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PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE eighty-seventh Annual General Meeting of the Society was held at 2.15 p.m. on Friday, March 3rd, 1961, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was occupied by the President, Mr. R. C. Chirnside, F.R.I.C. The Financial Statement for the year ending October 31st, 1960, was presented by the Honorary Treasurer and approved, and the Auditors for 1961 were appointed. The report of the Council for the year ending March, 1961 (see pp. 286–297), was presented by the Honorary Secretary and adopted.

The Scrutineers, Mr. H. E. Brookes and Mrs. H. I. Fisk, reported that the following had been elected officers for the coming year—

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

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

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

Honorary Treasurer—D. T. Lewis.

Honorary Secretary—R. E. Stuckey.

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

Other Members of Council—The Scrutineers further reported that 469 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—D. C. Garratt, 386; D. W. Wilson, 355; S. G. Burgess, 283; S. H. Jenkins, 272; R. A. Chalmers, 266; C. A. Parker, 247; A. G. Jones, 243; C. W. Herd, 230; N. R. Jones, 201.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—S. G. Burgess, R. A. Chalmers, D. C. Garratt, S. H. Jenkins, C. A. Parker and D. W. Wilson.

D. M. W. Anderson, B. Bagshawe, E. Bishop, E. Q. Laws, W. M. Lewis and J. T. Yardley, having been elected members of the Council in 1960, will, by the Society's Articles of Association, remain members of the Council for 1961.

J. Markland (Chairman of the North of England Section), A. F. Williams (Chairman of the Scottish Section), G. V. James (Chairman of the Western Section), H. C. Smith (Chairman of the Midlands Section), C. Whalley (Chairman of the Microchemistry Group), G. W. C. Milner (Chairman of the Physical Methods Group) and J. S. Simpson (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1961.

The retiring President, Mr. Chirnside, thanked the Honorary Officers for their services to the Society during his term of office, and especially Dr. Amos, under whose Honorary Treasurership much progress has been made. He then formally installed Dr. Amos in the Chair.

After the business outlined above had been completed, the meeting was opened to visitors, and the retiring President delivered his Presidential Address (see pp. 314–324).

DEMONSTRATION MEETING

A DEMONSTRATION Meeting of the Society was held at 6 p.m. on Wednesday, March 29th, 1961, at Chelsea College of Technology, Manresa Road, Chelsea, London, S.W.3.

The demonstrations were of laboratory-made equipment, and the following pieces of apparatus were shown—

Small-scale methods of heating and stirring, and miscellaneous small-scale techniques—M. A. Fill (Norwood Technical College).

Apparatus for alkaline isomerisation of fatty acids—D. M. Morgan (St. Mary's Hospital).

The apparatus provides a means of heating the isomerisation tubes under nitrogen at a controlled temperature of 180° C (Holman, R. T., and Hayes, H., *Anal. Chem.*, 1958, **30**, 1422).

Semi-micro Orsat apparatus—R. Moss and A. Slater (The Associated Ethyl Co., Ltd.).

The apparatus is designed for the analysis of gas samples of volume 1 to 4 ml. The gas burette is connected to two reservoirs by a three-way U-bore tap. This obviates the need to raise and lower the reservoir and gives precise control of the movement of the sample between the gas burette and the absorption pipettes.

Multiple stirrer unit for coagulation tests on water—R. F. Packham (Water Research Association).

The unit is designed to accommodate 1-litre samples. It has a built-in illumination system, two stirring speeds and a device that permits all the samples to be dosed with coagulant simultaneously.

Simple apparatus for continuous sampling of water—R. F. Packham (Water Research Association).

A series of collecting cups machined circumferentially in an aluminium table connect to the sample bottles. A tube delivering a continuous flow of water is moved in a circle so that each of the cups is fed in turn. The apparatus is set up to collect 24 hourly samples.

The following exhibits were demonstrated by J. E. Still and J. H. Konrath (G.E.C. Ltd., Hirst Research Centre)—

Automatic integrator for gas chromatography. (Designed by J. H. Konrath).

The areas of the successive peaks of a chromatogram are integrated and registered on a digital counter with zero reset. A potentiometer rotating with the chart-recorder pen drive supplies a varying direct voltage to an integrating motor on whose spindle is mounted a light mica disc, partly silvered. The rotation of this disc interrupts a light beam falling on a photo-transistor, and this operates the counter through a relay.

Atomiser for flame photometry, constructed entirely in a transparent plastic material. (Designed by J. E. Still).

This all-plastic atomiser permits solutions containing hydrofluoric acid to be sprayed. Another advantage of the mode of construction lies in its reproducibility; this feature leads to the possibility of using interchangeable jets of different tip dimensions to provide a range of atomising characteristics.

Tungsten-filament katharometer for gas chromatography. (Designed by D. G. Timms and J. H. Konrath).

A robust katharometer of high sensitivity with replaceable coiled-tungsten filaments supported under tension.

Sample-admission valve for vacuum fusion apparatus. (Designed by J. E. Still).

This valve provides for the admission of solid samples into a high-vacuum system without release of the vacuum. The use of a lubricated seal, which could contaminate the sample, is avoided.

Methods for quantitative assessment of psychotropic activity in mice—M. W. Parkes (Roche Products Ltd.).

Psychostimulant agents are estimated by (*a*) measurement of tremor in mice placed in canisters on gramophone pick-ups, the output of which is conventionally amplified and fed to an integrating motor operating a counter; (*b*) measurement of locomotor activity of mice walking on silica gel granules in tins with microphones under the floor, the output from these being treated as in (*a*).

Both psychostimulant and depressant agents may be estimated by rise or fall, respectively, in the body temperature of mice, measured by rectal thermistor probe (Designed by A. W. Lessin).

An anticoprophagic cup—or "Faecollector"—for the rat—A. E. Bender (Bovril Research Department).

A light aluminium cup is fixed over the tail of the rat to prevent it eating its faeces. It can be emptied without removing the device, so avoiding trauma to the tail. (Designed by B. H. Doell.)

A simple recording analytical balance designed for thermogravimetry—H. L. Evans and J. T. McAloren (Directorate of Chemical Inspection, War Office).

The balance has been constructed from an old free-swinging balance and operates on a simple hydrostatic principle. Electronic equipment is reduced to a minimum, is of simple design and transistorised. By simply changing the hydrostatic float, the balance may be made to operate over three ranges of weight change. These are (*i*) 0 to 150 mg, (*ii*) 0 to 50 mg and (*iii*) 0 to 20 mg, over a chart length of 10 inches. It is fitted with an oil-bath heating furnace designed for medium-temperature thermogravimetry, with a linear rate of heating as slow as 0·5° C per minute. Thermograms of oxalic acid and styphnic acid are shown.

"Sulphometer"—J. B. Clegg (The Permutit Co., Ltd.).

A device for turbimetric measurement of sulphate concentration (range 0 to 60 p.p.m.) in natural waters; barium chloride, hydrochloric acid and gelatin are used as reagents.

Humidator Cells—H. E. C. Powers (Tate & Lyle Ltd.).

Two cells designed to facilitate operations with vapour-pressure-sensitive systems. The enclosed atmosphere is maintained at the desired level by the presence of suitable salts or solutions. In the smaller cell progressive changes may be observed by transmitted light and photographically recorded.

Although designed for the study of crystallisation in thin films, the apparatus obviously has a wide range of possible applications, including even non-aqueous vapour-pressure operations, permitting molecular migration to equilibrium (*Nature*, 1960, **188**, 289; *New Scientist*, 1960, **8**, 1178; *Int. Sugar J.*, 1960, **62**, 307).

Semi-automatic compound dilution pipette—R. R. Goodall and W. Taylor (Imperial Chemical Industries Ltd., Pharmaceuticals Division).

A syringe is connected via two two-way taps A and B to a capillary pipette set below it. The syringe is filled to a stop-screw via tap A from a gravity head. The capillary pipette is filled with sample by suction through tap B. Taps A and B are then turned to the discharge position so that the contents of the syringe flush out the contents of the capillary pipette. The volume of the syringe can be varied. The apparatus is especially suitable for serial dilution, and on a 1 to 17·5 dilution the observed precision was 0·3 per cent.

Method for obtaining weighed micro samples of moisture- or oxygen-sensitive compounds —Miss I. Hall (Imperial Chemical Industries Ltd., Nobel Division).

An electrical arrangement for sealing a micro sample of liquid in a capillary tube, applicable to the micro-sampling of materials sensitive to atmospheric water vapour or to oxygen. (Designed by A. F. Williams and T. R. Prentice; see *Analyst*, 1960, **85**, 126.)

A.R.D.E. card sorting/punching machine—R. J. Loneragan (Armament Research and Development Establishment).

A card-sorting and punching machine for edge-punched cards. No special pre-punched cards are required. Punching and sorting are carried out on the same keyboard.

Assay of antibiotic mixtures using electrophoresis in agar—J. W. Lightbown and P. de Rossi (National Institute for Medical Research).

A mixture of two antibiotics of unknown concentration is placed with a mixture of standard preparations in punched holes, in a Latin Square design, at several dose levels, in a slab of buffered agar. After electrophoresis for a short period (*e.g.*, 5 to 10 minutes) the slab of agar is seeded and incubated. Independent assays are obtained for each antibiotic.

Apparatus for electro-chemical plating of polonium-210 on nickel—Mrs. M. P. Taylor (Medical Research Council Radiological Protection Service).

The apparatus consists of eight de-mountable cells, each containing a nickel disc. The solution containing the polonium is continuously agitated by means of a stream of air.

Punched-card index of analytical bibliography—D. R. Curry and P. J. Moore (Overseas Geological Surveys).

The index, which utilises single-sided *Analytical Abstracts*, is based on a novel punched-card system. Selected abstracts are indexed according to elements determined, method used, author, journal, etc. Considerable cross-referencing is possible without adding to the bulk of the system. In searching the index, the abstracts of all relevant papers—whether in a wide or narrow field of enquiry—can rapidly be produced for inspection. Present capacity of the system is 5000 abstracts. A similar system is in use for recording samples received by the laboratory, details of analysis, etc.

Induction heating applied to the micro-determination of carbon and hydrogen—Mrs. D. Butterworth (National Chemical Laboratory).

A radio-frequency generator is used as a source of heat for volatilising thermally-stable compounds in the rapid method for determining carbon and hydrogen.

Agar-gel plate immunoanalysis—J. G. Feinberg and Miss A. Temple (Beecham Research Laboratories Ltd.).

Special cutters have been designed and constructed for producing standardised well patterns in agar-gel plates. The plates are used for the qualitative and quantitative assay of macromolecular substances by serological precipitation in the agar-gel matrix. The cutters can be made in an instrument shop and are also now available commercially.

Magnetically driven fan—R. J. Jackson (Beecham Research Laboratories Ltd.).

An internal fan in a sealed humidity cabinet is driven magnetically from outside the cabinet.

Electrodes and cells for polarography—Mrs. B. Lamb and Mrs. D. Konczak (Evershed and Vignoles Ltd.).

Rotating solution for use with solid electrodes—The base on which the vessel rests is rotated to provide efficient stirring for amperometric titrations. This equipment may also be used with stationary solid electrodes.

Hanging-drop electrode—Hanging drop as described by Professor Kemula.

Vibrating electrode—The vibrating electrode is designed for the measurement of dissolved oxygen and also as an indicating electrode in amperometric titrations. It is based on the original design of Dr. Lindsey. The frequency is 50 cycles and the amplitude may be varied between 0·4 and 2·0 mm, but the exact amplitude will depend on the weight of the electrode. It is also possible to combine this vibrator with a silver - silver chloride electrode as shown. Further, it may be mercury plated for enhanced sensitivity with respect to oxygen.

Flow-through cell—A simple flow-through cell with constant-head device arranged as a polarographic cell to permit measurements to be made on a flowing solution. The conventional dropping-mercury electrode is used as the cathode and a pool of mercury as anode in this exhibit, but a solid electrode could be used as indicating electrode if desired.

The following exhibits were demonstrated by E. Bishop (Washington Singer Laboratories, University of Exeter)—

Automatic pre-heating self-flushing water still—R. G. Dhaneshwar and G. D. Short (University of Exeter).

An all-glass/quartz still with high reflux ratio and heat conservation, producing a sterile grease-free water of parts per thousand million purity, with automatic fail-to-safe operation, and which can be mounted high on a wall, out of the way.

Potentiometric titrimetry—R. G. Dhaneshwar and G. D. Short (University of Exeter).

A simple low-impedance apparatus assembled from radio components for routine use and teaching; a single meter, used as both null detector and voltmeter, allows potential measurements to be made with a precision of 0·1 per cent. without calibration. Facilities are included for polarisation and dead-stop titrimetry.

Differential electrolytic potentiometry—R. G. Dhaneshwar and G. D. Short (University of Exeter).

Automatic electrochemical differentiation of potentiometric curves. A versatile research assembly for the study of current - potential relationships at electrodes in the current range of 10^{-5} to 10^{-15} amp, with ballast resistors from 10^{6} to 10^{13} ohms, a variety of electrodes and facilities for the simultaneous study of the behaviour of individual electrodes.

Needle-valve weight burette—R. G. Dhaneshwar and G. D. Short (University of Exeter).

A 60-ml burette of minimum weight, obviating the use of lubricated taps, yet capable of precise manipulation and of delivering increments of the order of 0·001 ml.

Microcoulometry—E. Bishop (University of Exeter).

Conventional constant-current coulometry applied to small samples at high dilution. With the electrode-platform type of micro-cups, capillary-lock auxiliary electrodes and location of the end-point by D.E.P., determinations of 10^{-10} equivalent of oxidisable matter have been made.

Electronic constant-current/constant-potential source—E. Bishop (University of Exeter).

A simple, fairly conventional constant-potential supply of low output impedance, having a constant current output through a constant electronic resistance, based on cheap surplus valves, and regulating to $\pm 0{\cdot}02$ per cent. with a time-constant of 10 microseconds.

The following exhibits were demonstrated by F. Albert-Recht (Clinical Chemistry Department, Edinburgh University)—

Rocking extractor.

The instrument agitates 2-phase solvent systems contained in globular separating funnels by a rocking-pendulum movement. The gentle agitation assures adequate extraction, and formation of emulsions is minimised.

Ultrafiltration apparatus.

The instrument achieves ultrafiltration at high pressure (150 lb per sq. inch) through a length of "Visking" cellulose tubing. It provides speedy handling of relatively large volumes of colloidal solutions. Concentrated colloid and ultrafiltrate are available for subsequent analysis.

Sample cell arrangement for E.E.L. flame photometer.

A sample cell combined with distilled-water flushing and suction-emptying arrangements fitted on to a standard E.E.L. flame photometer. This combination speeds up the handling of samples and standards by efficient presentation of samples for spraying.

Electrophoretic tank for small-scale cellulose acetate strips.

The electrophoretic tank with small strip chamber and thermally insulated walls keeps water evaporation from strips to a minimum. The design of electrode vessels restricts movement of decomposed buffer on to the strip.

General-purpose integrating flame photometer—R. J. Webb and P. C. Wildy (U.K.A.E.A. Research Group, Woolwich Outstation).

A flame photometer of high sensitivity with provision for integrating or direct reading, use of internal standards and automatic background correction. The instrument is now being used for the determination of strontium in calcium at the 100 p.p.m. level, where the line - background ratio is 1 to 200.

Anodic stripping polarography—A. Parker and E. A. Terry (U.K.A.E.A. Research Group, Woolwich Outstation).

Controlled-potential electrolysis causes cations to deposit on a stationary mercury drop, and a reverse voltage sweep is then applied through a cathode-ray polarograph. Cadmium and lead can be determined at the 10^{-8} M level.

Anti-coincidence β-scintillation counter for low activity levels—J. L. Waddingham and J. D. Rowe (U.K.A.E.A. Research Group, Woolwich Outstation).

A thin plastic phosphor in contact with the sample is contained in a well in a cylindrical phosphor, which counts external radiation. The two associated photomultipliers are connected in anti-coincidence. The background for β-counting has been reduced to 0·4 count per minute, and the efficiency at the 2-MeV level is 50 per cent.

Coincidence scintillation counting for low-activity levels—J. L. Waddingham and J. D. Rowe (U.K.A.E.A. Research Group, Woolwich Outstation).

Scintillations from a thin phosphor in contact with the samples are viewed by the photomultipliers and only coincident pulses are accepted. This arrangement permits high gain to be used on the photomultipliers, since random thermal noise is minimised.

A simple gas chromatograph—C. J. Barker (The Metal Box Co., Ltd.).

A compact and robust apparatus, easily constructed in a laboratory workshop, operates at temperatures between 0° and 100° C and with columns up to 20 feet long. Detection is by thermal-conductivity measurements with a thermistor bead. (Designed by J. R. Bishop.)

Apparatus for coulometric determinations of free tin and tin - iron alloy on tinplate—J. R. Bishop and W. H. Hill (The Metal Box Co., Ltd.).

The tin coating layers are removed anodically in a cell made from a Tufnol cylinder. Changes in the potential at the anode half-cell are recorded by amplifying the current flowing in a high-resistance reference circuit. A magnetic amplifier feeds a recording milliammeter. Calibration is by a novel gravimetric technique.

A simple illuminated box for the incubation of stock cultures of *Ochromonas malhamensis* without overheating—S. A. Price and L. Gare (Vitamins Ltd.).

Ochromonas cultures, used for vitamin-B_{12} assay, should be grown under artificial light at 27° or 28° C, but temperatures only slightly higher than this inhibit growth of the organism. A bellows-type thermostat controlling the 60-watt lamp safeguards against overheating from the light source.

Titration assembly for acidimetric microbiological assays—L. Gare and S. A. Price (Vitamins Ltd.).

Cultures are titrated in a small beaker, magnetically stirred, the end-point being determined with a pH meter and the contents of the beaker emptied automatically by suction after titration.

Desiccator seal ring—P. R. Watt (Vitamins Ltd.).

The device consists of a flexible annular ring fitted over the upper flange of a standard vacuum desiccator. The seal is free from sticking and gives a greaseless joint: at the same time both flanges are protected from mechanical damage. As the lid lifts off vertically, the storage capacity of the desiccator may be nearly doubled.

Automatic micronitrometer—P. R. Watt (Vitamins Ltd.).

The apparatus is designed as a robust single unit to replace the conventional nitrometer and associated apparatus used in the Dumas nitrogen assay. It is self-balancing and reads the gas volume directly on a digital counter. No drainage period is necessary, and there are no errors due to drainage or etching.

Semi-micro molecular pot still—P. R. Watt (Vitamins Ltd.).

