk more about what has been accomplished by analytical chemistry and what it would be fair to say could not have been accomplished without the aid of analytical chemistry. Taking this point of view, I propose to give a brief survey this afternoon of some examples of the Service of Analytical Chemistry in Food and Agriculture, within the particular field in which I work.

ANALYTICAL CHEMISTRY IN THE SERVICE OF FOOD AND AGRICULTURE

In submitting my thoughts on the services of analytical chemistry to food and agriculture, I am immediately concerned with the fact that generally when food and agriculture are referred to collectively the emphasis is on food and matters connected directly with food, and the subject of agriculture is relegated to the background. It is of course natural that life should be considered in terms of food. Of all the forces that influence, govern, or determine the life of a people—religion, education, physical comfort, social amenities, the law—none is greater than food. But what is not so generally recognised is that food is co-existent with agriculture, its quality and quantity are dependent on the quality and quantity of agriculture; the question of food supplies cannot be properly considered independently of the question of agriculture. It is a biological law that man cannot live without plants. It is for this reason that in discussing, and putting forward instances of, the service of analysis, I have thought it desirable to deal, in the main, with agricultural matters.

At the present time, service to food and agriculture can scarcely have any real significance other than that of increasing productivity. The problem of an increasing population without a corresponding increase in the food supply is a topic of everyday conversation.

Although this question is outside the particular purpose of my talk and has been dealt with recently at length by Professor S. Zuckerman,[4] under the heading of "Food Production in Relation to National Economy," I should, however, like to show you a table from the 1947 F.A.O. report which shows vividly the position of the U.K. in this matter (see Table I).

TABLE I

F.A.O. REPORT, 1947

	Acres of arable land per person	Rate of population increase per 1000	Years needed to double population
Greece	0·74	11·8	59
Hungary	1·53	5·9	118
Rumania	1·70	10·1	69
Poland	1·33	11·2	62
Italy	0·74	9·4	74
Belgium	0·30	1·2	579
Netherlands	0·27	11·5	61
Germany	0·69	7·6	92
France	1·24	0·4	—
Sweden	1·46	3·1	224
Denmark	1·73	7·5	93
United Kingdom	0·27	—	—
England and Wales	—	2·2	314

It will be noted that the U.K. and the Netherlands have the smallest amount of arable land per person. This fact has the greater implication in an island like the U.K.

Agriculturists generally are being encouraged on the highest levels to increase productivity. It must be recognised, however, that there is little parallel between an increased productivity in industry of the necessities, other than foodstuffs, of our modern civilised life and an increased productivity of foodstuffs. With the former, articles are produced more or less unalterable and ready for use. On the other hand, the production on a farm of a certain amount of food, either animal or vegetable, does not mean that that same amount will be available for consumption. It may suffer, either while being grown or in the interval between full growth or harvesting and consumption, from one or more possible causes of deterioration, such as disease, breakdown and decomposition due to inherent natural vital activities, the action of bacteria or fungi, or the attack of insect or rodent pests. Viscount Bledisloe,[5] in his presidential address to the Second International Congress of Crop Protection, 1949, stated that a conservative estimate of the loss due to this cause, excluding weeds, is

given at 30 per cent. of crops growing, harvested and stored, and the F.A.O. has estimated the annual loss of grain at approximately 65 million tons.

Again, separate farms may yield the same weight of produce, yet the produce of one may have significantly greater nutritional value, quite apart from any question of decomposition or the effects of outside deteriorating agencies. That is to say, the productivity of agriculture cannot be assessed, from the national point of view, only in terms of weight or volume, it must also be assessed in respect of nutritional value. This fact is so important that it hardly needs stressing, but it brings me to my first example of the service of analytical chemistry.

Cobalt and animal health

Recently, an agricultural correspondent in an article on New Zealand in *The Times*[6] referring to the frequently repeated warning that the world must soon go hungry because human beings are increasing rapidly and there is no new land that can readily be brought into food production, points out that there are many square miles in the North Island of New Zealand waiting for development. To quote: "New Zealand's youngest soil was created with the Napier earthquake in 1931, but much more was made in 1886, when Mount Tarawera erupted and showered ashes and mud over 5700 square miles. This pumice soil, which grows useless tussocks and the scrub 'ti-trees' (Manuka) when left to nature, can quickly be transformed by burning, cultivating and fertilising into excellent grazing country for cows, beef cattle and sheep. The new soil which is friable and easily worked will grow abundant rye grass and clover. *The key to this new wealth was found* by incorporating a trace of cobalt (6 lb to 1 ton of superphosphate in the fertiliser dressing)."

You will observe this quite casual reference to cobalt, an element which cannot be described as well known to the average person. But, in fact, it was a considerable amount of analytical work that discovered this key.

The story of cobalt deficiency in animals is a fascinating one. For many years settlers in certain areas in New Zealand and Australia had experienced severe losses of sheep and cattle from "wasting diseases" of unknown cause. Animals, after grazing for several months, lost their appetites, wasted and finally died, although feeding in a luxuriant growth of pasture. Horses fed in the same areas remained in excellent health. Spectacular recovery followed change to other pastures, although apparently these were inferior in quality and quantity. The clinical picture was that of chronic starvation. It was natural enough, therefore, that the earliest treatment was for anaemia, and consisted in dosing with iron compounds. At first this seemed successful in New Zealand, as cures were obtained with the aid of massive doses. You will note the *massive* doses! But later work in Australia suggested that the curative agent was some impurity in the iron compounds. (Hence the need of massive doses.) It was also observed that while the amounts of iron found in good and bad pastures were not significantly different, there was often a very marked difference in the type of soils. Limonite soils were generally—though not invariably—good soils. So much so that treatment of the affected animals with drenches prepared from limonite had generally proved so effective that they were in common use. But these drenches were not invariably successful, so the next step was to add copper salts to the drenches, on the assumption that the value of the massive dosage of iron was due to traces of copper. This proved fallacious. It was at this point that the analytical approach to the problem began to appear of significant value. Dilute hydrochloric extracts of curative limonites proved effective, even after removal of iron from the extracts. Further fractionation showed that the potent element was in the fraction containing nickel, manganese, cobalt and zinc. Tests that followed with supposedly pure nickel oxide indicated nickel as the curative agent, until it was subsequently found that pure nickel chloride failed. Now, from another part of Australia, came the suggestion that the wasting disease, known locally as "coast disease," was due to lack of one of the trace elements, together with the further suggestion that cobalt might be required in ruminant nutrition, the latter suggestion being based on the demonstration a few years previously of the effect of traces of cobalt on rats. Analysis of the nickel compound showed the presence of substantial amounts of cobalt. The solution of the problem was found. In affected areas of Western Australia, sheep were kept in excellent condition by a daily dose of 0·1 mg of cobalt, and cattle by from 0·3 to 1·0 mg. In South Australia, however, it was found that copper as well as cobalt was necessary for complete cure. About the same time, in New Zealand, it was independently established by Askew and Dixon[7] that the effectiveness of ores and soil drenches was related to their cobalt content.

Consideration of some of the results of analysis are interesting (see Table II).

TABLE II

COBALT CONTENT OF PASTURES, ETC.

	Cobalt, p.p.m. (in dry matter)
"Pure nickel oxide"	7000
Ferric ammonium citrate	24
Limonite	2 to 55
"Nelson" soil	45
Acid extract of top-soils, bad	0·09 to 0·23
" " good	0·26 to 0·94
Unhealthy pasture	average 0·038
Healthy pasture	average 0·106
Livers of unhealthy sheep	0·02 to 0·03
Livers of healthy cobalt-treated sheep	0·07 to 0·25

Since then many other investigations have been carried out in various parts of the world and cobalt deficiency has been found to be the cause of apparent malnutrition in many places, even in some parts of Scotland.

One fact brought to light by this work was illuminating. While it was now established that cobalt is an essential factor in ruminant nutrition, it seemed clear that very much smaller amounts, if any, are required by non-ruminants. Though it might well be said that the original problem had been solved, the interesting problem of how the traces of cobalt function and why in one class of animal they should be necessary, and not in the other class, remained unanswered until quite recently, when light was thrown on this question by J. Tosie and R. L. Mitchell[8] with the aid of recently-developed methods of analysis using radio-active techniques. When radio-active cobalt was injected intravenously into adequately fed cattle and its course traced, somewhat surprisingly poor absorption of the element was shown, but some unexpected results were also shown which led to the examination of the micro-organisms in the rumen by the application of a spectrographic method for the determination of their cobalt content. This appears to have been an extraordinarily fertile line of investigation, for it established a reasonable possibility that the rumen micro-organisms accumulated cobalt from their external environment. The findings suggested that (1) in cobalt-deficient sheep the host and the microbes compete for the already low concentration of cobalt available in the feed; or (2) that cobalt may be essential for the micro-organisms and not for the host; or (3) that absorption of the element by the host would deprive the micro-organisms of a factor essential for their growth and metabolism. Conversely, if cobalt is an essential metabolite for the host, then its concentration in micro-organisms may reduce its availability for the host.

This is the picture to date. It is clearly not yet finished. But I would contend that it is an outstanding picture of how analytical chemistry first indicated the cure for a serious cattle disease and then, with the advance in the science, began to sketch in the cause of the trouble as a background to the picture. In their account in *Nature*, Tosie and Mitchell finally add the comment that it is of interest to note that cobalt has been found to occur to the extent of 4·0 per cent. of the crystals of the naturally occurring anti-pernicious anaemia factor.

GRASS IN ENSILAGE

It is accepted by many thoughtful agriculturists that from a national standpoint the greatest scope for increased home food production lies in raising the productivity of our grasslands. Sir George Stapledon[9] suggests that nearly one-third of the land surfaces of Great Britain is in rough and hill grazing and by far the larger proportion lies comparatively snug below the 1500 ft. contour. In general terms and on technical grounds there is no reason why this land should not be made the master instrument in producing an honest meat ration for all of us, here at home. The Minister of Agriculture[10] put the possibilities somewhat tersely when, at the Smithfield Show in London in December, 1949, he gave the farmers the slogan "Ten per cent. more grass from ten per cent. less land." Professor S. Zuckerman[4] puts the point that an increase from the present 11 cwt of starch equivalent per acre to 14 to 15 cwt of starch equivalent per acre would mean an additional approximate amount of 3½ million tons of starch equivalent, equal at the ruling price to £100 million.

Professor Zuckerman favours artificial drying of grass rather than ensiling, but this question is controversial.

The assessment of quality is largely dependent on chemical analysis, and of late years new factors, such as "trace elements," protein constitution and mineral composition have added to the difficulties of the assessment. Moreover, the calculations for that useful unit of measurement, "cwt of starch equivalent per acre," can only be made from analytical data.

The following table, by R. A. Hamilton,[11] illustrates the present-day value of grass—

TABLE III

ESTIMATED QUANTITIES OF STARCH EQUIVALENT AND PROTEIN EQUIVALENT PROVIDED BY CROPS AND GRASS IN THE U.K. IN 1948

	Million acres		Starch equivalent	Per cent. of total	Protein equivalent	Per cent. of total
			Million tons			
	13·1	Arable crops	11·0	49	1·1	37
	17·9	Grass—temporary and permanent ..	9·9	45	1·8	60
	17·2	Rough grazings	1·3	6	0·1	3
Total	48·2		22·2		3·0	

The available calculated figure for utilised starch equivalent for grasslands in the U.K. is from 10 to 12 cwt per acre.

Although man does not eat grass and the objection to these figures that they over-emphasise the importance of grass can therefore be raised, the extent to which arable crops are used for livestock feeding is often forgotten. It is illustrated in Table IV.

TABLE IV

ESTIMATED QUANTITIES OF STARCH EQUIVALENT AND PROTEIN EQUIVALENT PROVIDED IN THE U.K. IN 1948 BY CROPS AND GRASS WHICH WERE EATEN BY LIVESTOCK

	Starch equivalent	Per cent. of total	Protein equivalent	Per cent. of total
	Million tons			
Arable crops	6·8	38	0·7	27
Grass—temporary and permanent	9·9	55	1·8	69
Rough grazings	1·3	7	0·1	4
Total	18·0		2·6	

Grass is ordinarily utilised in several ways. It may be directly grazed, or cut frequently during the growing season and immediately artificially dried, or cut at or towards the end of its growing season and dried naturally to produce that age-old product, hay, or it may be cut and ensiled. Regarded as a source of protein—or meat in embryo—there must always be discussion as to the best way to treat grass that cannot be directly grazed. On this point it is to be observed that silage is a succulent and palatable article very largely used as a staple cattle food in the dairy countries of Denmark and Holland, and it is stated that most of the dairy farms of any size in the U.S.A. possess a silo, because in the early days young maize—a crop extensively grown there—is particularly suitable for ensiling. In the U.K., however, silage has had a chequered career. Prepared from a mixture of cereals and legumes, *e.g.*, oats and vetches, it attained considerable popularity at the end of the nineteenth century. But the practice declined, probably because although the silage then produced was a sweet and palatable food, it was produced at a high temperature from crops at an advanced stage of growth and its feeding value was low. Also it was in direct competition with hay-making. Now, within the last ten or twenty years, there has been a very strong revival, due without doubt to a better understanding of the chemistry involved in the underlying principles as interpreted by analysis of the constituents produced during the varying phases of its preparation. This is shown in detail and at considerable length by Sir S. J. Watson[12] in a recent article on the chemistry of ensilage. After describing grass silage as to-day's most important and most promising of the foodstuffs that can be produced on the farm, and further asserting that if we are to survive present-day economic conditions

its use on farms will have to increase in a marked degree, he deals convincingly with the nutritional evaluation of silage by consideration of analytical data. When cut, the crop is alive and respiring; in due course the cells die and the micro-flora come into action. The time interval and forms of organic breakdown can be controlled and influenced by physical means and aerobic and anaerobic conditions so that the silage produced shall be of the highest nutritional value and of a satisfactory palatability. Analytical investigation of the various types of silage produced under varying conditions of aeration due to packing, and of the temperature of the mass, led to an evaluation of such end-products as butyric, lactic and acetic acids, alcohol, carbon dioxide, amino-acids, fatty acids, volatile bases and ammonia. Thus, butyric acid over 1 per cent. means a silage that must be fed with caution, but is controllable because the butyric organisms cease growth at pH 4·2. Acidity produced by lactic acid organisms is considered a most important factor, and the lactic acid may reach 2 per cent. by weight of the fresh silage. Good quality means more than 1 per cent. of lactic acid, and in greater amount than the volatile acids. Mould growth with volatile bases and ammonia is restrained by high acidity, *i.e.*, a low pH. These essentials for a good silage would indicate that the crop should be harvested when it is richest in carbohydrate, that is at a late period in its growth; but this, unfortunately, is when it is poorest in protein. The difficulty has been resolved by adding extra carbohydrate to the grass in the silo; this makes it possible to reap the crop at an early stage of growth when its protein content is at a maximum. The English practice is to add molasses, in the U.S.A. the additional carbohydrate is supplied by the addition of sugar-beet pulp, potato meal or even whole potatoes. Another modern procedure to encourage the lactic acid organisms is by artificially lowering the pH below 4 by the addition of dilute mineral acids, usually hydrochloric and sulphuric acids, this procedure being in principle the well-known Continental A.I.V. process.

Finally, the feeding value of a silage can be quite properly judged by determination of the amounts of dry matter and nitrogen (crude protein) and the pH value. Colour is a good guide to the carotenoid value.

It would appear that present-day practice in the manufacture of good silage owes a very great deal to chemical analysis.

Metallic contamination of foodstuffs—crop protection: pest control

I have put these two apparently somewhat dissimilar subjects together because they are intimately associated. Commonly, the metallic contamination of foodstuffs occurs during the course of manufacture, that is, during the course of the journey from the raw material to the finished product. On the other hand, contamination due to crop protection or pest control occurs before the plant becomes the raw material of commercial practice. Nevertheless, the final result may be the same: a potential cause of toxicity or malnutrition or illness to the human or animal consumer.

It is well in the first place to consider the question of toxicity or poisonous quality. It is not easy to assess poisonous quality. There are some substances that appear to be potentially harmful, that is to say, poisonous, in the smallest quantities—and this quite apart from idiosyncrasy—while others, although definitely harmful if taken in any substantial amount, are apparently harmless in traces. Furthermore, the position is becoming increasingly complicated with the advance of analytical practice and the development of more sensitive and more comprehensive tests with the aid of which the physiologist or biochemist discovers more and more elements essential to human life in yet more minute traces. The question therefore arises: Is there in fact a proportion or amount of each of the so-called poisonous metals that is essential to life and can be assumed to be non-poisonous or harmless in the proportions naturally present? This question possibly really concerns only metallic contamination of foods, because the increasing tendency in crop protection and pest control is to use synthetic organic chemicals, such as DDT, or the phenoxyacetic acids, which can hardly be considered as natural to life in the same sense as may the minute traces of the now very large number of elements found to be normally present in vegetation. It seems likely that others will also be found to be essential. For instance, it is now suggested that that popular aid to murder and suicide—arsenic—belongs to this class. Bearing all this in mind it may well be regarded as fundamental to know whether any proportion of any one poisonous element can be considered as harmless. The answer to this question becomes of importance to the analyst when having found so many parts per million, or so many micrograms per ounce, of, say, arsenic or lead in a food, he is faced with the necessity of giving an

opinion as to whether or not the food is safe for human consumption. Clearly no analyst can answer this question from knowledge gained from personal experience. He must seek the aid of medical or physiological authorities. Let us then examine the evidence of these authorities. Perhaps the first to consider are the findings and recommendations of the Royal Commission on Arsenical Poisoning published in 1903. During the course of the year 1900 medical men in Lancashire and Staffordshire became aware of a serious increase in the illness generally diagnosed as alcoholic peripheral neuritis. This increase became so marked as to become epidemic in certain areas and to necessitate a closer and more critical examination. It was then observed that while alcoholic peripheral neuritis was normally an illness of spirit drinkers, the victims in this instance were generally beer drinkers. This led to examination of the beer particularly implicated, first for lead, then for higher alcohols, then for mineral poisons generally, these being the suggestions which arose successively. But these examinations yielded negative results. In November, 1900, however, Dr. Reynolds, of Manchester, recognised that one of the common skin symptoms—shingles—was also a common result of medicinal arsenical treatment. He applied the Reinsch test to the beer, obtained a good positive result; Dixon-Mann confirmed his findings, and so the cause of the trouble was found. It is estimated that from 2000 to 3000 illnesses, and about 100 deaths were caused by arsenical beer. In the period 1901 to 1903 (when the final report of the Royal Commission was published), an immense amount of investigational work was undertaken, both in respect of the analytical methods for the determination of arsenic, and in respect of arsenical contamination of foodstuffs; work in which our Society participated as well as the Government Laboratory and a brewers' research association. In 1903 the final report of the Commission, recommending maximum limits of 1/100th of a grain of arsenic per pound and per gallon respectively for solid and liquid foodstuffs, was published. Thus we have one authoritative recommendation, not an Order or Regulation, in respect of arsenic —and I shall return to it presently for another reason. But other than this the analyst will find himself in difficulty. Medical and physiological literature abounds in data concerning the toxicity of poisonous elements. But they are limited data. Mainly they are concerned with fatal, or near-fatal, doses, and the duration and character of the accompanying symptoms. On the question of what may be described as tolerances for human beings, there is little information. This is understandable, as experimental work on humans in order to ascertain degree of tolerance to poisons is not usually regarded as permissible. On the other hand, a very considerable amount of work has been done in connection with the reactions and well-being of animals, both large and small, and the available data is extensive and comprehensive. But however sound the general application of such data to humans may be, it cannot be accepted when the question arises as to whether or not a specified minute trace is harmful or beneficial, or whether a specified minute trace exceeds the safe limit.

The angle from which the problem in respect of human beings has been attacked so far—and it is difficult to see any other line of approach—is, in short, to add together the amounts of the particular element under consideration that are normally present in the daily diet, the amount normally present in the liquids that may be drunk daily and the amount inhaled in the dust of the atmosphere. The figure so obtained then constitutes the basis for an assessment of what may then be described as the safe daily limit. It will be seen that this approach is dependent on very comprehensive analytical data, and for many elements it is not available. That it is a sound approach, however, would appear to be very substantially confirmed when the applications of the recommendations of the report on arsenical poisoning referred to earlier are reviewed and considered. These recommendations have now been in force over forty-seven years, and have been generally accepted. During that long period I think it is safe to say that there is no significant clinical or physiological evidence that the daily ingestion of foods and liquids which may contain arsenic, but not in excess of 1·4 and 0·14 p.p.m. respectively, has led to any illness or other harmful effect. That is to say, such maximum limits for arsenic may now be accepted as safe limits for human beings. That is also to say, a safe limit for one poisonous element has been established practically entirely on the basis of data supplied by the analysis of foods. And I would venture to say that it could not have been established in any other way. So much for arsenic. Now official action seems likely in connection with limits for other potentially poisonous elements, particularly lead: so that if the same method of attacking the problem is pursued, then analysis still remains as the dominating factor for determining the answers.

It will be seen from the foregoing how intimately crop protection and pest control is connected with contamination of foodstuffs. When a crop is dusted or sprayed with a fungicide or an insecticide it is a reasonable requirement that these shall remain effective for a significant period of time. It follows that, despite the action of wind and rain, there is always the possibility that they remain still effective to some extent when the crop is marketed for human consumption. It will further be immediately observed that this widens the whole question enormously. Whereas the older kind of chemical used for the purpose of pest control can be generally described as metallic poisons, *e.g.*, lead, arsenic, and copper compounds, the newer methods of control depend on the use of synthetic organic chemicals, many, if not most, of which are of unknown toxicity to human beings. The problems that apply to the metallic contamination of foods, therefore, apply even more strongly to these newer poisons, particularly when it is realised that analytical control must now be dependent on the development of sufficiently sensitive and precise methods of analysis.

Commercialised photosynthesis as a source of increased food supply

In recent times consideration of the increased food needs of the present day and of any possible new sources of supply has focussed attention on the observation that while only a small proportion of the solar radiation suitable for the photosynthetic reduction of carbon dioxide by plants is actually converted to chemical energy in this way—the efficiency of the primary producers of agricultural economy, the so-called higher plants, amounting to only about 1 per cent. and not being susceptible to much improvement—certain uni-cellular forms of life can under suitable or appropriate conditions attain a much greater efficiency. Some algae, such as the Chlorella species, can utilise as much as 30 per cent. and may possibly

Table V

Yields from chlorella compared with crop plants

Source	U.S. tons per acre per crop year, dry weight	Percentage of fat	lb. fat per acre per growing season of 120 days
Chlorella	2·85	7·0	400
	1·74	17·0	593
	1·66	42·0	1390
	1·15	56·5	1303
	0·75	55·0	747
	0·46	75·0	687
Flax (seed)	0·70	37·0	518
Soya (seed)	0·63	18·0	227
Groundnut	0·60	30·0	360

attain a maximum efficiency of more than 80 per cent. In the higher plants the products of photosynthesis are translocated to non-photosynthetic structures or organs in the plant, but a Chlorella cell multiplies by simple division into daughter cells, each of which is capable both of growth and photosynthesis, and there occurs no diversion of the products of energy derived from solar radiation to support the growth elsewhere in the cell. It has now been found that the direction of what may be described as the metabolic activity and the determination of the end-products of such activity in algae is dependent, among others, on the following conditions: the supply of essential nutrient elements, the incidence of light of suitable wavelength and intensity, a controlled range of temperature and constant aeration, including a minimum of carbon dioxide. It has been found that the main product can be either protein, carbohydrate or fat, according to the stage of growth, the strain or variety of algae and the cultural conditions; and that in connection with the latter the most important factor is the concentration and nature of the combined nitrogen in the medium. The position to date, as shown in a very recent contribution by W. H. Pearsall and G. E. Fogg[13] from which this summary is taken, may be described as only in the experimental stage, although trials are reported of large-scale continuous culture in California for a period of over two months, where it is claimed that 5 per cent. of the incident sunlight was utilised in the production of organic matter. So far the investigational and experimental work show the following results. Different algal groups under differing cultural conditions and with differing nutrient media have specific tendencies towards predominance of protein or fat or carbohydrate.

The value of these algal proteins, fats or carbohydrates, from the point of view of human nutrition, is still however largely undetermined because the knowledge of this chemistry is incomplete, that is to say, they have not yet been subjected to comprehensive and detailed chemical analysis. What is known to date is that the proteins, theoretically the most economical food products of the controlled growth of algae, may well be of very low grade, lacking some of the essential amino-acids and containing substantial proportions of nitrogenous bases; the lipid fraction includes from 20 to 80 per cent. of fatty acids with a large proportion of unsaturated acids; and that although the carbohydrate portion includes some sugar and starch, there appears to be no published detailed analysis and it is thought to be largely of doubtful value in animal nutrition.

The authors conclude with an interesting table of yields from Chlorella compared with crop plants, and with the suggestion that as a means of supplementing our resources simple algae have considerable potentialities and are well worth further investigation from this point of view (see Table V). I would add that clearly such investigation waits on the analyst.

Irrigation and soil conditions

In the U.S.A., soils low in organic matter, poor in permeability to water, often containing an accumulation of salt and of extremely low fertility, occur in many river valleys and are known under the generic name of black-alkali soils. Usually the pH of these soils is in excess of 8, sodium is the predominant exchangeable base, and the organic matter may tend to dissolve in alkaline solution. The association of black-alkali formation with sodium carbonate and bicarbonate in irrigation waters was pointed out as far back as 1911, and was then used in rating formulae for irrigation waters; subsequently, the question of the influence of salts in irrigation waters was discussed when considering land reclamation and agricultural production in a north-western area of the U.S.A.; and in 1950, Frank M. Eaton, of the U.S. Department of Agriculture and Texas Agricultural Experimental Station,[14] published a paper entitled "Significance of Carbonates in Irrigation Waters," in which he first points out that "in terms of the difficulty and cost of reclamation and the severity of its effects, black-alkali continues to occupy a prominent position among the unfavourable consequences of irrigation," and then proceeds to postulate as fundamental that the problem can only properly be attacked by consideration, in the first place, of the character of the water, as indicated by fully detailed analytical examination; it is only when these data are known that the potential physical effects of the passage of the water through the soil can be forecast or assessed and a suitable method of reclamation outlined. Only occasionally does it occur that a water supply contains a sufficiently high concentration of salts to be directly harmful to plants; but as the irrigation water becomes the soil solution and loses volume and suffers changes due to concentration, to plant uptake, and to base exchange, then the picture alters. The author discusses at some length the quantitative significance of the relative amounts of Ca, Mg, Na and HCO_3 and CO_3 ions upon which depend the possibility of an ultimate condition of alkalinity due to sodium carbonate, and also the types of soil that may be developed in time and in absence of good drainage or when used too sparingly, namely: (1) calcium saline soils, produced by waters much higher in Ca + Mg than $HCO_3 + CO_3$ and which have relatively low Na value, usually readily reclaimable by draining and leaching; (2) sodium saline soils, produced by waters which initially or after partial evaporation and the precipitation of $CaCO_3$ have high Na values but no residual Na_2CO_3, which then deteriorate in permeability unless the water remains fairly saline; and (3) alkali soils, saline or non-saline, produced when irrigation waters containing more $HCO_3 + CO_3$ than Ca + Mg are used so sparingly that little leaching occurs. In the case of the last-mentioned type, however, if the Na is not too greatly in excess of Ca and Mg, and enough of such water is used that drainage continues to contain a substantial proportion of Ca and Mg, there may be no ill effects.

Perhaps the most generally interesting part of this paper is the author's observation that the discussion presented in it is the outcome of observations of the effects of prolonged use of water in two of the world's oldest irrigated areas: in Egypt, along the Nile, where black-alkali occurs, and where reclamation is now being accomplished in certain districts by providing drainage and then leaching with water from the same source as that which produced the condition; and in Iraq, along the Tigris and Euphrates, where the accumulation of salt in the land has been sufficient to account for a major decline in population and damage to a great civilisation. With regard to the Euphrates, it is pointed out that the character of the river water is such that it would have supported a flourishing irrigation agriculture had

the people, through the centuries, recognised the need of drainage to carry away the excess of salt; but there is no record of any ditch ever having been dug for this purpose.

Confirmation of at least one of the points emphasised in the above conclusions is independently afforded in a letter on problems of irrigation by E. Hayward,[15] in *Chemistry and Industry*, in December, 1950, when the writer deals with his personal study of the extensive irrigation system of the Punjab in North India. Here, owing to financial difficulties, the irrigation canals had been built without linings, with the result that in the course of fifty years large areas of the Punjab have been and are being thrown out of cultivation owing to constant seepage from the canals into the soil. The seepage gradually raises the sub-soil water level, which may ultimately produce swamps, but in any case brings the dissolved salts in the sub-soil water sufficiently near the surface of the soil for capillary action to come into operation, with the result that evaporation by heat of the sun causes a concentration of these salts in the surface soil and a consequential base exchange of *sodium* for aluminium, etc., in the surface soil. There is thus produced an untillable clay which will only support a sparse and reedy vegetation, and is quite incapable of bearing crops of foodstuffs.

Fertiliser technology research in the U.S.A.

If it is accepted that in any estimate of the potential crop possibilities of the agricultural land still in existence as such in this world, the assistance afforded by "artificial" fertilisers must have a significant bearing on the estimate, then the programme of future research in fertiliser technology, as recently outlined by K. D. Jacob,[16] will have a very great interest for us.

In the first place it may be briefly pointed out that while originally (1911) the emphasis in this research lay in exploration and investigation within the U.S. to determine possible sources of supply, it is now more particularly directed to transformation of nitrogen, phosphoric acid and potash into high analysis compounds of satisfactory physical condition and better efficiency for crop production, evaluation of new products as sources of plant nutrients and study of the consumption of plant nutrients—factors affecting consumption and trends in fertiliser usage.

The U.S.A. current programme includes the following general lines of investigation—

(1) Production of high analysis, synthetic nitrogen fertilisers of low solubility and controlled rate of availability to crops.

(2) Quality of water-insoluble nitrogen in commercial mixed fertilisers.

(3) Composition, properties and fertilising value of phosphates made by thermal and other processes.

(4) Factors influencing moisture absorption, caking, drillability and other physical properties of fertiliser materials and mixtures, including chemical reactions that cause loss of available plant nutrients during preparation and storage of mixed fertilisers.

(5) Development of improved methods of fertiliser analysis.

(6) Evaluation of agricultural liming materials.

(7) Studies of domestic and world resources, technology, production, consumption and trade of fertilisers and fertiliser materials.

Let us briefly consider this programme. Perhaps, in the first instance, it is of interest to glance at the approximate composition of Florida Land Pebble Phosphate, as compiled by K. D. Jacob and shown in Table VI.

Discussing the programme we have—

Item 1—This, at the moment, is particularly directed to the use of products known as "urea-form," *i.e.*, the plastic product of the interaction of urea and formaldehyde containing about 38 per cent. of nitrogen. Different ratios of the constituents result in products of different solubility. Greenhouse and field experiments indicate that owing to its low solubility and slow rate of availability it shows promise of being a superior fertiliser for long-growing crops that require substantial quantities of nitrogen throughout the season. Grass appears to be specially benefited by its application. A considerable amount of work is being done to assess rates of hydrolysis, nitrification and nitrogen availability of this material for the purpose of evaluating its fertilising value by an analytical method rather than by pot or field experiments.

In this connection I should like to refer to the outstanding work of one of our members, J. H. Hamence, in this field. For a number of years he has studied the nitrogen availability of fertilisers by an analytical method of a semi-biological nature, whereby the extent of the

nitrification that occurs when the fertiliser is mixed with soil in proportions common to agricultural practice, and with adequate controls, is measured by the amount of nitrate produced. The results of his earlier work has already been published,[17] but there is much more yet to come. Included in the fertilisers on which he has worked are the urea - formaldehyde plastics.

Item 2—This is really an extension of the work referred to under Item 1, as it is a comparative study of the present official (in the U.S.A.) method for determining the availability of water-insoluble nitrogen by treatment with permanganate, and of the rate of

TABLE VI

COMPOSITION OF FLORIDA LAND PEBBLE PHOSPHATE

	Per cent.
P_2O_5	30·0 to 36·0
Fe_2O_3	0·7 to 2·6
Al_2O_3	0·7 to 1·1
CaO	46·0 to 50·0
MgO	0·05 to 0·6
F	3·5 to 3·9
Cl	0·003 to 0·03
I	0·0008 to 0·002
SiO_2	7·0 to 10·0
MnO	0·002 to 0·05
Na_2O	0·05 to 0·6
K_2O	0·05 to 0·5
SO_3	0·2 to 1·5
TiO_2	0·03 to 0·08
BaO	trace
CuO	0·0005 to 0·003
NiO	0·003
ZnO	0·005
SnO_2	0·002
MoO_3	0·002
V_2O_3	trace to 0·02
Cr_2O_3	trace to 0·015
B_2O_3	0·002 to 0·01
As_2O_3	0·001 to 0·005
Se	trace
CO_2	1·5 to 4·5
Organic carbon	0·25 to 0·4
N	0·005 to 0·02
Total water	1·3 to 2·6

nitrification. In this brief account by Jacob[16] no indication of the methods adopted for determining rate of nitrification are given, but probably they are on the lines of the Hamence method.

Item 3—Comparison of solubility tests of phosphates produced at high temperatures, *e.g.*, glasses such as calcium metaphosphate and the phosphate rock - magnesium silicate fusion product cooled in such a way as to preclude partial crystallisation and then finely ground, as determined by such procedures as shaking with ammonium citrate solutions, with the yields obtained in field-growing experiments, seems to be giving interesting results.

Item 4—This clearly calls for over-all analytical control.

Items 5 *and* 6—These also are obviously analytical.

It would surely not be an exaggeration to say that the fertiliser technology research programme of the U.S. Department of Agriculture is based on the use of all resources of modern analytical chemistry.

GENETICS AND ANIMAL COMPOSITION

Doubtless most of us have been more than a little interested in the controversy which has recently seriously disturbed the quiet and even tenor of the Soviet scientific way of thought. I refer, of course, to the Vavilov - Lysenko controversy, which, fundamentally is a question whether genetic factors or environment influences directly determine the progressive evolution of life, particularly in respect of plant life. John Hammond,[18] in an illuminating discussion of the genetic differences in the composition of animal products, has clearly shown that if such genetic differences have any bearing in the controversy then it is only with the aid of

intensive methods of analysis for resolving the primary composition of animal products that any really powerful contribution to the discussion can be put forward. Thus, in the instance of milk—the only possible food for the just-born, and therefore presumably inevitably the vehicle for any continuing genetic factor that may be potentially operative—the statement that "the higher evolutionary forms of milk, such as that of the cow, repeat in general, in their development in the individual, the composition of milks of the lower evolutionary forms" can only be supported by analysis of the milks. For example, "at the seventh month of pregnancy in a heifer the secretions from the mammary gland contain about 9·1 per cent. of albumen and globulin and about 4 per cent. of casein—not very dissimilar to the proportion in cats' milk—and very different from the 0·4 per cent. of albumen and globulin and 3 per cent. of casein of normal cows' milk. Similar considerations apply to the casein - lactose ratios in some species, such as the mare and donkey, which have a higher lactose - protein ratio than the sheep, goat and cow." On similar lines, Hammond deals with the composition of meat and eggs. It seems clear from these studies of genetic differences that the interpretation is dependent on a profound knowledge of the primary composition of the relevant living and evoluting animal. A final lighter touch in this positive affirmation must, I think, be referred to when, in dealing with the inherited quality of the relative quantities of the different albumen layers of the egg, it is noted that this has a commercial importance from the point of view of the poaching of eggs.

The Truman Fourth Point and an Implementation

So far the examples quoted are of analytical work done or being done; looking forward, perhaps one of the most important investigations now being awaited in agriculture is that dealing with a better knowledge of the soil.

In January, 1949, President Truman put forward his now much discussed Fourth Point: a call for the intensification and sharing of American technological knowledge for the benefit of the undeveloped areas of the world. Later in 1949, the Parliamentary and Scientific Committee—an unofficial group of members of both Houses of Parliament and representatives of certain scientific societies and technical institutions—set up a sub-committee to consider the political and scientific implications, and the interim report of this sub-committee sets out the steps considered to be necessary for establishing or improving crops and crop production in these circumstances. Briefly stated these steps are—

(1) Supplementation of ordinary ground geological survey by stereoscopic examination of air photographs.

(2) Eradication of tsetse as preliminary to bush clearance.

(3) Establishment of research centres in pasture development.

(4) The fullest attention to water: supply, conservation, irrigation and drainage.

(5) Survey of crops and determinative factors, such as soil conditions, plant pathology, pests and fertilisers.

Clearly attention is here directed to such undeveloped areas as are now in existence in many parts of Central Africa, where regeneration and the establishment of fertile soil is a task of immense difficulty. When these five suggested steps are carefully considered it will be observed that they constitute a chronological sequence of work, from preliminary survey, through pest eradication, establishment of pasture research centres and attention to water, to examination of the soil and soil conditions. The endeavour to control or favourably influence conditions directly or indirectly affecting crop production, is quite properly of first importance, and is, of course, indispensable, but it is doubtful whether the enormous importance of a basic or fundamental knowledge of the soil is sufficiently appreciated. The ill-fated plan for the mechanised production of groundnuts in East and Central Africa was conceived as a solution of the end-of-the-war shortage of fats and animal feeding stuffs, and it may well be said, as it came into operation in 1948, that it anticipated the Truman Fourth Point. It may also be said that the major cause of the failure to attain any commercial success was lack of sufficient knowledge of the soil. Contrary to much public opinion, a very considerable amount of investigational and research work on the soil and groundnut production had been undertaken. The First Annual Report of the Overseas Food Corporation[19] includes a very full and complete account of the results of soil analysis and small plot experiments which had been undertaken. Samples of soil from the various districts were subjected to analysis on the conventional lines now customary in English agricultural institutions, covering the range of pH values and amounts of "available" P, Ca, Mg and K,

and, as was expected, a deficiency of P was found to be general. An interesting relationship of N to P, for these soils, was determined. Furthermore, experimental work with different types of phosphatic materials and resultant yields of groundnuts showed that the determination of citric-solubility of the phosphate in these materials was a useful criterion. So it may be fairly said that the major operation of growing groundnuts was not initiated without substantial preliminary work. But Africa has been gloomily described as a dying land,[20] presumably in the same sense that Babylonia may now be said to be dead. Sand and wild vegetation cover buildings and monuments, olive groves and cornfields in the Mediterranean littoral where once Roman colonies flourished; the Sahara and other deserts extend their boundaries year by year, and new deserts are stated to be emerging; the forests are being felled or burnt down, to be followed by soil and wind erosions and the silting up of rivers; lands are being over-grazed with the same ultimate result; the water table falls and the land dries up. It seems reasonable, therefore, to assume that as the soil is the food-store for all the minerals essential for plant growth, then in countries such as East and Central Africa, where the soil may have suffered seriously over many years from leaching and oxidation by a tropical sun, the soil analysis necessary to ascertain mineral deficiencies, the chemical and physical characteristics of the clay and organic fractions, and indeed possibly the condition of the population of micro-organisms, must of necessity be much more complete, intricate and searching than that normally required in lands such as England, where it has been under cultivation for very many years. It may well be that the unexpected poor yield of groundnuts was due to some such cause as the deficiency of a trace element.

Recently, Professor T. Wallace,[21] dealing with research on the status and functions of mineral nutrients, has stressed the importance of the inter-relationship between the various elements, and regards the various factors affecting the supply of mineral nutrients in soils as—

(1) The fixing power of soil.
(2) Soil reaction.
(3) Organic matter, drainage conditions and aeration.

Even more emphatic was the profound thought of Professor N. M. Comber at the 1949 meeting of the British Association, when he said: "We have considerable knowledge of genetics and plant breeding, there is much work done in the problems of plant pathology, bacteriology, mycology and entomology, the long-standing science of botany has brought detailed knowledge of the plant and the much more recent science of pedology is bringing new knowledge of the soil, knowledge of its formation, its morphology and the structure of its materials. But the basis of it all is the relationship of the soil and the plant and that is an almost unexplored field. . . . It used to be stated—indeed in some writings still is—that the root hairs dip into the soil solution and the root absorbs substances dissolved there just as in the case of plants grown in culture solutions. Some of us were able to show some time ago that the problem is much more complex than that. The plant and the soil are not two separate things that just touch one another: the intermingling of their colloids makes them one system—the soil colloids on the roots cannot be removed without rupturing the roots, they have come to be a part of the plant, and *what goes on in this soil - plant system* is the fundamental thing in all farming."

Briefly, it is important to know not only how the plant is fed, but also with what it is fed. For this purpose the aid of chemical analysis in its most advanced form is fundamental to the knowledge of the composition of the nutrients translocated from the soil through the semi-permeable rootlets or hairs of the plant roots into the plants.

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Anniversary Dinner

IN the evening of the day of the Annual General Meeting, a Dinner to celebrate the seventy-seventh anniversary of the Society was held, by kind permission of the Master, in the Hall of the Worshipful Society of Apothecaries of London, Blackfriars Lane, London, E.C.4.

The members and guests, numbering 82, were received by the President, Mr. George Taylor, O.B.E., F.R.I.C., and Mrs. Taylor. The President afterwards took the Chair at the Dinner.

The guests of the Society and of the President included: Professor E. K. Rideal, M.B.E., M.A., Ph.D., D.Sc., F.R.S., and Mrs. Rideal; Professor J. W. Cook, Ph.D., D.Sc., F.R.S., F.R.I.C.; S. Robson, M.Sc., D.I.C., M.I.Chem.E., M.I.M.M., F.R.I.C., and Mrs. Robson; H. W. Cremer, C.B.E., M.Sc., M.I.Chem.E., M.Inst.F., F.R.I.C.; N. C. Wright, B.A., D.Sc., Ph.D., F.R.I.C.; the Master of the Worshipful Society of Apothecaries, Dr. F. Howitt, and Mrs. Howitt; and the Clerk of the Worshipful Society of Apothecaries, E. Busby.

After the loyal toasts had been honoured, Professor J. W. Cook proposed the toast of the Society. He referred to the happy relationship that had ever existed between the Society and the Royal Institute of Chemistry, the last outstanding example of which had been the success that had attended the Summer School of Analytical Chemistry, sponsored by the two bodies, last year. This collaboration between the two bodies had also been exemplified by their united co-operation with the Ministry of Food in legislation in connection with the Food and Drugs Acts; this had resulted in improvements in the working of the Acts and in analytical chemistry. He congratulated the Society on its elevation to the Presidency of one who had for so long been an enthusiastic supporter of the Royal Institute of Chemistry. The election of Dr. Nicholls would also set the seal on the harmonious relationship that existed between the Public Analysts and the Government Laboratory. He also noted with great satisfaction that although the Society had been the leaders in the advancement of the science of analytical chemistry, the Universities were now beginning to take more interest in the subject. The toast was coupled with the name of the President.

The President, in response, thanked Professor Cook for his appreciative remarks on the work of the Society. He referred to the International Congress of Analytical Chemistry to be held at Oxford in September, 1952, and expressed the hope that all analytical chemists in this country would use their united endeavour to ensure its success. The proceedings of the Congress would be published in the Society's journal, *The Analyst*.

Dr. Roche Lynch, in proposing the toast of the guests, expressed his satisfaction that the Society should have chosen for the entertainment of such distinguished company the beautiful surroundings of the ancient hall of the Apothecaries, which had been made available to them by the kindness and generosity of the Master, who with his wife, was their honoured guest. He welcomed the ladies and the other eminent guests, most of whom were presidents or past presidents of learned institutions, and coupled with the toast the name of Dr. Norman Wright of the Ministry of Food.

Dr. Norman Wright, replying for the guests, said that he welcomed the opportunity of expressing on their behalf their appreciation of the entertainment and fare provided. He had had personal experience of the good work done by analytical chemists in their professional capacity on the Food Standards Committee of the Ministry, and was gratified to

find that in their pleasures they set themselves the same high standards and ideals as in their work. The Ministry of Food greatly appreciated the work, knowledge and background of experience that members of the Society put at their disposal; this experience had been enlarged by the recent visits to the United States of America of Mr. Adams and Dr. Nicholls, who had established personal contact with the Food and Drugs Administration in Washington. Dr. Wright expressed the hope that there would be some reciprocal visits.

The President then invested Dr. Nicholls with the presidential badge and wished him success during his term of office. Dr. Nicholls expressed his thanks for the honour that had been done him.

Report of the Joint Committee on Preservative Regulations

At the request of the Public Analysts and Official Agricultural Analysts Committee, the Council of the Society suggested to the Committee of the Food Group of the Society of Chemical Industry that a Joint Committee should be set up to report to the Ministry of Food and the Ministry of Health on the desirability of amending the Preservative Regulations. The Committee of the Food Group agreed to the suggestion and the Joint Committee of the two bodies was set up early in 1949, consisting of—

Representing the Society of Public Analysts and Other Analytical Chemists:

Dr. G. W. Monier-Williams (Chairman)
Dr. H. E. Cox
Mr. J. F. Clark
Mr. H. E. Monk
Mr. G. Taylor

Representing the Society of Chemical Industry—Food Group:

Dr. L. E. Campbell
Dr. J. M. B. Coppock
Dr. E. B. Hughes
Dr. C. H. Lea (non-voting)
Mr. R. Harold Morgan (Convenor and Secretary)

The report prepared by this Joint Committee was received by the Council of the Society in November, 1949, and was given their approval.

It was sent jointly by the Society and the Society of Chemical Industry to the Ministry of Food and the Ministry of Health in March, 1950.

In January, 1951, the Ministry of Food appointed a Sub-Committee of the Food Standards Committee with the following terms of reference—

> To review the Public Health (Preservatives, etc., in Food) Regulations and to make any recommendations the Sub-Committee may consider desirable for the amendment of the Regulations.

It is anticipated that the review will be concerned primarily with the technical and scientific as distinct from the administrative aspects of the Regulations, and the Sub-Committee has been invited, without prejudice to any other matters, to consider—

(*a*) The definition of "preservative" and the application of the Regulations specifically to anti-oxidants, anti-staling agents, anti-mould agents and similar substances.

(*b*) The permitted preservatives and similar substances, and the quantitative control of their use.

(*c*) The application of the Regulations to stabilising agents, emulsifying agents and allied chemicals.

(*d*) The provisions governing the control of added colouring matters and, in particular, whether a list of permitted colourings or dyestuffs should be substituted for the existing list of prohibited substances in Schedule I (Part 2) of the Regulations.

(*e*) The provisions relating to labelling of food containing preservatives, etc.

Professor E. C. Dodds, Director of the Courtauld Institute of Biochemistry at Middlesex Hospital, has agreed to act as Chairman; the following are particulars of the Government Departments and bodies that it is considered should be represented on the Sub-Committee

and of the individual representatives to whom invitations to serve on the Sub-Committee are being issued—

Ministry of Food	Mr. C. A. Adams
Ministry of Health	Dr. N. R. Beattie and Mr. P. N. R. Butcher
Department of Health for Scotland ..	Dr. J. M. Johnston
Department of the Government Chemist	Dr. J. R. Nicholls
Society of Public Analysts and Other Analytical Chemists	Dr. H. E. Cox
Food Manufacturing Industries	Mr. A. Glover, Co-operative Wholesale Society
Society of Chemical Industry (Food Group)	Dr. E. B. Hughes, Research Department, Messrs. J. Lyons & Co., Ltd.
Medical Research Council	Professor S. J. Cowell

Report of Joint Committee

The Preservatives Regulations of 1925–27 have been in existence with only slight modifications, for nearly 25 years. They have undoubtedly been of immense value in suppressing several undesirable methods of food preservation.

It is clear, however, that in 25 years, there have been many developments in food manufacture and processing that could not have been foreseen at the time, and that make it essential that the definition of the term "preservative" in the regulations be amended, and the application of the regulations more precisely defined. The Committee has noted below a number of specific instances in which the regulations as they stand have been found to be ambiguous or not in accordance with modern knowledge.

Admittedly it will be extremely difficult to frame a satisfactory definition of "preservative" that would be generally and permanently applicable. It will be necessary that a more detailed schedule than exists at present be drawn up, and that this schedule should be kept constantly under review.

The Committee has considered in detail the Public Health (Preservatives in Foods) Regulations, S.R. & O., 1925, No. 775, as amended, and makes the following suggestions—

PART I—

2 (1)—That the definition of "food" be replaced by that given in the Foods and Drugs Act, 1938, and Defence Regulations, *viz.*, "Food" means any article used as food or drink for human consumption, and includes any substance which is intended for use in the composition or preparation of food, any flavouring, sweetening matter or condiment and any colouring matter intended for use in food, and an article shall not be deemed not to be food by reason only that it is also capable of being used as medicine.

(N.B.)—The legal implications of the proposed definition should be considered, with particular reference to the final clause.

2 (1)—That in the definition of "preservative" the word "chemical" shall replace "substance" and the word "deterioration" shall be substituted for "decomposition."

2 (1)—That all exceptions to the definition of preservative should be put into the Schedule to the Regulations, and that provision should be made for amendment of the Schedule for which purpose suitable machinery should be established to permit of frequent consideration of suggested amendments.

That the definition of "thickening substance" appears out of place in the Preservatives Regulations. (This recommendation applies to all references to thickening substances wherever mentioned in the Regulations.)

That mention should be made of the various compounds of benzoic acid and of sulphur dioxide, which can be permitted for use in preservatives.

PART II—

4 (1)—That a list of the only colours permitted to be used in foods should be given, such a list to be subject to frequent revision. As a basis, the colours now in common use should be considered, and the whole matter should be investigated carefully in conjunction with the manufacturers of food colours.

4 (1) (ii)—That this paragraph needs clarification and re-drafting. The Committee is of the opinion that there is no objection to a Scheduled Food containing two preservatives provided that if any article of food specified in Part I of the said Schedule contains a second preservative necessarily introduced by the use of another Scheduled Food, the amount of preservative allowed by Schedule for the first named food should be reduced by the amount of the second preservative introduced by the use of the other Scheduled Food: 600 parts benzoic acid being regarded as equivalent to 350 parts sulphur dioxide for the purposes of calculation.

4 (1) (iii) (*a*) and (*b*)—That these paragraphs should be more specific and refer to foods not intended for retail sale.

4 (2)—That this sub-section be reconsidered in view of existing labelling regulations.

THE FIRST SCHEDULE—

1. That this food classification requires extension.
2. That this classification should also include fruit products and vegetable products, and that "for manufacturing purposes only" should replace "for conversion into jam or crystallised, glacé or cured fruit."
4. That this classification needs clarification and explanation of its specific purpose.
5. That "cordial" should be replaced by "concentrated soft drink" and that the comma after "juices" be deleted.
6. That the sulphur dioxide limit for jams, etc. be raised to 100 parts per million.
14. That "sweetened mineral waters" be replaced by "ready-to-drink soft drinks."
16. That "coffee and chicory extracts" should also be included.
17. That this classification needs extension.

60 C.A.A.—That the relaxation regarding the use of boric acid in 60 C.A.A. be reconsidered.

The Committee, in recommending a wider definition of the term "preservative" as mentioned heretofore, desires to bring under control the addition of substances to foods for other purposes, such as anti-oxidants, prevention of staling, anti-mould agents, stabilisers, etc., and recommends that a policy should be formulated with regard to such usages, giving a list of substances permitted for these purposes.

The following lists mention substances which appear to be added to food in various countries for the purposes mentioned.

ANTI-OXIDANTS

Tocopherols
Lecithin
Guaiacum resin
Nordihydroguaiaretic acid (NDGA)
Citric and phosphoric acids
Propyl gallate
Butylated hydroxy anisole

ANTI-MOULD AGENTS

Calcium propionate
Sodium di-acetate

PREVENTION OF STALING

Glyceryl stearates
Polyoxy ethylene stearates
Sorbitol stearates

EMULSIFYING AGENTS

Glyceryl mono-stearate and di-stearate
Glyceryl mono-oleate and di-oleate
Glyceryl mono-laurate
Cetyl palmitate
Pentaerythrityl stearates
Sulphonated laurol
Polymerised linseed oil

STABILISING AGENTS

Sodium and calcium pectates
Sodium alginate
Methyl cellulose
Ethyl cellulose
Sodium carboxymethyl cellulose

FATTY MATERIALS BUT NOT EMULSIFYING AGENTS

Lanette wax
Lanolin

MISCELLANEOUS

Diphenyl (orange preservative)
Methyl naphthyl acetate (potatoes in clamp)
Thiourea
Certain quinoline derivatives
Bromacetic ester (milk preservation)

Signed for and on behalf of the Joint Committee:

G. W. MONIER-WILLIAMS (*Chairman*)
R. HAROLD MORGAN (*Convenor and Secretary*)

Analytical Methods Committee

REPORT PREPARED BY THE SOAPLESS DETERGENTS SUB-COMMITTEE

Examination of Detergent Preparations

THE Analytical Methods Committee has received from its Sub-Committee on Soapless Detergents the following information based on its work to explore the advisability of standard methods for these preparations, and its publication has been duly authorised.

The members of the Sub-Committee were: W. H. Simmons (Chairman), H. E. Cox, C. G. Daubney, S. R. Epton, P. J. C. Haywood, A. MacArthur, K. A. Williams, D. C. Garratt (Honorary Secretary), and valuable assistance was given by W. J. Dwerryhouse and L. E. George of the Ministry of Food, Oils and Fats Division.

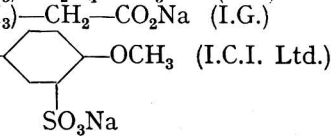
The Sub-Committee was formed primarily to consider whether in view of the Soap Substitutes (Labelling and Prices) Order, 1943 (S.R. & O., 1943, No. 638), standard methods of analysis of soapless detergents were possible or necessary.

Under the Soap Substitutes Order certain standards were laid down by the Ministry of Food for the formulation of these products, preliminary to the granting of a licence to label them for retail sale. Briefly these standards consisted of a specified minimum of active detergent and a maximum percentage of alkali and for the pH value when the product was claimed to be suitable for washing woollens, silks and other delicate fabrics.

The definition of "active detergent" is capable of very wide interpretation, but general agreement was reached that it referred to the water-soluble organic compounds capable of reducing the surface tension of water, in the molecule of which a hydrophilic group or groups is attached to a hydrophobic alkyl or alkyl-aryl chain. For quantitative purposes the description should refer to the anhydrous organic portion of the product, together with inorganic radicles chemically combined with it. The Sub-Committee do not wish to put this description forward as a definition, since to do so would be of little value unless the definition could be correlated to a performance test—and agreement on a specification for this is a matter of considerable difficulty.