An all-glass horizontal still for molecular distillation of charges in the size range 0·2 to 0·5 g. Up to six fractions may be collected from each charge. The still, high-vacuum pump, trap and controls are mounted compactly together as a unit.

An inclined drawing board fitted with a roll of tracing paper for the repeated use of a single piece of graph paper—P. G. D. Naylor (Oxo Ltd., Oxoid Division).

A roller supply of tracing paper is drawn over a fixed piece of graph paper and held in position on an inclined drawing board by polyurethane-foam-coated metal bands. Multiple graph records can be plotted by tracing over a single piece of printed semilog paper.

An illuminator-box for large plate microbiological assays—P. G. D. Naylor (Oxo Ltd., Oxoid Division).

An internally illuminated box containing two strip lights that provide side illumination for the measurement of zones of inhibition (or exhibition) in the microbiological assay of antibiotics (or vitamins) using large 12-inch × 12-inch assay plates.

Electrophoresis apparatus—T. H. Nelson (Oxo Ltd., Oxoid Division).

A simple apparatus for use with cellulose acetate strips for rapid electrophoretic separation of proteins.

An inexpensive incubator—T. H. Nelson (Oxo Ltd., Oxoid Division).

A simple inexpensive incubator that has been shown to give remarkably constant temperature control.

The diffusion plate-assay technique applied to enzymes and antibacterials in pharmaceutical analysis—D. V. Carter (Standards Department, Boots Pure Drug Co. Ltd.).

Examples of the adaptation of the method to substances other than antibiotics and vitamins.

JOINT MEETING

A JOINT Meeting of the Society with the Oil and Colour Chemists Association was held at 7 p.m. on Wednesday, April 12th, 1961, at the Wellcome Building, Euston Road, London, N.W.I. The Chair was taken jointly by the President of the Society, Dr. A. J. Amos, F.R.I.C., and the Chairman of the London Section of the Oil and Colour Chemists Association, Mr. J. A. L. Hawkey.

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

ORDINARY MEETING

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 3rd, 1961, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. A. J. Amos, F.R.I.C.

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

NEW MEMBERS

ORDINARY MEMBERS

Geoffrey Robert Andrews, A.C.T.(Birm.), A.R.I.C.; James Michael Bakes; Kenneth Bilson; Michael Rex Burgess, B.Sc.(Lond); Charles Edward Carpenter, A.R.I.C.; Douglas Vaughan Carter, B.Sc.(Nott.); Patrick Hamilton Cashman, B.A.(T.C.D.); Forster Cuthbertson, B.Sc., Ph.D.(Dunelm.); Peter Trevor Davies, M.A., Ph.D.(Cantab.), A.Inst.P.; Robert Ellerby, B.Sc.(Lond.); Joan Ann Philomena Gibson, M.Sc.(N.U.I.); Peter Gittins, B.Sc., Ph.D.(Birm.), A.R.I.C.; Geoffrey Green, F.I.M.L.T.; Arthur Frederick LeCore Holding, B.Sc., Ph.D.(Lond.), A.R.I.C.; George Frederick Hooke, A.R.I.C., A.C.T.(Liv.); Jack Lacy, B.Sc.(Dunelm.); Charles Frederick Luft, A.F.Inst.Pet., A.R.I.C.; Walter Roy Marris; Harry Marsland; Derek George Parsons; José M. Puigmarti-Codina; Robert Best Stirton; Francis Henry Strutt; Williams Alfred Stuart.

JUNIOR MEMBERS

Richard Martin Lee, B.Sc.(Aber.); Shirley Ann Lord.

NORTH OF ENGLAND SECTION AND PHYSICAL METHODS GROUP

A JOINT Meeting of the North of England Section and the Physical Methods Group was held at 2.15 p.m. on Saturday, March 25th, 1961, at the City Laboratories, Mount Pleasant, Liverpool, 3. The Chair was taken by the Chairman of the North of England Section, Mr. J. Markland, B.Sc., F.R.I.C.

The subject of the meeting was "The Analysis of Intact Samples" and the following papers were presented and discussed: "X-ray Fluorescence in General Analysis," by D. E. Bromley, B.Sc., A.Inst.P.; "The Use of Radioactive Isotopes in Simple X-ray Fluorescent Analysis," by C. E. Mellish, B.A., D.Phil.; "Analysis by Nuclear Magnetic Resonance Techniques," by D. J. Ferrett, M.A., D.Phil. (see summaries below).

X-RAY FLUORESCENCE IN GENERAL ANALYSIS

MR. D. E. BROMLEY said that X-ray fluorescence was widely applicable, gave good accuracy and was quick and non-destructive, but there were difficulties with light elements, there was only moderate sensitivity and apparatus tended to be expensive. Attention had concentrated on repetition analysis, but X-ray fluorescence could be useful in more general work. Focusing curved-crystal spectrometers having good resolution and requiring only a small specimen had been made at Admiralty Materials Laboratory. One of these was of very simple construction, requiring only hand tools and a drill to make. A typical application was in the analysis of artificial rubies for chromium. A satisfactory calibration had been made with mixtures of powdered oxides, and a limiting sensitivity of 40 p.p.m. had been obtained. In the measurement of plating thickness, by using radiation from either the grating or the underlying metal, an approximate calibration depending on known absorption coefficients was possible.

THE USE OF RADIOACTIVE ISOTOPES IN SIMPLE X-RAY FLUORESCENT ANALYSIS

DR. C. E. MELLISH said that for many applications of X-ray fluorescence spectroscopy the full performance of the conventional spectrometer was not required. In these applications it was possible to substitute a small radioactive source (1 millicurie) for the X-ray tube, provided that the crystal spectrometer was also dispensed with and resolution of the fluorescent X-rays produced was performed in a proportion or scintillation counter. He gave results of the application of this simple system to such problems as the measurement of metal-plate thickness and of solution strengths and also discussed the suitability of different isotope sources for different applications.

ANALYSIS BY NUCLEAR MAGNETIC RESONANCE TECHNIQUES

DR. D. J. FERRETT said that the phenomenon of nuclear magnetic resonance, in which responses could be obtained from nuclei that had spin, offered a technique for the analysis of intact samples of solids, liquids and gases. Equipment demands were rigorous, *e.g.*, magnets with highly uniform fields and electronic circuits with low noise levels. The information obtained could be both qualitative and quantitative and could be used as an aid to the elucidation of the structure of complex organic molecules.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held at 7.15 p.m. on Friday, March 24th, 1961, in the Royal College of Science and Technology, George Street, Glasgow, C.1. The Chair was taken by the Chairman of the Section, Mr. A. F. Williams, B.Sc., F.R.I.C.

The following papers were presented and discussed: "The Titration of Weak Acids in Non-aqueous Solvents," by G. R. Jamieson, B.Sc., F.R.I.C.; "High Frequency End-point Detection in Non-aqueous Titrimetry," by E. S. Lane, B.Sc., Ph.D., F.R.I.C.

MIDLANDS SECTION

THE sixth Annual General Meeting of the Section was held at 6.30 p.m. on Tuesday, March 14th, 1961, at Regent House, St. Philip's Place, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P. The following appointments were made for the ensuing year:—*Chairman*—Dr. H. C. Smith. *Vice-Chairman*—Mr. W. H. Stephenson. *Hon. Secretary*—Mr. G. W. Cherry, 48 George Frederick Road, Sutton Coldfield, Warwickshire. *Hon. Treasurer*—Mr. F. C. J. Poulton. *Hon. Assistant Secretary*—Mr. R. Adkins. *Members of Committee*—Mr. J. B. Aldred, Mr. B. E. Balfour, Professor R. Belcher, Dr. Bella B. Bauminger, Mr. H. J. G. Challis, Mr. W. T. Elwell, Miss C. J. Lloyd and Mr. A. Turner. Miss M. E. Tunnicliffe and Mr. J. Blenkin were reappointed as Hon. Auditors.

At the conclusion of the business of the Annual General Meeting, Dr. H. Weisz gave a short talk on "Advances in the Use of the Ring-oven Technique."

AN Ordinary Meeting of the Section was held at 7 p.m. on Thursday, March 23rd, 1961, at the College of Technology, Burton Street, Nottingham. The Chair was taken by Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P., Past Chairman of the Section.

The following paper was presented and discussed: "The Measurement of pH and Electrode Potential for Analytical Purposes," by G. Mattock, B.Sc., Ph.D., A.R.I.C. (see summary below).

THE MEASUREMENT OF pH AND ELECTRODE POTENTIAL FOR ANALYTICAL PURPOSES

DR. G. MATTOCK said that the principal applications of potentiometric measurements in analytical chemistry were in pH determinations and various types of titration. However, some recent developments in ion-selective electrodes showed promise in extending these fields.

pH measurement—

A pH determination was often an important parameter in many routine analytical procedures and might also be involved as a subsidiary control in analyses. Certain theoretical limitations existed, which, in general, precluded the significant determination of pH to better than 0·01 to 0·02 unit, particularly in media that could have widely varying compositions; the theoretical uncertainty might be even greater with only partially aqueous systems, where pH measurements could only be comparative. These uncertainties derived from the conventional nature of pH definitions and from variations in liquid-junction potentials. The conditions in which more discriminating measurements could be made were often too limiting for general analytical application.

Experimental criteria involved a consideration of possible temperature errors, the general behaviour and pH ranges of glass electrodes and the reproducibilities of liquid-junction devices. To take examples: at low and high pH values experimental reproducibility of a high order might be difficult to achieve; and pH - temperature coefficients of alkaline solutions might be sufficiently large to cause confusion unless allowed for.

Apparatus now available included highly discriminating pH meters of considerable stability. Single units incorporating both reference and glass-electrode components were available, permitting measurements on volumes of 1 to 2 ml, while for microvolumes electrode systems requiring only 60 to 80 μl were also available.

Potentiometric titration—

Apart from the common glass-electrode pH titrations, redox titrations were frequently performed with platinum or gold redox electrodes and a reference electrode, which might be a conventional calomel, or a glass electrode, or tungsten. Noble metals followed redox equilibria by providing electrons in the redox exchange and adopted a potential, E, corresponding to the redox activity ratio—

$$E = E_0 + \frac{RT}{F} \ln \frac{a_{ox}}{a_{red}}$$

The chief difficulty in redox-electrode titrations occurred when electrode sluggishness appeared. The causes of this were not always clear, but could sometimes be related

to the formation of oxide films on the "noble" metal surface, and possibly also to the redox system not being thermodynamically reversible. Examples where sluggishness might occur, for example, were in Fe^{2+} - $Cr_2O_7^{2-}$ and Fe^{2+} - VO^{2+} titrations; in others, such as Fe^{2+} - Ce^{4+}, no problems arose.

In non-aqueous acid - base titrations, glass electrodes found considerable application, together with suitable non-aqueous reference electrodes, particularly in protogenic (acidic) and amphiprotic media. In protophilic (basic) media, platinum or antimony electrodes were usually preferable as indicators.

An interesting new system was a mercury - Hg (EDTA) combination, which acted as an indicator electrode in potentiometric EDTA titrations. By suitable choice of pH conditions, groups of metals could be selectively titrated. One particularly useful example was in water hardness determinations, carried out at pH 8 to 10, where levels as low as 1 to 2 p.p.m. could be satisfactorily determined by the use of an amalgamated gold electrode and a calomel reference electrode, with addition of the mercuric salt of EDTA.

Cation-responsive glass electrodes—

A recent development in glass electrodes had been the introduction of stable glasses that were highly selective to singly charged cations, such as Na^+. Sodium electrodes, for example, gave, analogously to pH, a "pNa" value and permitted direct measurement of sodium levels in solutions. The measuring range covered approximately molar to 10^{-5} molar (0·2 p.p.m. Na^+), and could even be extended to 10^{-6} molar or weaker with certain controls. Their most obvious application was in continuous monitoring of sodium levels in water supplies, but they had been applied to determinations of saline content in processed fluids, such as yeast mixes.

As a subsidiary item of possible analytical interest, it should be noted that sensitivity to univalent ions, such as silver and thallium[I], had also been observed.

MICROCHEMISTRY GROUP

THE twenty-ninth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, March 22nd, 1961, at "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Chairman of the Group, Mr. C. Whalley, B.Sc., F.R.I.C.

A discussion on "The Separation and Determination of Traces of Iron" was opened by D. M. Peake and E. J. Newman, B.Sc., A.R.I.C.

BIOLOGICAL METHODS GROUP

A DISCUSSION Meeting of the Group was held at 6.30 p.m. on Thursday, April 6th, 1961, in "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Chairman of the Group, Mr. J. S. Simpson, F.I.M.L.T.

A discussion on "Principles Involved in Collaborative Studies" was opened by S. A. Price, B.Sc., F.R.I.C.

Annual Report of the Council: March, 1961

It has become customary in the Annual Reports of Council presented in recent years to record the increasing and widening activities of the Society. The work of the Programmes Committee has been particularly important, and with it the planned provision of meetings that attempt to cover the whole field of modern analytical methods. It has also been a pleasure in previous years to record successful meetings organised by the Society in conjunction with Groups and Sections. Even judged against such a background, 1960 has been a particularly full and varied year.

As an innovation this year, the Society's Annual General Meeting and the Bernard Dyer Memorial Lecture were held, at the invitation of the Midlands Section, in Birmingham. This was the first occasion on which the Bernard Dyer Memorial Lecture had been given outside London, and Professor A. C. Frazer gave an address entitled "The Contribution of Analytical Chemistry to Medical Progress." The lecture was followed in the evening by the Society's Annual Dinner at which members of the Midlands Section and members from other parts of the country attended in almost equal numbers. The success of this function may well encourage the Society to plan future Annual General Meetings in centres other than London.

During the year there have been some outstanding Joint Meetings with other Societies to whom analysis is an important and vital matter. In April, for example, a joint Symposium with the Fertiliser Society on the subject of "Fertiliser Analysis," lasting 2 days, was held in Church House, Westminster; almost 200 people attended, of whom 20 were from overseas. In May, a 2-day Symposium was organised jointly with the Iron and Steel Institute and the Institute of Metals, in London. The subject was "The Determination of Gases in Metals"; more than 300 people attended, and it was particularly gratifying to have papers presented by leading workers from the United States. There was also a large attendance from European countries. The Proceedings of the Symposium have now been published in book form by the Iron and Steel Institute.

Another important event in which the Society played a prominent part was the Third Gas Chromatography Symposium held in Edinburgh in June. This was organised jointly by the Society and the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum. The meeting extended over 4 days and was held in the Assembly Rooms, George Street, Edinburgh. There were more than 560 delegates, including 160 from overseas, and a large number of applications had to be refused. The Organising Committee, of which Mr. L. Brealey was Secretary, was nobly supported in Edinburgh by the Scottish Section, who undertook a great many of the local arrangements.

The year 1960 has also been eventful for the President, Mr. R. C. Chirnside. In July he presented an Address on behalf of the Society to the Royal Society on the occasion of its Tercentenary—the invitation from the Royal Society acknowledging the status of the Society among other learned bodies. In September, at the invitation of the Chemical Societies of Sweden and Denmark, he made a lecture tour, during which he conveyed greetings from the Council to those Societies. The Ramsay Chemical Dinner, in December of this year, was the first occasion at which the President of the Society for Analytical Chemistry was Chairman. Mr. Chirnside also gave the Ramsay Lecture, entitled "Ramsay, Chemistry and the Electrical Industry."

Activities of the Sections and Groups have again been widespread, joint meetings with other bodies forming an increasing proportion of the total meetings. Of particular interest were the 2-day Symposium on "Analytical Chemistry in the Service of Agriculture" held in Nottingham in July, and the joint meeting of the Scottish Section with the Polarographic Society and the Caithness Technical Society at Dounreay in September.

The Analytical Methods Committee has again extended its activities, and during the year the work of its many committees has progressed. Methods of analysis for additives in animal feeding stuffs—work being undertaken at the request of the Scientific Sub-Committee of the Ministry of Agriculture, Fisheries and Food—has reached an advanced stage and publication can be expected in the near future. A research scholar has been appointed to work at Rothamsted Experimental Station on the investigation of bioassay methods for determining toxic

pesticide residues in foodstuffs, this appointment following on the report by Mr. P. H. Needham on the use of such methods, published in *The Analyst*.

The Annual Conference of Honorary Secretaries of Sections and Groups was held on May 17th, 1960. Once again the meeting proved of great value to the Honorary Secretaries in enabling them to meet and discuss questions of mutual interest. The advisability of altering the date of the Conference was discussed so that it might be easier for joint meetings to be planned.

Council records with pleasure the award of the C.B.E. to Mr. E. J. Vaughan, the award of the O.B.E. to Mr. M. Lovett and Mr. A. A. Smales and the award of the M.B.E. to Mr. C. H. Allen.

The Society now has 1998 members, an increase of 57 over the membership of a year ago.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to Sir Harry Jephcott and Mr. P. N. Mould, who have completed 40 years of membership.

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

F. W. F. Arnaud	A. Lees	W. B. Shaw
A. Bacon	H. Lowe	W. H. Simmons
H. Baggesgaard-Rasmussen	W. Marsden	L. H. Smith
E. Brodaty	J. McCrae	G. Taylor
A. S. Carlos	J. H. Oliver	G. Thomas
R. D. T. E. Chandler	J. W. Paterson	T. Tickle
E. M. Hawkins	P. Schidrowitz	R. F. Wright
L. G. S. Hebbs		

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

March, 1960, in London, Joint Meeting with the Fine Chemicals Group of the Society of Chemical Industry on Techniques of Automatic Analysis:

"Automatic Analysis in the Chemical Industry," by R. M. Pearson, A.R.I.C.
"Automation in Clinical Biochemistry," by I. D. P. Wootton, M.A., M.B., Ph.D., F.R.I.C.

April, 1960, in London:

"A Combined Gravimetric and Photometric Procedure for the Determination of Silica in Silicate Rocks and Minerals," by P. G. Jeffery, M.Sc., Ph.D., D.I.C., A.R.C.S., F.R.I.C., and A. D. Wilson, B.Sc.
"The Estimation of Trimethylene Glycol in Glycerol by Gas Chromatography," by J. Clifford, B.Sc., M.A.
"Direct Colorimetric Determination of Trace Chloride," by T. Nash, M.A., B.Sc., A.R.I.C.

April, 1960, in London, Joint Symposium with the Fertiliser Society on Fertiliser Analysis:

Nine papers were read at this meeting; for details see *The Analyst*, 1960, **85**, 305.

May, 1960, in London, Joint Symposium with the Iron and Steel Institute and the Institute of Metals on The Determination of Gases in Metals:

Sixteen papers were read at this meeting: for details see *The Analyst*, 1960, **85**, 385.