The various types of modern detergents generally commercially available in this country have been listed. This list is in no way complete but it should be useful to illustrate the difficulties that were manifested in the attempt to collate the analytical data available as a preliminary to investigating a method applicable as a standard procedure to all products.

PRODUCTS CONTAINING FATTY ACID RESIDUES—

Igepon A type .. .. .. $R—CO—O—C_2H_4—SO_3Na$ (I.G.)
Igepon T type .. .. .. $R—CO—N(CH_3)—C_2H_4—SO_3Na$ (I.G.)
Medialan A type .. .. .. $R—CO—N(CH_3)—CH_2—CO_2Na$ (I.G.)
Lissapol LS .. .. ..  (I.C.I. Ltd.)
Breeze (active constituent) .. $R—CO—NH—C_2H_4—O—CH_2SO_3Na$ (Levers, U.S.A.)

The fatty acid residues used in the foregoing types are varied, from around C_{12} upwards, depending on the particular use for which the detergent is intended.

SULPHATED PRIMARY ALCOHOLS—

These are products of the general type R—O—SO_3Na, where R generally ranges from C_{12} to C_{18}. Commercial examples are Lissapol C (I.C.I.), Gardinols (I.G.), Blansols, Empicols L and LQ (Marchon Products Ltd.) and Dreft (Hedleys). The triethanolamine salts also appear as shampoos, *e.g.*, in Drene.

SULPHATED SECONDARY ALCOHOLS—

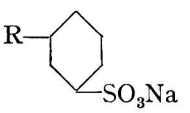
These are products of the type R—CH(O—SO_3Na)—R′. Teepol (Shell Chemicals Ltd.) and Comprox (Irano Products Ltd.) are examples. Comprox has also been known as Iranopol and By-Prox.

ALKANE SULPHONATES—

General formula: R—CH(SO_3Na)—R′. Examples are MP.189 (Du Pont) and Mersolats (I.G.).

ALKYL ARYL SULPHONATES—

For example:



and similar products based on alkylated naphthalene sulphonates. Commercial examples are Perminal BX and Dispersols L and T (I.C.I.) and Nansa (Marchon Products Ltd.), some of the Nacconols (National Aniline & Chemical Co.), Santomerses (Monsanto), Igepon NA and sulphonated Oronite. Petroleum sulphonates are generally of this type.

ESTERS AND ETHERS—

Polyglyceryl stearates and ethylene oxide condensates of fatty alcohols, phenols, amides, etc., containing, for instance, a long polyethylene glycol chain. Lubrol W and Lissapol N (I.C.I.), Igepals (I.G.), Stergene (Domestos Ltd.) and some of the Tritons (Rohm & Haas) are commercial examples.

SULPHOSUCCINIC ESTERS—

For example, sodium dioctyl sulphosuccinate

$$\begin{array}{l} C_8H_{17}\text{—OOC.CH.SO}_3\text{Na} \\ \qquad\qquad\qquad\quad | \\ C_8H_{17}\text{—OOC.CH}_2 \end{array}$$

as commercially represented by the Aerosols OT, etc. (American Cyanamid).

SULPHATED VEGETABLE OILS, FATTY ACID ESTERS, ETC.—

For example:

$$C_{17}H_{32}\begin{cases} \text{O.SO}_2\text{ONa} \\ \text{COO(Na or R)} \end{cases}$$

as commercially represented by the long-established Turkey Red Oils (sulphated castor oil) and Calsolene Oil HS (I.C.I.).

All the foregoing types are anionic surface active agents, except those of the ester and ether type, which are classed as non-ionic agents.

In addition there are the cationic detergents. These are quaternary ammonium compounds, such as cetyl trimethylammonium bromide. Cetavlon, Lissolamine A, Cirrasol OD (I.C.I.) and cetyl pyridinium bromide, Fixanol C (I.C.I.), are commercially available types.

All these various types of surface active agents, with possibly the present exception of the cationic types, may appear either singly or admixed with each other and also mixed with other detergent "boosters," solubilising agents, etc.

With the rescinding of the Soap Substitutes Order in November, 1949, the need for standard methods of analysis became less urgent. This was fortunate, as the Sub-Committee had reached the conclusion that, with our present knowledge and the diversity of materials grouped together under this class of product, a method of quantitative determination suitable for all was impracticable. In fact, it is doubtful whether much progress can be made in devising accurate methods of analysis unless each product is considered as an individual rather than as one of a type. Hence the Sub-Committee consider that it is unable to recommend any standard method for the analysis of these detergents.

Throughout the work the Sub-Committee has had unstinted assistance from those of its members who are connected with commercial firms manufacturing particular products (Shell Refining & Marketing Co., Ltd., Monsanto Chemicals Ltd. and Imperial Chemical Industries Ltd., Dyestuffs Division), also from Mr. C. G. Daubney of the Department of the Government Chemist and from the Ministry of Food, Oils and Fats Division. It was obvious that this analytical information would be of value to analysts if published collectively. But it must be emphasised that a particular quantitative method is only recommended for a specified product, although it may be found that many of the methods are of wider or even of general applicability for products of the same class.

QUALITATIVE TESTS

A qualitative examination to ascertain the presence of one or more of the under-noted classes of substances is a primary necessity in dealing with a detergent of unknown composition.

(*a*) True soap (fatty or resin acids with alkali, ammonium or ethanolamine base).
(*b*) Alkali carbonate, phosphate or silicates; abrasives and fillers.
(*c*) Synthetic organic detergents of the sulphated or sulphonated type.
(*d*) Sulphated glycerides.
(*e*) Polyethylene glycol derivatives.
(*f*) Quaternary bases.
(*g*) Methyl and carboxymethyl cellulose.
(*h*) Naphthenic acid soaps.

To this end a few simple tests can be applied; the following procedure will give useful information.

A portion of the sample is taken up in water and any insoluble matter removed by filtration or centrifuging to give the test solution.

(*i*) Some of the test solution is boiled. The formation of a gel may indicate cellulose ethers, see (*vii*); separation of an oil may indicate polyethylene glycols.

(*ii*) A portion of the test solution is tested for alkalinity and, if alkaline, made acid to methyl red. The separation of fatty acids indicates soap (note that silica may also separate here). If, after removal of any fatty acid, the solution still froths on shaking there is presumptive evidence of a synthetic detergent.

(*iii*) If a synthetic detergent is indicated, chloroform and a few drops of methylene blue solution are added and the mixture is shaken. If the chloroform is coloured blue, a sulphated or sulphonated product is indicated. Absence of colour in the chloroform suggests a polyethylene glycol or cationic product or both.

(*iv*) If a polyethylene glycol product is indicated, 5 ml of a 1 per cent. solution of the glycol in water (*i.e.*, test solution) are treated with 5 ml of thiocyanate reagent (174 g of ammonium thiocyanate and 2·8 g of cobalt nitrate per litre) at room temperature. After 2 hours the colour of the liquid (not of any precipitate) should still be blue-violet if a polyethylene glycol is present. Vigorous shaking is necessary.

(*v*) A fresh portion of the test solution is boiled under a reflux condenser with *N* sodium hydroxide for half an hour. An increase in the fatty acid liberated on acidification compared with that from the untreated material indicates a sulphated glyceride.

(*vi*) Two further portions of the test solution are taken. One is shaken with chloroform and methylene blue, the other with chloroform and bromophenol blue. Quaternary bases cause the bromophenol blue to colour the chloroform but the methylene blue remains in the aqueous phase. For this test a strong electrolyte must be present.

(*vii*) Methyl cellulose and carboxymethyl cellulose can sometimes be detected in preparations by their typical fibre-like structure under the microscope. To distinguish between

them, the following tests can be applied to suitably purified aqueous extracts after concentration under reduced pressure or at a low temperature (not exceeding 50° C).

The reagents are added to the concentrate.

Substance	Boiling	Fehling's copper reagent	Aluminium sulphate, 10 per cent.
Methyl cellulose	Coagulation	No reaction	No reaction
Carboxymethyl cellulose ..	No reaction	Heavy, pale blue ppt.	Gelatinous white ppt.

A portion of the aqueous extract is evaporated to dryness on a watch glass. Saturated lithium chloride solution is added and mixed intimately with the film of residue. Addition of 0·01 *N* iodine solution produces a red colour with methyl cellulose and a blue colour with carboxyl cellulose.

There is little information in the literature on the qualitative examination of detergent preparations, but the schemes of analysis set out by Linsenmeyer[1] and Van der Hoeve,[2] although they have not been tried out fully, will be found useful and might well form the basis for further work.

QUANTITATIVE METHODS OF ANALYSIS

Although quantitative methods are generally given in outline only, the Sub-Committee decided to republish *in extenso* those methods that have been used satisfactorily for certain surface active materials in the laboratories of its various members. These methods appear in the appropriate places in the text.

TOTAL ORGANIC MATTER—

(*a*) A given weight of sample is extracted by boiling with alcohol under a reflux condenser or by means of a Soxhlet extractor. If inorganic chloride is present in the sample, some may be extracted by the solvent. It should be determined in the usual way and its weight deducted.

(*b*) A given weight of sample is dissolved in dilute acid and extracted with ether in a Werner - Schmidt tube. Other solvents that dissolve less water, *e.g.*, methyl *iso*butyl ketone, can be used. The extract is evaporated, the residue freed from traces of moisture by warming with a little acetone, dried at as low a temperature as possible and weighed. Re-extraction of the dry residue with dry ether is sometimes advisable.

This method gives a measure of the total organic matter as sodium salt or as free acid and includes neutral bodies.

See also, "Official and Tentative Methods of the American Oil Chemists Society," Section F.[3]

SOAP - DETERGENT MIXTURES—

Berkowitz[4] describes a method based on a difference figure, whereby the percentage of synthetic detergent = per cent. alcohol-soluble matter — (per cent. soda soap plus per cent. fatty matter plus per cent. NaCl in alcohol-soluble matter).

ANIONIC DETERGENTS—

A given weight of the organic matter extracted from the original sample is dissolved in water and a suitable aliquot titrated with standard 0·004 *M* cetyl pyridinium bromide with methylene blue as indicator.

The following method is described by Epton[5]—

Ten millilitres of an approximately 0·005 *M* solution of the anion-active material is transferred by means of a pipette to a 250-ml stoppered reagent bottle. To this is added 25 ml of a solution containing 0·003 per cent. of methylene blue (B.P. quality), 1·2 per cent. of concentrated sulphuric acid, 5·0 per cent. of sodium sulphate (anhydrous) and then 15 ml of chloroform. The bottle is shaken with just sufficient force to ensure that the phases mix thoroughly. At this stage the upper layer is a pale blue and the lower layer dark blue. A solution of cetyl pyridinium bromide containing about 2 g per litre of purified material is added about 2 ml at a time with intermittent shaking. When the colour of the upper layer begins to deepen the rate of addition is reduced. The end-point is reached when both layers, viewed in reflected light, are the same colour.

The molar concentration of the cetyl pyridinium bromide solution is determined as follows—

Fifty millilitres of the solution are transferred by means of a pipette to a beaker and 25 ml of 0·01 *M* potassium dichromate solution are added. This precipitates insoluble cetyl pyridinium dichromate. The solution is heated to 90° C to coagulate the precipitate and then filtered through a No. 40 Whatman paper. The excess of dichromate in the filtrate is determined iodimetrically.

Another method of determination is due to Barr, Oliver and Stubbings,[6] who use the following reagents and procedure—

Reagents—

(*a*) Bromophenol blue indicator solution, a 0·04 per cent. solution in 20 per cent. aqueous alcohol.
(*b*) Chloroform B.P.
(*c*) Cetyl trimethylammonium bromide solution, approximately 0·001 *M*.
(*d*) Sodium oleyl sulphate (the reference sample).

Procedure—Weigh accurately such a quantity of the sodium oleyl sulphate, reagent (*d*), as will contain about 0·4 g of active agent, dissolve in about 200 ml of distilled water at 50° to 60° C (not above 60° C) and add a few drops of *M* sodium carbonate solution until the solution is faintly alkaline to Brilliant Yellow indicator paper. Cool the solution to 20° C, transfer to a measuring flask, dilute to 1 litre and mix well. Transfer 25·0 ml of this reference solution by means of a pipette to a glass-stoppered bottle and add 100 ml of water, 50 ml of chloroform and 5 drops of bromophenol blue indicator solution. Titrate the mixture with the cetyl trimethylammonium bromide solution, reagent (*c*), shaking after each addition of titrant. In the early stages of the titration, the chloroform emulsifies in the aqueous phase, but ready separation into two layers occurs as the titration proceeds, particularly as the end-point is approached. About 1 minute is allowed to elapse between successive additions of titrant, added in 0·1-ml increments towards the end-point, which is taken as the point at which the first indication of blue colour appears in the chloroform layer. The blue colour intensifies with further additions of cetyl trimethylammonium bromide solution. The cation active solution (*c*), thus standardised against the reference sample, is used for the titration of other anion active compounds by an exactly similar titration procedure, using as far as is practicable an approximately 0·001 *M* solution of each substance to be titrated.

SCHINDLER SEPARATION—

This method is described in "Sulphated Oils and Allied Products," by Burton and Robertshaw,[7] and has been widely used for the separation of the components of detergent preparations.

The various fractions recovered are—

(1) Free fatty acids from soap, which can be weighed and titrated to check the equivalent weight.
(2) Sulphated compounds. These tend to darken when the solvent, carbon tetrachloride, is removed.
(3) Highly sulphated compounds and sulphonic acids. This fraction can be titrated as desired.
(4) Higher alcohols, mineral oil and other neutral fatty bodies.

It should be noted that the method fails for sulphated glycerides, which do not dissolve in carbon tetrachloride. Further, cellulose ethers upset the method, for they stabilise emulsions and prevent the proper separation of the initial aqueous and solvent layers.

SULPHATED BODIES—

These are regarded as substances that can be hydrolysed by heating under a reflux condenser with *N* hydrochloric acid for several hours, after which the liberated sulphuric acid is titrated. If it is difficult to see the end-point, the hydrolysate can be extracted with ether before titration. The ether-soluble hydrolysis product can be weighed as a check.

Total alkalinity—Weigh out accurately from 10 to 15 g of the sample into a litre beaker, make into a thin cream with water, dilute to 600 ml and titrate with 0·1 *N* hydrochloric acid and not more than 4 drops of the mixed indicator (see below).

Let alkalinity expressed as milligrams of potassium hydroxide per gram of sample = A.

Concentration of organic sulphates—Weigh out accurately about 15 g of the prepared sample in a 500-ml Geissler flask and add 50 ml of *N* hydrochloric acid. Heat gently under a reflux air-condenser, until the layer of oil covering the aqueous layer is clear and frothing has entirely ceased; this may take from 4 to 24 hours. During the heating, the flask should be supported by a clamp, about a half to three-quarters of an inch above an asbestos gauze with the flame carefully regulated so that the liquid is just kept gently boiling. If boiling is vigorous there is a danger of loss of hydrochloric acid, with consequent vitiation of the results. A piece of congo red paper loosely inserted in the upper end of the air condenser will indicate whether or not volatile mineral acid is being lost during the hydrolysis.

Allow the flask to cool and wash down the condenser with a little ether and then a little distilled water. Add 25 ml of ether (free from acid or alkali) to dissolve the fatty layer; then add 50 ml of neutral saturated sodium chloride solution and mix the contents of the flask by swirling. Add not more than 4 drops of mixed indicator and titrate with *N* sodium hydroxide solution. Near the end-point care must be taken to allow the ethereal layer to separate after each addition of alkali, as the dark colour of the ethereal solution tends to mask the colour change of the indicator. It is preferable to separate and wash the ether layer and then to titrate the combined aqueous extracts.

Let the titre = B ml of *N* sodium hydroxide.

Titrate 50 ml of *N* hydrochloric acid with *N* sodium hydroxide solution and 4 drops of mixed indicator as before.

Let the titre = C ml of *N* sodium hydroxide.

The increase in acidity after hydrolysis = B − C ml of *N* sodium hydroxide.

This is equivalent to (B − C) × 56·1/wt. taken = D milligrams of potassium hydroxide per gram of sample.

(A + D)/56·1 × 36 = per cent. sodium alkyl sulphate (m.wt. 360).

The molecular weight used in calculating the result is empirical and is based on the results of analysis. For Lissapol C, m.wt. = 360, for Teepol, m.wt. = approximately 320.

Mixed indicator—Methyl orange and xylene cyanol FF.

(*a*) Xylene cyanol FF (Disulphine Blue FFS), 1·4 g, dissolved in 250 ml of 50 per cent. alcohol.

(*b*) Methyl orange, 1 g, dissolved in 250 ml of 50 per cent. alcohol.

Two drops of (*a*) and 2 drops of (*b*) are used in each titration.

Note—A mixture of solutions (*a*) and (*b*) tends to deteriorate on keeping.

This mixed indicator is to be preferred to methyl orange alone, which is not very sensitive in artificial light.

SULPHONATED BODIES—

A method suitable for Igepon type detergents[8] is based on the precipitation of the sulphonate with benzidine. The insoluble portion is filtered off and dissolved in alcohol, and aliquots are taken for titration with alkali and for direct weighing. The method is unsuitable for sulphated bodies since it involves boiling with hydrochloric acid.

A similar method by Marron and Schifferli[9] is based on the fact that alkyl aryl sulphonates react in aqueous solution with an amine salt of a mineral acid, *p*-toluidine hydrochloride, to produce an amine salt that can be extracted with carbon tetrachloride. The carbon tetrachloride extract is mixed with neutral alcohol and titrated with 0·1 *N* sodium hydroxide. On titration the compound is broken up into *p*-toluidine and the sulphonic acid, which reacts with the alkali. The weakly basic amine does not interfere.

It is essential, however, that the molecular weight of the alkyl aryl sulphonate is known. This molecular weight can be ascertained by carrying out several determinations on a sample of known composition.

METHOD—

Reagent—*p*-Toluidine hydrochloride. Thirty-four grams of the salt, after recrystallisation from industrial methylated spirit, are dissolved in distilled water and made up to 1 litre. Further recrystallisation must be carried out if the solution is not clear, or if the titration blank is too high.

Indicator—A 0·5 per cent. solution of *m*-cresol purple. Dissolve 0·250 g of *m*-cresol purple in 6·5 ml of 0·1 *N* sodium hydroxide. Rinse into a 50-ml volumetric flask with

sufficient water to make a total volume of 25 ml and then dilute to 50 ml with industrial methylated spirit.

Procedure—Weigh out by difference from a weighing bottle 2 to 3 g of the detergent into a 250-ml separating funnel. Add 100 ml of *p*-toluidine hydrochloride solution, stopper the funnel and shake well. Continue with alternate shaking and settling until all the solid dissolves. Add 50 ml of carbon tetrachloride and shake well. Allow to stand until there is complete separation of the phases. Run off the lower layer into a 500-ml iodine flask. Make further extractions with 25 and 10 ml respectively of carbon tetrachloride. To the combined extracts add 100 ml of neutral industrial methylated spirit and 6 drops of *m*-cresol purple indicator. Titrate with 0·1 *N* sodium hydroxide with vigorous shaking between the additions. At the end-point, the grey colour of the emulsion takes on a blue or lavender tint. The two phases will separate if allowed to stand and a reddish purple colour in the upper layer denotes the end-point.

Carry out a blank determination of the *p*-toluidine hydrochloride solution. Subtract any value, which should not exceed 0·3 ml of 0·1 *N* sodium hydroxide, found for the blank from the value obtained when the sample is present.

The percentage of alkyl aryl sodium sulphonate contained in the sample is given by—

$$\frac{\text{Volume (ml) of 0·1 } N \text{ NaOH required for the titration} \times \text{F} \times \text{M}}{\text{Weight of sample taken} \times 100}$$

where F is the factor for the 0·1 *N* sodium hydroxide and M is the molecular weight of the alkyl aryl sodium sulphonate.

NON-IONIC DETERGENTS—

Polyethylene glycol compounds. The method given by Oliver and Preston[10] has been found satisfactory. The factor used for converting the weight of the precipitate to weight of detergent must, however, depend on information obtained by experiment.

Reagents—The reagents required are: (*a*) Detergent solution of known concentration. (*b*) Hydrochloric acid solution, 1 volume of the concentrated acid diluted to 4 volumes with distilled water. (*c*) Barium chloride, 10 g of $BaCl_2.2H_2O$ dissolved in 100 ml of distilled water. (*d*) Phosphomolybdic acid (B.D.H.), 10 g of $P_2O_5.20MoO_3.51H_2O$ dissolved in 100 ml of distilled water.

Sulphates, if present, interfere with the determination and must be removed by treatment with barium chloride solution before the following procedure.

Procedure—An aliquot part of solution (*a*), containing a known amount of detergent, usually not more than 100 mg, is placed in a 250-ml beaker, to which are added, in the following order, 5 ml each of hydrochloric acid (solution *b*), barium chloride (solution *c*) and phosphomolybdic acid (solution *d*); the contents of the beaker are then diluted to 150 ml with distilled water. The yellowish-green precipitate formed is flocculated by heating the mixture to boiling-point; the beaker is then covered and allowed to stand overnight (18 hours). The precipitate is filtered through a tared No. 4 sintered-glass crucible that has been previously heated for 15 minutes at 100° C and cooled in a desiccator, washed with a minimum of 100 ml of distilled water and dried at 100° C to constant weight. After two 1-hour periods, no substantial change in weight should be found. Solutions of the detergent under test are then precipitated in the same way.

This procedure establishes the ratio of the weight of the complex to the weight of the detergent for the particular detergent preparation under test.

The ammonium cobalt thiocyanate test mentioned above (qualitative test *iv*) as described by H. Gnamm[11] and by Van der Hoeve[2] is said to be available as a quantitative method.

CATIONIC DETERGENTS—QUATERNARY BASES—

These can be determined by a reversal of the methylene blue titration method. A sample of Teepol is titrated against 0·004 *M* cetyl pyridinium bromide (see "Anionic Detergents") and this standardised Teepol used to titrate the quaternary base under test.

NAPHTHENIC ACID SOAP—

This can be determined as described in "Standard Methods for Testing Petroleum and its Products"[12] by separating the copper salt, in presence of excess copper sulphate, and dissolving it in benzene.

NEUTRAL ELECTROLYTE AND ALKALINE ELECTROLYTE—

Since the type and quantity of these materials vary enormously in a given product from time to time, it is impossible to give general methods for their analysis. The presence of the detergent usually interferes seriously with any precipitation method involving aqueous solution, because of its dispersing action on the precipitate. It is therefore usually necessary to remove, extract or destroy the active material before estimating inorganic salts.

Alkalinity as hydroxide, carbonate or bicarbonate may be estimated by electrometric titration or by the indicator method. In the latter method indicators must be selected with care, as the active material tends to alter the apparent pH value of certain indicators.

For the estimation of sodium sulphate, which is a very common constituent of detergent preparations, the following method can be recommended. It will be noted that alkalinity is neutralised by sulphuric acid before the determination is begun.

Sufficient sample to yield approximately 0·2 g of sodium sulphate as final precipitate is weighed to the nearest milligram into a 400-ml beaker. Five millilitres of water are added and thoroughly mixed with the sample by stirring with a glass rod. One drop of bromophenol blue indicator is added and the solution is titrated with 0·5 *N* sulphuric acid until exactly neutral. The solution is rapidly raised almost to boiling-point by heating over a gas burner, but is not actually boiled. (This process must not take longer than 1 minute.) One drop of phenolphthalein indicator is added and then 1 to 2 drops of 0·5 *N* sodium hydroxide solution, which will make the test solution just alkaline to phenolphthalein. Two hundred millilitres of neutral ethyl alcohol are added and the mixture is boiled gently for 30 minutes, with the beaker covered by a clock-glass during this period. The mixture is cooled to about 50° C and the precipitated sulphate is removed by filtration through the tared sintered-glass crucible and washed with 100 ml of warm neutral ethyl alcohol. The crucible is then dried repeatedly in the oven, cooled in a desiccator and weighed to the nearest milligram until it reaches constant weight.

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Applications of Paper Chromatographic Methods in the Sugar and Allied Industries

By H. C. S. de WHALLEY, N. ALBON and D. GROSS

It is shown that separation of sugars of industrial interest can be made rapidly and quantitatively by the paper chromatographic procedure first used by S. M. Partridge of the Low Temperature Research Station, Cambridge, whose advice and assistance at the beginning paved the way for the later investigations. The procedure adopted and the construction of the apparatus is described. The chromatogram is sprayed with various reagents that give colour reactions with the sugars. The sugars are identified by comparison with controls of pure sugar run on the same piece of paper.

By means of paper chromatography it is possible to demonstrate the Lobry de Bruyn conversion and show the equilibrium concentrations of glucose, fructose and mannose; the presence in the conversion products of a fourth sugar, allulose, is also made evident. The heat degradation products of fructose have been separated and, by co-operation with Zerban and Sattler, were shown to be identical with the non-fermentables of cane molasses; some "compounds" were shown to be mixtures. Raffinose can be estimated in raw beet sugar with precision and certainty for the first time. The degree of purity of sugars such as raffinose has been determined; freedom from traces of sucrose could previously only be inferred, as the exact physical constants of the sugar were, and still are, open to conjecture. Mixtures of starch hydrolysis products, such as those present in beer, can be separated and identified quantitatively. At intermediate stages of the inversion of sucrose by invertase the appearance of at least one synthesised tri-saccharide has been noticed.

Chromatographic methods enable the organic and inorganic non-sugars, including colouring matters, to be separated, and make their examination a relatively simple matter; much still remains to be done in the identification of the separated products.

Limitations of the Traditional Control Instruments

Although scientific control of process operations in the sugar industry has been progressively improved during the last twenty-five years, the greater part of this control is still very empirical.

The most important instruments used in a control laboratory include the polarimeter, refractometer, Brix hydrometer, pH meter, conductivity ash meter (which indicates the amount of salts present), colorimeters and narrow-waveband light absorption instruments. All of these have been and will remain invaluable to the industry, but they are not sufficient to solve many of the problems that occur daily.

The optical rotation provides an exact measure of the concentration of pure sugar solutions, but in the sugar industry most of the samples examined are far from pure, as they contain mixtures of sugars together with non-sugars, some of which possess optical activity that varies with concentration or pH; measurement of polarisation gives only a commercial approximation to the sucrose content. The use of lead acetate defecants in solution or powder form confuses the result still further. Even with refined white granulated sugar[1] the sucrose content must be indirectly calculated by difference from 100 of the separately determined percentages of moisture, ash and reducing sugars, because the polarimeter is limited to an accuracy of 0·05, or with more recent instruments 0·02, and this is sufficient only for commercial purposes.

The Lane and Eynon method for determining reducing sugars, which has received international acceptance as a standard method, gives, with sugar-house products, only the total reducing value expressed as invert sugar, which is rarely, if ever, found in any samples from juice to finished sugars, syrups or molasses. The reducing effect of large quantities of sucrose with a low content of reducing sugars vitiates the accuracy of the method;

some of the reducing power may not even be due to sugars.[2] Tables based on the refractive index of sucrose solutions give values for the total solids whose accuracy is limited by the content of non-sugars. The Brix hydrometer at 20° C gives a true value for total solids for pure sucrose solutions, but with solutions of lower purity it gives values that are correct only for density purposes. The determined pH at 20° or 25° C does not necessarily correspond to the pH found at the factory working temperature, nor is there any precise relation between the two figures owing to the unknown dissociation of the non-sugars.

Abnormal discrepancies between ash determined by conductimetric and gravimetric methods depend on the composition of the non-sugars.