June, 1960, in Edinburgh, Joint Symposium with the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum:

Thirty-five papers were read at this meeting. A report of the Symposium appears in *The Analyst*, 1960, **85**, 457.

September, 1960, in London, on The Chemist and Food Quality:

"The Food Analyst To-day and Yesterday," by A. J. Amos, B.Sc., Ph.D., F.R.I.C.
"Some Applications of Research to the Study and Control of Consistency in Certain Foods," by E. H. Steiner, B.Sc., F.R.I.C.
"Estimation of the Polyphenolic Oxidation Products in Tea as an Assessment of Tea Quality—The Spectrophotometric Estimation of Theaflavins and Thearubigins in Black Tea Liquors," by E. A. H. Roberts, M.A., D.Phil., and R. F. Smith, B.Sc., F.R.I.C.
"The Analysis of Volatile Strawberry Flavours," by D. S. Bidmead, A.R.I.C.

October, 1960, in London:

"Paper Chromatography of Some Organo-tin Compounds," by D. J. Williams, B.Sc., and J. W. Price, Ph.D., F.R.I.C.
"A Procedure for Determining the Molar Extinction Coefficients of Metal Dithizonates," by H. M. N. H. Irving, M.A., D.Phil., D.Sc., F.R.I.C., and R. S. Ramakrishna, B.Sc.
"The Spectrophotometric Determination of Microgram Amounts of Calcium," by J. R. W. Kerr.

November, 1960, in London, on Analysis of Semi-conductors:

Introductory Remarks by C. A. Parker, B.Sc., Ph.D., F.R.I.C.
"The Determination of Some Trace Impurities in Gallium Arsenide by Square-wave Polarography," by V. J. Jennings, B.Sc., Ph.D.
"The Determination of Phosphorus in Silicon by a Fluorimetric Method," by R. E. Minns, A.R.I.C.
"Experiments on the Detection and Determination of Impurities in Silicon by Means of Gas Chromatography," by J. E. Still, B.Sc., F.R.I.C., and R. C. Chirnside, F.R.I.C.
"The Determination of Boron in Silicon by Isotope Dilution," by D. C. Newton, B.Sc., J. Sanders, A.I.M., and A. C. Tyrrell.
"The Spectrographic Analysis of Trace Impurities in Indium, following Chemical Concentration," by J. F. Duke, B.A., H. R. Whitehead, B.Sc., and H. R. Sullivan.
"Determination of Impurities in Semi-conductors by Spark-source Mass Spectrometry," by R. Brown and J. D. Waldron, B.Sc., Ph.D.
"Radioactivation Analysis," by J. A. James, M.A., B.Sc., A.R.I.C.

December, 1960, in London, on The Flask Combustion Technique:

Introduction by W. Schöniger, Dr.ing.
"Apparatus for Electrical Ignition," by J. Haslam, D.Sc., F.R.I.C., J. B. Hamilton and D. C. M. Squirrell, B.Sc., F.R.I.C.
"Determination of Halogens," by C. A. Johnson, B.Pharm., B.Sc., F.P.S., F.R.I.C.
"Determination of Boron," by Miss M. Corner, B.Sc., F.R.I.C.
"Determination of Phosphorus," by E. Q. Laws, B.Sc., F.R.I.C.
"Determination of Sulphur," by Miss J. P. Dixon, A.R.I.C.

February, 1961, in London, on X-ray Fluorescence, organised by the Physical Methods Group:

"X-ray Fluorescence Spectroscopy," by K. M. Bills.
"Some Analytical Applications of X-ray Fluorescence Spectrometry," by F. Brown, B.Sc., Ph.D., A.R.I.C.

NORTH OF ENGLAND SECTION—The membership of the Section is 430, compared with 411 last year. During 1960, ten meetings were held, including four Joint Meetings and the usual Summer Meeting. The following papers were read and discussed—

Manchester, January, 1960, Annual General Meeting:

"Analytical Methods in Clinical Biochemistry," by H. Varley, M.Sc., F.R.I.C.

Manchester, March, 1960:

"The Analysis of Non-soapy Detergent Products," by G. F. Longman, B.Sc., F.R.I.C.

Liverpool, April, 1960:

"The Application of Isotopes to Analysis," by G. B. Cook, Ph.D., and J. W. Lucas, B.Sc., F.R.I.C.

Hull, May, 1960, jointly with the Microchemistry Group and the University of Hull Chemical Society, on Corrosion:

"Oxidation of Metals by Oxygen at High Temperatures," by S. J. Gregg, D.Sc., F.R.I.C., A.R.C.S.
"X-ray Studies of Some Metal Oxidation and Corrosion Problems," by H. P. Rooksby, B.Sc., F.Inst.P.

Llandudno, June, 1960, Summer Meeting:

"The Baking Scientist," by J. B. M. Coppock, O.B.E., Ph.D., F.R.I.C.

Chester, September, 1960, jointly with the Physical Methods Group:

"Applications of X-ray Spectrometry in the Oil Industry," by R. W. Toft, A.R.I.C., D.I.C.
"The Identification of Substances of Low Volatility by Pyrolysis - Gas Liquid Chromatography," by G. C. Hewitt, B.Sc., Ph.D., and B. T. Whitham, B.Sc., A.R.I.C.

Bangor, September, 1960, jointly with the Microchemistry Group and the North Wales Section of the Royal Institute of Chemistry:

"Techniques and Scales of Analysis," by Professor R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F., and Professor C. L. Wilson, Ph.D., D.Sc., F.R.I.C., F.I.C.I.

Leeds, November, 1960:

"The Analytical Chemistry of Phosphorus," by N. T. Wilkinson, F.R.I.C.

Newcastle, November, 1960, jointly with the Newcastle and North-East Coast Section of the Royal Institute of Chemistry:

"The Changing Aspect of Chemical Analysis," by H. N. Wilson, F.R.I.C.

Liverpool, December, 1960:

"Experiences in the Estimation of Some Elements in Foodstuffs," by H. Pritchard, M.Sc., F.R.I.C.

SCOTTISH SECTION—The membership of the Section has decreased by 11 to 116.

The Section has had a particularly active year, despite one scientific meeting less than in 1959; of the meetings held, four were in Glasgow, two in Edinburgh, and the seventh took the form of a Joint Meeting with the Polarographic Society and the Caithness Technical Society, held at Dounreay in the Lecture Hall of the Experimental Reactor Establishment of the U.K.A.E.A. After the papers and afternoon tea, the visitors were taken on a most interesting tour of the Establishment, which included the Fast Reactor and the Analytical Laboratories.

Of the Glasgow meetings, the first was the twenty-fifth Annual General Meeting, which took the usual form of a lunch, followed by the business meeting and an address from our Past President, Dr. D. W. Kent-Jones.

The last meeting in Glasgow was of particular significance, not only as the annual occasion when the Society now combines with the three Chartered Bodies as joint sponsor, but in that responsibility for arranging the meeting fell this year on the Society. The Section was very fortunate in being able to call on our President, who was in Glasgow from the previous evening, where he had most successfully Chaired the 1960 Ramsay Dinner, at which the Principal Guest was Sir Alexander Fleck.

Last, but certainly not least, the major activity of the Section during the first half of the year was in the organisation of many aspects of the Third Gas Chromatography Symposium, jointly with the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum, and our Society, culminating in the highly successful holding of the Symposium in the Assembly Rooms, Edinburgh, during the second week of June.

The following papers have been presented and discussed—

Edinburgh, January, 1960:

"Applications of Infra-red Spectroscopy," by L. J. Bellamy, B.Sc., Ph.D.
"An Application of G.L.C.—Infra-red Spectroscopy Technique," by D. M. W. Anderson, B.Sc., Ph.D., A.R.I.C.

Glasgow, January, 1960, Annual General Meeting:

"The Work of the Cereal Chemist: Some Aspects of New Techniques," by D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.

Glasgow, February, 1960:

"Analytical Methods in the Hygienic Control of Industrial Atmospheres," by J. C. Gage, B.Sc., Ph.D., F.R.I.C.
"Analytical Problems in the Isolation and Measurement of Traces of Radioactivity in Foods," by Professor J. Hawthorn, B.Sc., Ph.D., A.R.C.S.T., F.R.I.C.

Edinburgh, March, 1960:

"The Control of Quality in Synthetic Foodstuff Colours," by H. E. Stagg, B.Sc., F.R.I.C.

Glasgow, April, 1960:

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

Dounreay, September, 1960, jointly with the Polarographic Society and the Caithness Technical Society:

"Tesla-luminescence in Inorganic and Organic Systems," by R. J. Magee, M.Sc., Ph.D., A.R.I.C.
"Applications of Polarography in Industrial Analysis," by G. F. Reynolds, M.Sc., F.R.I.C.
"The Assay of Carbon-14 and Other Low-energy β-emitters," by J. C. Bevington, M.A., Ph.D., D.Sc.

Edinburgh, October, 1960:

"Some Aspects of the Analytical Chemistry of the Heteropolymolybdates," by R. A. Chalmers, B.Sc., Ph.D., and A. G. Sinclair, B.Sc.
"A Colorimetric Determination of Sulphite," by W. Moser, B.Sc., R. A. Chalmers, B.Sc., Ph.D., and A. G. Fogg.
"Some Factors Affecting the Use of Amalgams as Reductants," by R. A. Chalmers, B.Sc., Ph.D., W. Moser, B.Sc., and D. A. Thomson, B.Sc.

Glasgow, December, 1960, jointly with the Chemical Society, the Society of Chemical Industry and the Royal Institute of Chemistry:

"Ramsay, Chemistry and the Electrical Industry," by R. C. Chirnside, F.R.I.C.

WESTERN SECTION—The membership of the Section is 102, an increase of 1 during the year.

Since the beginning of 1960, 6 meetings have been held, including the A.G.M. All have been joint meetings with the Royal Institute of Chemistry or the Society of Chemical Industry, or both, or with other sections of our own Society. As in previous years, the meetings have been widely separated over the area of the Section and attendances have been good, except for isolated instances when the meeting has clashed with other meetings in the area.

The following papers have been presented and discussed—

January, 1960, Bristol, jointly with the Bristol and District Section of the Royal Institute of Chemistry:

"Radiochemical Analysis," by J. N. Andrews, B.Sc., Ph.D., D.I.C., A.R.I.C.

March, 1960, Swansea, jointly with the South Wales Section of the Royal Institute of Chemistry:

"Advantages and Disadvantages of Visual Colorimetry," by G. J. Chamberlin.

May, 1960, Poole, jointly with the Physical Methods Group, on Atomic-absorption Spectroscopy:

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

May, 1960, Plymouth, Summer meeting jointly with the South Western Counties Section of the Royal Institute of Chemistry:

"Trace Elements in Sea-water," by L. H. N. Cooper, Ph.D., D.Sc.

October, 1960, Salisbury, jointly with the Mid-Southern Counties Section of the Royal Institute of Chemistry:

"Some Observations on Analytical Chemistry," by J. Haslam, D.Sc., F.R.I.C.

December, 1960, Newport, jointly with the Cardiff and District Section of the Royal Institute of Chemistry and the South Wales Section of the Society of Chemical Industry:

"Radioactivity in Relation to Water Supplies," by F. P. Hornby, B.Sc., F.R.I.C.

MIDLANDS SECTION—The membership of the Section on December 31st, 1960, was 344, consisting of 310 ordinary members and 34 junior members. This is an increase of 8 ordinary members and 1 junior member during the year. There are 9 Honorary Members.

The programme for 1960 has been marked by three events of outstanding interest.

Continuing the practice of the Section to invite every year an eminent chemist from abroad to speak on some topic of direct interest to analytical chemists, Professor Gutmann of Vienna gave a stimulating talk on "Some Analytical Aspects of Reactions in Non-aqueous Solutions." This meeting was held on February 24th jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry. In July the Section organised a successful 2-day Symposium on "Analytical Chemistry in the Service of Agriculture." Held in one of the Halls of Residence of Nottingham University, this venture attracted upwards of 80 delegates, including a number of visitors from the Continent. Mr. R. C. Chirnside, President of the Society, made the opening address, and in the subsequent sessions the Chair

was taken by Dr. D. C. Garratt, Professor R. Belcher and Dr. S. H. Jenkins. During the Symposium, visits were paid to the Veterinary and Horticultural Research Stations of Messrs. Boots Pure Drug Co., and an informal dinner was held in the Portland Building of the University. Seven papers were read and summaries appear in *The Analyst*, 1960, **85**, 617.

Three of the papers submitted in the competition for the Elwell Award were read at a meeting of the Section in September, 1960. The Award consists of a silver cigarette box having an inlaid plaque in some of the newer industrial metals and is held for 1 year by a chemist not over 30 years of age who, in the opinion of a panel of judges, submits the best paper on an analytical topic. A gift of books to the value of 3 guineas accompanies the Trophy, which on this occasion was awarded to Mr. D. J. Brindley for a paper on "The Polarographic Determination of Niobium in Highly Alloyed Steels."

The following papers have been presented and discussed—

January, 1960, Birmingham: presentation of papers for the Elwell Award, 1959:

"The Polarographic Determination of Small Amounts of Tin and Lead in Zirconium and its Alloys," by R. T. Clark.
"Neutron Activation Analysis of High Purity Aluminium," by D. Hazelby.
"The Assay of Sodium Citrate and Sodium Potassium Tartrate by (*a*) Cation Exchange and (*b*) Non-Aqueous Titrimetry," by M. L. Richardson.

January, 1960, Birmingham, jointly with the Microchemistry Group:

"Micro Gas Analysis," by G. J. Minkoff, D.Sc., D.I.C.

February, 1960, Birmingham, jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry:

"Some Analytical Aspects of Reactions in Certain Non-aqueous Solutions," by Professor V. Gutmann.

March, 1960, Birmingham:

"Plant Growth Promoting Substances—Some Analytical Aspects," by Professor R. L. Wain, D.Sc., Ph.D., F.R.I.C.

March, 1960, Nottingham:

Annual General Meeting.

April, 1960, Birmingham:

"The Analytical Chemistry of Titanium and Zirconium," by W. T. Elwell, F.R.I.C., and D. F. Wood, B.Sc., A.R.I.C.

May, 1960, Nottingham:

"The Application of Gas - Liquid Chromatography to the Analysis of Essential Oils," by D. Holness, B.A.

July, 1960, Nottingham, Symposium on Analytical Chemistry in the Service of Agriculture:

Seven papers were read at this meeting; for details see *The Analyst*, 1960, **85**, 617.

September, 1960, Birmingham: presentation of papers for the Elwell Award, 1960:

"The Polarographic Determination of Niobium in Highly Alloyed Steels," by D. J. Brindley.
"The Identification of Vapour-phase and Liquid-phase Gums Found in Gas Plant and Appliances," by P. M. Owens.
"Moisture Determination in Carbon Dioxide Gas", by J. A. Roff.

October, 1960, Coventry:

"The Analytical Chemistry of Chromium and Vanadium," by G. M. Holmes, F.R.I.C.

October, 1960, Nottingham:

"Paper Chromatography of Dyestuffs," by J. C. Brown.

November, 1960, Birmingham, jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry:

"Analytical Problems in Forensic Toxicology," by F. L. Cann, B.Sc., A.R.I.C.

December, 1960, Birmingham:

"The Analysis of Waters Used in Industry," by K. B. Coates.

December, 1960, Nottingham:

"The Development of the Analytical Balance," by K. M. Ogden.

MICROCHEMISTRY GROUP—The membership of the Group is now 718, an increase of 29 in the past year.

During 1960 four Ordinary Meetings of the Group were held: in Birmingham on January 12th (together with the Midlands Section); in London on February 19th (the Annual General Meeting of the Group followed by a Joint Meeting with the Biological Methods Group); in Hull on May 13th (jointly with the North of England Section and the University of Hull Chemical Society); and in Bangor on September 30th and October 1st (together with the North of England Section and the North Wales Section of the Royal Institute of Chemistry). The following papers were read—

Birmingham:

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

London:

"Micro-analysis in Clinical Biochemistry," by Professor E. J. King, M.A., D.Sc., F.R.I.C.
"Completely Automatic Methods in Micro-analysis," by I. D. P. Wootton, M.A., M.B., Ph.D., F.R.I.C.
"Automatic Titration Apparatus," by Ruth Haslam, M.B., D.C.P., and I. D. P. Wootton, M.A., M.B., Ph.D., F.R.I.C.
"Flame Photometric Analysis of Divalent Cations in Biological Materials," by I. MacIntyre, M.B.
"Optical Rotatory Dispersion," by W. Klyne, M.A., D.Sc.
"Spectrofluorimetric Determination of Alkaline Phosphatase in Micro Quantities of Serum," by D. W. Moss, M.A.

Hull:

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

Bangor:

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

Five informal discussion meetings were held in London and one in Bangor. The following are the topics discussed, and the speakers who introduced them—

"Treatment of Inorganic and Organic Materials for the Determination of Metals," introduced by C. Whalley, B.Sc., F.R.I.C.
"Titrations in Non-aqueous Solvents," introduced by E. H. Tinley, B.Sc., F.P.S.
"The Direct Determination of Oxygen," introduced by D. W. Wilson, M.Sc., F.R.I.C.
"Techniques and Scales of Analysis," introduced by Professor R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F., and Professor C. L. Wilson, Ph.D., D.Sc., F.R.I.C., F.I.C.I.
"Analytical Aspects of Corrosion," introduced by H. C. J. Saint, A.R.I.C.
A Review of Topics in Organic Micro-analysis.

PHYSICAL METHODS GROUP—The membership of the Group is now 782, an increase of 32 since the last Annual Report.

During the past year the Group has held four Ordinary Meetings and organised a Joint Meeting of the Society with the Oils and Fats Group of the Society of Chemical Industry in February. Two of the Ordinary Meetings were held in London and one each in Poole, Chester and Oxford. The Poole meeting was held jointly with the Western Section, the Chester meeting with the North of England Section and the Oxford meeting with the Thames Valley Section of the Royal Institute of Chemistry.

Following the Annual General Meeting on November 24th, 1959, the retiring Chairman, Mr. R. A. C. Isbell, delivered a lecture entitled "The Design of Optical Instruments for Chemical Analysis."

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

Automatic Analytical Instrumentation—London, April, 1960:

"Auto Analyzer," by A. L. J. Buckle, M.Sc., Ph.D., A.R.I.C.
"E.I.L. Model 24 Automatic Titrimeter," by G. Mattock, B.Sc., Ph.D., A.R.I.C.
"D. C. L. Null-balance Magnetic Oxygen Analyser," by C. W. Munday, B.Sc., A.R.I.C.
"Mervyn - CERL Automatic Sulphur Dioxide Recorder," by Mrs. M. W. Redfearn.

Atomic-absorption Spectroscopy—Poole, May, 1960:

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

Chester, September, 1960:

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

Nuclear Magnetic Resonance—Oxford, October, 1960:

General Introduction by R. E. Richards, M.A., D.Phil., F.R.S.
"The Application of Broad-line Nuclear Magnetic Resonance to Inorganic Analysis," by D. J. Ferrett, M.A., D.Phil.
"Applications of Nuclear Magnetic Resonance in Organic Chemistry," by L. M. Jackman, Ph.D.

BIOLOGICAL METHODS GROUP—During the year the membership of the Group has decreased from 310 to 308.

In the year ending October 31st, 1960, the Group has held, in addition to the Annual General Meeting, five Ordinary Meetings and made one laboratory visit. The following papers were read and discussed—

December, 1959, London, on Biological Methods in Forensic Science:

"Biological Methods in Forensic Toxicology," by A. S. Curry, M.A., Ph.D., A.R.I.C.
"Some Experiments on the Determination of Alcohol in Biological Fluids by the Alcohol Dehydrogenase Method," by H. J. Walls, B.Sc., Ph.D.
"Enzymes and Antibodies in Forensic Science," by S. S. Kind, B.Sc.

January, 1960, London:

"Antibiotic Assays in Body Fluids," by Professor L. Garrod, M.A., M.D., F.R.C.P.

February, 1960, London, jointly with the Microchemistry Group:

Details of the papers read at this meeting are given in the report on the Microchemistry Group.

April, 1960, London, on Hormones in Clinical Practice:

"Assay of Gonadotrophins in Body Fluids," by J. A. Loraine, M.D., Ch.B., M.R.C.P.
"Insulin Assay in Plasma by the Rat Diaphragm Method," by P. H. Wright, M.Sc., M.B., Ch.B.

October, 1960, London, on The Biological Assay of Insecticidal Residues:

Introduction by J. H. Hamence, M.Sc., Ph.D., F.R.I.C.
"Biological Techniques for the Detection and Estimation of Insecticidal Residues," by P. H. Need ham, B.Sc.
"Industrial Approach to the Biological Assay of Insecticidal Residues," J. G. Reynolds, F.R.I.C., and R. Goulden, F.R.I.C.

ANALYTICAL METHODS COMMITTEE—During the past year the Committee, its Sub-Committees and Panels, and the Joint Committee with The Pharmaceutical Society, have maintained the level of activity reported a year ago. Three new Committees have been appointed and one Panel of the Joint Committee has been disbanded on completion of its work: the total number of Committees is now 22, an increase of 2 over last year.

In addition to the Annual Report of the Committee, 6 Reports of Sub-Committees and Panels and 2 Reports of special investigational work have been published in *The Analyst*. These are—

Reports of Sub-Committees and Panels:

"Fiore Method for Determining Linalol: Amendment," by the Essential Oils Sub-Committee (*March*).
"The Determination of Small Amounts of Arsenic in Organic Matter," by the Metallic Impurities in Organic Matter Sub-Committee (*September*).
"Methods for the Destruction of Organic Matter," by the Metallic Impurities in Organic Matter Sub-Committee (*September*).
"Assay of Rauwolfia," by the Joint Committee of The Pharmaceutical Society and the Society for Analytical Chemistry (*October*).

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

"The Determination of Small Amounts of DDT in Flour and Other Foodstuffs" (*August*).
"The Determination of Malathion Residues in Cereals and Oilseeds" (*December*).

Reports of Special Investigational Work:

"The Determination of Trace Quantities of Silver in Trade Effluents," by T. B. Pierce (*March*).
"Investigation into the Use of Bioassay for Pesticide Residues in Foodstuffs," by P. H. Needham (*November*).

The investigational work published in the last-named Report formed the basis of an evening meeting organised by the Biological Methods Group in October.

A further development arising from Mr. Needham's investigations has been the appointment of the Society's second Scholar, Dr. J. H. Stevenson, to carry out research for a year at Rothamsted Experimental Station under Mr. Needham's supervision. The research work is directed, in the first instance, to a comparison of the general sensitivities and convenience in use of a limited number of organisms that are already known to be reactive to small amounts of toxic pesticides.

The various Sub-Committees and Panels of the Analytical Methods Committee have continued to be active throughout the year and special mention may be made of the progress made by the Additives in Animal Feeding Stuffs Sub-Committee and its associated Sub-Committee on Trace Elements in Fertilisers and Feeding Stuffs. The latter Sub-Committee is nearing the end of its programme and it is hoped to publish within the next year a full report of its work covering investigations into methods of analysis for 15 elements and giving details of the methods finally recommended. All the five Panels of the former Sub-Committee have been very active during the year and a number of reports are in course of preparation; it is hoped that these will be published during the coming year. The Metallic Impurities in Organic Matter Sub-Committee published two reports in the September issue of *The Analyst*, and work is now proceeding on methods for copper and mercury

One new Sub-Committee of the Analytical Methods Committee—that on primary analytical standards—has been appointed, following a request from the Analytical Chemistry Section of I.U.P.A.C. for a critical examination of the various substances that have been proposed as standards, with a view to making specific recommendations on behalf of the United Kingdom.

Two new Panels of the Joint Committee with The Pharmaceutical Society were appointed during the year—one to investigate methods of assay of pyrethrum and the other to investigate the biological methods of assay of anthraquinone drugs. After the publication of the report on the Assay of Rauwolfia, the Panel concerned with its preparation has been disbanded. Two of the other Panels of the Joint Committee, whose first Reports were published in 1959, are continuing their work.

Mr. S. C. Jolly, whose appointment as part-time Publications Secretary was announced a year ago, is engaged in revising the Bibliography of Standard, Tentative and Recommended or Recognised Methods of Analysis, originally published in 1951, and is also editing all the recommended methods that have been published from time to time in Reports of the Analytical Methods Committee with a view to their publication as a collection of the Society's recommended methods of analysis.

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

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

Joint Library Committee, Chemical Society:

Dr. J. G. A. Griffiths.

British Iron and Steel Research Association:

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

Parliamentary and Scientific Committee:

Dr. J. H. Hamence.

Royal Institute of Chemistry, Summer School Organising Committee:

Mr. A. N. Leather and Mr. C. Whalley.

Chemical Council:

Dr. A. J. Amos.

B.S.I. Committees:

Mr. S. A. Price: Chemical Divisional Council.
Dr. R. A. Lawrie: Meat and Meat Products.
Dr. J. H. Hamence: Cereals and Pulses.
Dr. K. A. Williams: Oils, Seeds and Vegetable Oils.
Mr. L. J. Hamilton: Antibiotics in Dairy Products.
Dr. J. G. Davis: Sampling of Dairy Products.
Mr. A. G. Hill: Lovibond Colour Scale—C.I.E. System.
Dr. K. A. Williams: Home Produced Technical Tallow.
Dr. K. A. Williams: Home Produced Technical Bonegrease.

Standing Advisory Council, Fertilisers and Feeding Stuffs Act:

Dr. J. H. Hamence.

British National Committee for Chemistry:

Dr. R. E. Stuckey.

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

HONORARY TREASURER'S REPORT—The income derived from each of the sources from which the Society obtains most of its revenue, namely, members' subscriptions, sales of *The Analyst* and *Analytical Abstracts*, advertisements and interest on investments, was greater in the year ended October 31st, 1960, than in the previous year, the total increase in revenue from these sources being £3137, but the profit on "other publications" was less in 1960 by £425 because of the concentration of sales of the Decennial Index in 1959. The net result was a rise in income of £2712.

On the expenditure side the cost of producing and distributing *The Analyst* and *Analytical Abstracts* rose by £3823, an increase greater than the total increase in income, and sums of £303 and £445 were spent respectively upon the publication of a new List of Members and upon redecoration of the Council Room. Hence, despite the enhanced revenue the surplus of income over expenditure excluding money put to reserves was less than that of 1959 by £1557.

Despite this expected fall in the disposable surplus of income over expenditure, the sum available for distribution between reserves and the Accumulated Fund at the close of the Society's books in 1960 was £6827, an outcome that fully justifies the confident outlook reported last year.

The cost of administering the Society's activities, excluding expenditure on publications, the finances of the Analytical Methods Committee and money put to reserves, represents a charge of £2 10s. 0d. per member. For the remaining 13s. of his subscription each member receives each year copies of *The Analyst* and *Analytical Abstracts*, the annual subscription for which to non-members is £8 8s. 0d.

PROGRAMMES COMMITTEE—The Committee arranged an ambitious series of meetings during 1960. A glance down the list given earlier in this report will indicate how an attempt was made to break away from the usual type of programme and also to cater for as wide a section of Society members as possible. The policy of establishing closer contacts with other learned Societies and Groups is indicated by the fact that out of ten meetings or Symposia arranged, four were held jointly with other bodies.

As in previous years, two evening meetings were devoted to the presentation of papers submitted for publication in *The Analyst*. These attracted somewhat larger audiences than had attended previous meetings of this kind, but the attendances in general were still somewhat disappointing. On the other hand the joint meeting with the Fine Chemicals Group of the Society of Chemical Industry on "Techniques of Automatic Analysis," the meeting on "Analysis of Semiconductors" and that on "The Flask Combustion Technique" proved extremely popular.

Special mention should be made of the three Symposia. The first one, held jointly with the Fertiliser Society on "Fertiliser Analysis," provided a platform for the presentation of work done by Committees from both Societies, and many of the methods described during the meeting may well become standard in the Fertiliser Industry. The Symposium arranged jointly with the Iron and Steel Institute and the Institute of Metals was important, not only for the fact that it was the first time "The Determination of Gases in Metals" had been the subject of a Symposium in this country, but because it was the first time that the two Institutes had come together for a meeting of any kind. The response so greatly exceeded the expectations of the Organising Committee, over 330 delegates being registered, that a new hall had to be booked a few days before the meeting to provide sufficient seating. The result of this was that tea and coffee could not be provided and the delegates were not as comfortable as one would have hoped, but despite these shortcomings the meeting was highly successful. The Gas Chromatography Symposium in Edinburgh was organised jointly with the Gas Chromatography Discussion Group, and a great deal of help was given by the Scottish Section of the Society. It was by far our most ambitious project and 560 delegates were attracted, 160 of them from overseas. Apart from the scientific programme an exhibition of commercial equipment was organised and receptions were held for delegates and their ladies on three evenings. Two of these functions were given by the Lord Provost of Edinburgh and the British Petroleum Company, respectively. A ladies' programme of visits to local industries and beauty spots was arranged, and on the final day the delegates had an opportunity to visit Scottish industries. The proceedings of all these three Symposia were published in book form.

The Committee intends to continue a policy of close co-operation with other Groups and hopes that Society members will give full support to these activities.

THE ANALYST—The Council and the Publication Committee have continued to consider *The Analyst* and to seek ways in which its value to analysts can be enhanced. Innovations during the year include the publication of an important general lecture on "The Changing Aspect of Chemical Analysis," originally given by H. N. Wilson to the North of England Section in October, 1959, and it is hoped that other lectures of a similar calibre will follow. This is in addition to the biennial Bernard Dyer Memorial Lecture, given in 1960 by Professor A. C. Frazer, which was published in May. The first of the monographs forecast in last year's Report will appear shortly; it is on "Methods for the Analysis of Non-soapy Detergent Products," by G. F. Longman and J. Hilton.

The Publication Committee has compared the numbers of papers in various fields of analysis published in *The Analyst* with the numbers of abstracts in the same fields appearing in *Analytical Abstracts* during the corresponding period. In this comparison with world analytical literature, it appears that *The Analyst* carries its fair share of papers on most topics. The Publication Committee is also discussing the sources from which papers come with a view to taking steps to increase the number of papers from certain quarters.

The 1960 volume of *The Analyst* contained 928 pages, against 756 in 1959. This is greater than any previous volume except that for 1952, which in addition to its normal contents contained the full proceedings of the International Congress on Analytical Chemistry held that year at Oxford. More papers and notes were published in 1960 than ever before: 118 and 66, respectively, compared with 89 and 52 in 1959. As last year, six Review Papers are included in this total, and also two Reports to the Analytical Methods Committee on Special Researches and one Lecture of general interest.

The number of copies of each issue being printed is 6900.

Summaries of 28 papers presented at meetings but not being published in full anywhere were printed in the Proceedings of the Society. Fifty-six books were reviewed.

Fifteen issues of the Bulletin were distributed with *The Analyst* during the year. Although it is published only when there are announcements to be made, the Bulletin has appeared in all twelve months this year (two in each of the first three months); this has been brought about by the increasing activity throughout the year of the Society, its Sections and its Groups.

ANALYTICAL ABSTRACTS—The steady growth of *Analytical Abstracts* has continued during the year in spite of difficulties of maintaining an adequate staff. The number of abstracts published in Volume 7 was 5522, contained in 732 pages, as compared with 5073

abstracts in 692 pages in 1959. In spite of this the number of abstracts remaining unpublished, and consequently the interval between publication of the original paper and the abstract, has not been substantially reduced; this interval is now on the average about eight months.

The Index for 1959 was published on April 27th, which was the scheduled date, a month earlier than in the previous year.

Although the printing number for 1960 was fixed at 6800, stocks have been reduced almost to vanishing point owing to the fact that sales have increased to an unexpectedly high figure.

The membership of the Abstracts Committee remains unchanged.

R. C. CHIRNSIDE, *President.*
R. E. STUCKEY, *Honorary Secretary.*

Report of the Analytical Methods Committee 1960

THIS sixth Report of the Analytical Methods Committee of The Society for Analytical Chemistry reviews the progress of work during 1960; however, the period covered is from March 1st to December 31st, *i.e.*, ten months only.

GENERAL REVIEW

The Committee was sorry to learn of the death in December of Mr. W. H. Simmons. Mr. Simmons's long association with the Committee goes right back to its formation in 1924, when he became its first Honorary Secretary, an office he held until 1946, and he was also Chairman of the Essential Oils Sub-Committee from 1933 to 1956. On his retirement from the active work of the Sub-Committee he was elected an honorary member in recognition of his long and devoted service and in gratitude for all the valuable help and guidance he so willingly gave over the years.

During the year, the Committee was sorry to lose, through resignation, Mr. W. T. Elwell, and the opportunity is taken here to thank him for his help.

During the year, also, the Committee was glad to welcome two ex-members, namely, Dr. J. Haslam and Dr. R. F. Milton, and a new member, Mr. E. Bishop.

PROGRESS OF WORK—

The Committee is again able to report steady progress in its work, as evidenced by the continued output of published reports and by an increase in the number of committees, which now total 22, two more than last year. The willingness with which all members of committees have undertaken the tasks before them cannot be too highly rated, and their constant enthusiasm in collaborative tests in their own laboratories has made possible the successful development of the Committee's work during the past few years.

This is illustrated by the progress of work in the five panels dealing with methods for Additives in Animal Feeding Stuffs. The Sub-Committee responsible for co-ordinating the work of these panels was appointed at the end of 1958 in response to a request for help from the Standing Advisory Committee, Fertilisers and Feeding Stuffs Act, 1926, of the Ministry of Agriculture, Fisheries and Food. It immediately set to work to review any methods that might be available for determining in the supplemented or medicated feed any of the large number of additives that are, or are likely to be, used. The list of additives to be considered was a formidable one, and, after the preliminary review of methods for the additives *per se* had shown that few, if any, of them could be applied to the determination of those additives when contained in the feed, a somewhat gloomy picture was presented in an Interim Report to the Ministry's Advisory Committee at the end of 1959. Much investigational work was envisaged and the prospects of an early success in finding suitable methods were not particularly encouraging.

However, after a further year in which intensive collaborative work has been carried out, the outlook as presented in a second Interim Report to the Advisory Committee is much brighter. A number of methods can now be recommended (some with certain limitations), and the panels are at present engaged in preparing reports on the work carried out in connection with them: it is hoped that these reports will be published during the coming year. Meanwhile, collaborative investigations into methods for the remaining additives are proceeding, but success in these projects may not be so rapid, since the problems to be solved are acknowledged to be more difficult than in the first group.

The rôle of a sixth panel of this Sub-Committee, dealing with the group of mineral additives, was undertaken by the existing Sub-Committee engaged in the preparation of methods for determining Trace Elements in Fertilisers and Feeding Stuffs. This Sub-Committee had already been in existence for about a year and a half before the Additives Sub-Committee was appointed and, like the latter, had been set up as a result of an approach by the same Advisory Committee to the Ministry. The lengthy programme of work that it undertook is now virtually complete, methods for 15 elements having been agreed upon. In a few cases more than one method is to be recommended for the same element, according to the level to be determined (the content in a fertiliser may differ markedly from that in a feeding stuff) and also according to the nature of the sample, since the types of ingredients may demand a different technique.

The results of this Sub-Committee's work are now being prepared as an integrated report, and it is hoped that this will be ready for publication within the next few months.

Another Sub-Committee to complete part of its programme of work is that engaged on methods for determining Metallic Impurities in Organic Matter. The term "organic matter" here covers a wide variety of materials and can be said to include any organic substance whose use is affected by the presence of toxic or deleterious traces of metals, *e.g.*, foodstuffs, drugs, plastics, lubricating oils. For this reason, the Sub-Committee aims at recommending a method that is satisfactorily selective for a particular trace metal and can be used in any normal up-to-date laboratory. Further, because the organic materials to be examined are of such diverse types, the correct preparation of the sample is of the utmost importance. The Sub-Committee therefore decided that it would be expedient to make a comprehensive collection of accepted and reliable procedures for the destruction of the organic matter, arranged on a systematic basis and depending on the ease with which this can be achieved without loss of the metal to be determined.

This has been done and the collected methods were published in the September, 1960, issue of *The Analyst*. Also in the same issue was the Sub-Committee's report on The Determination of Small Amounts of Arsenic in Organic Matter. This report recommends a method

in which molybdenum blue is used, and it also includes a revision of the standard Gutzeit procedure.

Another committee report to be published during the year was that by a panel of the Joint Committee with the Pharmaceutical Society, on The Assay of Rauwolfia. Mention was made a year ago of the imminent completion of this panel's programme of work, and the report was subsequently published in the October, 1960, issue of *The Analyst*.

Two other reports mentioned last year as being in the press were concerned with special investigational work commissioned by the Analytical Methods Committee: both were subsequently published in *The Analyst* during the year. One, on The Determination of Trace Quantities of Silver in Trade Effluents, appeared in the March issue, and describes the investigations carried out by Mr. T. B. Pierce at Oxford in an attempt to evolve a sufficiently sensitive method for determining down to 0·01 p.p.m. of silver in the presence of organic matter. The Joint Committee of The Society for Analytical Chemistry and the Association of British Chemical Manufacturers, whose book of collected Recommended Methods for the Analysis of Trade Effluents was published in 1958, had suggested that a suitable method should be sought, since silver (although it is an unlikely contaminant of trade effluents because of its economic value) adversely affects the anaerobic bacterial processes in sewage treatment and is toxic to fish and other aquatic life. As a result a method is recommended that satisfactorily concentrates and separates the silver, which is then determined absorptiometrically. Other possible techniques are also described.