A figure for colour content, whether found by use of Lovibond glasses or by light absorption at 5600 A, gives no information about the composition of the colouring materials, nor does it give information about their selective adsorption during carbonatation or by bone charcoal.

New tools for industrial research

How then are we able to investigate problems that, owing to the presence of non-sugars in relatively low concentration, cannot be solved with the instruments available? The most satisfactory procedure is to make use of chromatography in one or other of its several forms. Chromatography, sometimes with the use of ion-exchange agents, wavelength spectrophotometers, flame spectrometers and recording polarographs, will go far to assist research in the sugar and allied industries.

General possibilities of chromatography

This paper is concerned with chromatography. It is appropriate at this stage to quote from Dr. R. C. Hockett's foreword to the scientific report on Chromatography of Sugars and Related Substances[3] published in 1948—

> "The close chemical similarity of the various sugars to one another has always made the problem of sugar analysis a fundamentally difficult one. The progress of biochemistry, physiology, botany and food technology has been impeded for many years by the lack of quick and accurate methods by which the various carbohydrates might be differentiated from one another and estimated quantitatively. The recent developments of chromatographic adsorption methods of analysis have provided investigators in many fields with an exceedingly powerful and useful tool for separation and purification. The application of such methods to the sugars has required ingenuity and painstaking work but has attained a notable degree of success. Although they are not generally useful as quick routine procedures, they do provide means of separating sharply the constituents of many mixtures composed of substances that are chemically similar. They have also the extremely important merit of isolating these constituents in tangible and usually crystalline form so that the identification is not a matter of surmise or deduction. Qualitatively they meet the ultimate specification and are capable also, in conjunction with more traditional methods, of providing quantitative information."

Methods—

Some progress has been made since these words were written.

Chromatography has been described as a specialised type of adsorption. Solutions are run through a bed or column of adsorbent and, with subsequent percolation of the proper solvent or mixed solvent down the column, the least strongly adsorbed compounds move down the column faster than the more strongly adsorbed compounds. This results in a series of bands or zones that can be separated by mechanical extrusion of the adsorbent in fractions or alternatively can be fractionally eluted by the solvent. A practical example of adsorption in the sugar refinery is provided by bone charcoal contained in cisterns. Colour and non-sugars and even sugars themselves are adsorbed, and the sugars are desorbed together with some colour and non-sugars when the charcoal is "sweetened off" or washed prior to regeneration of the charcoal. As bone charcoal is a black adsorbent, no zones are visible in the earlier stages of running, although some of the coloured zones would be visible if the adsorbent were colourless.

Even colourless adsorbents may fail to show zones if the adsorbed compounds are colourless, but sometimes they can be made to fluoresce in ultra-violet light and at other

times they can be made visible by addition of mixed dyestuffs that have individual adsorption characteristics resembling those of the main compounds being separated.

For standard column chromatography, a narrow glass tube with a constriction at the lower end with a perforated disc, sintered-glass disc or a cotton wool plug just above the constriction can be used when the adsorbents are to be eluted. When the adsorbent is to be extruded mechanically, a straight tube of glass or plastic is selected; it should have a slight taper to assist extrusion. The tube is attached by means of a ground joint to a lower portion containing a perforated cap and ending in a constriction.

The adsorbent used must be selected in accordance with the required characteristics. Many different substances have been used; they include carbon, alumina, silica gel, kieselguhr, magnesia, clays of different types, sucrose, starch and cellulose powder.

Generally the particle size of the adsorbent should not be larger than would pass a 200-mesh screen, and the material should be freed from very fine particles that hinder flow. The packing of the tube is an art acquired only by experience. Flow may be facilitated by use of a hydrostatic head or by gentle suction.

The first advances in the separation of sugars came with the discovery of suitable coloured sugar derivatives. However, these methods did not commend themselves to the sugar industry because the yields of the derivatives were not quantitative, nor were the preparations entirely free from products of side reactions; also one simple sugar might yield several derivatives.

After flow-through or elution chromatography the eluates of colourless sugars could be examined by physical means, *e.g.*, by measurement of the refractive index, or by chemical means, *e.g.*, by oxidation with periodate or Fehling's solution. The method was tedious and empirical, however.

The interest of the sugar industry was aroused when Partridge,[4] who used the method elaborated by Consden, Gordon and Martin[5] for separating the amino-acids of wool hydrolysates, separated simple sugars by what is now known as paper chromatography. Goppelsroder, in the nineteenth century, was the first to use sheets or strips of filter-paper for separation, and he found it extremely useful. Consden, Gordon and Martin revived this dormant technique and placed it on a more scientific basis; it has since been applied more generally to other problems, including that of the separation of sugars, by Partridge and his colleagues at the Low Temperature Research Station, Cambridge. With the helpful advice and guidance of Dr. Partridge we were able to make an easy start, although we were forewarned by Dr. Bate-Smith that in many of the investigations planned we should have to work out our own salvation.

The technique of paper chromatography lies in placing a drop of the test solution on a filter-paper strip at a point near the top end; the paper is then hung from a trough containing a suitable solvent or mixture of solvents into which the top end of the paper dips. The trough and the paper strip are enclosed in a chromatographic cabinet, a lagged air-tight compartment in which the atmosphere is saturated with the vapours of water and the solvents. As the solvent is drawn into the paper by capillary forces and starts flowing vertically over the strip it extracts the individual constituents of the spot at different rates, carries them down the strip to form a series of invisible spots each containing a separate constituent, and so effects the desired separation. The strip is removed from the solvent trough and dried, and then sprayed with suitable reagents to make the spots visible; coloured compounds that are already visible do not need to be sprayed. The resultant strip is termed a chromatogram.

THEORY OF THE PROCESS—

To explain the mechanism, it is assumed that the water in the paper (cellulose) forms a static liquid phase and the solvent a mobile liquid phase. Hence the paper takes no part in the actual process and acts only as an inert support for the water. From the moment the solvent flows over the original spot of test solution there is a distribution or partition of the constituents of the mixture between the water and the solvent, the solvent carrying more and more away until the extraction is complete. Every constituent is extracted according to its partition coefficient, which is a constant characteristic of each compound. The differences in the partition coefficient account for faster or slower movement and hence for the ultimate separation of the constituents of a mixture. By dividing the distance each substance moves by the distance moved by the solvent front on the chromatogram, a constant,

the R_F value, is obtained; it is characteristic of the compound in a given solvent under standard conditions, is easily reproducible and can be used for the identification of the compound. As the partition coefficients vary with each solvent, the selection of a suitable solvent for various mixtures of compounds is very important. The solvents are used saturated with water to help to attain phase equilibrium and also to increase the solvent power. Mixtures of several solvents are often more efficient, and the addition of small quantities of acidic or basic compounds has also been found useful. The partition ratio is proportional to the solubilities of the compounds in the solvent concerned; a knowledge of the solubilities is therefore helpful in the selection of solvents. Indeed, because the partition principle was assumed to be the basis of the method, the process was called "paper partition chromatography." However, it is not possible always to exclude the action of adsorption on the paper, as various workers have reported more or less strong adsorption effects when running paper chromatograms. It is sometimes difficult to decide what part is played by partition and whether partition is still the only governing factor. It can, however, be safely assumed that both partition and adsorption, and possibly some other factors of minor importance, are responsible for the functioning of paper chromatography.

Paper is very convenient as an adsorbent because it is easily stored in a small space, is ready for instant use, is inexpensive and can be photographed for permanent record. A large number of different samples can be run in parallel under identical conditions. Minute quantities down to a microgram can be analysed, which helps to conserve precious compounds. The paper strips can be of various sizes, or large sheets can be used, as is necessary with two-dimensional chromatograms when the paper is developed in two directions with two different solvents selected according to the requirements of the substances to be separated.

The one serious limitation to the use of paper in chromatography is the very small amount of material that can be placed upon a single sheet of paper. However, the small volume of solution applied to the spot can be dried and a further volume superimposed upon it, so doubling the quantity of material to be separated, although if the quantity is greatly increased, clean separation is hindered. An alternative method of increasing the yield is by making a series of sample drops across the paper and, after separation, collecting them together by water elution; in this way quantities can be increased up to tenfold.

For larger quantities recourse must be made to column separation with powdered cellulose as the adsorbent and the appropriate solvent. Extensive work has been carried out by this method by Jones, Hirst *et al.*[6] at Birmingham and later at Bristol and Edinburgh. The completeness of separation of the fractions can be tested by subjecting a drop of each fraction to the paper technique. A very minor constituent can sometimes be concentrated on a column and from the still impure mixture so prepared the required constituent can be separated cleanly on paper for identification or quantitative measurement.

DETAILS OF THE TECHNIQUE—

For the identification of the separated sugars a supply of pure sugars is required, as it is necessary to run solutions of these on the paper as controls.

If a micro-technique is used, only minute quantities of samples and controls are required. The drops applied to the paper are measured with a micro-pipette, an Agla micrometer syringe or, for routine purposes, carefully calibrated capillary tubes. For quantitative work exact measurement of the volume is essential. The areas of the spots of reacted sugars are compared with those of the controls for quantitative estimation. The filter-paper must be carefully selected, as different grades are required for different purposes. Even with one grade of paper, because no two sheets of paper are exactly identical in thickness or density, it is essential to make control tests on the same sheet as the test sample. Trouble has been caused by merely following directions to use a particular grade of paper, when the results obtained have conflicted with those of other workers. The suppliers request that when a particular grade of filter-paper is ordered it should be stipulated that it is to be used for chromatographic work; such supplies are vetted to ensure that the tolerance in weight and thickness is much smaller than for paper supplied for less critical analytical work.

Other requirements that, unless fulfilled, are almost certain to cause trouble to the beginner are as follows—

(1) The sample spots applied to the paper must be air-dried before the strip is transferred to the chromatographic cabinet.

(2) The solvent or mixed solvents must be saturated with water before use by shaking the two liquids together in a separating funnel; the solvent phase must be free from fine droplets of water. This phase is used in the trough and the aqueous phase is placed in the bottom of the cabinet.
(3) The atmosphere of the cabinet should be in equilibrium with respect to the mixed vapours before the paper is dipped in the trough and suspended in the cabinet, and in consequence it is advisable to prepare the cabinet in advance.
(4) The paper should nearly reach the liquid in the base of the cabinet but must not touch it.
(5) The cabinet should be lagged to prevent or slow down temperature changes, as increase or decrease of temperature will alter R_F values. Small changes are immaterial as control tests are likewise affected, but large changes of temperature may speed operations and run the spot off the paper.
(6) When the separation of mixtures is not satisfactory the cause may be insufficient time in the chromatographic cabinet. If increased time produces no improvement, the solvents may require modification. As the R_F value is increased, the separation in a given time first improves, but then becomes less satisfactory because the spots spread.

Experimental

Apparatus—

Figs. 1, 2 and 3 show the chromatographic cabinet and constructional details; the cabinets are made inexpensively from glass accumulator boxes by cutting off and grinding the base of one and fitting it above another, the joint being made with adhesive tape. The trough is of glass or polythene; the latter is more easily worked by making use of hot nitrogen welding.

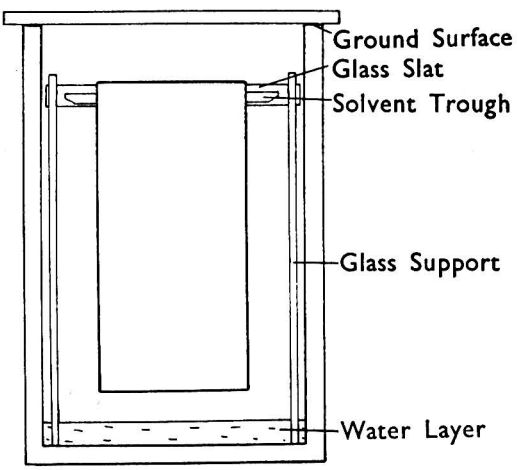

Fig. 2. Chromatographic cabinet

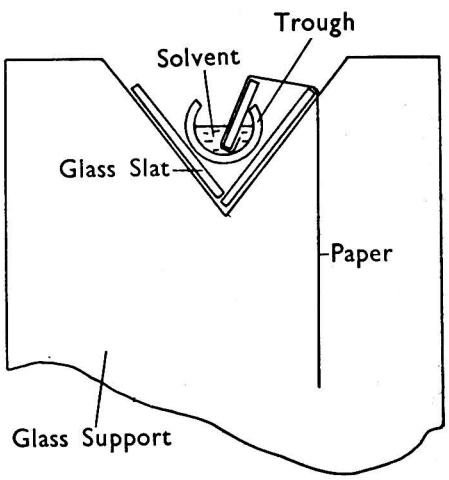

Fig. 3. Trough assembly, showing solvent and paper

After removal from the chromatographic cabinet, the paper is suspended in the drying cabinet, as shown in the photograph, Fig. 5. This cabinet has been constructed in our workshops from angle-iron, which forms a framework that is fitted with asbestos-cement sheet sides and a hinged top. The base of the cabinet is a perforated plate under which is fitted an electric resistance heater. Through the heater and the perforated bottom plate a current of air is drawn by suction from the fan situated on one side at the top of the cabinet; the air exhausts through a duct to the fume cupboard—a necessary precaution, as the solvent vapours, especially when pyridine or collidine are used, are unpleasant and may be toxic. The paper must not be overheated or it will become discoloured; uniform heating, not entirely satisfactorily attained with this particular design, is most desirable. The function of the cabinet is simply to remove water and solvent.

If colourless substances are being separated, it is necessary to spray the paper with a suitable reagent, and this is done as shown in Fig. 4 by means of an atomising spray bottle actuated by compressed air. It is essential to spray the paper evenly and completely. During this operation the paper is suspended in a fume cupboard. When sprayed, the paper is returned to the drying cabinet for drying and sometimes for further heating to complete the reaction of the reagent; Fig. 5 shows the sprayed chromatogram in the drying cabinet.

REAGENTS—

External heat for reaction is applied when the paper has been sprayed with α-naphthol. Molisch's reagent, as ordinarily used in testing for sugar in refinery or factory waste waters, relies on the addition of concentrated sulphuric acid to the water sample to which an alcoholic solution of α-naphthol has been previously added. The heat generated serves two purposes; one is to hydrolyse sucrose, the other is to enable the breakdown product of fructose, methyl hydroxy furfural, to react with the phenol to give the characteristic colour reaction. As such a reagent as sulphuric acid must not be used on a paper chromatogram, the alcoholic solution is acidified with phosphoric acid and heat is applied externally. The α-naphthol - phosphoric acid reagent serves to indicate not only ketoses, but also di-saccharides containing ketoses, *e.g.*, sucrose or raffinose, which are completely hydrolysed by the phosphoric acid. It gives no reaction for aldoses or compound aldose sugars such as maltose. An alcoholic solution of ammoniacal silver nitrate containing caustic soda serves to indicate all reducing sugars and reacts slightly with non-reducing sugars.

An alternative reagent for sugars is aniline oxalate, and the chromatogram prepared in this way shows spectacular fluorescence in ultra-violet light.

When it is required to show aldoses and ketoses on the same chromatogram, an alcoholic solution of naphtho-resorcinol containing phosphoric acid can be used; this produces a pink spot with ketoses and a green spot with aldoses.

It is evident from the foregoing that the reagent has to be selected to suit the particular mixture of sugars. Many other reagents have been tried, but those described have given the most successful results. Sometimes the reagent gives a fugitive colour reaction, *e.g.*, that with α-naphthol, and then a photographic copy must be made within fifteen minutes if a record is to be kept. With colouring matters separated from raw sugar solutions or intermediate products, the coloured spots are visible; however, some are pale in colour and some are present in sufficiently low concentration to be invisible. Examination in ultra-violet light will enable them to be seen clearly, and exposure to ammonia gas will intensify all the coloured spots.

USES OF PAPER CHROMATOGRAPHY

Paper chromatography has been applied by the authors to many problems, some of which have been readily solved; others have been partly solved and much information has been gained, but further work is required for their complete solution.

The separation of sucrose, glucose, fructose and other simple sugars by the technique of Partridge is shown in Table I.

TABLE I

CONDITIONS FOR SEPARATION OF SUGARS

Paper used	Whatman No. 1
Solvent	Ethyl acetate, 2 parts by volume Pyridine, A.R., 1 part by volume Water, 2 parts by volume
Time in cabinet	16 hours at 17° C
Time and temperature of drying	½ hour at 90° C
Reagent used	Naphtho-resorcinol and phosphoric acid
Time and temperature of heating	10 minutes at 90° C

In the chromatogram, Fig. 6, the individual sugars, each of different R_F value, are shown to have travelled different distances downwards. In addition, a mixture of the sugars has been separated into its constituents. Several practical applications of this procedure have been useful. In one, a sample of supposed mannose was quickly shown to contain no mannose but only sucrose with traces of glucose and fructose (invert sugar) and a patch of colour; it was in fact a low purity granulated sugar of unknown origin.

A sample of Dutch fondant was found to be composed of sucrose and high conversion glucose, with only a trace of invert sugar formed by hydrolysis in manufacture. Sugar confectionery containing a mixture of sugars can easily be examined by this procedure and such constituents as lactose, sucrose, maltose, glucose and fructose may be shown to be present.

Once the approximate amounts of the components of these mixtures are known, it is possible to make a quantitative assessment by polarimetric and reducing methods and simple calculation.

LOBRY DE BRUYN CONVERSION OR EFFECT OF ALKALI ON HEXOSES—

The re-arrangement of simple sugars in aqueous alkaline solution can be clearly demonstrated. Glucose, fructose and mannose in saturated lime-water solutions are shown in Figs. 7 and 8 to have formed equilibrium mixtures of all three sugars from each individual sugar through the common enolic form. With the chromatogram sprayed with the reagent aniline oxalate, glucose and mannose are shown in Fig. 7. With α-naphthol reagent, Fig. 8 shows fructose and, in addition, a spot that is almost certainly *d*-allulose, the epimer of fructose, but as yet we have no specimen of *d*-allulose as a control. The demonstration of this conversion is not as academic as it may seem, as it is connected with the problems of alteration or loss of reducing sugars in the operations of liming, carbonatation and charring. Samples of brewer's caramel produced by the action of heat and ammonia on sugars such as sucrose, invert sugars, glucose and hydrol all showed a quantity of fructose among the residual sugars present.

DESTRUCTION OF SUGARS DURING THE HEATING OF RAW CANE SYRUP—

An investigation was being made into the relative advantages of heating syrup by steam coil or by hot-water coil through equal temperature ranges in the same time, the upper temperature limit being maintained for twelve hours. In the normal estimation of total sugars after inversion, which were expressed as the proportion of invert sugar in the total

TABLE II

CONDITIONS FOR SEPARATION OF FRUCTOSE DECOMPOSITION PRODUCTS

Paper used	Whatman No. 1
Solvent	Ethyl acetate, 2 parts by volume Pyridine, A.R., 1 part by volume Water, 2 parts by volume
Time in cabinet	24 hours at 17° C
Time and temperature of drying	1 hour at 90° C
Reagent used	Naphthol
Time and temperature of heating	10 minutes at 90° C

solids, the errors of estimation were found to be of the same order as the expected differences. A chromatographic examination of destruction products showed, as might be expected, that some were present in the original sample. A number of compounds could be separated but not identified. It was then realised that these compounds, some still possessing optical rotation or reducing power, resembled one class of the non-fermentables of cane molasses, that produced by destruction of fructose, into which Zerban and Sattler were carrying out an investigation. By their procedure,[7] pure fructose was partly destroyed by long heating of its solution and fermentation of the residual fructose; the unfermentable syrup that remained was chromatographed and showed many similar spots to those found with raw cane syrup. Chemical fractionation of the residue by the procedure of Zerban and Sattler followed by chromatographic treatment of the separated fractions showed that some that had previously been considered to be simple were really more complex. Collaborative work with the New York Sugar Trade Laboratory has enabled some of the compounds to be identified. Minute samples for examination have been flown from the U.S.A. to England and chromatograms have been flown back. As a result the joint knowledge of all the collaborators has been much advanced.

A full paper on the subject by Zerban, Sattler and their various collaborators is being prepared for publication in the near future.

With the conditions shown in Table II, a chromatogram of some of the fructose decomposition products has been prepared.

The three dimers have been isolated as described from the mixture, but only two of the pure dimers have been identified on the chromatogram; we were unable to carry out the identification as we had no pure specimens, but Zerban and Sattler were able to do so. In the chromatogram, Fig. 9, the compounds visible include (*a*) the three dimers of fructose, the di-hetero levulosans, (*b*) a compound that is probably *d*-allulose and (*c*) the monomeric anhydride of fructose.

In following the procedure of Zerban and Sattler in fermentation of residual fructose, it was found by chromatographic examination that all fructose had been removed by one instead of by two fermentations. Any attempt at quantitative measurement of destruction of fructose by heating had to be postponed to allow work to be concentrated on the estimation of raffinose in beet sugar.

PURITY OF SUGARS—

Pure sugars are used for controls and now that more exact methods are available for testing for impurities, the purity of purchased sugars should not be assumed. A sample of pure fructose was found to contain traces of the breakdown products already described, and a laboratory reagent maltose contained dextrins. A sample of purified raffinose was submitted to us for estimation of traces of sucrose. It was part of a larger quantity intended for use in preparation of International tables of refractive indices and no other means existed for determination of small quantities of sucrose. The physical constants that were available had probably been determined on sugars of even lesser purity.

Direct chromatographic tests on 400 μg of the raffinose sample in a 10 per cent. solution did not reveal any sucrose spot, but this only meant that the sucrose, if present, was less than 0·5 per cent. of the total. Larger quantities, limited by the solubility of raffinose, of 800 and 1200 μg still did not reveal a sucrose spot; this placed the content of sucrose below 0·25 and 0·16 per cent. respectively, although under such concentrated conditions the separation could not be perfect as overloading would occur. A series of spots, each containing 1000 μg of the raffinose sample, were chromatographed on one sheet of thicker paper (to prevent overloading) and the portion where the sucrose should have appeared was cut off, extracted with water, concentrated *in vacuo* and re-chromatographed. The result was the appearance of a sucrose spot indicating that the original sample contained 0·15 per cent. of sucrose. The test had to be carried out in an atmosphere free from traces of sucrose, a requirement not easily met in a sugar laboratory. When the result was reported, the bulk was once recrystallised and another sample submitted. This was tested in a similar manner and showed less than 0·02 per cent. of sucrose, which was the limit of the test. The bulk of the raffinose was then recrystallised twice more as an added safeguard before being used for its intended purpose.

RAFFINOSE IN RAW BEET SUGARS—

Our work on the subject of raffinose in raw beet sugars has already been reported,[8,9] but as the subject is of some importance and interest, a brief account is included in this paper. By the use of paper chromatography, raffinose in raw beet sugars can be detected and estimated with precision and certainty for the first time. The classical two-enzyme method is useless for determining small quantities in raw products and may be unreliable even with amounts of the order of 0·5 per cent. Table III shows the conditions of the separation.

TABLE III

CONDITIONS FOR RAFFINOSE SEPARATION

Paper used	Whatman No. 1
Solvent	*n*-Butanol, 5 parts by volume Pyridine, A.R., 3 parts by volume Water, 3 parts by volume Benzene, 1 part by volume
Time in cabinet	24 hours at 16° C
Time and temperature of drying	1 hour at 90° C
Reagent used	α-Naphthol
Time and temperature of heating	10 minutes at 90° C

A chromatogram of a number of British raw beet sugars with controls of raffinose is shown in Fig. 10. The ash, or more correctly the salts present in raw beet sugars, hinders,