The other report, on An Investigation into the Use of Bioassay for Pesticide Residues in Foodstuffs, was by Mr. P. H. Needham, who made an extensive survey of the extent to which bioassays are used in laboratories in the United Kingdom and in European countries as a rapid "screening" test for detecting or determining toxic residues. Mr. Needham's report was published in the November issue of *The Analyst*, having previously formed the basis of an evening discussion meeting organised by the Biological Methods Group of the Society in October.

The results of this survey were most illuminating, because they showed that bioassay techniques involving small arthropods are being used much more extensively than had been suspected from a scrutiny of the literature. This was due to the fact that most of the laboratories have developed internally their own techniques to suit individual requirements —usually to give a quick comparative assessment of the toxicity of samples in which the identity of the pesticide is known. Although some investigational work, principally in continental laboratories, is being done in an attempt to use bioassay as a qualitative "screening" test for foodstuff samples in which the identity of the pesticide is unknown, most laboratories still rely on chemical and chromatographic methods for identification purposes: in only one laboratory that was visited was any attempt being made to develop a biological technique for classifying pesticides into groups.

The need for a rapid sorting test has been evident for some time, since the usual chemical methods for identifying or assaying pesticide residues in foods are so lengthy as to be of little value for use on perishable foodstuffs. Mr. Needham's survey showed the considerable potentialities of bioassay techniques, but it was clear that a considerable amount of standardisation would be required before bioassay could be used on a more general basis. Further consultation with representatives of laboratories using bioassays indicated that research work would first be needed to establish the correct conditions of breeding and use of a selected number of organisms and to determine their comparative sensitivities towards certain pesticides. A second stage of investigational work would be to ascertain the best methods of preparing foodstuff samples for bioassay to avoid extraneous toxic effects.

As a result, it was decided that the Society should appoint a research scholar to initiate this work of standardisation, and it was encouraging to learn that a number of laboratories in this country were willing to co-operate in any way possible. At the beginning of November, therefore, Dr. J. H. Stevenson, an entomologist, was appointed as the Society's Scholar to undertake this work at Rothamsted Experimental Station under the general guidance of Mr. Needham, and the Society is most grateful to the Director of the Station for his generosity in providing the necessary facilities.

Two other reports to be published during the year are those on Recommended Methods of Analysis of Pesticide Residues in Foodstuffs. Early in 1958, two Panels were set up jointly by the Society for Analytical Chemistry (represented by the Analytical Methods Committee), the Scientific Sub-Committee of the Interdepartmental Advisory Committee on Poisonous

Substances Used in Agriculture and Food Storage and the Association of British Insecticide Manufacturers (now the Association of British Manufacturers of Agricultural Chemicals). These two Panels undertook collaborative studies of analytical methods for DDT and BHC residues. Later, in 1959, two more Joint Panels were set up to study methods for determining malathion and organo-mercury residues. Of these four Panels, those concerned with DDT and malathion have completed their programmes of work, and their reports were published, respectively, in the August and December issues of *The Analyst*. Recently it has been agreed to set up two more Joint Panels—on fluoracetamide and Phosdrin residues.

Mention was made earlier in this Report of the appointment of new committees during the year. One of these is undertaking a critical examination of the various substances that have been proposed for use as primary standards in acidimetry and alkalimetry, and it has been set up as a result of a request from the Analytical Chemistry Section of the International Union of Pure and Applied Chemistry for recommendations of suitable substances—these recommendations to be made on behalf of the United Kingdom. Since a similar programme of work for primary standards as a whole had been proposed for consideration by the Microchemistry Group of the Society, it was agreed to amalgamate the work into a single Sub-Committee under the aegis of the A.M.C., since the personnel of both committees would be virtually the same. The Sub-Committee, with Mr. E. Bishop as Chairman, began its work in June; a classification of the various proposed standards has been made, and these are being examined critically with a view to evaluating them according to certain criteria.

The second committee to be appointed is concerned with the assay of crude drugs being undertaken by the Joint Committee with the Pharmaceutical Society. This particular Panel is examining the various biological techniques used for the assay of anthraquinone drugs (senna, cascara, aloes, etc.), since it was found that the existing Panel concerned with methods for the chemical assay of these substances could not usefully proceed until some measure of agreement of results obtained by different bioassay methods could be established.

A third new Sub-Committee of the A.M.C. is also to be appointed as soon as possible to make a comprehensive review of Methods for Particle Size Analysis, with a view to evaluating the various principles underlying the instrumental methods used for determinations of particle size in the sub-sieve range. This Sub-Committee will be under the chairmanship of Mr. E. Q. Laws.

The other Sub-Committees and Panels have continued to make progress during the year, and details of their personnel and reports of work will be found below.

ANALYTICAL METHODS TRUST—

The number of industrial organisations that gave donations to the Trust Fund during the year was 32 (the same as in 1959) and the total amount received was approximately £4500. This sum represents approximately £400 less in subscriptions than in 1959.

INCOME AND EXPENDITURE—

The statement of accounts (see Appendix I) for the financial year ending October 31st, 1960, shows an expenditure of £4577 (including Scholarship Grants and Awards for Research). The gross income of £6283 includes £955 income tax recovered on Covenanted Subscriptions over a period of five years.

REPORTS OF SUB-COMMITTEES OF THE ANALYTICAL METHODS COMMITTEE

PUBLICATIONS SUB-COMMITTEE

CONSTITUTION—

D. C. Garratt, Ph.D., D.Sc., F.R.I.C. (*Chairman*)	*Chairman, Analytical Methods Committee*
J. B. Attrill, M.A., F.R.I.C.	*Editor*, The Analyst
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Member, Analytical Methods Committee*
D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.	*Member, Analytical Methods Committee*
H. N. Wilson, F.R.I.C.	*Member, Analytical Methods Committee*
S. C. Jolly, B.Sc., B.Pharm., M.P.S., A.R.I.C. (*Secretary*)	*Editor, Scientific Publications, The Pharmaceutical Society of Great Britain*

PROGRESS OF WORK—

Progress has been made on the preparatory editorial work necessary for the publication in 1961 of the proposed book of Standard Methods of Analysis, which is to consist of a

collection of the recommended methods of analysis included in the published Reports of the various Sub-Committees and Joint Committees, together with a bibliography based on that published by the Analytical Methods Committee in 1951. The revision and expansion of this bibliography has been started and should be completed early in 1961.

Additives in Animal Feeding Stuffs Sub-Committee

Constitution—

D. C. Garratt, Ph.D., D.Sc., F.R.I.C. (*Chairman*)	*Boots Pure Drug Co. Ltd.*
A. J. Amos, B.Sc., Ph.D., F.R.I.C.	*Analytical and Consulting Chemist*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
R. F. Phipers, B.Sc., Ph.D.	*Cooper Technical Bureau*
S. A. Price, B.Sc., F.R.I.C.	*Vitamins Ltd.*
C. J. Regan, B.Sc., F.R.I.C.	Formerly *Chemist-in-Chief, London County Council*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C.	*British Drug Houses Ltd.*
F. R. Williams	*Ministry of Agriculture, Fisheries and Food*
Miss C. H. Tinker (*Secretary*)	

Terms of reference—"To investigate and prepare methods for determining the amounts of additives (nutrients, stimulants and prophylactics) in animal and poultry feeding stuffs."

Progress of work—

The general progress of work in the Sub-Committee and in its six Panels has been reviewed earlier in this Report (see p. 298), and the detailed reports of the Panels are given below. The question of animal dietetics is receiving a considerable amount of attention these days, and there is an increasing demand for adequate methods of analysis for the control of feeding stuffs; at a Symposium on "Analytical Chemistry in the Service of Agriculture" organised by the Society at Nottingham in July, 1960, the Sub-Committee's work in this connection was presented in a paper by Dr. R. F. Phipers, Chairman of the Prophylactics Panel.

Antibiotics Panel

Constitution—

S. A. Price, B.Sc., F.R.I.C. (*Chairman*)	*Vitamins Ltd.*
A. J. Cavell, M.Sc., A.R.C.S., D.I.C., F.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
Mrs. J. Gammon, B.Sc. (*née* Stephens)	*Cyanamid of Great Britain Ltd., Lederle Laboratories*
O. Hughes	*Pfizer Ltd.*
W. P. Jones, F.P.S., F.R.I.C.	*Cyanamid of Great Britain Ltd., Lederle Laboratories*
G. Sykes, M.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
J. H. Taylor, Ph.D., M.R.C.V.S.	*Cyanamid of Great Britain Ltd., Agricultural Division*
S. Varsanyi, A.I.S.T.	*Glaxo Laboratories Ltd.*
Miss A. M. Parry (*Secretary*)	

Progress of work—

Early in its work the Panel confirmed that each of the three antibiotics, penicillin, aureomycin and oxytetracycline, could be assayed by chemical or microbiological methods in their respective pre-mixes (*i.e.*, at the level of a few grams per pound).

Chemical methods are not applicable at the levels at which antibiotics are added to feeding stuffs (a few grams per ton), and the Panel has therefore examined microbiological methods with a view to recommending procedures that would be similar for all three antibiotics. Methods have now been agreed upon by which reproducible results can be obtained on feeding stuffs containing any one of the three antibiotics. However, these methods require a sample of the unfortified feed for use as a blank; since in normal practice this is unlikely to be available, investigations are now in progress on procedures for producing a "blank" by destruction of the antibiotic in the fortified sample.

The development of methods for the assay of samples containing more than one antibiotic and those containing additives, such as prophylactics or other drugs, in addition to the antibiotic will require more extensive investigations and probably original research.

HORMONES PANEL

CONSTITUTION—

R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C. (*Chairman*)	*British Drug Houses Ltd.*
J. Allen, A.R.I.C.	*British Drug Houses Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
J. A. Potter, A.R.I.C.	*Analytical and Consulting Chemist*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
Miss A. M. Parry (*Secretary*)	

PROGRESS OF WORK—

Chemical methods for the assay of stilboestrol and hexoestrol in feeding stuffs have been examined and tested collaboratively. The methods are now considered to be satisfactory and reports are being prepared.

PROPHYLACTICS PANEL

CONSTITUTION—

R. F. Phipers, B.Sc., Ph.D. (*Chairman*)	*Cooper Technical Bureau*
C. W. Ballard, B.Sc., F.P.S., F.R.I.C.	*May & Baker Ltd.*
N. C. Brown, M.A., B.Sc., A.R.I.C.	*Cooper Technical Bureau*
H. G. Dickenson, B.Sc., Ph.D.	*Ward, Blenkinsop & Co. Ltd.*
A. W. Hartley, F.R.I.C.	*Spillers Ltd.*
A. Holbrook, F.R.I.C.	*Imperial Chemical Industries Ltd.* (*Pharmaceuticals Division*)
S. G. E. Stevens, B.Sc., F.R.I.C.	*Smith Kline & French Laboratories Ltd.*
J. A. Stubbles, B.Sc.	*May & Baker Ltd.*
Miss A. M. Parry (*Secretary*)	

PROGRESS OF WORK—

The use of complex feeding stuffs in collaborative assays revealed the need for further modification of the method for nitrofurazone, but the Panel now considers the method to be satisfactory, and a report is being prepared. Similarly, the colorimetric method for the assay of sulphaquinoxaline was found to be inapplicable to certain feeding stuffs, and collaborative work on the sulpha drugs has therefore been deferred pending the outcome of investigations by one member of the Panel into a paper-chromatographic method of separation.

After preliminary trials by individual members of the Panel, methods are now being considered for the assay of nicarbazin and of acinitrazole, and collaborative tests on the latter are in progress.

The Panel is keeping under review the introduction and use of new coccidiostats and anti-blackhead drugs and will, as necessary, revise the list of prophylactics to be investigated.

VITAMINS (FAT-SOLUBLE) PANEL

CONSTITUTION—

W. L. Sheppard, F.R.I.C. (*Chairman*)	*Unilever Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
C. R. Louden, B.Sc., F.R.I.C.	*R. Silcock & Sons Ltd.*
H. Pritchard, M.Sc., F.R.I.C.	*Analytical and Consulting Chemist*
S. A. Reed, B.Sc., A.R.I.C.	*British Cod Liver Oils (Hull and Grimsby) Ltd.*
G. Walley, B.Sc., F.R.I.C.	*Unilever Ltd.*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
Miss C. H. Tinker (*Secretary*)	

PROGRESS OF WORK—

No meetings of this Panel were held during the year, but collaborative tests have nevertheless continued, and the Panel is now satisfied that the spectrophotometric method is suitable, provided that strict attention is given to procedural detail, for the determination of vitamin A and of β-carotene in most types of feeding stuffs. The Panel's report is now being prepared, and it is hoped to publish it shortly. Meanwhile, further collaborative work has been proceeding in the hope that an alternative quick method can be included in the report; this method depends on the formation of anhydro-vitamin A, which is determined colorimetrically.

VITAMINS (WATER-SOLUBLE) PANEL

CONSTITUTION—

A. J. Amos, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
J. E. Ford, B.Sc., Ph.D.	*National Institute for Research in Dairying*
B. M. Gibbs, B.Sc., A.R.I.C.	*Unilever Ltd.*
S. A. Price, B.Sc., F.R.I.C.	*Vitamins Ltd.*
H. Pritchard, M.Sc., F.R.I.C.	*Analytical and Consulting Chemist*
F. Clermont Scott, B.Sc., F.R.I.C.	*Vitamins Ltd.*
G. Sykes, M.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
S. Varsanyi, A.I.S.T.	*Glaxo Laboratories Ltd.*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
Miss C. H. Tinker (*Secretary*)	

PROGRESS OF WORK—

Accepted methods for the following B-group vitamins have been investigated to ascertain whether or not they can be made applicable to the determination of those vitamins when present at low concentration in feeding stuffs: nicotinic acid; vitamin B_{12}; pantothenic acid; riboflavin; pyridoxin (vitamin B_6); and choline.

For all these vitamins microbiological methods have been investigated, but chemical methods for pyridoxin and choline are also under consideration.

For the first three vitamins in the above list—nicotinic acid, vitamin B_{12} and pantothenic acid—methods can now be recommended for use in feeding-stuff assays, the order of accuracy of the determinations being about ± 30 per cent. in the hands of experienced microbiologists. It is hoped that these reports will be published shortly.

In all tests the total vitamin is determined, *i.e.*, naturally occurring plus added vitamin. However, the total reported may not necessarily be a measure of the biological value of the feeding stuff as a source of the vitamin in question, since it is known that in some instances the naturally occurring vitamin may be present in a "bound" form. For instance, nicotinic acid can occur as a bound form in cereal products, and this, though unavailable to the domestic animal, is extracted completely during the normal assay procedure; on the other hand, some bound forms of naturally occurring pantothenic acid may not be wholly available to the test organism unless a special dual-enzyme system is employed for extraction.

Methods for the remaining three vitamins—riboflavin, pyridoxin and choline—are still under investigation. For riboflavin, although reproducible results were obtained by all the Panel members when assaying the same extract, the extraction procedure itself requires more investigation than the Panel members can carry out on a collaborative basis, and this is being looked into privately by one of the laboratories concerned.

ANALYTICAL STANDARDS SUB-COMMITTEE

CONSTITUTION—

E. Bishop, B.Sc., A.R.C.S.T., A.R.I.C. (*Chairman*)	*University of Exeter (Department of Chemistry)*
P. R. W. Baker, M.Sc., A.R.I.C.	*Wellcome Research Laboratories*
A. G. Hill, F.R.I.C.	*British Drug Houses Ltd.*
R. M. Pearson, A.R.I.C.	*Imperial Chemical Industries Ltd. (Billingham Division)*
W. I. Stephen, B.Sc., Ph.D., A.R.I.C.	*University of Birmingham (Department of Chemistry)*
C. Whalley, B.Sc., F.R.I.C. (*deputy* S. Andrus, A.R.I.C.)	*Laporte Chemicals Ltd.*
J. T. Yardley, B.Sc., F.R.I.C.	*Hopkin & Williams Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To examine existing analytical standards and to select suitable substances."

PROGRAMME OF WORK—

As mentioned earlier in this Report (see p. 300), this Sub-Committee was set up in response to a request from the Analytical Chemistry Section of the International Union of Pure and Applied Chemistry that a critical examination be made of the various substances that have been proposed for use as primary standards in acidimetry and alkalimetry, with

a view to making recommendations on behalf of the United Kingdom. Work on titrimetric standards in general, which was being considered by the Microanalytical Reagents and Standards Sub-Committee of the Microchemistry Group of the Society, will also be undertaken by the present Sub-Committee.

The substances submitted to the Sub-Committee for consideration in the first place were listed in two groups, (*a*) established standards and (*b*) newer proposed standards, as follows—

(*a*) *Established standards*	(*b*) *New standards*
Sodium carbonate	Sodium hydrogen diglycollate
Constant-boiling hydrochloric acid	2,4,6-Trinitrobenzoic acid
Borax	Sulphuric acid
Potassium hydrogen phthalate	3,3′-Dinitrosulphimide
Sulphamic acid	Calcium hydrogen malate hexahydrate
Potassium bi-iodate	4-Aminopyridine
Benzoic acid	Tris(hydroxymethyl)aminomethane
	Potassium hydrogen 3,5-dinitrobenzoate

Hydrazine sulphate was added to list (*a*) at the Sub-Committee's first meeting in June, 1960.

PROGRESS OF WORK—

Since its first meeting in June, 1960, the Sub-Committee has defined its objectives as follows—

(*a*) To survey existing standard substances suitable for acid - base titrimetry.

(*b*) To classify these according to (*i*) their purity, (*ii*) their facility of preparation and handling and (*iii*) their titrimetric application.

(*c*) To select one or more substances for recommendation as reference standards in compliance with the I.U.P.A.C. referendum.

(*d*) To draw up specifications for the preparation, handling, purity and use of the standards chosen.

(*e*) To draw up specifications within their own categories for other substances found suitable for general application.

Reports prepared by members on each of the established standards, and on some of the newer ones, have enabled the Sub-Committee to evaluate the suitability of these substances as primary standards and to select the most promising for immediate examination. Collaborative tests on the first phase of the experimental work are being designed.