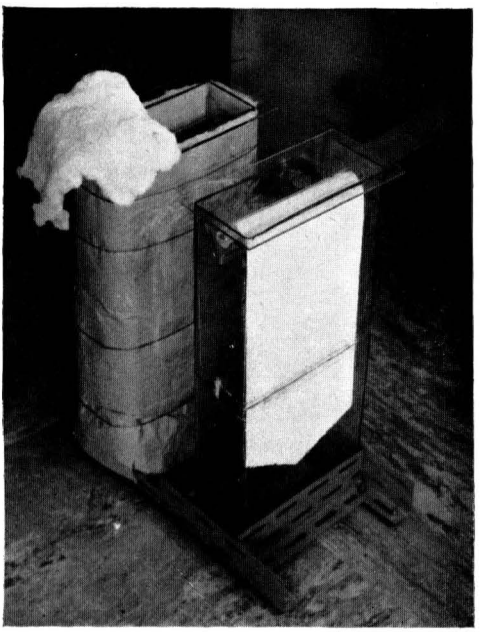

Fig. 1. Chromatographic cabinets, lagged and unlagged

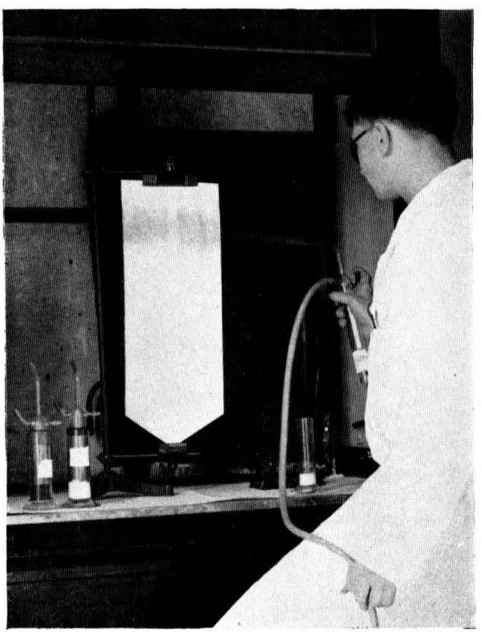

Fig. 4. Spraying the reagent

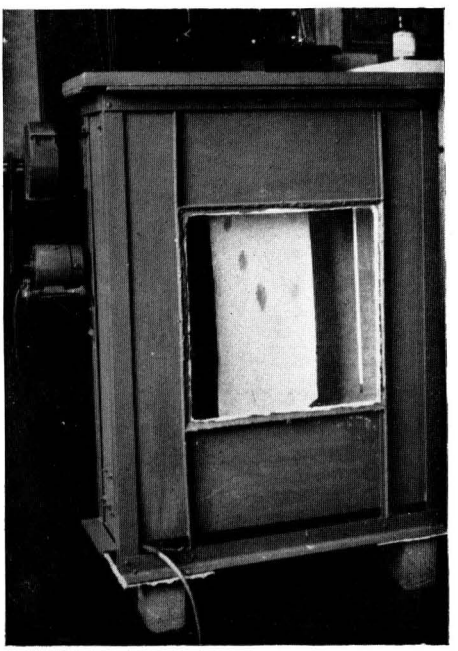

Fig. 5. Heating the sprayed paper in the drying cabinet

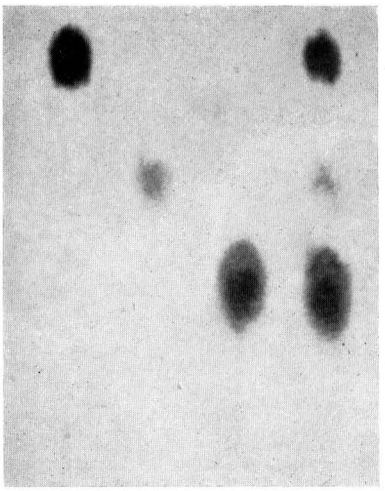

Fig. 6. Chromatogram of sucrose, glucose and fructose

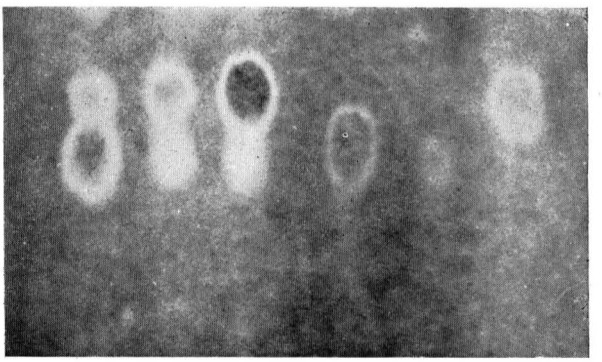

Fig. 7. Lobry de Bruyn conversion; glucose and mannose

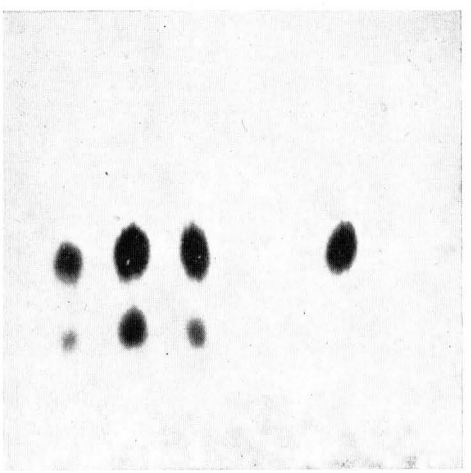

Fig. 8. Lobry de Bruyn conversion; glucose, mannose and fructose

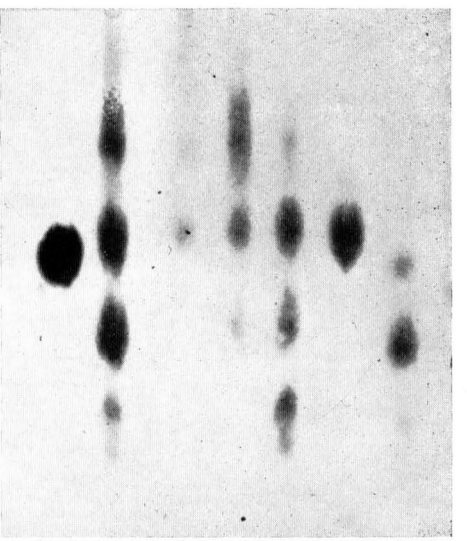

Fig. 9. Chromatogram of fructose decomposition products

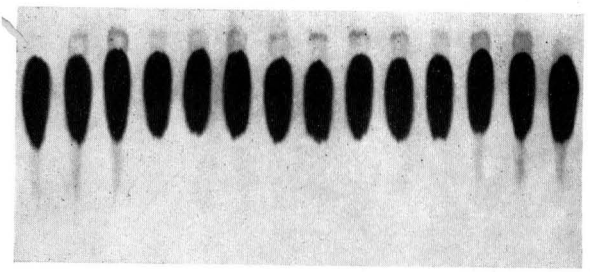

Fig. 10. Chromatogram of raffinose separation from raw beet sugars

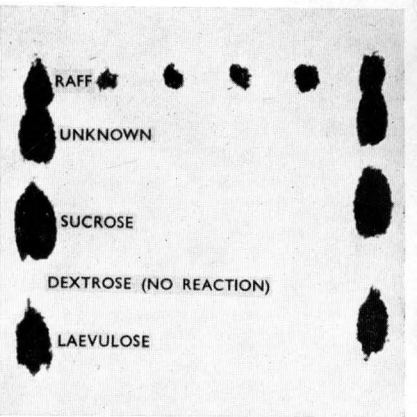

Fig. 11. Chromatogram of raffinose in U.K. beet molasses

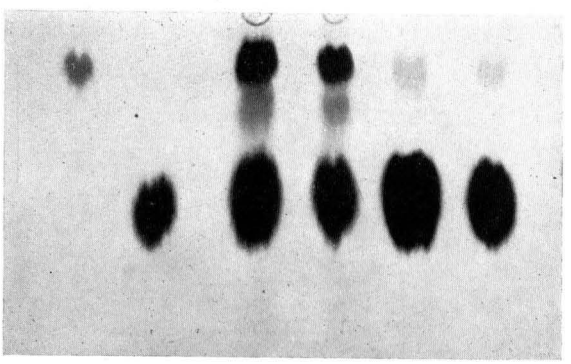

Fig. 12. Chromatogram of raffinose in U.S. white beet sugars from baryta-treated Steffenised molasses and in residual molasses

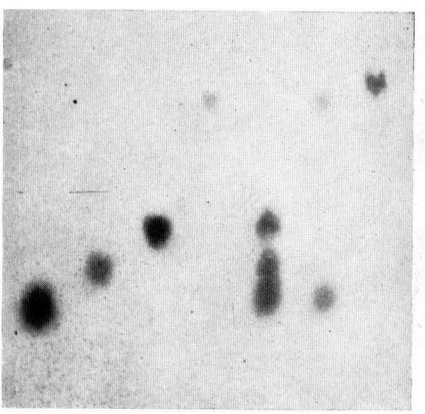

Fig. 13. Chromatogram of raffinose hydrolysed by enzymes

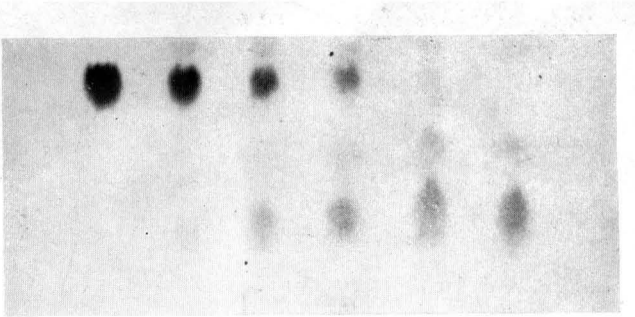

Fig. 14. Sucrose partly hydrolysed by invertase

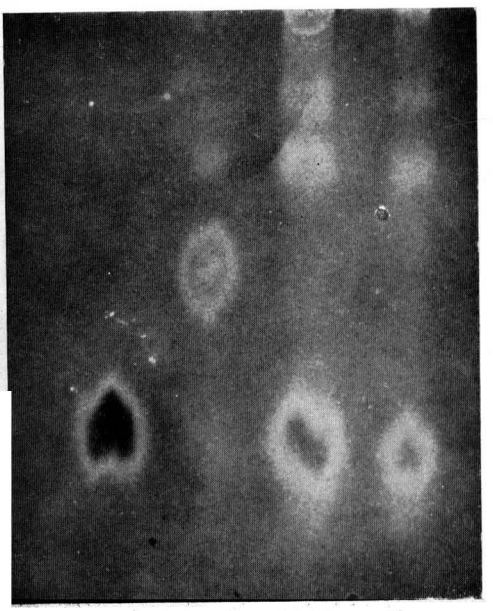

Fig. 15. Sugars in beer

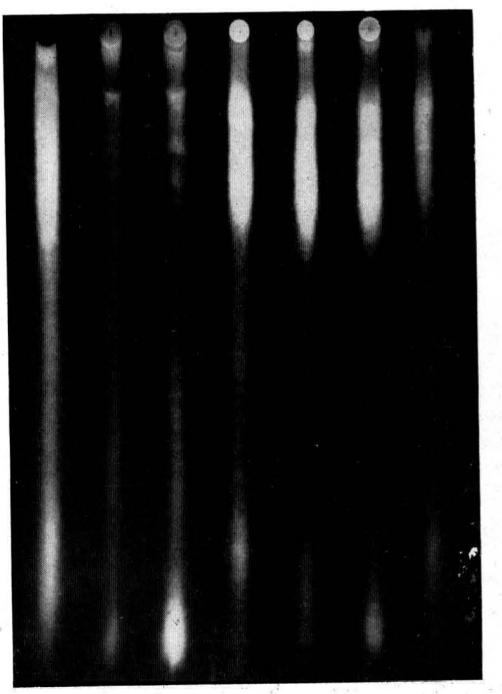

Fig. 16. Colouring matters in raw sugar solution

to a slight degree, the movement of the raffinose, and to compensate for this in the controls the pure raffinose is dissolved in a solution of raw cane sugar that has been tested and shown to be completely free from raffinose. The spots now known to be raffinose were at first identified with caution as it was considered that they might possibly be a non-sugar of R_F value equal to raffinose, but this was disproved by the following procedure. A number of equal volumes of raw sugar solution were chromatographed together on a paper sheet and the portion of the paper containing spots corresponding to raffinose was cut out and extracted with water. After concentration *in vacuo* and precipitation by acetone characteristic needle-shaped crystals were deposited; they were indistinguishable from those precipitated from pure raffinose. In other experiments the spots were extracted and concentrated to give a 2 per cent. solution of the supposed raffinose. On inversion with Wallerstein's invertase this solution gave fructose and melibiose, and on inversion with invertase containing Wallerstein's melibiase it yielded fructose, glucose and galactose. The presence of these sugars in the expected yields was demonstrated chromatographically, as also was the complete inversion of the supposed raffinose.

All the samples of raw beet sugars received for refining at our two London refineries during the 1949 to 1950 campaign have been tested for raffinose by paper chromatography with the results summarised in Table IV. No sample was free from raffinose. The total number of samples from both refineries was 429; they contained an average of 0·28 per cent. of raffinose hydrate.

TABLE IV

RAFFINOSE IN RAW BEET SUGARS

Factory	No. of samples	Raffinose hydrate			Average ash, %
		Max., %	Min., %	Average, %	
Refinery P—					
1	90	0·48	Trace	0·22	0·96
2	77	0·60	0·15	0·32	2·12
3	42	0·40	Trace	0·21	0·69
4	34	0·50	0·05	0·23	0·56
Miscellaneous	8	0·50	0·20	0·33	0·79
Refinery T—					
1	22	0·50	0·30	0·39	0·98
3	12	0·45	0·15	0·32	0·68
5	139	0·48	0·02	0·28	0·76
Miscellaneous	5	0·28	0·10	0·24	0·81

As 1 per cent. of raffinose polarises 1·52°, the amount of fictitious sucrose shown by polarisation is 0·42 per cent. This is equivalent to a thousand tons of fictitious sucrose for which payment has been made. The figures of apparent sucrose losses in refining require an adjustment of sucrose input because, although the raffinose appears in an output item, *viz.*, the molasses, the method of analysis takes only partial account of this. The value of the apparent sucrose in molasses is considerably lower than that in the major output item, *viz.*, refined sugar.

RAFFINOSE IN FACTORY BEET MOLASSES—

The effect of the high ratio of salts to sucrose makes direct chromatography of a molasses solution unsatisfactory. If, however, the salts are removed by passing the solution through a mixed bed of cation and anion removal material, *e.g.*, Zeocarb and De-acidite B (Permutit), it is found that a clean chromatographic separation of raffinose can be made, as shown in Fig. 11.

A number of samples of factory beet molasses has been tested. They were obtained through the courtesy of the British Sugar Corporation to assist in our search for a supply of molasses containing a high proportion of raffinose for culturing melibiase yeasts. The results of these tests showed that raffinose hydrate was present in amounts of 1·1 to 2·4 per cent. A larger supply of one of these samples showed 2 per cent. of raffinose by the paper test and 2·1 per cent. by the two-enzyme method.

RAFFINOSE IN WHITE SUGAR RECOVERED FROM MOLASSES—

No processing of molasses for recovery of sucrose is practised in the United Kingdom, but various countries in Europe use the lime, strontia or baryta processes. The Great Western Sugar Company of Denver, Colorado, uses the Steffen lime process in about half of their beet sugar factories in order to get a double dose of the lime for juice purification and for the recovery of sugar. When the raffinose in the final molasses from the Steffen process accumulates to the extent of 5 per cent. or thereabouts it is termed Steffen discard. This amounts to 40,000 to 50,000 tons per year and is further processed in the barium process plant at Johnstown, Colorado, which works for eight to ten months of the year entirely on molasses. A considerable elimination of the raffinose takes place in the mother liquors from the barium saccharate precipitation, but some goes through and builds up in the final molasses to about 20 per cent. The total quantity of this molasses is very small, but it is reported that several thousand pounds of high-purity crystalline raffinose have been recovered from it. The refined white granulated sugar crystals produced at Johnstown[10] are distinctive in appearance, being rather long and needle shaped in comparison with normal sucrose crystals. This variation is attributed to crystallisation in presence of raffinose. Fig. 12 is a chromatogram of the sugar and the molasses. On the molasses chromatogram there appeared an unknown spot, afterwards identified; this is referred to later in the paper.

The raffinose hydrate in the sugar was estimated at 0·8 per cent. by paper chromatography and as 0·9 per cent. by the two-enzyme method. The analysis showed—

	%
Polarisation	100·18
Sucrose	98·88
Raffinose hydrate	0·90
Moisture	0·05
Ash	0·027
Organic non-sugars	0·143
	100·00

In the molasses the proportion of raffinose as shown by paper tests was about 16 per cent. and as shown by the two-enzyme method 15·5 per cent. The analysis was as follows—

	%
Raffinose	15·48
Sucrose	55·84
Ash	2·67
Moisture	23·4
Organic non-sugars	2·61
	100·0

From these figures it can be deduced that the shape of the sugar crystals is due to the fact that they are mixed crystals and that the effect on the shape has not merely been caused by crystallisation in presence of raffinose.

It is now known that raffinose is widely distributed in the vegetable kingdom and that it is generally found together with the tetra-saccharide stachyose. Raffinose is not sweet, but it is in all probability assimilated and utilised in human metabolism like most other naturally occurring sugars. Molasses cattle foods may contain up to 1 per cent. or more of raffinose.

RAFFINOSE IN NORMAL WHITE BEET SUGARS—

If white beet sugars are of good quality they contain very little raffinose, but if the quality is low, the amount, although very small, is measurable. One such sample showed the following curious analysis—

	%
Polarisation	99·93
Ash	0·030
Reducing sugars	0·014
Moisture	0·048
Organic non-sugars	?
	100·022

The total, 100·022 per cent., indicates that the percentage of organic non-sugars, found by subtracting the figures for the other items from 100, is either absent or negative. The former is unlikely with an ash figure of 0·03 per cent., and the latter is impossible.

A chromatogram showed the presence of 0·15 per cent. of raffinose hydrate, which enabled the polarisation to be corrected and the analysis re-arranged as follows—

	%
Corrected polarisation (sucrose)	99·705
Raffinose hydrate	0·15
Ash	0·030
Reducing sugars	0·014
Moisture (½ hour at 105° C)*	0·048
Unestimated or organic non-sugar	0·053
	100·000

* The loss of water from raffinose hydrate under these conditions is negligible.

There is no doubt that the raffinose present is optically active and is affecting the polarisation reading to the extent of 1·5 per cent. for every 1·0 per cent. of raffinose present.

HYDROLYSIS OF SUGARS WITH ENZYMES—

Mention has already been made of the use of the enzyme invertase and the mixed enzymes invertase and melibiase to prove the identity and estimate the quantity of raffinose in raw beet sugar. Fig. 13 is a chromatogram of raffinose after treatment with the enzymes. With invertase the raffinose has yielded fructose and melibiose, and with the mixed enzymes the raffinose has completely hydrolysed to the three constituent hexoses, fructose, glucose and galactose. Another worker had informed us that he had experienced difficulty in the separation of lactose and melibiose; hydrolysis of either with acid yielded the same two sugars, glucose and galactose. Our experience showed that a satisfactory separation could be achieved with a suitable ethyl acetate - pyridine - water solvent.

If the hydrolysis was made with melibiase instead of with acid, lactose was unaffected, whereas melibiose was broken up and a very clearly defined separation was obtained.

ENZYME PURITY—

A sample of invertase was found to hydrolyse melibiose slightly, so showing that a trace of melibiase was also present. It is almost certain that without chromatographic separation of the sugars this could not have been detected.

HYDROLYSIS OF SUCROSE BY INVERTASE—

During the examination of the activity of melibiase in culture yeasts, the progress of hydrolysis was followed by chromatography of minute samples.

A preparatory study was made of the hydrolysis of sucrose by invertase. In the early stages of the hydrolysis the chromatogram (Fig. 14) showed much unchanged sucrose and some glucose and fructose. In addition to these there is an unknown spot above the sucrose spot. Our colleague, P. Blanchard, who was engaged on this study, was interested in the nature of this compound, the quantity of which decreased as hydrolysis proceeded and finally disappeared when hydrolysis was complete. The portion of the paper containing this spot of unknown material was cut out, extracted, and re-chromatographed after complete hydrolysis with invertase. From the position of the spot on the original chromatogram and the proportion of the hexoses produced by hydrolysis the material appears to be a new tri-saccharide composed of two fructose and one glucose units. This compound is the cause of the unknown spot in Fig. 12.

Further investigation of this reaction revealed the presence of yet another compound, which is thought to be another tri-saccharide of slightly different structure. These new compounds have been separated by adsorption chromatography on activated charcoal and small quantities have been crystallised. Bacon and Edelman, working with a similar technique at the University of Sheffield, have also observed this effect with invertase preparations.

This complication could be due to the reactive fructofuranose first liberated by the hydrolysis of sucrose linking up with some unchanged sucrose. It may be catalysed by invertase or by some other enzyme occurring in invertase preparations. No similar effect has yet been observed during the hydrolysis of sucrose by acids.

BEER—

Small amounts of sugar remain after the normal course of fermentation, and for the determination of these we suggested paper chromatography. A trial gave satisfactory results. In Fig. 15 dextrins appear at the top of the chromatogram as a string of compounds. The sugars maltose, glucose and fructose are also clearly separated in that order. The investigations were not pursued, but they indicate the possibilities of the method for the separation of the hydrolysis products of starch.

COLOURING MATTER—

The study of the colouring matter present in raw materials and also of that formed during refining processes is made difficult by the presence of a multitude of coloured compounds of several types. Spectrophotometric absorption curves over the range of the visible spectrum show no characteristic peaks to assist identification. It was thought that if separation into components could be effected, more information could be obtained either chemically or spectrophotometrically from each isolated component.

The colour in a solution of a raw cane sugar was isolated by column chromatography and the concentrated colour was re-chromatographed on paper with a solvent consisting of a mixture of butanol, acetic acid and benzene. The resultant chromatogram when viewed in ultra-violet light showed a number of strongly fluorescent, well-separated spots in addition to those visible by normal light, as shown in Fig. 16. Further investigations showed that sufficient quantities for the identification of the separated compounds could be obtained by the use of adsorption columns packed with adsorbents such as activated alumina, or magnesia. According to the adsorbent used the coloured compounds can be divided into several components by the formation of distinct bands or zones that can be separated by extrusion or elution. It is now possible to treat each component or group of coloured compounds separately and to obtain information specific for the particular component; this represents an obvious advance over previous investigations in this field.

WORK OF OTHER INVESTIGATORS

Some mention should be made of the valuable contributions to the subject by other investigators. Brown and Dahlberg[11] have separated various nitrogenous compounds from Steffen waste waters and then applied paper chromatography to the identification of the various amino-acids. They have identified aspartic acid, glutamic acid, serine, glycine, alanine, tyrosine, valine and leucines in both protein-free beet juice and in Steffen waste.

Pratt and Wiggins[12] have adsorbed all the amino-acids present in cane juice on a column of Zeocarb 215 and eluted the column with 2 *N* hydrochloric acid. The concentrated eluate was submitted to paper chromatography, first with a mixed solvent of collidine and lutidine and then in a second dimension with phenol as solvent. They identified the following amino-acids: aspartic acid, glutamic acid, serine, glycine, alanine (and possible glutamine), amino-butyric acid, lysine, valine and leucine or an isomer.

Binkley and Wolfrom[13] used chromatographic fractionation with various concentrations of ethanol on columns of clay and obtained four crude fractions, characterised by their copper reduction values before and after hydrolysis. Re-fractionation of two of these crude fractions followed by the extraction of sections yielded crystalline sucrose, *d*-glucose and *meso*-inositol; these were also isolated, together with *d*-fructose and *d*-mannitol, as crystalline acetates by acetylation and subsequent chromatographic separation. *d*-Glucose is present in excess of *d*-fructose; reducing substances other than hexoses were present in the reducing fraction. Application of similar procedures to a residue from the fermentation of molasses led to the isolation of crystalline sucrose and *d*-mannitol and their crystalline acetates, and also crystalline acetates of *d*-glucose, *d*-fructose, *d*-erythritol, *d*-arabitol and an unidentified substance.

We desire to thank those of our colleagues who have given us a great deal of time and help, and in particular D. Harrison for the preparation of the photographs and F. Carman for his advice and guidance on these. We also thank W. Underwood and A. Graves for their skill and ingenuity in constructing, at low cost, the apparatus required. Finally, we express our thanks to the Directors of Tate and Lyle Limited for permission to publish the results of the work carried out in their Research Laboratories.

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Discussion

Mr. L. Eynon congratulated the authors on their very important contribution to sugar analysis. In particular, they had solved the problem of the estimation of raffinose in raw beet sugars. Before the 1914–18 war, we had imported large quantities of raw beet sugar from the Continent and a considerable proportion of Continental sugar was so-called "process" sugar, extracted from beet molasses by the lime or strontia extraction method. This sugar contained considerable amounts of raffinose; with the methods of estimating raffinose available at that time it was not possible to estimate less than 0·3 to 0·5 per cent. with certainty. With the chromatographic method developed by the authors it was now possible to estimate as little as 0·05 per cent. Mr. Eynon opened the discussion by asking whether any attempt had been made to determine the melassigenic factor of raffinose.

Mr. de Whalley replied that not much was known about the melassigenic factor of raffinose. A. Herzfeld, in 1910, stated that joint work with Foerster at an earlier date had shown it to be negligibly small.

Dr. J. R. Nicholls said that from a scientific point of view the paper was a highly valuable contribution. It showed that minor constituents could now be separated and determined to a high degree of accuracy and that the presence of hitherto unsuspected constituents could be demonstrated. The method showed great promise for the separation of such vague constituents as the colouring matters, and the identification of the separated components should be greatly facilitated.

Dr. A. Carruthers said that as a representative of the Corporation that produces sugar from beet, he offered congratulations to Mr. de Whalley and his colleagues on their work. He referred to the degree of accuracy pertaining to the estimation of raffinose in raw beet sugar and asked whether the results of comparisons between the test material (raw sugar) and the same test material with added known quantities of pure raffinose would differ from the results found by comparing the test material with mixtures of raw cane sugar and known amounts of raffinose.

Mr. de Whalley replied that there was no reason to expect a difference in the results. The addition of raffinose to the sample under test had been tried and it had been found that raw cane sugar containing no raffinose was a more suitable adjunct to the pure raffinose to balance the slowing of the separation by the salts present.

Mr. H. E. Monk enquired about the possibility of using these methods in the examination of honey for the presence of invert sugar made either with acid or enzymes.

Mr. de Whalley replied that they had not examined honey. If invert sugar had been made by invertase and the sucrose was not completely inverted, some of the newly discovered tri-saccharides would be present. These might normally be present in honey. Hydroxymethylfurfural was formed either by heating or on inversion with acid.

Miss E. I. Beeching asked the lecturer if he had tried precipitation of the protein before making chromatographs.

Mr. de Whalley replied that removal of fat and protein, if present, was desirable, but that in his laboratory no work had been done on this subject as neither were present in their sugar products.

Dr. J. H. Hamence said that there were two questions concerning technique that he would like to ask the authors. First, the authors had shown paper chromatography to be an extremely valuable analytical tool for the differentiation and estimation of the different sugars present in mixtures, but from the description given by Mr. de Whalley, it took at least 18 hours before results were obtained. Was it

possible to shorten this time in order to obtain a qualitative indication of the sugars present in a mixture? Secondly, was it essential that the form of apparatus used by the authors be strictly adhered to? For a number of years they had worked in their laboratory with strips of filter-paper between two sheets of glass plate, following the technique described by Rutter. Was it possible to use this technique for the separation of sugars qualitatively, instead of using the rather more elaborate technique described by Mr. de Whalley?

MR. DE WHALLEY said that separation was normally achieved overnight and did not consume operator's time.

MR. N. ALBON said it was possible in qualitative work and simple investigations to obtain separations more quickly by variation of the solvent mixtures by inclusion of more water in the solvent phase or by use of faster paper. The spots were less well defined and the method was unsatisfactory for quantitative work. Various types of apparatus could be used to give similar results. The apparatus described sounded more elaborate than it actually was. It could be further simplified for short-travel separations designed for qualitative use. The glass-plate method described by Dr. Hamence had not been tried.

MR. E. M. LEARMONTH enquired whether it was necessary to have control spots at both edges and to keep a stock of pure sugars. Was there any method of assaying photometrically?

MR. ALBON said that a photometric method was possible and there were a number of references in the literature. A large number of test samples could be run on one sheet of paper. However, when only a few samples had to be tested, controls need only be on one edge.

MR. DE WHALLEY pointed out that the quantities of stock sugar required were very small as only microgram amounts were used for controls.

DR. E. H. CALLOW asked what were the minimum amounts that could be estimated. He also asked whether the authors had tried the use of a higher temperature.

MR. ALBON replied that the minimum amount required depended on the particular sugar; it could be less than 5 μg or even as little as 1 μg. The use of a higher temperature appeared to be a useful modification, but the design of the apparatus would become more complicated.

MR. R. F. MILTON asked if two-dimensional paper chromatography was useful for separating closely related sugars.

MR. ALBON replied that it had on occasion been used for rarely occurring constituents, but that they had found it better to use one-dimensional chromatography and suitably modify the solvent as required.

The Determination of Carbon Dioxide Derived from Carbonates in Agricultural and Biological Materials

BY J. TINSLEY, T. G. TAYLOR AND J. H. MOORE

Methods for the estimation of carbonate are reviewed.

A simple titration procedure for the determination of carbonate in a wide variety of materials is described. Decomposition by acid and absorption of carbon dioxide by alkali are accomplished under reduced pressure within one reaction vessel. Amounts of carbon dioxide ranging from 1 to 80 mg can be determined to within ± 1 per cent.

Part 1. Introductory Review

METHODS for determining carbon dioxide released by the action of acids on carbonates comprise three main groups according to the way the measurement is made.

GRAVIMETRIC METHODS—

In these the carbon dioxide may be weighed either (*i*) directly, by the gain in weight of an absorbent, or (*ii*) indirectly, by the loss in weight of the system.

For the most accurate results a direct procedure is usually employed in which the gas evolved from the reaction vessel is dried and purified by passing through a suitable absorption train. Formerly the carbon dioxide was usually absorbed in potash bulbs, but now it is more convenient to use solid absorbents such as soda-lime, soda-lime - asbestos (Carbosorb) or sodium hydroxide - asbestos (Ascarite).

However, for many purposes an indirect method is less tedious to operate. Provided that other gaseous products are not derived from, *e.g.*, nitrite, sulphite or sulphide, accurate

results are secured if due precaution is taken to prevent loss of water from the system. Several designs of apparatus have been used but probably the best known is the Schrötter tube.

An apparatus of simpler construction designed by Scott and Jewell[1] was recommended by Scott and Furman.[2] The reaction vessel consists of an ordinary conical flask in which is placed a small volume of acid solution. The test material, contained in a squat flat-bottomed tube, is carefully introduced, and the flask is then closed with a rubber stopper carrying a calcium chloride exit tube and an inlet tube dipping below the surface of the acid. After weighing, the assembled apparatus is tilted to overturn the small tube and gently shaken to mix the contents. A slow stream of dried air is passed through the apparatus for 30 minutes before the final weighing is performed.