CHLORINE IN ORGANIC COMPOUNDS SUB-COMMITTEE

CONSTITUTION—

R. Belcher, Ph.D., D.Sc., F.Inst.F., F.R.I.C. (*Chairman*)	*University of Birmingham (Professor of Analytical Chemistry)*
J. H. Dunn, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
K. Gardner, B.Sc., F.R.I.C.	*Fisons Pest Control Ltd.*
R. Goulden, F.R.I.C.	*"Shell" Research Ltd.*
C. A. Johnson, B.Sc., B.Pharm., F.P.S., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
Miss A. M. G. Macdonald, M.Sc., Ph.D., A.R.I.C.	*University of Birmingham (Department of Chemistry)*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To prepare methods for the determination of organically-bound chlorine, having special reference to commercial preparations such as pesticides."

PROGRESS OF WORK—

The Sub-Committee met only once during the year. The application of the oxygen flask combustion method to the semi-micro determination of organically bound chlorine in technical grades of pesticides and in solid and liquid formulations is considered satisfactory for products containing not less than 10 per cent. of chlorine, but not for low-concentrate dusts, since the high proportion of inorganic filler prevents complete combustion. The Sub-Committee's report on its investigations, together with details of the recommended analytical procedure, is to be prepared for publication.

Essential Oils Sub-Committee

Constitution—

G. W. Ferguson, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
A. J. M. Bailey, B.Sc., F.P.S., F.R.I.C.	*W. J. Bush & Co. Ltd.*
D. Holness, B.A.	*Proprietary Perfumes Ltd.*
H. T. Islip, B.Sc., F.R.I.C.	Formerly *D.S.I.R., Tropical Products Institute*
P. McGregor, B.Sc., A.H.-W.C., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
T. L. Parkinson, B.Sc., Ph.D., F.R.I.C.	*Beecham Foods Ltd.*
Miss H. M. Perry, M.Sc., F.R.I.C.	*Stafford Allen & Sons Ltd.*
G. B. Pickering, B.Sc., Ph.D.	*D.S.I.R., Tropical Products Institute*
J. H. Seager, M.Sc., F.R.I.C.	*Yardley & Co. Ltd.*
S. G. E. Stevens, B.Sc., F.R.I.C.	*Smith Kline & French Laboratories Ltd.*
B. D. Sully, B.Sc., Ph.D., A.R.C.S., F.R.I.C.	*A. Boake, Roberts & Co. Ltd.*
Miss C. H. Tinker (*Secretary*)	

Progress of work—

In the Sub-Committee's Report on the Determination of Linalol, published in 1957, the Glichitch method was recommended as being preferable to the Fiore method. Subsequently, however, one of the Sub-Committee members has conclusively demonstrated by the use of gas - liquid chromatography that the mechanism of the Fiore method is the sounder (Holness, D., *Analyst*, 1959, **84**, 3). The Sub-Committee therefore decided to reverse its original recommendation, and an Amendment to the 1957 Report has been published accordingly (*Analyst*, 1960, **85**, 165). This use of gas - liquid chromatography for tracing the course of certain chemical reactions has already been applied by the Sub-Committee to demonstrate the inaccuracies of hot-formylation methods for determining citronellol (*Analyst*, 1959, **84**, 690).

The Sub-Committee is continuing its collaborative investigations of various methods for the determination of citral and of carbonyl compounds.

Meat Products Sub-Committee

Constitution—

S. M. Herschdoerfer, Ph.D., F.R.I.C. (*Chairman*)	*T. Wall & Sons Ltd.*
S. Back, B.Sc., F.R.I.C.	*Crosse & Blackwell Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.*	*British Food Manufacturing Industries Research Association*
P. O. Dennis, B.Sc., F.R.I.C.	*Oxo Ltd.*
J. R. Fraser, B.Sc., A.C.G.F.C., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
R. A. Lawrie, B.Sc., Ph.D., F.R.I.C.	*A.R.C., Low Temperature Research Station*
A. McM. Taylor, B.Sc., Ph.D., F.R.I.C.	*British Food Manufacturing Industries Research Association*
E. F. Williams, M.A., F.R.I.C. (*deputy* H. C. Hornsey, F.R.I.C.)	*J. Sainsbury Ltd.*
H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.	*Public Analyst*
Miss C. H. Tinker (*Secretary*)	

* Resigned July, 1960.

Terms of reference—"(*a*) The determination of the meat content of products containing meat; (*b*) the determination of the constituents of meat and meat products.

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

Progress of work—

A year ago it was announced that the Sub-Committee had prepared an interim report on nitrogen factors for pork. However, in view of the receipt of additional data from various meat research organisations in this country and in Europe, together with some data for the nitrogen content of rusk filler made from present-day flour, the Sub-Committee decided to expand the report considerably and to add a short report on rusk filler. This has now been completed, and it is hoped to publish the full report shortly. Meanwhile, similar data on the nitrogen contents of beef, veal and chicken meat are being collected.

METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

W. C. Johnson, M.B.E., F.R.I.C. (*Chairman*)	*Hopkin & Williams Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.*	*British Food Manufacturing Industries Research Association*
J. C. Gage, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
T. T. Gorsuch, B.Sc., Ph.D., A.R.I.C.	*U.K. Atomic Energy Authority, The Radiochemical Centre*
E. I. Johnson, M.Sc., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
Miss E. M. Johnson, M.Sc.	*British Food Manufacturing Industries Research Association*
T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C.†	*Public Analyst*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
E. J. Newman, B.Sc., A.R.I.C.	*Hopkin & Williams Ltd.*
W. G. Sharples, A.R.I.C.	*Imperial Chemical Industries Ltd. (Dyestuffs Division)*
Miss A. M. Parry (*Secretary*)	

* Resigned July, 1960. † Resigned October, 1960.

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

PROGRESS OF WORK—

As mentioned earlier in this Report (see p. 298), two reports from the Sub-Committee were published in the September issue of *The Analyst*, namely, The Determination of Arsenic in Small Amounts of Organic Matter, containing details of a method in which molybdenum blue is used and of the Gutzeit procedure, and Methods for the Destruction of Organic Matter, in which are assembled methods for both wet and dry decomposition, which are in general use and are of fairly wide applicability.

The Sub-Committee has considered the relative merits of a number of reagents and methods recognised for the determination of copper; because a recommended method should be as widely applicable as possible both in selectivity and sensitivity, comparative tests are being carried out before a decision is made as to the most suitable method.

Several methods are under review for the determination of mercury, since it is unlikely that a single method will be applicable to all types of sample.

The Sub-Committee is being kept informed of the work of the following bodies—

Trace Elements in Fertilisers and Feeding Stuffs Sub-Committee.

Mercury Residues Panel set up jointly by the Scientific Sub-Committee on Poisonous Substances used in Agriculture and Food Storage, the Analytical Methods Committee and the Association of British Manufacturers of Agricultural Chemicals.

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

CONSTITUTION—

D. W. Wilson, M.Sc., F.R.I.C. (*Chairman*)	*Sir John Cass College (Department of Chemistry)*
P. R. W. Baker, M.Sc., A.R.I.C.	*Wellcome Research Laboratories*
Miss B. B. Bauminger, Ph.D., A.I.R.I., F.R.I.C.	*Dunlop Research Centre*
W. T. Chambers, B.Sc., Ph.D., A.R.I.C.	*British Rubber Producers' Research Association*
A. F. Colson, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Alkali Division)*
Miss M. Corner, B.Sc., F.R.I.C.	*D.S.I.R., National Chemical Laboratory*
Miss J. Cuckney	*Imperial College of Science and Technology (Department of Chemistry)*
F. Ellington, B.Sc., A.R.C.S., F.R.I.C.	*National Coal Board, Coal Research Establishment*
F. J. McMurray	*Wellcome Chemical Works*
M. P. Mendoza, B.Sc., A.R.C.S.	*British Coal Utilisation Research Association*
F. H. Oliver	*Parke, Davis & Co.*
H. J. Warlow	*D.S.I.R., Tropical Products Institute*
C. Whalley, B.Sc., F.R.I.C.	*Laporte Chemicals Ltd.*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To investigate the Unterzaucher method, and its modifications, for the micro-determination of oxygen."

PROGRESS OF WORK—

The Sub-Committee has carried out preliminary collaborative tests on the final stage of the method—*i.e.*, the reaction between pure carbon monoxide and iodine pentoxide—and, as a result of these tests, a statistically planned experiment is being devised.

PESTICIDES RESIDUES IN FOODSTUFFS SUB-COMMITTEE

CONSTITUTION—

R. A. E. Galley, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C. (*Chairman*)	*"Shell" Research Ltd.*
J. C. Gage, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
G. S. Hartley, D.Sc.	*Research Centre of Fisons Pest Control Ltd.*
C. O. Harvey, B.Sc., A.R.C.S., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
J. G. Reynolds, F.Inst.Pet., F.R.I.C.	*"Shell" Research Ltd.*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To consider the analytical problems that arise, or may arise, in connection with the presence of pesticide residues in foodstuffs; and to advise as to analytical procedures for the detection and determination of any such residues or their breakdown products."

PROGRESS OF WORK—

This Sub-Committee acts in an advisory capacity only and is not called upon to meet frequently. The progress of work on methods for pesticides residues has been covered in some detail earlier in this Report (see p. 299)—research on bioassay methods being undertaken at Rothamsted Experimental Station by Dr. J. H. Stevenson under the direction of Mr. P. H. Needham, and collaborative testing of chemical methods being undertaken in collaboration with the Association of British Manufacturers of Agricultural Chemicals and the Scientific Sub-Committee of the Interdepartmental Advisory Committee on Poisonous Substances used in Agriculture and Food Storage.

TRACE ELEMENTS IN FERTILISERS AND FEEDING-STUFFS SUB-COMMITTEE

CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C. (*Chairman*)	Formerly *Chemist-in-Chief, London County Council*
S. M. Boden, B.Sc., A.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
S. G. Burgess, B.Sc., Ph.D., F.Inst.Pet., M.Inst.S.P., F.R.I.C.	*London County Council*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
E. I. Johnson, M.Sc., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
R. L. Mitchell, B.Sc., Ph.D., F.R.I.C., F.R.S.E.	*Macaulay Institute for Soil Research*
J. B. E. Patterson, M.Sc., F.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
Miss C. H. Tinker (*Secretary*)	

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

PROGRESS OF WORK—

Methods for all the 11 elements mentioned above have now been agreed upon. A method for small amounts of selenium, which was causing some difficulty a year ago, is now considered suitable for contents down to 2 μg when a colorimetric finish is used or down to 0·5 μg when a fluorimetric finish is used.

In addition to its programme of work, as defined by the Terms of Reference, this Sub-Committee also acts as the Minerals Panel of the Additives in Animal Feeding Stuffs Sub-Committee (*q.v.*) and to this end has now agreed on methods for calcium and salt (as chloride).

Methods for the determination of chromium and nickel in fertilisers are also to be recommended, since these elements may be present if sewage sludges are used.

In all, some 18 methods have been completed, and a comprehensive report is being prepared for publication.

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

MAIN COMMITTEE

CONSTITUTION—

Representing the Pharmaceutical Society of Great Britain—

K. R. Capper, Ph.D., B.Pharm., F.P.S., D.I.C. (*Chairman*)	*Pharmaceutical Society of Great Britain*
J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S., F.R.I.C.	*University of London (Professor of Pharmacognosy)*
R. Higson, F.P.S.	*Ministry of Health, Supplies Division*
W. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Stafford Allen & Sons Ltd.*

Representing the Society for Analytical Chemistry—

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

Representing the Tropical Products Institute, D.S.I.R.—

A. J. Feuell, B.Sc., Ph.D., A.R.I.C.

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*
Miss A. M. Parry, B.Sc. (*Assistant Secretary*)	*Assistant Secretary to the Analytical Methods Committee*

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

PROGRESS OF WORK—

The Main Committee, which acts in a steering capacity, is able to report steady progress in most of its working Panels. In two Panels, however, work has been suspended for the time being to enable some investigations outside their scope to be carried out elsewhere. The suspension of work by Panel 1, pending the outcome of research at Manchester University on chemical and biological methods for digitalis, was announced in last year's Report: the work of Panel 3, on chemical methods for anthraquinone drugs, has been suspended until a reliable biological assessment can be made; until this is achieved, it will not be possible to correlate the chemical methods under investigation. A new Panel, 3A, is undertaking the work on bioassay methods.

The publication in October of the report on the Assay of Rauwolfia brought to an end the programme of work of Panel 4, and this has now been disbanded.

Panels 2 and 5, on methods for capsicum and lonchocarpus, respectively, are continuing their investigations after the publication of their reports last year. The work of Panel 6,

on methods for pyrethrum, has progressed satisfactorily during the twelve months since the Panel's appointment.

Details of the progress by each Panel are given below.

PANEL 1: *Digitalis purpurea*—CHEMICAL METHOD

CONSTITUTION—

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

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

PROGRESS OF WORK—

Research on the separation and assessment of the relative biological activities of the main constituents of digitalis leaf is being carried out by individual workers; meanwhile the work of the Panel has been suspended.

PANEL 2: CAPSICUM—CAPSAICIN CONTENT

CONSTITUTION—

H. B. Heath, M.B.E., B.Pharm., F.P.S. (*Chairman*)	*Stafford Allen & Sons Ltd.*
E. A. Elsbury, F.R.I.C.	*Parke, Davis & Co.*
C. F. G. Fost, M.P.S.	*W. J. Bush & Co. Ltd.*
C. A. MacDonald, B.Sc., F.R.I.C.	*Evans Medical Research Laboratories*
G. R. A. Short, F.P.S., F.L.S.	*W. J. Bush & Co. Ltd.*
G. I. Smales, B.Sc., A.R.I.C.	*Parke, Davis & Co.*
Miss G. M. Wells, B.Sc., A.P.I.	*Beecham Research Laboratories Ltd.*
A. J. Woodgate, B.Sc.	*Stafford Allen & Sons Ltd.*
Miss A. M. Parry (*Secretary*)	

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

PROGRESS OF WORK—

The Panel is now satisfied that its published methods for the determination of capsaicin (*Analyst*, 1959, **84**, 603) can, with suitable modifications, be applied to capsicum wool and to highly coloured chillies: these modifications will be included in the Panel's next report. Since paprika is used mainly as a colouring agent and not for its capsaicin content, there appears to be no need for a method of assaying it.

The Panel is re-considering the colorimetric method for the assay of capsaicin. The published procedure, involving the preparation of the dry diazo compound, is known to be hazardous, and a variation of the method in which the salt is formed in solution is being investigated.

A simplified spectrophotometric procedure, suitable for routine control tests, is also being examined.

The methods already published do not distinguish between pure capsaicin and a synthetic capsaicin-like derivative that is used in certain preparations. Investigations are proceeding into two possible methods, one by selective oxidation and the other by infra-red spectrophotometry, for differentiating between the vanillylamides of isodecanoic acid (capsaicin) and of nonylic acid (synthetic capsaicin).

The Panel is grateful to Messrs. Pfizer Ltd. for gifts of samples of the pure vanillylamide of nonylic acid.

Panel 3: Anthraquinone drugs

Constitution—

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

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

Progress of work—

After examination and modification of a colorimetric chemical method for determining the sennoside content of samples of powdered senna pod, the Panel succeeded in obtaining reasonably good inter-laboratory agreement on samples of Alexandrian senna pods, but rather less satisfactory inter-laboratory agreement on samples of Tinnevelly senna pods. However, biological tests on the same samples gave inconsistent results, and it was not possible to use these to assess the validity of the chemical method as a means of estimating the purgative activity of the drug. The Joint Committee therefore decided to set up another Panel (3A) to examine biological methods of assaying anthraquinone drugs; pending the outcome of this new Panel's work, chemical investigations have been discontinued.

If and when a reliable biological assessment becomes available, chemical work will be resumed on the lines suggested by the Panel in a report to the Joint Committee.

Panel 3A: Biological assay of anthraquinone drugs

Constitution—

K. L. Smith, M.P.S. (*Chairman*)	*Boots Pure Drug Co. Ltd.*
P. F. D'Arcy, B.Pharm., Ph.D., M.P.S.	*Allen & Hanburys Ltd.*
J. W. Fairbarin, B.Sc., Ph.D., F.P.S., F.L.S., F.R.I.C.	*University of London (Professor of Pharmacognosy)*
G. A. Stewart, B.Sc., Ph.D., A.R.I.C.	*Wellcome Biological Control Laboratories*
Miss A. M. Parry (*Secretary*)	

Terms of reference—"To study biological methods for the assay of anthraquinone drugs."

Programme of work—

Biological assays of powdered senna pods, made in order to attempt to correlate results obtained by chemical methods with the purgative activity of the drug, were found to be at variance in assessing the relative potencies of the samples. It was therefore decided that, before the chemical results could be interpreted in terms of biological activity, it would be necessary to establish the conditions under which the biological method of assay would give reproducible results. Accordingly, this Panel was set up to investigate biological methods for the assay of senna and other anthraquinone-containing drugs.

Progress of work—

The Panel held its first meeting in August, 1960, and collaborative work on the assay of senna pods is now in progress.

Panel 4: Rauwolfia

Constitution—

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

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

PROGRESS OF WORK—

As mentioned earlier in this Report (see p. 299), the Panel has completed its programme and its Report was published in the October, 1960, issue of *The Analyst*. The Panel has now been disbanded.

PANEL 5: LONCHOCARPUS AND DERRIS

CONSTITUTION—

R. F. Phipers, B.Sc., Ph.D. (*Chairman*)	*Cooper Technical Bureau*
R. Buckley, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
J. A. Dawson, B.Sc., A.R.I.C.	*D.S.I.R., Tropical Products Institute*
W. E. Drinkwater, F.R.I.C.	*Boots Pure Drug Co. Ltd.*
R. V. Foster, M.Sc., A.R.I.C.	*Cooper Technical Bureau*
S. C. Jolly, B.Sc., B.Pharm., M.P.S., A.R.I.C.	*Pharmaceutical Society of Great Britain*
J. T. Martin, D.Sc., F.R.I.C.	*University of Bristol (Long Ashton Research Station)*
R. A. Rabnott	*Analytical and Consulting Chemist*
F. H. Tresadern	*Stafford Allen & Sons Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate methods of assay of derris, lonchocarpus and their preparations, with particular reference to the determination of their rotenone content."

PROGRESS OF WORK—

The gravimetric method for The Determination of Rotenone in Rotenone-bearing Plants with Special Reference to Lonchocarpus, published by the Panel (*Analyst*, **1959**, **84**, 735), is not applicable to preparations having a very low rotenone content or containing interfering substances. The Panel has therefore been examining a colorimetric method that is used commercially for the control of preparations containing rotenone. This method, although empirical and not necessarily giving the true rotenone content, has been found satisfactory by individual firms. However, when it was applied to preparations in collaborative tests, the results were disappointing, and it was clear that more specific definition of the details of the procedure was required. The Panel is therefore using solutions of pure rotenone to investigate the technique of the method and to determine the optimum conditions for the development of the colour; some progress has been made on these lines, and it is hoped that as a result a method that gives reproducible results will be recommended.

PANEL 6: PYRETHRUM

CONSTITUTION—

W. Mitchell, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Stafford Allen & Sons Ltd.*
H. E. Coomber, B.Sc.	*Mitchell Cotts & Co. Ltd.*
L. Donegan	*D.S.I.R., Tropical Products Institute*
M. Elliott, Ph.D.	*Rothamsted Experimental Station*
A. D. Harford	*British Petroleum Research Centre*
S. C. Jolly, B.Sc., B.Pharm., M.P.S., A.R.I.C.	*Pharmaceutical Society of Great Britain*
W. S. Manson, B.Sc., A.R.I.C.	*Cooper Technical Bureau*
R. A. Rabnott	*Analytical and Consulting Chemist*
F. H. Tresadern	*Stafford Allen & Sons Ltd.*
T. F. West, Ph.D., D.Sc., A.M.I.Chem.E., F.R.I.C.	*African Pyrethrum Technical Information Centre Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate methods of assay of pyrethrum flowers and pyrethrum extract with a view to recommending a standard chemical or physical method of assay."

PROGRESS OF WORK—

For many years difficulties have been experienced in trading in pyrethrum owing to the variations in results of analyses from different laboratories ostensibly using the same or similar methods of assay; despite collaborative trials on an international scale, these difficulties have remained unresolved. In view of the obvious need for a reliable method of assay for pyrethrum, the Joint Committee decided to set up a Panel to investigate the problem.

The Panel began work at the beginning of 1960 and, after reviewing the various types of chemical and physical methods that have been published for the assay of pyrethrum, selected for detailed study a mercury-reduction method, variants of which are most widely used in commerce. It was thought that, since reproducible results could be obtained within individual laboratories, the inter-laboratory discrepancies might arise from differences in technique or quality of reagents; accordingly, the method was drafted in precise detail and tested by seven laboratories, all using portions of the same samples of extract. The inter-laboratory agreement between these laboratories, two of which are in Kenya, was most encouraging.

Work is now in progress to try to establish the critical features of the procedure that may have been responsible for past divergencies in results and to define the techniques that will give the most reproducible results.

The Panel has so far been concerned with extracts of the drug, but intends to extend its work to include the assay of flowers of pyrethrum.

APPENDIX I

THE SOCIETY FOR ANALYTICAL CHEMISTRY ANALYTICAL METHODS TRUST ACCOUNTS FOR THE YEAR ENDED OCTOBER 31ST, 1960

Income and Expenditure Account for the Year Ended October 31st, 1960

1959 £		£	£	*1959* £		£	£
	Rent, Light, Heat and			*4857*	Subscriptions from Industry..	4461	
314	Telephone	246			Income Tax recovered on Covenanted Subscriptions for the years 1954–55 to		
3140	Salaries	3497		—	1958–59	955	
115	Office Equipment ..	46					5416
266	Printing and Stationery	138			Interest from Investments		
23	Travelling Expenses ..	23		*10*	(gross)		10
65	Expenses of Meetings ..	136		*360*	Bank Deposit Interest ..		521
21	Audit Fee and Accountancy	42*			Sales of "Recommended Methods for the Analysis of Trade Effluents," received from Society for Analytical Chemistry		
119	Postage and Petty Expenses	101		*235*	.. .. ..		336
4063			4229				
107	Scholarship Grants and Awards for Research		200				
—	Contribution to Decorations and Fittings of Council Room ..		148				
1292	Excess of Income over Expenditure for the year ended October 31st, 1960, transferred to Accumulated Fund		1706				
£5462			£6283	*£5462*			£6283

Accumulated Fund

1959 £		£	*1959* £		£
14,086	Balance carried to Balance Sheet	15,831	*12,794*	Balance at October 31st, 1959 ..	14,086
			—	Increase in value on Redemption of £100 Government of Ceylon 3½% Stock, 1959	39
			1292	Excess of Income over Expenditure for the year ended October 31st, 1960	1706
£14,086		£15,831	*£14,086*		£15,831

* Including fee for recovering Income Tax on Covenanted Subscriptions.

Balance Sheet at October 31st, 1960

1959			*1959*				
£		£	£	£		£	£
14,086	*Accumulated Fund*	15,831			*Investments (at Cost):*		
3264	*Sundry Creditors*	2728			£100 Government of Ceylon 3½% Stock, 1959 (redeemed		
				61	15.12.59) ..		
					£100 3½% Conversion Stock ..	83	
				83			
				100	£100 3½% War Stock	100	
			244				183
					(Market Value at 31.10.60, £121)		
			22		*Sundry Debtors* ..		36
					Cash:		
					At Bank on—		
				9000	Deposit Account	11,000	
				8084	Current Account	7340	
			17,084				18,340
£17,350		£18,559	*£17,350*				£18,559

Signed on behalf of the Analytical Methods Trust Fund G. H. LLOYD-JACOB, *Chairman*,
J. HUBERT HAMENCE, *Honorary Treasurer*.

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

We have examined the above Balance Sheet which in our opinion gives a true and fair view of the state of affairs of the Trust at 31st October, 1960.

10 New Court,
Lincoln's Inn,
LONDON, W.C.2.
6th February, 1961.

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

APPENDIX II

SUBSCRIBERS TO THE TRUST FUND DURING 1960

Albright & Wilson Ltd.
The Associated Ethyl Co. Ltd.
Boots Pure Drug Co. Ltd.
The British Aluminium Co. Ltd.
The British Drug Houses Ltd.
British Glues & Chemicals Ltd.
British Oxygen Research & Development Ltd.
Brotherton & Co. Ltd.
Central Electricity Generating Board
The Distillers Co. Ltd.
Dunlop Research Centre
Esso Research Ltd.
Glaxo Laboratories Ltd.
Arthur Guinness, Son & Co. (Park Royal) Ltd.
Hopkin & Williams Ltd.
Horlicks Ltd.
Huntley & Palmers Ltd.
Imperial Chemical Industries Ltd.
Laporte Chemicals Ltd.
J. Lyons & Co. Ltd.
Macfarlane, Lang & Co. Ltd.
May & Baker Ltd.
The Metal Box Co. Ltd.
The Millers' Mutual Association
Procea Products Ltd.
Quaker Oats Ltd.
Rowntree & Co. Ltd.
"Shell" Research Ltd.
John & E. Sturge Ltd.
Unilever Ltd.
Vitamins Ltd.
Weston Research Laboratories Ltd.

Address of the Retiring President

R. C. CHIRNSIDE, F.R.I.C.

(Delivered after the Annual General Meeting, March 3rd, 1961)

The Enlargement of Horizons in Analytical Chemistry

IT has been my privilege during the past 33 years to have listened to every Presidential Address to this Society, starting with that of E. R. Bolton in 1928. Bolton opened his address to what he termed "our little Society," with its 580 members, with the following words—

> "The report I have to make to you this evening upon the activities of the past year is a happy story of unprecedented progress, unpunctuated by any very startling events."

I hope that you will not be disappointed or too greatly alarmed when I say that 33 years later, and after a total of 16 years of service on Council, I do not feel quite so confident as Bolton about the state of our health.

I shall not attempt to burden you with an account of my stewardship over the last 2 years—instead I want to invite you first to look a good deal further back over the history of our Society.

It was nearly 50 years ago, in 1912 to be exact, when E. W. Voelcker, the father of our good friend Eric Voelcker, introduced the new President, Leonard Archbutt, Chief Chemist of the Midland Railway, in the following terms—

> "Mr. Archbutt has the distinction of being the first President of this Society who has never held the post of Public Analyst and I think it was a very happy suggestion that the gradual *enlargement of our horizons*—which a few years ago resulted in our incorporation as a Society which embraced all branches of the analytical profession—should now be marked by the election of Mr. Archbutt as President."

May I draw your attention to the phrase from which, like the Scottish preacher, I take my text—"the enlargement of our horizons."

By 1913 we find Archbutt himself saying—

> "I think we ought to have a much larger membership."

and again—

> "I am afraid the amplification of our title in 1905 to the Society of Public Analysts and Other Analytical Chemists has not entirely removed the misconception that we are essentially a Society of Public Analysts."

A few years later, in 1919, Samuel Rideal, the father of Sir Eric Rideal, was President, and he too had something to say about the name—

> "I am not certain," he said, "whether we might not consider shortening the long name of our Society to that of the Society of Analysts and thus bring our title in accord with that of our Journal."

I mention this because Rideal's comment suggests that by 1919 our Journal, *The Analyst*, was thought to be reflecting the gradual enlargement of the Society's horizons.

We now have just on 2000 members, and the misconception to which Archbutt referred as long ago as 1913 is, I hope, dispelled. We have not shortened our name as Rideal suggested, but have changed it, though only after another "40 years on."

It might be argued that the "gradual enlargement" to which Voelcker referred has indeed been gradual, perhaps too gradual. It was certainly a surprise to me to discover, for example, that in the last 50 years the Society has only twice gone outside the rather narrower field of its earlier interests for its President. On the other hand, our journal, *The Analyst*, now has a circulation of nearly 7000, has had several "new looks" and may yet have more. *Analytical Abstracts*, with an even larger circulation, begun in 1954, has already established itself not only in this country but also in some European countries, Scandinavia and the Netherlands, for example, and also in the United States of America.

It has always seemed to me that a learned Society, and we may lay claim since our change of name to be one, stands to be judged primarily by its publications and by its meetings. I have already touched on publications in passing, and I shall have something more to say about them and about meetings in due course. Suffice it to say that much of our thinking has of late gone into both and both continue to be the object of further study. Why, then, in the face of our achievements, do I not radiate satisfaction and optimism like Bolton? It may need greater discernment than I can hope to bring to the task to give you a simple and concise answer.

My main doubt, as I see it, arises from an awareness that, while the Society of recent years has been catching up, analytical chemistry itself has not been standing still. So much so that he would be a brave man who would to-day attempt a proper definition of analytical chemistry or chemical analysis, or indeed a description of the analyst himself. On reflection, however, I did not think this should deter me from trying to put before you at least some aspects of the situation as I see it. The laying down of the seal of office brings with it, I trust, certain freedoms, and possibly a unique opportunity, and a responsibility, to speak —and if necessary to speak out—on the things that seem of greatest import.

Those of us who were born near the beginning of the century can, I think, count ourselves privileged to have lived through such exciting times. In a span of little more than my own lifetime science has grown from an academic pursuit to become an integral part of the background of much of modern industry. Although we must all look with mixed feelings at the undeniable fact that two wars have accelerated this process, it would seem that nothing short of such a crisis can render palatable new ideas, and not only new ideas in chemistry, to naturally conservative minds.

When I entered chemistry just after the end of World War I, few industrial concerns had begun to think really scientifically. They did not in many instances have laboratories of their own—this was true even of some of our basic industries, the coal industry, for example. They certainly did not have research laboratories, for these were not yet fashionable. Analysis as I remember it would in the main have been more properly described as assaying. Analytical determinations were made so as to be able to assess the commercial value of a material. It might, for example, be a determination of the iron or manganese content of an ore, the sulphur content of pyrites, the available chlorine in bleaching powder, the "proximate" analysis and the calorific value of coal. Another requirement of analysis was to check conformity with a standard or a specification. Metals and alloys were subject to specifications of composition and of levels of impurity which, it was fondly believed, could be transmuted by mathematical skill into a satisfying description of mechanical properties. Other materials might have to comply with regulations: mine dusts and mine airs with safety regulations; foods and drugs to certain legal standards or to those established by custom. I well remember on Tyneside how even the grease that was to be used during the launching of a ship had to be tested shortly before the event, and one of my nightmares, when I had been so engaged, was to wonder whether the great ship would slide smoothly into the water the next day or whether, because of some error of mine, the whole ceremony would end in disaster.

Some parts of industry had, it is true, set up analytical laboratories as a first and a laudable effort to introduce science into industry. It was believed, with some justification, that a measure of control in manufacture would result from the analytical information provided about chemical composition or the nature and amount of impurities in raw materials, or in the finished product. The steel industry, for example, has a better record than most in this respect, and I have never ceased to admire the skill and the speed of their "shift" chemists.

Nevertheless, when I first began work in a laboratory, analysts as a whole were in the depressed classes of the chemical community; to be fair, let us add, at a time when there was much depression about. The whole atmosphere of this period is reflected in the closing words of G. Rudd Thompson's address in 1925; they were enough to deter any young man from entering the profession—

> "I appeal therefore," he said, "to those already engaged in analytical chemistry and especially teachers of chemistry to discourage all students who contemplate chemistry as a profession other than that minority who show an exceptional aptitude for this type of work and who are in addition convinced that the satisfaction of chemistry for its own sake can outweigh the very limited prospect of material success which now obtains.

> "The older I get," he went on to say, "the more sympathetic and possibly more pessimistic do I become in regard to this question of the failure of recognition of merit and knowledge acquired after many years of hard work and honest intention. As a Society, as a Council, as individual members, we can do very little to remedy this for we are all more or less in the same boat. A change for the better may come and probably will come in time but how is not for me to suggest nor do I see a means of improvement other than that mentioned."

That was in 1925. My span of professional life has extended over two social extremes; this period of depression in the twenties to the present day, when the analyst begins to have a scarcity value.

I was fortunate not very long after the time of Rudd Thompson's depressing prophecy to find myself in the environment of industrial research, in a pioneer research laboratory. Its work was directed to the scientific and technological problems of a large Company, a Company that was in itself really a collection of industries, ranging from the very old, founded on the arts, like glass and ceramics, to the very new, founded on and derived from basic scientific developments. This was the context in which I was called upon to provide a professional analytical service.

It began to be clear before long that even in those days I had to do some new thinking about analysis and its place in the scheme of things. I came soon to realise that a conception of analysis restricted to a statement of percentage composition, expressed in the arbitrary way that I had come to accept, was often inadequate, and sometimes useless. I learned, too, that even scientists and engineers often did not know the right question to ask of the analyst and almost as often did not fully appreciate or understand the answers they were likely to get from him.

There have been many more lessons to learn since that time during the formative years of a group whose primary objective has been to give scientific service to a number of research groups and also to works engineers and technologists. Over so long a period and with such a variety of interests to cover, I have not unnaturally developed a philosophy about analysis and its purpose, and I venture to think that it comprises some matters of sufficiently general concern to be of interest to you here to-day.

Sooner or later the research worker engaged on any problem in which materials are involved will require certain basic measurements. You will remember Lord Kelvin's classic dictum—

> "When you can measure what you are speaking about and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind."

All analysis ends in measurement, and measurement is a physical process. If this were better remembered or better understood I think there would be less extravagant talk about physical methods of analysis.

Your research worker often finds that his academic training and his experience do not enable him to make these measurements. He may therefore have to choose one of two courses —either to step aside and spend his time in becoming a quasi-expert, or, because this process may have to be repeated many times and because it takes a deal of time to become expert, to go instead for help to a professional service group where they are not only expert in the measurement, but where nowadays the necessary and often extremely expensive equipment for that measurement exists.

At first sight, the second of these choices would seem to be the more profitable, but this is to oversimplify a problem which is often not even diagnosed, and where it is, is by no means completely solved. If for the moment you will accept the term "analysis" to cover what I have referred to as "measurements," although these seldom have any intrinsic value, taken singly or together they often serve to indicate the potentialities of some substance or material.

If you were to ask what do I mean by analysis, and if I were to be allowed to exclude assaying or testing, I could find no more apposite definition than that given some years ago by one of our Past Presidents, E. B. Hughes. He defined analysis as "the examination of a material to ascertain its composition, its properties, its qualities," and I want to suggest to you that the greatest of these is no longer necessarily composition. In my opinion it is just because the term analysis has for so long been interpreted to mean only composition

that so much useless analysis has been and is being carried out, that so many of those who wanted information about the properties or the qualities of a material have been discouraged and are confirmed in their view that the analyst is a poor fellow and that he is giving them an inadequate and sometimes an out-of-date service.

It is in these circumstances that the scientific worker may be tempted to make the first of the choices to which I referred; he will try to get the information he needs himself and, what is more, he will not restrict himself to the use of the tools and techniques that the analyst has been accustomed to think of as his own. Trained though I was as an analyst, I have never been able to share the complaints and protests of the analyst that such a situation seems to engender—indeed, I incline to the view that most of the advances in analytical techniques and tools in the last 20 revolutionary years have come, not from analysts, but from those whom the analyst might in one sense be said to have failed. Some of the most revolutionary and exciting have come from the biochemist, to whom we all owe a great debt; consciously or unconsciously, these developments have arisen because the analyst so often has not been able to give the biochemist or the research worker in some other field the kind of information or measurement he required. I need mention only gas chromatography to illustrate my point.

In my own laboratory we had to learn that our function at times was to resemble that of the physician, and that we had to use our knowledge, our senses and our skills to diagnose, and to help in prescribing remedies for industrial ills. This implied a responsibility and a willingness on the part of the analyst so to enlarge his own field of knowledge as to be able to comprehend the nature of his customers' problems. How otherwise would he be able to scrutinise critically analytical requests, to ensure that they were properly stated, that they were likely to furnish useful information and that their cost would not be wholly incommensurate with their probable value?

I was fortunate to come into contact early in my professional life with sympathetic physicist colleagues, sympathetic, that is, to the philosophy I have been trying to outline. The physicist was himself a newcomer to industry, and he brought with him some new thinking—and some sorely needed new thinking—from which the analyst could not fail to profit. When we began to consider what tools and techniques we had available among us, and what kinds of information we could obtain by an intelligent selection from, or combination of, these various techniques, the possibilities seemed unlimited. It became evident at once that we had to think of a newer and wider conception of the science and the craft that we used to call analytical chemistry and, also, of the person whom we used to call an analytical chemist.

You will, I think, agree at once that to accept the wider conception of analysis that I am suggesting involves a drastic revision of our thinking. The place of the analyst himself may sometimes be taken by a team of specialists, some of whom would formerly have had no place in the traditional analytical laboratory. The professional analyst was always something of a specialist among chemists; he is now often a specialist and not always a chemist among analysts.

I would differentiate, very sharply, analysis from assaying; the determination of the composition of a substance, an important and often enough a difficult matter calling for the highest skill, may nevertheless frequently give only the minimum information required.