A very similar type of apparatus was used by Erickson, Li and Gieseking[3] for the determination of carbonate in soils. A small tube was fused to the inside of the reaction flask to hold 5 ml of a concentrated solution of trichloroacetic acid and the reaction was allowed to proceed for 12 hours after mixing.

GASOMETRIC METHODS—

In these the carbon dioxide is released and measured in a closed system either (*i*) volumetrically, at known temperature and pressure, or (*ii*) manometrically, at known temperature and volume.

The form of apparatus depends somewhat on the type of material being analysed. For solids such as powdered limestone or soil, Collins[4] developed a volumetric apparatus from an earlier design by Scheibler. A full description of the Collins calcimeter and its operation is given in Wright's textbooks of agricultural and soil analysis.[5,6] Briefly, it consists of a gas-measuring unit immersed in a water jacket and connected by rubber tubing to a reaction vessel. For this a 150-ml bottle or flask is used to contain the test sample together with a small horn tube holding diluted hydrochloric acid (1 + 2). This arrangement is the reverse of that used by Scott and Jewell, but the same result is achieved by tilting the flask to discharge the acid on to the carbonate material. The maximum volume of carbon dioxide that can be handled in the apparatus at room temperature and pressure is less than 50 ml, corresponding to about 0·2 g of calcium carbonate. If carefully calibrated, the apparatus gives reliable results, except with small quantities of carbon dioxide.

An alternative form of apparatus for soils and other solid materials was described by Singh and Mathur.[7] This was adapted from a design used originally for biological fluids, embodying a manometric tube filled with Brodie's solution. Burns and Henderson[8] employed the Barcroft manometric apparatus for the determination of carbonate in bone tissue.

However, for measuring carbon dioxide and other gases evolved from biochemical solutions, the well-known Van Slyke apparatus has attained great popularity. The original tube described by Van Slyke[9] was calibrated for volumetric measurement of the gas over mercury at atmospheric pressure. Later, Van Slyke and Neill[10] introduced the manometric version for measuring the pressure of the gas when reduced to a standard volume of 0·5 or 2·0 ml. Greater accuracy was possible with this apparatus, a full description of which is given in the textbooks of Peters and Van Slyke[11] and of Hawk, Oser and Summerson.[12]

Robinson[13] described a modification of the original Van Slyke tube in which powdered solids were admitted through an opening fitted with a ground-glass stopper. Bowes and Murray,[14] in studies on the composition of teeth, used a Van Slyke - Neill tube having a stopcock with a large bore of 7 mm diameter, through which the powdered material was introduced from a weighing funnel. Such arrangements have not persisted, because it is more generally convenient to use the separate reaction vessel devised by Van Slyke, Page and Kirk[15] for connection to the standard Van Slyke - Neill tube. These workers first used it for the micro-determination of carbon in organic compounds by a wet combustion procedure, which was later modified by Van Slyke and Folch.[16] The carbon dioxide is absorbed in a 0·5 *N* solution of sodium hydroxide containing 0·5 *M* hydrazine, to reduce any halogens, and then regenerated with 2 *N* lactic acid solution. MacFadyen[17] used the same apparatus for determining carbon dioxide released from amino-acids by the ninhydrin reaction but, in order to reduce the solubility of carbon dioxide, the alkali and lactic acid solution were almost saturated with sodium chloride. For the micro-estimation of carbonate in bone, Sobel, Rockenmacher and Kramer[18] found that it was necessary to use a water jacket around the connecting arm to prevent fumes passing into the Van Slyke - Neill tube when the bone sample was boiled with 3 *N* hydrochloric acid in the reaction vessel. The great utility of the Van Slyke - Neill

apparatus with attached reaction vessel is further illustrated by a method for the determination of inorganic and organic carbon in the same soil sample that has recently been devised by Bremner.[19]

Rapid manometric devices that involve no adjustment in volume of the gas are available for carbonate solutions and materials such as limestones. For use when moderate accuracy suffices, Piper[20] has described a modification of Passon's method that is used for soils at the Waite Institute in Australia. Dixon and Williams[21] developed a stainless steel vessel fitted with a false base forming two compartments. These hold the carbonate material separate from a 20 per cent. solution of phosphoric acid until mixing is performed by tilting.

TITRIMETRIC METHODS—

In these the carbon dioxide is absorbed in a standard alkali solution, usually barium or sodium hydroxide. Methods differ in points of detail according to the form of the reaction vessel, the means of absorption and the mode of titration.

The reaction vessel may consist simply of a flask with provision for the inlet of acid and the outlet of carbon dioxide to the absorption vessel. In the method described by Amos[22] for the determination of carbonate in soils, the sample, containing not more than 0·5 g of calcium carbonate, was boiled with a solution of approximately 2 *N* hydrochloric acid. The carbon dioxide passed through a condenser into a Reiset absorption tower containing 0·5 *N* sodium hydroxide solution. When absorption was complete, the solution was titrated with standard hydrochloric acid in two stages, according to the method used by Brown and Escomb.[23] The first stage was titrated with phenolphthalein as indicator and the second stage with methyl orange. The difference between these two titration values represents bicarbonate.

However, such a method is not employed at present for soils, because boiling with hydrochloric acid often gives high results, as was emphasised by the Report of the Organic Carbon Committee to the Third International Congress of Soil Science.[24] The high results are due to decomposition of organic matter, especially uronides, and also to the formation of chlorine by oxidation when manganese oxides are present. These errors can to a great extent be avoided either by carrying out the reaction at room temperature or by boiling at a low temperature under reduced pressure with hydrochloric acid containing a reducing agent such as ferrous or stannous chloride. The lower the temperature and the lower the concentration of acid the less is the danger of decarboxylation of the organic matter, but when magnesian limestone granules are present in the sample, they often dissolve very slowly in dilute acid at room temperature.

In the tentative A.O.A.C. method[25] for soils, the sample, ground to pass a 60-mesh sieve, is treated with approximately *N* hydrochloric acid solution containing 5 per cent. of stannous chloride. The reaction flask is mounted on a reciprocating shaker and connected by rubber tubing either to an absorption train or to a tower containing 0·5 *N* sodium hydroxide solution, depending on whether the determination is to be made gravimetrically or titrimetrically.

For titration, the procedure of Winkler[26] is followed, the alkali being first washed out of the tower into a 500-ml graduated flask, 10 ml of a neutral 25 per cent. barium chloride solution being then added to precipitate barium carbonate. After dilution and mixing, the flask is set aside for 4 hours before the excess of hydroxide is titrated with standard acid, phenolphthalein being used as indicator. For soils containing resistant carbonates, the reaction vessel is heated with a condenser inserted before the absorption vessel. It should also be noted that Fraps[27] examined this method for the determination of carbonate in feeding stuffs and found it necessary to use stronger hydrochloric acid (diluted 1 + 1) for the complete decomposition of bone meal.

In place of this rather lengthy procedure, Schollenberger's method has been widely used in America for soils and limestone materials. Decomposition is effected by boiling with acid under reduced pressure at about 30° C; although the method has undergone minor modifications since it was first described in 1930,[28] the essential features remain unchanged in the latest (1945) description.[29] The sample, containing not more than the equivalent of 0·25 g of calcium carbonate, is placed in a 200-ml reaction flask, which is connected through an upright condenser with a one-litre absorption flask. The system is evacuated to about 2 cm of mercury, and then 50 ml of 0·2 *N* barium hydroxide solution are admitted to the absorption flask. Dilute hydrochloric acid containing ferrous or stannous

chloride is sucked into the reaction vessel and the contents are heated to maintain a steady rate of boiling at about 30° C. Generally the reaction is completed within a few minutes, after which the inlet to the reaction flask is opened to admit a slow stream of air, free from carbon dioxide. The barium hydroxide solution must be agitated by shaking the apparatus to break the film of carbonate and so ensure complete absorption of carbon dioxide before the flask is disconnected. Finally, the excess of hydroxide is titrated with 0·1 *N* hydrochloric acid, thymolphthalein or phenolphthalein being used as indicator. The volume of acid solution in the reaction vessel should be about 100 ml, but the strength is varied from a dilution of 1 in 25 for ordinary use to 1 in 10 for use with resistant carbonates. Normally the determination can be completed within an hour.

A quicker method is that described by Shaw and MacIntire[30]; in this, steam distillation is used to ensure rapid decomposition. The reaction flask is fitted with a stopper carrying a steam inlet tube and a tap funnel for introducing acid. A Liebig condenser forms the exit tube, which leads through a gas-scrubbing bottle to the absorption vessel. This consists of a 500-ml suction flask containing dilute sodium hydroxide solution, and is provided with a special reservoir tube that can be moved vertically in the neck of the flask while maintaining an airtight joint with a rubber sleeve. Inorganic carbonate materials are decomposed by introducing approximately *N* hydrochloric or perchloric acid solution, which is diluted to a concentration of about 0·4 *N* within the reaction vessel. It is necessary to pass steam for about 2 minutes and, if 1 minute is allowed for shaking the absorption vessel, the whole operation of decomposition and collection is completed within 5 minutes. The absorbent is then titrated with 0·1 *N* hydrochloric acid, either directly to the bicarbonate stage at pH 8·4, with phenolphthalein as indicator, or after the addition of barium chloride solution. For soil samples, the same procedure is followed except that the acid introduced into the reaction vessel contains 5 per cent. w/v of stannous chloride ($SnCl_2.2H_2O$). Even with this reducing agent and short digestion period, the error due to carbon dioxide released from the soil organic matter is slightly greater than by Schollenberger's method because of the higher temperature.

In all these titrimetric methods so far described, each piece of apparatus, besides requiring individual attention during operation, needs to be heated for decomposition to take place. Hutchinson and MacLennan,[31] however, devised a method in which the carbonate was decomposed *in vacuo* at room temperature, and a slight modification of their method was recommended by Piper[20] for accurate determinations. The reaction vessel is connected through a simple spray trap to a larger absorption vessel, containing 0·1 *N* sodium hydroxide. After assembly the apparatus is evacuated as completely as possible before admitting approximately *N* hydrochloric acid into the reaction vessel from a tap funnel. For soil samples this acid may contain 3 per cent. w/v of ferrous chloride ($FeCl_2.4H_2O$). The apparatus is shaken intermittently for 20 minutes before admitting a slow stream of air, free from carbon dioxide, through the tap funnel. The shaking is repeated to complete the absorption of carbon dioxide, and then barium chloride solution is added to the absorbent before titration with 0·1 *N* hydrochloric acid. If the end-point is taken as the stage when thymolphthalein just becomes colourless, it may be checked by addition of phenolphthalein, which should then give a pink colour that requires only another one or two drops to discharge it.

A very similar method was used by Williams[32] for the determination of carbonate in calcareous soils before the extraction of exchangeable bases. An excess of 0·5 *N* acetic acid was used in place of hydrochloric acid and the system was allowed to stand overnight under reduced pressure. Instead of sodium hydroxide, 0·2 *N* barium hydroxide solution was used as absorbent.

In order to avoid individual manipulation during the absorption process, several workers have endeavoured to simplify this form of apparatus still further by carrying out decomposition and absorption within one closed vessel under reduced pressure. Van Slyke[33] devised the apparatus illustrated in Fig. 1 for the determination of carbonate in powdered bone and other materials.

The powdered material is weighed into the bottom of a suitable tube about 20 mm in diameter, and this is placed inside a 250-ml suction flask containing a measured volume of 0·1 *N* barium hydroxide. The stopper carrying the tap funnel is inserted and the flask evacuated to less than 50 mm of mercury through the side tube, which is then closed with a screw clip. An excess of approximately *N* hydrochloric acid, usually about 5 ml, is dropped cautiously on the carbonate material from the tap funnel. When the first reaction has

subsided, the flask is shaken with a rotary movement for 3 minutes and then set aside for 5 hours, for bone or other resistant material, with occasional shaking to break the carbonate film.

Afterwards the vacuum is broken and, according to the original method, the barium carbonate is filtered on a Gooch crucible before the excess of hydroxide is titrated with 0·1 *N* hydrochloric acid, phenolphthalein being used as indicator. The same equipment and procedure was used by Robinson[13] for soils, limestones and marls. Materials containing much

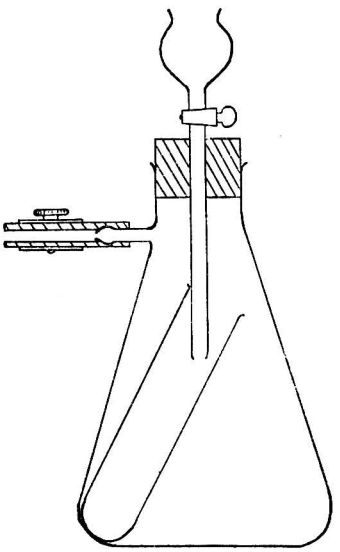

Fig. 1. Van Slyke's apparatus

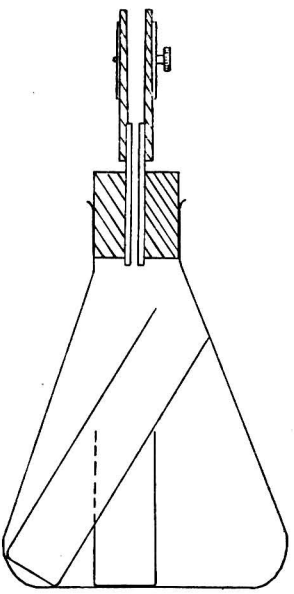

Fig. 2. Simplified apparatus

carbonate should be covered with water in the tube, a drop of octyl alcohol being added to minimise frothing when the acid is admitted. For soils containing little carbonate he suggested placing the sample in the flask and the barium hydroxide in the tube.

Independently, Hepburn[34] devised an almost identical form of apparatus and used approximately 3 *N* hydrochloric acid for decomposition and 50 ml of 0·1 *N* barium hydroxide solution as absorbent. For resistant materials the flask was allowed to stand overnight and the excess of hydroxide was then titrated directly in the flask with 0·1 *N* oxalic acid solution, phenolphthalein being used as indicator. The accuracy claimed for the method was $\pm$0·5 per cent.

The same principle underlies the well-known micro-diffusion method of analysis developed by Conway.[35]

Part 2. Proposed Method

Preliminary investigations

The authors required a convenient method for the determination of carbonate in amounts equivalent to 1 to 100 mg of carbon dioxide in such diverse materials as bones, fresh intestinal contents from experimental animals, feeding stuffs, soils and liming materials. For some materials the yields of carbon dioxide are minute, yet most of the foregoing methods are not designed primarily for dealing with small amounts. A Van Slyke - Neill apparatus was not available, and it did not appear feasible to use Conway's micro-method because of the difficulty of drawing small representative samples from such heterogeneous materials. Therefore recourse was made to the Van Slyke type of apparatus shown in Fig. 1.

Preliminary trials were made with measured volumes of a standard sodium carbonate solution placed in the tube with the absorbent in the flask, and then with solution and absorbent interchanged. Initially, 0·2 *N* barium hydroxide solution was used as absorbent and the excess was titrated with hydrochloric acid, a mixed indicator solution of thymolphthalein and phenolphthalein being used, as suggested by Conway. The surface of the

absorbent became coated with a film of barium carbonate and, although this could be broken by repeatedly shaking the flask, in the narrow tube it quickly reformed and prevented complete absorption. Attempts were made to avoid this caking by adding various reagents to the absorbent, but neither synthetic surface active agents nor glycols proved successful. Of the various alcohols tried only ethyl alcohol gave any promise. By adding an equal volume of rectified spirit to the 0·1 *N* barium hydroxide solution just before evacuation, caking was prevented, but this procedure could not be adopted because absorption of carbon dioxide was not quantitative in the presence of alcohol.

In view of this difficulty and because it seemed desirable to retain the absorbent in a tube for convenience of titration, it was decided to use sodium hydroxide instead. Winkler's procedure was first used for titration, barium chloride solution being added to precipitate carbonate, but results were variable with standard carbonate solutions and it was discontinued. It appears difficult to ensure the right conditions for precipitation of the normal barium carbonate, although greater success might possibly have been secured with strontium chloride in place of barium chloride, as used by Benedetti-Pichler, Cefola and Waldman.[36] Instead, titration of the absorbent in two stages was investigated and finally adopted, as described later. This gave satisfactory results when a good vacuum was maintained in the flask overnight, but all too frequently air leaked in. Eventually the simpler form of apparatus illustrated by Fig. 2 was devised. This arrangement embodies features from several of the methods described previously, the absorbent, carbonate material and acid all being placed within the flask before evacuation. The method has proved very successful and is described in detail below.

Method

Apparatus for release and absorption of carbon dioxide—

For quantities of carbon dioxide up to 10 *mg*—A convenient number of thick-walled 200-ml conical Pyrex flasks are selected for uniform neck dimensions to allow a long and a short tube to be placed within each flask (Fig. 2). These are supplied with well-fitting one-holed rubber stoppers (size M or N) carrying a short length of capillary tubing to which is joined about 8 to 10 cm of 2-mm bore rubber pressure tubing with a screw clip attached. Two sets of flat-bottomed specimen tubes are used, each of 19 mm ($\frac{3}{4}$ inch) diameter; the larger, in which is placed the absorbent, is 80 mm long and the smaller is cut to 60 mm long.

For quantities of carbon dioxide exceeding 10 *mg*—For larger quantities of carbon dioxide, 500-ml suction flasks are convenient, the rubber tubing being joined to the side-arm and the neck closed with a solid rubber stopper. Appropriate sizes for tubes are 25 mm (1 inch) in diameter, the larger being 127 mm (5 inches) long and the smaller either 51 mm (2 inches) or 76 mm (3 inches) long.

Reagents—

Distilled water—Boil vigorously for 20 minutes to free from carbon dioxide and protect with a soda-lime guard tube.

Sodium hydroxide stock solution—Prepare a carbonate-free stock solution containing 1 g per ml of water. Allow to stand until clear and then siphon off the supernatant liquid from the carbonate residue. About 10·5 ml of this solution diluted to 1 litre is used as a 0·2 *N* solution.

Sodium hydroxide solution for adding to intestinal contents—Dilute the stock solution with carbon dioxide-free water to give an approximately *N* solution.

Sodium hydroxide solution for absorption—Dilute the stock solution to 0·05 *N*, 0·1 *N* or 0·2 *N*, according to the amount of carbon dioxide to be determined. These solutions need not be accurately standardised, but must be protected from carbon dioxide by soda-lime guard tubes.

Hydrochloric acid—Prepare a solution for titration by dilution of A.R. concentrated acid (approximately 11 *N*) with carbon dioxide-free distilled water to a strength equivalent to the alkali absorbent. This solution must be accurately standardised.

Acid solutions for decomposition—(*i*) Perchloric acid, 20 per cent. w/w, approximately 3 *N*, for soils, etc. (*ii*) Hydrochloric acid or trichloracetic acid, approximately *N*, for bone tissue, etc.

Thymol blue indicator—Prepare a 0·1 per cent. solution by triturating 1 g of thymol blue with 21·5 ml of 0·1 *N* sodium hydroxide and dilute to 1 litre with water.

Screened methyl orange indicator—Prepare a solution containing 0·2 per cent. of methyl orange and 0·28 per cent. of xylene cyanol FF in 50 per cent. ethanol.

Standard sodium carbonate solution—Prepare from A.R. anhydrous sodium carbonate heated in an electric muffle at 270° C for half an hour. Dissolve 9·6355 g in 1 litre of water, to give a solution equivalent to 4 mg of carbon dioxide per millilitre. This solution is further diluted as desired.

These solutions readily absorb atmospheric carbon dioxide and must be protected with soda-lime guard tubes.

Buffer solutions—(*i*) 0·05 *M* potassium hydrogen phthalate adjusted to pH 3·8 with hydrochloric acid. (*ii*) 0·05 *M* borax adjusted to pH 8·2 and 8·3 with hydrochloric acid.

PROCEDURE FOR RELEASE AND ABSORPTION OF CARBON DIOXIDE—

All glassware is thoroughly cleaned in chromic acid mixture, washed and dried before use.

For 1 to 10 mg of carbon dioxide in small flasks—

(*i*) If no more than about 2 g of dry powdered material is to be taken, weigh the sample into the short tube and insert it in the flask into which 10 to 25 ml of decomposition acid has been measured with a pipette. For this operation hold the flask at an inclined angle in one hand and gently slide the tube into an upright position with the aid of the index finger of the other hand. Finally, carefully introduce the larger tube, containing 5 ml of 0·05 *N* or 0·1 *N* sodium hydroxide solution for absorption, and then insert the rubber stopper in the neck of the flask after wetting it with distilled water to obtain a good seal. To minimise errors due to absorption of carbon dioxide from the air in the flask, *immediately* connect the rubber tube to a suction line operated by a vacuum pump or water jet and evacuate the flask until small bubbles of gas arise in the absorbent. At this point, corresponding to a pressure of about 5 cm of mercury, close the screw clip and disconnect the suction line. Tilt the flask to overturn the smaller tube and allow the contents to react with the acid. Ensure thorough mixing by gentle swirling and set the flask aside overnight for 18 hours to allow complete absorption. A ring of water placed around the stopper helps to maintain the seal.

The sodium hydroxide solution should be measured into the larger tube just before evacuation; it is convenient to draw each aliquot from a flask in which the solution is protected from the atmosphere by a layer of petroleum ether. If possible, it is convenient for one worker to measure the sodium hydroxide solution while another evacuates the flasks, when a batch of analyses is being made.

(*ii*) If the material is so bulky and low in carbonate content that a large sample must be taken, weigh it into the flask and place 5 ml of acid in the short tube. For dry materials, such as feeding stuffs, add 10 to 20 ml of carbon dioxide-free water to ensure thorough wetting and mixing with the acid, provided that there is no risk of losing carbon dioxide from the wetted material. Follow the remainder of the procedure as usual. With wet material, such as intestinal contents, no extra water is needed, but the operations should be performed without delay to avoid loss of carbon dioxide or gain from the atmosphere. Samples of intestinal contents that are liable to lose carbon dioxide during evacuation of the flasks should be made alkaline with 5 ml of approximately *N* sodium hydroxide added to about 5 g of wet material in the flask. After evacuation and mixing with 5 ml of 20 per cent. perchloric acid solution a sufficiently large excess of acid remains.

For more than 10 mg of carbon dioxide—

For soils and ground limestone samples 500-ml flasks are used, but essentially the same procedure is followed. Weigh from 0·5 to 5 g of soil into the flask, depending on the carbonate content. Place 10 ml of 20 per cent. perchloric acid solution in the smaller tube and 20 ml of 0·2 *N* sodium hydroxide in the larger one. Theoretically this amount allows for the absorption of 88 mg of carbon dioxide to the sodium carbonate stage.

For soils with a very low carbonate content more than 5 g can be taken and a larger volume of acid (15 or 20 ml) used to ensure thorough mixing. The use of reducing agents in the acid solution has not been examined, as it was considered that the error due to decomposition of organic matter would be very small under these conditions.

Whichever procedure is followed, blank determinations on the reagents must be carried out in duplicate or, preferably, triplicate for each batch of analyses.

After the flask has stood overnight, release the vacuum by unscrewing the clip on the inlet tube. Originally carbon dioxide-free air was admitted through an absorption tube,

but this proved unnecessary provided the titration was performed immediately. A convenient precaution is to add 1 or 2 ml of petroleum ether to the absorption tube as soon as the flask is opened. This serves to protect the solution from atmospheric contamination and to prevent the escape of carbon dioxide during the first stage of the titration.

TITRATION PROCEDURE—

To the small tubes containing 5 ml of absorbent, add 4 drops of thymol blue indicator and titrate the solution to the bicarbonate stage with hydrochloric acid of appropriate strength. It is convenient to use a 5-ml burette with a rubber tube and pinchcock connected to a capillary jet of sufficient length to reach to the bottom of the tube. Add the acid in small amounts until the indicator begins to change colour from blue to green. At this point make further additions very carefully, use the jet itself for stirring, and allow adequate time after each addition. Match the colour against two standard tubes of the same dimensions containing about the same volumes of the indicator and buffer solutions adjusted to pH 8·3 and 8·2 respectively. At least one minute should elapse between the addition of the last fractions of acid required to bring the colour to between those of the two standards. The standards can be used for some time provided that the tubes are kept well stoppered and are stored in the dark when not in use. If the end-point is overshot it may be quickly recovered by a small addition of carbonate-free sodium hydroxide solution. Record the volume of acid required for this first titration, and then add 2 drops of screened methyl orange indicator to the tube before continuing the titration rapidly to the second stage. For this end-point, match the tube with a tube of buffer solution at pH 3·8. We have found it convenient to use a separate 2-ml or 5-ml burette for this second titration to avoid errors due to draining of the first burette on standing. Alternatively, a micro-burette of Rehberg or Conway type could be used with acid of suitable strength.

For the larger tubes the same procedure is followed, except that 10 drops of thymol blue and 5 drops of screened methyl orange indicator are adequate for 20 ml of absorbent. It is best to agitate the solution with a glass rod with a flat circular disc at the end; care must be taken not to break the surface of the petroleum ether layer during the first stage of the titration. It is convenient to use 25-ml and 10-ml burettes and, if desired, these may be of a self-levelling type, connected with a reservoir.

CALCULATION—

The carbon dioxide content is represented by the second titration value.

(*i*) $NaOH + Na_2CO_3 + 2HCl \rightarrow 2NaCl + NaHCO_3 + H_2O$ (pH 8·3)

(*ii*) $NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$ (pH 3·8)

From equation (*ii*), 1 ml of N hydrochloric acid $\equiv$ 44 mg of carbon dioxide.

A correction must be made for the blank on the apparatus and reagents. Hence—

Carbon dioxide content $= 44x(y - z)$ mg,

where x = normality of acid

y = millilitres of acid used in second titration

z = mean value for blank in millilitres.

If the volume of standard sodium hydroxide solution is carefully measured by pipette, the total volume of acid used for the titration will be the same each time within the limits of experimental error. For routine operation it is therefore unnecessary to perform the second stage of the titration once the mean values for the total titration and the blank have been determined. Alternatively, the acid used for the first part of the titration need not be recorded in routine work. However, it is safest to record both titrations because they afford a useful check on the accuracy of working, particularly if some acid should perchance be carried into the absorption tube as spray or splash. This we have found to happen only very occasionally during many determinations, but even so, provided an excess of alkali remains in the tube, the second titration is unaltered and the result is valid.

DISCUSSION OF TITRATION PROCEDURE

The procedure adopted is essentially that devised by Warder[37] and developed by Brown and Escombe.[23] It has been fully described and discussed by Kolthoff and Stenger[38] in their textbook of Volumetric Analysis. A careful examination of the method was made by

Benedetti-Pichler, Cefola and Waldman[36] and also by Shaw and MacIntire.[30] Since the accuracy of this method for the determination of carbonates depends so largely on the estimation of the carbon dioxide absorbed by sodium hydroxide solution it is worth considering the main features of the titration.

TITRATION TO THE BICARBONATE STAGE—

According to Kolthoff and Stenger the pH of sodium bicarbonate solution is 8·35 whether the solution is 0·1 *N* or 0·01 *N*, but other workers have accepted values as low as 8·2 for the equivalence point. Because the inflexion point of the titration curve is not very sharp, phenolphthalein and thymolphthalein are not very suitable indicators. Thymol blue is more satisfactory, but it is still necessary to employ a solution of the indicator at known pH for matching the end-point of the titration. Some workers have used sodium bicarbonate solution for this purpose, but it is not stable and readily loses carbon dioxide with a consequent rise in pH value. It is convenient to use two comparison tubes of borate buffer solution adjusted to pH 8·3 and 8·2 respectively. These show a distinct colour difference with thymol blue when viewed against a white background, the lower value being more

TABLE I

RECOVERY OF CARBON DIOXIDE FROM SODIUM CARBONATE SOLUTIONS

	Carbon dioxide, mg	Recovery, %	Number of determinations	Standard deviation	Coefficient of Variation
(*a*)	*With small flasks*—				
	1	100·7	8	0·012	1·22
	2	100·4	9	0·023	1·15
	3	100·5	9	0·018	0·61
	5	100·2	9	0·004	0·07
	10	100·5	8	0·029	0·29
(*b*)	*With large flasks*—				
	12·5	100·4	9	0·120	0·96
	40	100·3	8	0·186	0·46
	66	99·4	10	0·626	0·60
	82·5	99·2	8	0·295	0·36

yellow than green. Alternatively, the indicator mixture of Simpson[39] may be used. This contains 6 volumes of 0·1 per cent. thymol blue to 1 volume of 0·1 per cent. cresol red and changes colour sharply from violet at pH 8·4 to blue at 8·3 and rose at 8·2. However, the presence of cresol red renders the end-point with methyl orange at the second stage of the titration somewhat less distinct.

It is most important to realise that the reaction proceeds relatively slowly, especially as the end-point is approached and the addition of hydrochloric acid forms carbonic acid locally in the solution. The dehydration reaction, $H_2CO_3 \rightarrow H_2O + CO_2$, then proceeds much more readily than the formation of bicarbonate, $CO_2 + OH' \rightarrow HCO_3'$. Consequently the titration to the first stage should be performed slowly with gentle stirring to avoid local concentrations of acid. When the end-point is almost reached, about 1 minute should elapse between the last two additions. Benedetti-Pichler, Cefola and Waldman showed the need to prevent loss of carbon dioxide from the system and recommended that a stoppered flask be used as the titration vessel. In the present investigation good results were obtained in narrow titration tubes by having the surface of the alkali solution protected with a layer of petroleum ether and directing the tip of the capillary jet to the bottom of the tube.

TITRATION TO THE CARBONIC ACID STAGE—

Originally, Warder[37] removed carbon dioxide by boiling the solution with an excess of acid, but Brown and Escombe[23] used methyl orange as indicator for the direct titration of the bicarbonate. The second inflexion point of the titration curve occurs around pH 4, but it becomes less sharp as the concentration of carbonate is decreased and it is also influenced by the amount of carbon dioxide retained in solution. Cooper[40] demonstrated that the pH value of the equivalence point approached 5 at very great dilutions, such as occur in natural water. We have found for concentrations of the order of 0·1 *N* that screened methyl

orange is satisfactory when used in conjunction with a comparison tube containing phthalate buffer solution adjusted to pH 3·8. Vigorous stirring to facilitate removal of carbon dioxide sharpens the end-point.

Results

The accuracy of the method described was first established with standard solutions of sodium carbonate, and a summary of the results obtained is shown in Table I.

Further, the method has been used for extensive analyses on various materials, and a comparison with other methods was made on samples of bone and soils.

With the small flasks, replicate determinations were made of the carbon dioxide content of a standard sample of powdered bone kindly supplied by Dr. A. E. Sobel of the Jewish Hospital, Brooklyn, U.S.A. The results, given in Table II, show close agreement with his value obtained with the Van Slyke - Neill apparatus.

With the larger flasks, a group of ten soil samples, air-dried and passed through a 40-mesh sieve, were analysed for their carbonate content, and the results agreed closely with the values obtained gravimetrically with a Schrötter tube, as shown in Table II.

Table II

Determination of carbonate in bone and soils

(*a*) *In powdered bone, with small flasks and N hydrochloric acid for decomposition*—

Bone sample	Weight, mg	Carbon dioxide, %
1	29·6	3·397
2	29·9	3·274
3	32·8	3·306
4	37·3	3·327
5	42·4	3·439
6	45·8	3·274
7	52·0	3·263
8	62·2	3·288
9	99·7	3·375
10	117·2	3·384
11	126·9	3·333
12	149·6	3·292

Mean carbon dioxide content, 3·329 per cent.; Std. dev., 0·053. Coefficient of Variation, 0·456.

By Van Slyke - Neill—Mean carbon dioxide content, 3·315 per cent. ±0·0157.

(*b*) *In soils, with larger flasks and 20 per cent. perchloric acid*—

Soil sample	Calcium carbonate: By titration method, %	Calcium carbonate: By Schrötter tube, %	Deviation, %
1	0·00	0·002	−0·002
2	0·010	0·013	−0·003
3	0·020	0·016	+0·004
4	0·020	0·018	+0·002
5	1·19	1·17	+0·08
6	1·82	1·85	−0·03
7	2·24	2·23	+0·01
8	7·08	7·06	+0·02
9	32·50	32·22	+0·28
10	46·80	46·63	+0·17

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DEPARTMENT OF AGRICULTURAL CHEMISTRY
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October, 1950

The Colorimetric Determination of Palladium with 2-Mercapto-4:5-dimethylthiazole

BY D. E. RYAN

A method is described for the determination of palladium based on the colour produced by its reaction with 2-mercapto-4:5-dimethylthiazole. Rhodium and gold in amounts up to 10 μg per ml do not interfere. Iridium ($IrCl_6''$) solutions are nearly completely decolorised; large amounts of iridium, therefore, do not interfere. Platinum interferes, but an extraction procedure that permits small amounts of palladium to be separated quickly and easily from platinum, iridium and rhodium is described.

WHILE investigating the use of 2-mercapto-4:5-dimethylthiazole for the colorimetric determination of rhodium[1] it was found that palladium interfered by reacting to give a colour similar to that for rhodium. Further investigation has shown that this reaction can be used to determine palladium colorimetrically. It is practically instantaneous and is independent of the amount of reagent present provided that an excess is used. It is not sensitive to variations in the acidity of the solution or in the concentration of salts present. The reaction is selective in that platinum is the only platinum metal causing serious interference; this interference is easily eliminated, moreover, by an extraction procedure that allows small amounts of palladium to be separated from large quantities of the platinum metals.

Maximum absorption, as with rhodium, occurs in the ultra-violet, but excellent results can be obtained in the visible region of the spectrum. A Spekker photo-electric absorptiometer, with an Ilford No. 601 filter (maximum transmittancy at 430 mμ), was used to obtain the data below.

The colour developed in aqueous solution is stable for a time, but the palladium complex has a tendency to precipitate, particularly with increasing palladium concentration. Samples containing 2 μg of palladium per millilitre show less than 5 per cent. deviation in the values for optical density after 12 hours, whilst those containing 8 μg per ml are stable for less than 15 minutes. The difficulty is overcome by making the solution 20 per cent. v/v in ethyl alcohol; under these conditions the following optical densities were obtained for a solution containing 8·6 μg of palladium per millilitre—

Time	5 min.	30 min.	1 hour	2 hours	20 hours
Optical density	0·548	0·548	0·549	0·548	0·546

The amount of alcohol added should be closely controlled as the optical density decreases with increasing alcohol concentration; solutions containing 8·6 μg of palladium per millilitre gave the following optical densities at various alcohol concentrations—

Alcohol concentration, %	0	5	10	20	30
Optical density	0·590	0·576	0·565	0·543	0·517

The maximum concentration that can be used with a 1·00-cm cell is 15 μg of palladium per millilitre, whilst a concentration of 0·5 μg per ml gives a minimum transmittancy of 92 per cent.

Method

Reagents—

2-Mercapto-4:5-dimethylthiazole—The reagent solution was prepared as previously described.[1]

Standard palladium solution—Palladium sponge was dissolved in aqua regia, the nitric acid removed by evaporating to dryness several times with concentrated hydrochloric acid, and the residue finally dissolved in a solution containing 1 ml of concentrated hydrochloric acid per litre. This solution, standardised by the dimethylglyoxime method, contained 0·862 mg of palladium per millilitre. Suitable concentrations were prepared by diluting this standard with a solution containing 1 ml of concentrated hydrochloric acid per litre.

Procedure—

Measure palladium samples into 100-ml volumetric flasks, add about 2 ml of concentrated hydrochloric acid and 20 ml of 95 per cent. ethyl alcohol, and dilute to about 70 ml. Add the reagent (1 ml is sufficient for each 5 μg of palladium present per millilitre) and dilute to the mark with distilled water. The optical density can be measured immediately.

The optical densities for solutions under varying conditions are shown below. These results were obtained with 1·8 μg of palladium per millilitre and show that variations in the acid, reagent, or salt concentration have little effect on the sensitivity.

Condition	Optical density
100 *ml of solution containing*—	
1 ml of hydrochloric acid	0·133
5 ml of hydrochloric acid	0·129
20 ml of hydrochloric acid	0·132
5 ml of hydrochloric acid + 5 ml of sulphuric acid	0·132
5 ml of hydrochloric acid + 3 ml of nitric acid (nitrous-free)	0·130
1 ml of reagent	0·134
6 ml of reagent	0·133
0·2 *M* ammonium chloride	0·132

Fig. 1 shows that the system deviates from Beer's law. This deviation was found also in solutions in which no alcohol was present.

Composition of complex—

The palladium complex with 2-mercapto-4:5-dimethylthiazole was precipitated from a neutral solution. The average value obtained for the palladium content, on analysis of the complex dried in a desiccator over silica gel, was 27·9 per cent. This suggests that the palladium complex is $(C_4H_6NSCS)_2Pd$, which contains 27·0 per cent. of palladium.

EFFECT OF VARIOUS IONS—

The reactions of various cations with 2-mercapto-4:5-dimethylthiazole have been previously described.[1] Under the conditions of reaction with palladium, however, the following differences should be noted. Rhodium does not react and does not interfere except for the colour of the rhodium solution itself; this becomes troublesome above 10 μg of rhodium per millilitre. Iridium solutions are almost completely decolorised and palladium can be determined without interference in solutions containing 35 μg of iridium per millilitre. Gold is not precipitated from solutions containing 10 μg per ml and palladium can be determined without interference at such gold concentrations; attempts to eliminate interference from gold at high concentrations by precipitating the gold complex in aqueous medium and filtering were unsuccessful owing to loss of palladium. Platinum interferes by giving a yellow colour or precipitate and must be absent.

No interference was noted when 200 μg per ml of the following ions were present in solutions containing 2 μg of palladium per ml: NO_3', $C_2H_3O_2'$, F', Cl', Br', I', SO_4'', SO_3'', C_2O_4'', PO_4''', ClO_3', AsO_4''', $K^{\cdot}$, $Na^{\cdot}$, $NH_4^{\cdot}$, $Pb^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot\cdot}$. Particularly noteworthy are the non-interferences of iodide and stannous tin, which have been used as drop reagents for detecting palladium.

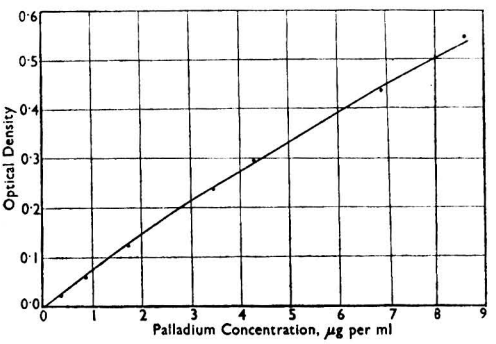

Fig. 1. Deviation from Beer's law

Cyanide and carbonate must be absent as they inhibit the reaction; even 2 μg of cyanide per millilitre gives results that are low by 20 per cent. Nitrite interferes by reacting with the reagent to give a greenish-yellow colour and must be absent.

SEPARATION OF PALLADIUM FROM PLATINUM, RHODIUM AND IRIDIUM—

Palladium can be separated from platinum by applying the hydrous oxide method of Gilchrist and Wichers[2] to quantities of the order of 5 μg. This method was used to separate palladium before determining it colorimetrically with 2-mercapto-4:5-dimethylthiazole and

TABLE I

DETERMINATION OF PALLADIUM WITH 2-MERCAPTO-4:5-DIMETHYLTHIAZOLE

Palladium taken, μg per ml	Palladium found, μg per ml	Other metal present, μg per ml
2·2	2·2	10 Au, as $AuCl_4'$
8·6	8·7	20 Au "
2·2	2·3	35 Ir, as $IrCl_6''$
8·6	8·6	20 Ir "
2·2	2·2	10 Rh, as $RhCl_6'''$
4·3	4·4	15 Rh "
1·7	1·8	10 Rh.* Hydrous oxide procedure used
1·7	1·7	20 Ir* " " "
1·7	1·7	20 Pt Hydrous oxide procedure used to separate Pt
1·7	1·8	10 Ir + 20 Pt* " " "
1·7	1·9	10 Rh + 20 Ir + 20 Pt* " " "

* Rhodium and iridium precipitate with the palladium; good results are obtained, however, on applying the hydrous oxide procedure to solutions containing the concentrations shown.

was primarily as that given by Yoe and Overholser.[3] Since, however, palladium is determined in acid solution with this reagent there was no necessity to evaporate to dryness after dissolving the oxide in hydrochloric acid. In obtaining the results shown in Table I, when applying the hydrous oxide procedure, it was necessary to boil the solutions vigorously for 15 minutes to eliminate the greenish-brown colour obtained on first dissolving the dioxides.

The hydrous oxide procedure accomplishes a separation from platinum only. The possibility of separating palladium from platinum, iridium and rhodium was suggested in a previous paper by Ryan[4] in which the palladium was allowed to react with *p*-nitrosodiphenylamine and the palladium complex extracted with an organic solvent. Results shown in Table II prove that small amounts of palladium can be separated in this manner.

Procedure—Evaporate the platinum metal solution to dryness on a steam-bath and dissolve the residue in 10 ml of water containing one drop of concentrated hydrochloric acid. Add 3 to 4 ml of a 0·005 per cent. solution of *p*-nitrosodiphenylamine and, after 10 minutes, extract with 10 ml of ethyl acetate or chloroform. Repeat the reagent addition and extraction and combine the two extracts. Evaporate to dryness, add 5 ml of concentrated sulphuric acid and heat until the organic matter is well charred before adding nitric acid to destroy organic matter completely. Since nitrous acid is liberated in this operation and this is a positive interference in the determination, it must be completely removed; this is ensured by fuming at least twice, washing down the sides of the beaker after each fuming. Cool, dilute and determine the palladium with 2-mercapto-4:5-dimethylthiazole.

In extracting the palladium complex, the colour of the organic layer is a good guide to the completeness of extraction; a yellow colour of reagent appearing in this layer rather than the red of the complex indicates complete extraction. It is advisable to let the aqueous layer that wets the walls of the separatory funnel drain down, after nearly all the aqueous layer has been drawn off, in order to remove the last few drops; since two extractions are made it is convenient to have two funnels available. Although both chloroform and ethyl acetate were used in this work, the latter is preferred as there is less tendency to form emulsions or for the complex to gather at the interface.

TABLE II

DETERMINATION OF PALLADIUM WITH 2-MERCAPTO-4:5-DIMETHYLTHIAZOLE AFTER SEPARATION (BY EXTRACTION AS ITS *p*-NITROSODIPHENYLAMINE COMPLEX) FROM PLATINUM, RHODIUM AND IRIDIUM

Palladium taken, mg	Palladium found, mg	Other metal present, mg
0·172	0·172	4 Pt
0·172	0·170	10 Pt
0·085	0·087	6 Pt
0·085	0·082	5 Ir
0·085	0·084	5 Rh
0·034	0·034	10 Rh
0·018	0·018	4 Pt
0·018	0·019	5 Rh
0·018	0·018	5 Ir
0·018	0·017	5 Pt + 5 Rh + 3 Ir
0·022	0·023	5 Pt + 5 Rh + 3 Ir
0·022	0·023	5 Pt + 5 Rh + 3 Ir
0·007	0·007	4 Pt
0·007	0·007	5 Rh + 5 Ir

The author thanks Mr. L. S. Theobald for his encouragement and help in this work. Sincere appreciation is expressed to Lord Beaverbrook for providing the scholarship, through the Beaverbrook Overseas Scholarship Fund, which enabled this work to be completed.

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DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY
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October, 1950

The Analysis of Manganese Bronze

By GEORGE NORWITZ

A new method is proposed for the analysis of manganese bronzes. The sample is dissolved in a mixture of perchloric and nitric acids, hydrogen peroxide is added, and the copper and lead electrolysed. Manganese, nickel, iron, aluminium and tin are determined on aliquot parts of the electrolyte.

The methods that have been proposed[1,2,3,4,5] for the analysis of manganese bronze require many time-consuming operations such as filtrations and hydrogen sulphide precipitations. In this paper a method is proposed for the analysis of manganese bronze that entirely eliminates filtrations and hydrogen sulphide precipitations. The time required is one-quarter of that required for the most rapid of the older methods. It is based on the observation by the author that copper and lead can be separated by electrolysis from as much as 2 per cent. of tin by the use of a perchloric - nitric acid electrolyte. After the copper and lead have been separated by electrolysis, the manganese, nickel, iron, aluminium and tin are determined on aliquots of the electrolyte by means of conventional procedures.

Apparatus and reagents—

A Klett - Summerson photo-electric colorimeter.

Platinum gauze cathodes—Height 50 mm, diameter 45 mm and *platinum spiral anodes* (with a spiral width of 10 mm).

Benzoic acid solution—A 10 per cent. solution in methanol.

Buffer solution—Mix 470 ml of ammonium hydroxide and 430 ml of glacial acetic acid. Cool to room temperature and add more acid or base as necessary to make the pH value lie between 5·25 and 5·35 when 1 volume is diluted to 20. Dilute to 1 litre.

Gelatin solution—A 1 per cent. w/v solution.

Aluminon reagent—Dissolve 0·3 g of aluminon in 200 ml of water and add 60 ml of benzoic acid solution (10 per cent.). Dilute to 300 ml, add 300 ml of buffer solution and 300 ml of gelatin solution and shake. Allow to stand for 3 days before using. The reagent will keep for at least 2 months if stored in a dark place.

Procedure

Copper and lead—Take 1 g of the sample in a 300-ml electrolytic beaker. Add, in the following order, 5 ml of water, 10 ml of perchloric acid and 10 ml of nitric acid. Allow the sample to dissolve without heating (this will take about a minute). Add 1 ml of 30 per cent. hydrogen peroxide to oxidise the lower oxides of nitrogen, mix and dilute to 190 ml with water. Electrolyse for copper and lead at 2 amperes per square decimeter for 75 to 90 minutes. During the electrolysis stir the solution by suitable means. Immerse the electrodes in water and in alcohol. Dry the cathodes at 110° C for 3 minutes, cool and weigh the deposit as metallic copper. Dry the anodes at 110° C for 15 minutes, cool and weigh the deposit as PbO_2. The factor for converting PbO_2 to Pb is 0·866.

Manganese—Dilute the electrolyte from the copper and lead determinations to 250 ml. Pipette 25 ml into a 100-ml graduated flask, add 5 ml of 85 per cent. phosphoric acid and 0·5 g of potassium periodate. Heat to boiling and boil gently for 15 minutes. Cool to room temperature and dilute to 100 ml. Measure the absorption at 540 millimicrons in a photo-electric absorptiometer (1-cm cell) that has been set to zero against water. Convert the readings to percentage of manganese by means of a graph prepared from standard permanganate solution.

Nickel—Transfer 10 ml of the test solution to a 100-ml graduated flask, add 5 ml of 10 per cent. citric acid solution, 5 ml of bromine water and 5 ml of diluted ammonium hydroxide solution (1 + 1). Mix after the addition of each reagent. Add 3 ml of a 1 per cent. alcoholic solution of dimethylglyoxime and dilute to 100 ml with water. Measure the absorption at 540 millimicrons in a photo-electric absorptiometer (1-cm cell) that has been

set to zero against water. Convert the readings to percentage of nickel by means of a graph prepared from standard nickel solution.

Iron—Pipette 10 ml of the test solution into a 100-ml graduated flask and add 1 ml of 3 per cent. hydrogen peroxide. Add 25 ml of 10 per cent. ammonium thiocyanate solution and dilute to 100 ml with water. Measure the absorption at 470 millimicrons in a photo-electric absorptiometer (1-cm cell) that has been set to zero against water. Convert the readings to percentage of iron by means of a graph prepared from standard iron solution.

Aluminium[6,7]—Pipette 25 ml of the test solution into a 200-ml graduated flask. Dilute to the mark and pipette a 5-ml aliquot into a 100-ml graduated flask. Add $15 \pm 0{\cdot}5$ ml of the aluminon reagent from a pipette. Do not allow the aliquot or the aluminon reagent to run down the neck of the flask. Heat on the steam-bath for 20 minutes in such a way that the steam comes in contact with the sides of the flask. Cool and dilute to 100 ml. Measure the absorption at 540 millimicrons in a photo-electric absorptiometer (4-cm cell) that has been set to zero against a reagent blank. Read from a graph prepared from pure aluminium solution the percentage of aluminium represented by the combined aluminium and iron colours, and then make a correction for the iron. The iron colour was found by the author to be 0·364 times as intense as the aluminium colour. The exact ratio should be determined by each laboratory by means of standard aluminium and iron solutions.

Tin—Measure 150 ml of the test solution into a 500-ml Erlenmeyer flask. Add 20 ml of sulphuric acid and evaporate to fumes. Continue to fume strongly for a few minutes to drive off the perchloric acid. Allow to cool, add 150 ml of water and 45 ml of hydrochloric acid and reduce with lead in the usual way.[8] Titrate with 0·01 *N* iodine solution from a short accurately-calibrated burette.

Results

The results obtained by the author in analysing two representative manganese bronzes by the above method are shown in Table I.

Table I

Results for two samples of manganese bronze

	Present,* %	Found, %
	Sample 62*b*	
Copper	57·39	57·40, 57·37, 57·39
Lead	0·28	0·29, 0·27, 0·28
Manganese	1·29	1·28, 1·29, 1·29
Nickel	0·27	0·27, 0·27, 0·26
Iron	0·82	0·82, 0·82, 0·81
Aluminium	0·97	0·98, 0·95, 0·96
Tin	0·96	0·98, 0·96, 0·95
	Sample R	
Copper	56·82	56·86, 56·82
Lead	0·18	0·18, 0·17
Manganese	0·98	0·97, 0·98
Nickel	0·02	0·02, 0·02
Iron	1·02	1·02, 1·01
Aluminium	0·88	0·86, 0·89
Tin	0·34	0·37, 0·34

* Values for 62*b* are National Bureau of Standards certified values; values for sample R were obtained by using A.S.T.M. umpire methods.[1]

Notes—

The samples must be dissolved without heating, otherwise some metastannic acid may precipitate. It is essential that 30 per cent. hydrogen peroxide be used to oxidise the lower oxides of nitrogen. The use of the equivalent amount of 3 per cent. hydrogen peroxide is not satisfactory, since this grade usually contains sufficient phosphate (added as a preservative) to interfere with the deposition of lead dioxide.

When spiral anodes are used there is no appreciable contamination of the lead dioxide by manganese dioxide.

The method described is designed for the analysis of the MnC type of manganese bronze. This is the type usually encountered in commerce. It has maximum permissible limits of 1·5 per cent. of manganese, 0·35 per cent. of lead and 1·0 per cent. of tin.

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Notes

THE CHROMATOGRAPHIC ESTIMATION OF AQUEOUS SOLUTIONS OF ACIDS

THE separation and estimation of the lower fatty acids is easily effected by partition chromatography.[1] One slight difficulty is that acids in aqueous solution have to be transferred to a solvent before being placed on the column. It has been found possible to eliminate this step by mixing an aliquot of the aqueous solution with a small amount of silica gel and then adding this to the top of the column.

PROCEDURE—

Prepare the column by adding dilute hydrochloric acid to silica gel,[1] forming it into a sludge with chloroform and packing it into the tube with a tightly-fitting glass piston. Place a circle of

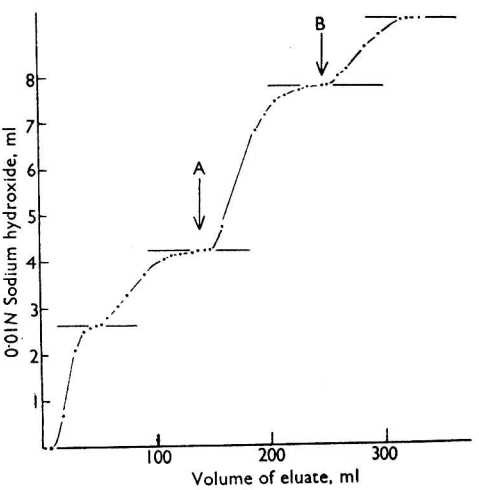

Fig. 1. Titration curve of acidity of eluate

filter-paper on the top of the column. Take a quantity of silica gel, about 5 to 10 per cent. of that used for the column, and add to it an aliquot of the aqueous solution so that the silica gel remains powdery after the addition. The aliquot should contain 0·001 equivalent of total acid. With a spatula, mix the solution and the silica gel thoroughly in a small beaker. Tap the powder on to a folded filter-paper and thence on to the column. There should be just enough chloroform above the column to cover the surface after the extra silica gel has been added. Press the surface firmly with the glass piston, add three 1-ml portions of chloroform to wash in the acids and then develop the column in the usual way, titrating the eluate with 0·01 *N* sodium hydroxide solution.

The method has been found to work well for the routine estimation of mixtures of butyric, propionic, acetic and formic acids. The result of a typical separation of these acids is shown in Fig. 1.

In this experiment a column containing 10 g of silica gel was used. The eluate from the column was titrated continuously with 0·01 *N* sodium hydroxide solution; a stream of air, free from carbon

dioxide, was bubbled continuously through the mixture of eluate and water. The solvents used were: chloroform up to the point A, chloroform containing 5 per cent. of butanol by volume up to B, and benzene containing 10 per cent. of butanol by volume beyond B. The acids appear in the order butyric, propionic, acetic and formic. The quantitative results were—

Acid	Found, %	Taken in mixture, %
Butyric	28·1	28·4
Propionic	15·6	15·1
Acetic	39·1	39·5
Formic	17·2	17·1

I should like to thank the Directors of the Distillers Company Limited for permission to publish this note.

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THE DISTILLERS COMPANY LTD.
RESEARCH AND DEVELOPMENT DEPT.
GREAT BURGH, EPSOM, SURREY

W. S. WISE
November, 1950

THE PHOTOMETRIC DETERMINATION OF COPPER IN ALUMINIUM ALLOYS WITH SODIUM DIETHYLDITHIOCARBAMATE

WE have examined the method described by Williams[1] for the photometric determination of copper in aluminium alloys with tetra-ethylene pentamine and, although we agree that sodium diethyldithiocarbamate may have certain disadvantages (*e.g.*, its high sensitivity) when compared with tetra-ethylene pentamine, we wish to emphasise that, in spite of this, it can be and is used successfully for the analytical control of alloying quantities of copper in a wide variety of normal industrial aluminium alloys. Moreover, in the important group of aluminium - copper - nickel alloys, interference caused by the presence of nickel is not insurmountable, as it may be reduced to negligible proportions by suitable adjustment of the ammonia concentration in the final solution. Table I shows the typical accuracy attainable in routine copper determinations carried out over a period of several months on two normal aluminium alloys. Table II shows the composition of these alloys. The results are quite satisfactory for control purposes.

TABLE I

DETERMINATION OF COPPER IN ALUMINIUM ALLOYS BY SODIUM DIETHYLDITHIOCARBAMATE

Standard result (volumetric), %	Average of routine results, %	Number of determinations	Standard deviation, σ	Standard deviation, %	Alloy
1·53	1·555	64	0·0274	1·76	HID55 (483)
1·53	1·55	39	0·0225	1·45	HID55 (483)
2·02	2·015	98	0·0522	2·58	HIDRR50 (461)
2·57	2·58	144	0·0399	1·55	HID55 (484)

TABLE II

COMPOSITION OF ALLOYS

Alloy	Cu, %	Ni, %	Mg, %	Fe, %	Si, %	Ti, %	Mn, %	Zn, %
HID55 (483) ..	1·53	1·43	1·31	0·40	1·52	0·20	0·31	0·055
HID55 (484) ..	2·57	0·92	0·78	0·88	0·92	0·15	0·50	0·10
HIDRR50 (461) ..	2·02	1·82	0·064	0·69	1·61	0·23	0·13	—

In 1945, Phillips and Edwards[2] published some results of their work on a method that used sodium diethyldithiocarbamate for the determination of copper in the presence of a wide variety of elements normally encountered in aluminium alloys. Their method was tested with particular reference to Y-alloy containing 3·5 to 4·59 per cent. of copper and 1·8 to 2·3 per cent. of nickel. With regard to nickel interference, they demonstrated that turbidity caused by this element could be avoided by ensuring a suitable concentration of ammonia in the final solution. Their

method in practice covered ranges of from 0·2 to 5 per cent. for copper and 0·2 to 3 per cent. for nickel. Typical standard deviations were given for a Y-alloy and are quite satisfactory for most purposes.

Stross[3] has also investigated the influence of large quantities of various elements likely to be present in aluminium alloys. With a 10-mg sample, the determination of from 0·5 to 2 per cent. of copper is not affected by the presence of 2 per cent. of nickel, and with a 5-mg sample 4 per cent. of nickel is without any appreciable influence on the determination of 4 per cent. of copper.

Similarly, Steele and Russell[4] have shown the efficacy of a suitable ammonia concentration in reducing the effect of nickel on the determination of copper in nickel-bearing steels and cast irons.

By way of confirmation we have recently carried out a limited number of experiments with synthetic solutions, all of which contain aluminium, together with various concentrations of copper, nickel and iron. These solutions were prepared by dissolving suitable weights of the highest purity metal available in the minimum quantity of nitric - hydrochloric acid solution. After dilution to a convenient volume in a graduated flask, aliquots representing the amounts of the above metals contained in 0·1 g of alloy sample were transferred to beakers and evaporated almost to dryness in order to remove any excess of acid. The solutions were diluted with water and filtered into 200-ml graduated flasks. From the latter, 10-ml aliquots (representing 5 mg of the alloy sample) were then transferred by means of a pipette to 100-ml graduated flasks, to each of which was added 10 ml of 30 per cent. aqueous citric acid solution, 20 to 21 ml of fresh ammonia solution, sp.gr. 0·880, cooled to 20° C, 5 ml of fresh 1 per cent. aqueous gum arabic solution, 10 ml of fresh 0·1 per cent. aqueous solution of sodium diethyldithiocarbamate and sufficient water to make up to the 100-ml mark. The extinctions were measured on the Spekker absorptiometer in a 4-cm cell with Ilford violet 601 filters and a tungsten filament lamp. The measurements were carried out immediately after the solutions were coloured. The results are shown in Table III.

With alloys, including calibration standards, 0·1 g of sample is dissolved in 10 ml of aqua regia (1 volume of hydrochloric acid + 1 volume of nitric acid) and evaporated almost to dryness. From this stage the procedure is the same as that outlined above. Blank determinations are always carried out.

TABLE III

DETERMINATION OF COPPER IN SYNTHETIC SOLUTIONS

Elements present in addition to aluminium			Observed extinction; average of two separate determinations
Copper, %	Nickel, %	Iron, %	
1·81	—	—	0·529
1·81	2·0	—	0·535
1·81	2·0	1·08	0·531
2·94	—	—	0·826
2·94	2·0	—	0·824
2·94	2·0	1·08	0·828
2·94	3·0	0·54	0·841
4·08	—	—	1·089
4·08	2·0	—	1·105
4·08	2·0	1·08	1·103

Inspection of Table III shows that variations in extinction caused by the presence of nickel and iron are quite small, and the measurements are capable of giving sufficient accuracy for control purposes. Moreover, in our laboratories, these variations are still further reduced by calibration on actual standard alloys representative of the alloys under investigation.

We wish to thank the Directors of High Duty Alloys Limited for permission to publish this note.

REFERENCES

1. Williams, L. H., *Analyst*, 1950, **75**, 425.
2. Phillips, D. F., and Edwards, L. L., *Metal Ind.*, 1945, **66**, 409.
3. Stross, W., *Metallurgia*, 1945, **32**, 257.
4. Steele, S. D., and Russell, L., *Analyst*, 1949, **74**, 105.

CENTRAL RESEARCH LABORATORIES
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E. C. MILLS
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November, 1950

Apparatus

PREPARATION OF GLASS-DISTILLED WATER

GLASS-DISTILLED water is essential for the preparation of media for microbiological assays. The apparatus shown in Fig. 1 is suitable for the production of a continuous supply of glass-distilled water and can be constructed from apparatus common in any laboratory. Water distilled in this apparatus was used in the assay of vitamin B_{12} as described by Pritchard.[1]

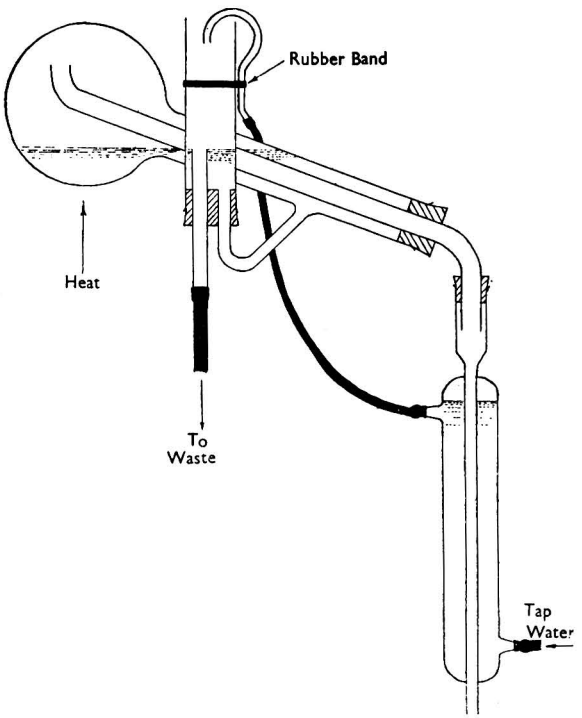

Fig. 1. Simple still for the continuous supply of glass-distilled water suitable for microbiological assays

The "boiler" consists of an ordinary distilling flask inclined at an angle of about 20° to the horizontal. The side-arm, after shortening if necessary, is bent in the form of a U-tube in a plane at right angles to the axis of the flask in such a fashion that the free limb of the U-tube is vertical when the flask is inclined downwards at an angle of about 20°.

The cylinder of a constant-level device can be made from 1½ or 2-inch diameter glass tubing or from a boiling tube, the bottom of which has been cut off. At one end it is fitted with a stout rubber bung, bored with two holes. One hole carries the bent side-arm of the flask, the other carries a wide-bore tube to lead water to waste. The height that this tube reaches into the cylinder determines the depth of the water in the distilling flask. The constant-level apparatus is completed by bending a length of tubing and attaching it by a rubber band so that one end enters the cylinder and the other is conveniently attached to the outlet of the condenser by a length of rubber tubing. The bore of the inlet should, of course, be less (about half) than that of the waste pipe.

Steam is conveyed from the flask to a vertical condenser by a wide tube fitted into the flask and condenser by rubber bungs. The end of the conduit that is in the flask must be so bent that the open end is directed away from the freely boiling surface of the water to avoid contamination from priming. The angle of this bend is determined by trial and is so made that the tube can be passed down the neck of the flask when the apparatus is assembled.

The condenser is of the ordinary single-surface type. It is more convenient to have an all-glass condenser, as thin rubber connections become rotted after the still has been working for some weeks.

In this laboratory the boiler is a distilling flask of 700-ml capacity. The steam conduit and waste tubes are 7-mm bore tubing. The cylinder of the constant level device is made from a boiling tube of 3 cm diameter and the inlet to it is made from 4-mm bore tubing.

REFERENCE

1. Pritchard, H., *Analyst*, 1951, **76**, 155.

13, HAMILTON SQUARE
BIRKENHEAD

D. R. WRAIGE
February, 1951

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1951, **76**, 244).

Public Analyst	*Appointments*
HAMENCE, Jack Hubert (Joint)	County of Rutland.
JAMES, George Vaughton	County Borough of Bath.
RYMER, Thomas Edward (Deputy)	Urban District of Merton and Morden.

OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1951, **76**, 180).

Agricultural Analyst	*Appointments*
HAMENCE, Jack Hubert (Deputy)	County of Rutland.
JAMES, George Vaughton	County Borough of Bath.

Ministry of Food

STATUTORY INSTRUMENTS*

1951—No. 314. The Meat Products and Canned Meat (Amendment) Order, 1951. Price 2d.

This Order, which came into operation on March 4th, 1951, permits the manufacture and sale of pork sausages and beef sausages of less than the prescribed minimum meat content, if the deficiency in meat is compensated by the use of milk powder in the proportion of 6 parts of milk powder to 10 parts of meat. The actual meat content may not be reduced in this way below 55 per cent. for pork sausages and 40 per cent. for beef sausages.

The Order amends the Meat Products and Canned Meat (Control and Maximum Prices) Order, 1948 (S.I., 1948, No. 1509; Analyst, 1948, 73, 341), as amended by S.I., 1949, Nos. 782, 1303 and 2045 and S.I., 1950, No. 1764 (Analyst, 1951, 76, 119), as follows—

(*a*) by adding after the definition of "Meat product" in Article 1 thereof the following definition:

"'Milk powder' means milk, partly skimmed milk or skimmed milk, buttermilk or whey which has been concentrated to the form of powder or solid by the removal of its water."

(*b*) by substituting for Article 3 thereof the following Article:

"3. A person shall not by way of trade prepare or manufacture or sell or have in his possession for sale any description of specified food mentioned in column 1 of the First Schedule to this Order the meat content of which is less than the minimum meat content prescribed as respects that description in column 2 of the said Schedule:

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

Provided that—

(i) any milk powder used in the manufacture of pork sausages, pork sausage meat and pork slicing sausage and beef sausages, beef sausage meat and beef slicing sausage shall be deemed to be equivalent to 5/3 of its own weight in meat for the purpose of assessing the meat content of any of the said products, if the quantity of such milk powder so used does not exceed 6 per cent. of the total weight of the product, and

(ii) any fat of vegetable origin used in the manufacture of beef sausages, beef sausage meat, or beef slicing sausage shall be deemed to be meat for the purpose of assessing the meat content of any of those products, if the total quantity of such fat so used does not exceed 25 per cent. of the prescribed minimum meat content of the product."

CIRCULARS MF 17/50 AND 5/51

Approved Oxidising and Preservative Agents

Circular MF 17/50 (*price* 1*d.*), *dated September* 19*th*, 1950, *refers to Circular MF* 11/50, *dated June* 27*th*, 1950 (*Analyst*, 1950, **75**, 504), *and gives the names of two further products whose use for the cleansing of milk tankers, vessels or appliances has been approved by the Minister of Agriculture and the Minister of Food.*

Circular MF 5/51 (*price* 2*d.*), *dated March* 1*st*, 1951, *gives the names of three further products similarly approved.*

The further list of products is as follows—

CLORFECT, UNIVPURI CHLORSOL, DUROS, GASCOIGNE—RED LABEL, SOLCHLOR.

British Standards Institution

NEW SPECIFICATIONS*

B.S. 997 : 1951. Sperm Oil. Price 2s. 6d.
B.S. 1365 : 1951. Short-range, Short-stem Thermometers. Price 2s.
B.S. 1704 : 1951. General Purpose Thermometers. Price 2s.

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and may be obtained on application to the Secretary, Miss D. V. Wilson, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee LBC/2—Glassware for Medical and Bacteriological Use.

CM(LBC) 9917—Draft B.S. for Petri Dishes (Revision of B.S. 611).

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

CN(LBC) 36—Draft B.S. for Nessler Cylinders (Revision of B.S. 612).

CM(LBC) 9886—Draft B.S. for Density Bottles (Revision of B.S. 733).

Draft Specification prepared by Technical Committee DAC/6—Rennet, Annatto and other Colours for Dairying Purposes, Sub-Committee DAC/6/2—Annatto and other Colours (drafting).

CN(DAC) 80—Draft B.S. for Annatto for Dairying Products.

Draft Specification prepared by Non-ferrous Metals Industry Standards Committee NFE/–, Sub-Committee NFE/–/3—Sampling and Analysis of Aluminium and Aluminium Alloys.

CM(NFE) 9831—Draft B.S. Method for the Determination of Zinc in Aluminium Alloys (Polarographic Method).

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

Book Reviews

THE NATIONAL FORMULARY. Ninth Edition. Pp. xl + 877. Washington: American Pharmaceutical Association. 1950. Price $8.00 (in U.S.A.); $8.75 (elsewhere).

This book should not be confused with the British publication having a similar title, which is a compilation of prescriptions for use in connection with the National Health Service Act, 1946, whereas the book under review may conveniently be regarded as being approximately the American equivalent of our British Pharmaceutical Codex. Its purpose is to present a compilation of standards for widely used drugs and preparations that are not included in the United States Pharmacopoeia. The importance of the National Formulary has steadily increased since the appearance of the first edition in 1888 and by the terms of the Federal Food and Drugs Law of 1906 it was designated an official compendium along with the United States Pharmacopoeia, and this arrangement was confirmed by the Federal Food, Drug and Cosmetic Act of 1938.

The body of the work comprises 562 pages devoted to monographs giving detailed standards for drugs and their preparations. These monographs are arranged in the same way as those of the United States Pharmacopoeia and, in general, include a description of the medicament, statement of solubility, tests for identification, examination for likely impurities and, where applicable, a procedure for assay. For nearly every substance there is a direction about packaging and storage.

After the monographs there follows a compilation of reagents and preparations for use in the clinical laboratory and then an important section devoted to standards for reagents, for ingredients of preparations and for dyes used as biological stains. Together, these two portions of the work occupy 114 pages of small print. Many of the specifications are very exhaustive, particularly those applying to the dyestuffs.

The next section of 98 pages is entitled general tests, processes and apparatus and defines numerous analytical operations, such as the test for arsenic, the determination of boiling range, disintegration tests for tablets, standards for light transmission, the measurement of viscosity, microbiological methods for the assay of nicotinamide and riboflavine and many more general and special analytical procedures.

A further list of general reagents and volumetric solutions, two tables of permitted coal-tar dyes for colouring purposes, a short addendum and an index occupying 57 pages complete this handsomely bound volume.

From all these thousands of tests and analytical processes it would not be difficult to make suggestions for alternatives or improvements, the more easily by concentrating on one's own specialities. But no useful purpose would be served. It is sufficient to say that every page reveals the immense care that has been devoted to the production of this compendium. Much of the matter has, of necessity, been derived from previous editions or from earlier Pharmacopoeias of the United States; but, on the other hand, much is new and the whole is dovetailed together to produce a work of reference invaluable to all concerned with the examination of medicinal substances.

N. L. ALLPORT

DDT AND NEWER PERSISTENT INSECTICIDES. By T. F. WEST, D.Sc., Ph.D., F.R.I.C., and G. A. CAMPBELL, M.Sc., F.R.I.C. Second Edition. Pp. xiv + 632. London: Chapman and Hall Ltd. 1950. Price 50s.

The first edition of this book appeared in 1946 when DDT was still something of a novelty. Even so, it ran to some 300 pages in recording the large amount of research results published up to 1945. In the succeeding years an even greater volume of publications on the applications of DDT in the control of animal and plant pests has appeared. Hence it is not surprising that the authors have found it necessary to produce a revised and extended second edition, or that the new edition should run to some 500 pages devoted to DDT, with a further 70 pages devoted to newer chlorinated hydrocarbon insecticides. Inclusion of the latter has, incidentally, necessitated an appropriate change in the original title.

Part One of the book, dealing with DDT, follows the pattern of the first edition. Chapter I, describing the development of DDT, has been completely rewritten on the basis of more detailed information obtained from Switzerland since 1945. Similarly, advances in knowledge of the chemistry of DDT have necessitated considerable revision of Chapter II, which now includes a valuable tabulation of the many analogues that have been synthesised and gives an indication of their relative insecticidal activity, with references. This chapter deals with assay methods

for DDT and its estimation in residues on biological or other treated surfaces, and also gives much more information on the solubility of DDT than appeared in the first edition. It is to be regretted that this latter information refers in the main to the pure *p-p'*-isomer and that the solubilities are expressed as "grams per 100 ml" and "grams per 100 grams" of solvent. The ordinary user is likely to be much more interested in the solubility characteristics of *technical* DDT, and even then on a weight/volume percentage basis. The remaining chapters, while preserving much of the matter presented in the first edition, have been considerably extended by references to more recent work.

Part Two deals, rather briefly, with the newer chlorinated hydrocarbon insecticides, chapters being devoted respectively to benzene hexachloride, chlordane, toxaphene and "various new insecticides."

The authors are to be congratulated on the manner in which they have undertaken the task of surveying the vast literature on this subject. Wisely, they have not attempted to do more than report on all work that appears to be relevant. In fact, they specifically disclaim any effort to make, at this stage of development, a "critical résumé." It does, however, seem unfortunate that a book published in 1950 should review the literature only up to 1946; although, through unavoidable delay in production of the book, opportunity has been taken to include, as an appendix, lists of references tabulated according to chapter headings up to 1948.

It is quite impossible in a short review to single out items of particular interest. Suffice it to say that this is a book that must be available to all those who, as chemists or biologists, are interested in insecticides. The book is well produced and bound, contains relatively few misprints, and includes 13 plates, most of which appeared in the first edition.

W. MITCHELL

ORGANIC REAGENTS FOR ORGANIC ANALYSIS. By the Staff of the Research Laboratory of Hopkin and Williams Ltd. Second Edition. Pp. viii + 255. Published by Hopkin and Williams Ltd., Chadwell Heath, Essex. 1950. Price 12s. 6d. (plus 5d. postage) from the publishers.

The first edition of this laboratory handbook to the use of organic reagents in the identification of organic compounds by means of derivatives with diagnostic melting-points has already received favourable notice in *The Analyst* (1946, **71**, 503).

The general plan of the second edition follows that of the first, but the book has undergone enlargement by the inclusion of about half a dozen new reagents and many additions, revisions and corrections to the melting-point tables. This increase in subject-matter fulfils, in some measure, the hope expressed by the reviewer of the first edition.

From the large number of reagents that are continually being proposed for the identification of organic groups and compounds by means of the melting-points of characteristic derivatives, a selection is made of those that are, in the opinion of the authors and for reasons stated, the most useful and readily obtainable; for these, the properties and methods of use are described and the melting-points of the derivatives listed.

Bibliographies to the literature of the selected reagents are supplied and the properties of many other reagents that are, for various reasons, considered to be of less general importance or usefulness are critically reviewed.

The book is well indexed, and bound in proofed cloth for bench use. It forms a useful companion to the standard textbooks on practical organic chemistry.

F. L. OKELL

Publications Received

THE MODERN SOAP AND DETERGENT INDUSTRY. Volume II. THE MANUFACTURE OF SPECIAL SOAPS AND DETERGENT COMPOSITIONS. Revised by E. I. COOKE, M.A., B.Sc., A.R.I.C. Third Edition. Pp. xii + 448. London: The Technical Press Ltd. 1951. Price 50s.

LEAF ANALYSIS. Translated by R. L. MITCHELL from "DIE BLATTANALYSE" by H. Lundegårdh. Pp. viii + 176. London: Hilger & Watts, Ltd. 1951. Price 22s. 6d.

HANDBOOK OF ANTIBIOTICS. By A. L. BARON. Pp. viii + 303. New York: Reinhold Publishing Corporation. London: Chapman & Hall, Ltd. 1950. Price $6.50; 52s.

ORGANIC CHEMISTRY. By I. L. FINAR, B.Sc., Ph.D., A.R.I.C. Pp. xv + 696. London: Longmans, Green & Co. 1951. Price 40s.

LES MÉTHODES D'ANALYSE DES RÉACTIONS EN SOLUTION. By G. CHARLOT and R. GAUGUIN. Pp. viii + 328. Paris: Masson et Cie. 1951. Price 2200 fr.

CHIMIE MINÉRALE THÉORIQUE ET EXPÉRIMENTALE (CHIMIE ELECTRONIQUE). By F. GALLAIS. Pp. 808. Paris: Masson et Cie. 1950. Price 2800 fr.

BENTLEY AND DRIVER'S TEXTBOOK OF PHARMACEUTICAL CHEMISTRY. Revised by J. E. DRIVER, M.A., Ph.D., M.Sc., F.R.I.C. Fifth Edition. Pp. viii + 671. London: Oxford University Press. 1951. Price 32s. 6d.

ELECTRIC EYES. By A. J. FAWCETT. Pp. 28. Salisbury: The Tintometer Ltd. 1951. Price 1s. 6d.

A description of the uses and limitations of the photo-electric cell.

VACUUM. A Review of Developments in Vacuum Research and Engineering. Volume I, No. 1, January, 1951. Pp. v + 72. London: W. Edwards & Co. (London), Ltd. Subscription fees 25s. (British Isles); 30s. (Abroad).

A journal incorporating papers and abstracts.

THE PURIFICATION OF THE WATER OF SWIMMING BATHS. Report issued by the Ministry of Health. Pp. 36. London: H.M. Stationery Office. 1951. Price 1s. 6d.

MICRODIFFUSION ANALYSIS AND VOLUMETRIC ERROR. By E. J. CONWAY, M.B., D.Sc., F.R.S. Pp. xxiv + 391. London: Crosby, Lockwood & Son, Ltd. 1951. Price 25s.

PHYSICAL METHODS IN CHEMICAL ANALYSIS. Volume II. Edited by W. G. BERL. Pp. xii + 639. New York: Academic Press Inc. 1951. Price $13.50.

METHODS OF VITAMIN ASSAY. By the ASSOCIATION OF VITAMIN CHEMISTS, INC. Second Edition. Pp. xviii + 301. New York: Interscience Publishers, Inc. 1951. Price $5.50.

THE CHEMICAL ANALYSIS OF WATERS, BOILER- AND FEED-WATERS, SEWAGE AND EFFLUENTS. By DENIS DICKINSON, M.Sc., Ph.D., F.R.I.C., F.R.San.I. Second Edition. Pp. xii + 144. London: Blackie & Son, Ltd. 1950. Price 6s. 6d.

Sulphuric Control Order, 1950

INFORMATION has been received that it is not intended to restrict supplies of acids and other chemicals used by analysts under the Sulphuric Control Order, 1950. Members having difficulty in obtaining supplies are recommended to write to the Honorary Secretary.

PHYSICAL METHODS GROUP

THE Thirty-second Ordinary Meeting of the Group will be held in the afternoon and evening of Tuesday, May 22nd, 1951, in the Lecture Room of the Institute of Physics, 47, Belgrave Square, London, S.W.1. The subject of the meeting is "Radiochemistry."

The first part of the meeting will be at 4.0 p.m., when the following papers will be presented and discussed: "Radio-active Tracer - Paper Chromatography Techniques," by F. P. W. Winteringham, A. Harrison and R. G. Bridges; "Paper Chromatography of Radio-active Penicillin," by E. Lester Smith and D. Allison.

The second part of the meeting will be at 5.45 p.m., when the following papers will be presented and discussed: "The Determination of Sub-microgram Quantities of Arsenic by Radio-activation," by A. A. Smales and B. D. Pate; "Micro-determination of Sodium and Potassium by Activation Analysis," by R. D. Keynes.

In the interval between the two parts of the meeting, tea will be provided at a nominal charge.

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ASSISTANT CHEMISTS required for analytical research laboratory attached to Home Counties chemical works. Applicants should have had some experience in analytical work. Salary according to experience and qualifications. Write stating age, details of qualifications and experience and salary required to Box No. 3771, THE ANALYST, 47, Gresham Street, London, E.C.2.

ANALYSTS required by a Major Oil Company for its London Laboratory handling a wide variety of problems affecting oils, greases and special petroleum products. Good education and Honours B.Sc. degree or A.R.I.C. are essential qualifications. Those appointed will be required to assist the Head of the Analytical Section in applying standard oil test methods and special analytical techniques to samples of new and used lubricants, engine deposits, etc. The vacancies carry opportunities for progress for young, energetic men, and involve some responsibility for the supervision of others. Salary will be commensurate with qualifications and experience; conditions of employment include pension and sickness benefit schemes. Applicants should write giving full particulars, quoting reference (Z.1706) to Box No. 3772, THE ANALYST, 47, Gresham Street, London, E.C.2.

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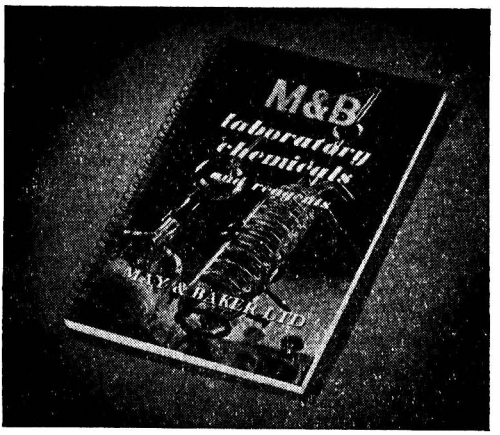

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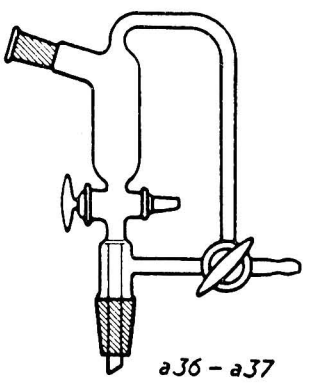

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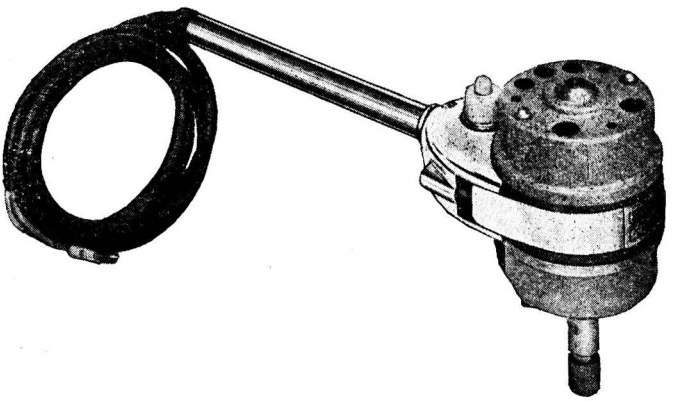

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Refs : 1. Higgins, M. Monthly Bull. Min. of Health & Pub. Health Lab. Service. Feb. 1950 p. 49. 2. Higgins, M. & Hobbs, B. ibid, p. 38.

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