But it is not only techniques of analysis that change: it is also the kind of information they give. There can be no static or permanent conception of what constitutes analytical information. This, too, must change as our understanding grows, particularly our knowledge of the solid state. Some of the latest instrumental techniques enable us to get conventional information in a very much shorter time, and their principal application is therefore to testing. I may add that the achievements in this direction, particularly with automatic, direct-reading spectroscopy, are nothing short of sensational.

But I am more concerned to bring to your notice the new kind of information that instrumental and other new techniques make it possible to obtain. I have in mind identification of compounds, or phases, or solid-solution effects, the distinguishing between polymorphic forms of a substance, information on fundamental crystal size and crystal shape, on lattice strain, on inhomogeneity, on inclusions, on differences in surface and body composition, on the nature and amount of impurity at levels in the parts per million, ten million or a hundred million range, on the nature and amount of gases dissolved in solids. All this and more, in my experience, is becoming vital to the study of the behaviour and uses of materials.

I could give examples from my own experience of materials that, on the basis of every conventional chemical method of examination, appear to be identical, yet behave quite differently in some modern application. Two that spring to mind at once, it may surprise you, are the "simple" compounds ferric oxide, Fe_2O_3, and aluminium oxide, Al_2O_3.

Gray and Bacharach[1] have drawn attention recently to some of the equally pressing and more vital analogous problems in biochemistry, "where there is often a need to distinguish between substances for which there do not exist, and possibly never can exist, differential chemical tests." "Nowhere," they say, "has the need for meticulous separation, sometimes on a millimicrogram scale, of closely related compounds been more urgently felt or more diligently sought than in the field of . . . biochemical analysis."

Some of the problems that arise in the analysis of food provide perhaps the best examples of the inadequacy of our present knowledge. Dr. Hamence rightly drew attention in his address 2 years ago to the need for techniques for the separation and determination of natural substances when they are present in a mixture, in contrast to the indirect methods of assessment on which much of our present work has to be based. In this context one has only to think of the arbitrary calculation of "protein" content from a figure for nitrogen, itself derived from an actual determination of ammonia.

This is an occasion when, with some regret, I must resist the temptation to talk in particular about the potentialities and the applications of any one of the modern techniques, chemical, physical or instrumental. I have in any case already given many concrete examples of their use and application in my papers to the Congress on Modern Analytical Chemistry in Industry at St. Andrews in 1957 and to the International Symposium on Microchemistry at Birmingham in 1958.

The analytical revolution of which everyone has become so conscious during the last 15 to 20 years began with us many years earlier when, as I have already mentioned, we invited the help of the physicist in attempting a more novel approach to some of the problems that arose in our own laboratories. This new situation is not without its dangers; indeed, they are already evident. Despite the wonderful new techniques that have been put into our hands, we may merely succeed in amassing many more analytical results in a much shorter time. So far as it goes this may well offer a solution to the vital requirement of speed in many testing laboratories, but it may sometimes be prudent to ask if the results are really necessary. There is, however, a greater hazard. The enthusiasts for many of the modern techniques are in danger of spreading the thought that instrumental techniques render superfluous the classical analyst. This is not yet true; indeed, we are already in difficulties because he is so scarce.

It is true, however, that in some applications of modern instrumental techniques it is not only the analyst but also the analytical laboratory that is rendered superfluous, for with these techniques some qualities of a material in a chemical plant can be continuously monitored and effective automatic control of the process established—the true meaning of automation.

The term "instrumentation" is often enough that used in connection with the measurement of some physical quality other than mass or volume, and we need to remind ourselves sometimes that the chemical balance is a physical instrument. It is of the greatest importance that we use the newer techniques to supplement, or to complement, as well as to replace, classical analytical methods in the measurement of the things that matter, to obtain information that offers the greatest possibility of translation into a useful and satisfying statement of properties of a material, be they mechanical, electrical, biochemical, nutritional, or what you will. In short, we should move away from the nineteenth-century idea that analysis is wholly concerned with a statement of composition and that this, in the inorganic field at least, can be set down as a list of arbitrarily defined oxides or radicals. I would hope also that, as another consequence of the acceptance of such a philosophy, the distinction, hitherto often obscured, between testing and analysis might become more clear.

Seen in retrospect, the golden age of analysis in the last century, to which so many nostalgic references have been made by my predecessors, and the lowering of the status of the analyst in the earlier half of this century are understandable. The present structure of chemistry, geology, mineralogy and some other sciences was built up on analysis: the composition of much that goes to make up our material world was charted and a vast collection of basic information was established. In mineralogy alone the analyst and the microscopist carried out a herculean task. Much of the work was truly heroic, and it was directed to scientific ends. When, later, the emphasis shifted to the commercial control of materials

by analysis or test, to fix a price, to meet a specification, to comply with a regulation—when, in other words, the objective seemed no longer to be so unambiguously scientific—then the status of analysis fell and that of the analyst with it.

We are probably all confident that the status of analysis has now risen again. Can we be quite so confident about the status of the analyst? Paradoxically, I am inclined to think that we cannot, perhaps because it is no longer so easy to identify the analyst. The "tester," of course, presents no such difficulty: "he" is now often "she" or "it," "she," a girl, not necessarily a qualified chemist but having a high degree of skill and intelligence; "it," an instrument, sometimes large, often expensive.

A great deal of what I would regard as true analytical work is now carried out by chemists or physicists who do not consider themselves to be analysts and would describe their work by some name other than analysis. Only a minority of these people may think it appropriate to join the Society for Analytical Chemistry, and I suggest that we cannot begin too early to ask ourselves why this is so. Does the fault lie with the chemist or the physicist, does it lie with the Society, is there indeed a fault, or are we witnessing a change that is in the natural order of things? These are questions to which I suggest an answer must be sought in the next 10 years. You have only to look back at the dramatic developments of the last 10 years to appreciate the force of my argument.

How does the Society stand in relation to what I have been trying to advocate? What has it been doing these 30 years? Perhaps the first stirring from the mood of self-satisfaction reflected by Bolton was towards the end of the war, in late 1944, when the Society, in an effort to meet the changing situation, formed Groups—first the Microchemistry Group and then the Physical Methods and the Biological Methods Groups. May I just quote you two or three sentences from my Chairman's address on the foundation of the Physical Methods Group.[2] I said—

> "Although analysis has made great and essential contributions to all branches of chemistry, there has been a long interval in which it has remained a neglected branch of the science but there are welcome signs of renewed interest in analytical chemistry and in the analyst himself."
>
> "This Society, whose main object as laid down in the Memorandum of Association is to encourage, assist and extend the knowledge and study of analytical chemistry, in forming Groups to deal first with microchemistry, and to-day, with physical methods of analysis, has in my view, given impetus to some sort of movement towards a renaissance in analytical chemistry. It is clear that the activities of such a Group will be concerned with some of the newer tools and techniques by which we may add to our knowledge about the composition, properties and qualities of materials either in or outside the normally accepted problems of analysis."

I think it will be agreed by all that these Groups have done magnificent work, that they have brought to the Society a new breadth of outlook. Indeed, I sometimes wonder whether they have not already accomplished the task they set out to do and whether some re-fusion or coalescence of interest is not now both possible and desirable, for we are frequently faced with the dilemma that a technique is both "physical" and "microchemical" and that it belongs to both Groups, and why not therefore to the Society?

What is much more disturbing to my mind is the whole range of measurements that do not lie specifically without our province. From the first, the Physical Methods Group could provide a platform for only a limited number of techniques in a given period of time. The policy during its early life was frankly educative; after that the changes were rung as often as might be on the newer techniques—of polarography, chromatography, and the like. We once had a Polarographic Discussion Panel and, by what I now believe to be an error of judgment, we disbanded it, only to find its place taken by the Polarographic Society. But the whole issue is now becoming more complex, for analysis now rests on a number of disciplines. Let me give you a picture of the present situation.

Under the auspices of the Institute of Physics, for example, there is an Applied Spectroscopy Group, an Electron Microscopy Group, an X-ray Analysis Group, a Non-destructive Testing Group. There are, operating as "free radicals," the Polarographic Society, to which I have already drawn attention, the Photoelectric Spectrometry Group and the Infra-red Discussion Group. Under the auspices of the Institute of Petroleum there is a very special and in some ways wholly admirable organisation. This is a body, known as the Hydrocarbon

Research Group, born in some special circumstances during the war. This body has now nine members; five are oil companies, one is a national board and the three others are large chemical companies. They each contribute a substantial sum of money to the Group and the Group administers these funds for the support of fundamental research in the universities in a number of fields—in spectroscopy, over the whole range of the electromagnetic spectrum, including, for example, nuclear magnetic resonance, in mass spectrometry, and in hydrocarbon chemistry.

The Gas Chromatography Discussion Group—a body of whose enthusiasm and whose size you need no reminder, for it was with them last summer that we were able to organise such a successful Conference in Edinburgh—was formed in association with the Hydrocarbon Research Group; it was they who were quick to recognise the potentialities of the technique. I well remember how A. J. P. Martin was persuaded to demonstrate gas chromatography for the first time publicly at the International Congress of Analytical Chemistry at Oxford in 1952, and it has been a matter of some disappointment to me that this technique, developed by two of our most brilliant biochemists, should for the moment seem to have passed into other hands. It could be argued that all this was for the best, that no one Society with interests as wide as ours could have lavished so much of its energies in any one particular direction.

I have no doubt at all that these various Discussion Groups have done much to speed up the development of their respective techniques and that we have all benefited as a consequence and owe them a debt. Nevertheless, I do not think we could claim that this factor was uppermost in our minds at the time; rather do I think that there was a lack of immediate realisation of the significance of some of these new techniques. Our Physical Methods Group has now devised a new mechanism to enable it to keep in direct touch with developments. It has set up advisory panels for each of the new techniques and will hope to provide a platform for a meeting on any of these topics at the appropriate time.

All this is not without influence on our publications. In the first instance the coverage required in our Abstracts is very wide. We can also, I think, look not without some pride at our journal, *The Analyst*, transformed out of all recognition since I first had a sight of it in 1922. But the multiplicity of Societies to which I have referred is reflected in an almost equally long list of specialist analytical journals—the Journals of Chromatography, of Polarography, of Electroanalytical Chemistry, etc., not to mention at least one other British and one European journal covering the field of general analytical chemistry.

Apart from any other aspects, it is clear that the subject of analytical chemistry is now among the "best sellers." A learned Society starts with something of a handicap compared with a commercial publishing house, but again, I would think this a cause neither for complaint nor for complacency, and much thought is being given at the moment to future developments in our journal. Review papers and monographs are among the other contemporary developments. I would mention, moreover, that on the cover of *The Analyst* its objectives are set out clearly for all to read—"a publication dealing with all branches of analytical chemistry"—and there is no reason why this should not be as comprehensive as possible. During this last year the proceedings of the two major symposia, which we have helped to organise, have been published in two handsome books—"Gases in Metals" and "The Third Gas Chromatography Symposium"—in both of which we cover many of the techniques of the modern investigator.

What about our meetings, the other main responsibility of the Society? These are revolutionary times and even a scientific society cannot expect to escape the wind of change. It cannot and should not assume that, on the first Wednesday of every month at seven in the evening, a large number of its members will continue to choose to listen to three papers on three diverse problems in analysis just because they have done so in the past, and in preference to the counter-attractions that are now available within or without their homes. It is already evident that we were wise, 2 or 3 years ago, to set up a Programmes Committee and that they in their turn have been wise to fashion a new pattern of meeting.

I would like to refer in more detail to some aspects of the meetings that the Society has held jointly during this last year, first with the Fertiliser Society, then with the two metallurgical institutions—the Iron and Steel Institute and the Institute of Metals—on the determination of Gases in Metals, and later with the Gas Chromatography Discussion Group. The 2-day meeting with the metallurgical institutions, for example, attracted over 300 people, including a number of distinguished workers from the United States of America and from

the continent of Europe. Among the techniques discussed were vacuum fusion, emission spectroscopy, isotope dilution, X-ray emission and even the measurement of internal friction. Close on 600 people, 160 of them from overseas, came to the 4-day meeting in Edinburgh on Gas Chromatography.

These events serve to illustrate a changing pattern of scientific meeting, which we have done well to recognise. But they illustrate something else that we also have to recognise; that not more than about one third of those attending such meetings are members of this Society. For some, the reasons are obvious and valid, but of the others, many, I would suggest, belong to that section of chemical society to which I have already made reference: they do not admit to the practice of analysis and they reject the label of "analyst."

In pointing out these problems I am offering no ready solution, but it is part of my thesis to suggest that we shall have to enlarge our horizons—that we shall have to face up to the diversity of disciplines now involved in what used to be called analytical chemistry. "Like it or not," says Liebhafsky in the preface to his recent book on "Spectrochemical Analysis with X-rays,"[3]

> "the chemistry is going out of analytical chemistry. For a long time indeed, Chaucer with his
>
> 'The lyf so short, the craft so long to lerne
> Th' assay so hard, so sharp the conquering'
>
> proved a better prophet than he knew. But nowadays physics and electronics are in part being fused with analytical chemistry to make the assay easier and the conquering less painful."

In passing, we should note the dependence of pure science on technology—to which G. P. Thomson[4] has recently drawn our attention—both the material return and also in the realm of ideas. A modern laboratory could not work without the instruments developed for technology and obtainable more cheaply because industry has required them to be made in reasonably large numbers.

I referred earlier to the many other groups that are concerned with the techniques of measurement, measurements which, I submit, are, or sooner or later will be, thought to constitute analytical data. Some of these groups, for example, the Applied Spectroscopy Group or the X-ray Analysis Group of the Institute of Physics, are firmly attached to other learned Societies; some, like the Gas Chromatography Discussion Group, are more loosely attached to other bodies; some others have no such affinities and one associates them mainly with the fields of work, say biochemistry or metallurgy, for which they were perhaps first developed or in which they were first applied.

This is the crux of the matter and this is the reason why, unlike Bolton in 1928, I do not see our future as one of uneventful, steady progress. The loyalties of all these groups lie in the main well outside the bounds of this Society. There is at once paradoxically a gap and an overlap. Despite the efforts of the Physical Methods Group since 1945, the Society for Analytical Chemistry will, I think, have to do still more to try to bridge this gap, to accept at a faster rate the need for new kinds of measurement with new kinds of tools. Ultimately this means the acceptance of a new conception of "analysis."

There is perhaps an even greater need for the exponents of and enthusiasts for these new techniques to recognise the overlap, to accept perhaps a little more humbly that there are skills, and there is art, in classical analytical chemistry; that spectrography is not the most sensitive technique for many elements; that iron, for example, can be determined more readily, accurately, and at a lower level by chemical methods than by radioactivation methods; that classical analysis is not necessarily always more tedious or time-consuming than other methods, and that even troublesome "blanks" can be just as troublesome when they are called "signal to noise ratio."

I said that I did not see the future as one of uneventful steady progress. I do see, however, an exciting and a stimulating challenge—a challenge to the analyst to establish closer contacts with those working in the newer fields of measurement—to set up some mechanism for collaboration during this period of transition from classical analytical chemistry to analysis based more broadly on other types of measurement besides those of mass and volume and on information that includes, but sometimes only as an essential minimum, a determination of composition. I have the strongest conviction on this matter, based as

it is on so long an experience of the value of the co-ordination and application of many diverse analytical techniques in my own environment.

I would like to touch briefly on another matter in which I feel this country rather than our Society has been dragging its feet, and I do so only because I think it has a bearing on my general theme. I refer to the establishment of University Chairs in Analytical Chemistry —for which our President, Chaston Chapman,[5] put in a plea over 40 years ago. The satisfaction we must all feel that two have now been set up in Great Britain is tempered for some of us by the fact that they have come, if not too late, certainly at a time when we have begun to cross new frontiers—when, as I have already mentioned, some of the chemistry is going out of analytical chemistry and when it now begins to rest on a diversity of disciplines and often looks like analytical physics. While, therefore, this revival of interest in analytical chemistry is indeed welcome, both in our Universities and in our Colleges of Advanced Technology, they too will have to face some of the problems I have been trying to delineate. I may add that already in one College of Advanced Technology the students for the Diploma of Technology in Applied Chemistry include in the third and fourth years a course in electronics and instrumentation.

May I offer another thought to those in the Universities? It is this—I think that they would be imprudent, if not unwise, to assume that even in purely chemical matters the analyst in industry is a benighted creature, steeped in empiricism and sadly in need of theoretical enlightenment. Ostwald came near to making this mistake, as Lundell pointed out in his now famous lecture on "The Analysis of Things as They Are."[6] "A system," he said, "containing ten to twenty diverse components can hardly be handled on a strictly scientific basis and any handling of it requires actual experience in analysis." To this I would add that physico-chemical data, however valuable, can seldom be applied to really complex mixtures.

Nor let any one, either in industry or in university, minimise the value of the good classical analyst. There is still much that he has to do and that can be accomplished only by his skill and his art and through his fund of knowledge based on long experience. H. N. Wilson emphasised this point in his lecture on "The Changing Aspect of Chemical Analysis"[7] when he drew attention to the fact, too often overlooked or not even understood, that so many of our instrumental techniques depend for their calibration on standards that have been accurately analysed by an expert classical analyst.

As this is an occasion, perhaps a unique occasion, when I may air some personal views, may I be so bold as to mention one other matter? There has sometimes seemed to me to be a pre-occupation in University analytical circles with microchemistry. I have never disguised the fact that I am in this matter a heretic. Nor have I ever been able to discover whether microchemistry is the determination of a relatively large concentration of one or more constituents of a very small sample, or the determination of a very small concentration of one or more constituents of a relatively large sample. It is unfortunate also that the term should often seem to be used in the restricted field of the determination of a few elements, carbon, hydrogen, oxygen, sulphur, fluorine, etc., in organic compounds, and of the apparatus and technique as often restricted to small pieces of glassware or porcelain.

I have been concerned much over the last few years, through the development of both solid-state chemistry and of nuclear power, with the determination of fantastically small concentrations of certain elements in very small samples, and I am prepared to use an apparatus 10 feet by 6 feet, if necessary, to determine, shall we say, 1 part per 100 million of boron in 5 milligrams of a sample of a semiconductor. This more closely accords with my ideas of microchemistry. Whatever the definition, this kind of demand is going to be made on the analyst, and here, above all, new frontiers may have to be crossed.

Consider, for example, the special technique known as the electron microprobe; this is already in use in many establishments for research in metallurgical problems, but it is also an extraordinary new analytical tool. In 1951 Castaing[8] published results to show that an electron microscope could be converted into a useful X-ray emission spectrograph for point-to-point exploration on a micron scale. Outstanding features of the technique were the small size of the sample, a 1-μ cube or thereabouts, and the absence of pronounced adsorption and enhancement effects. Castaing gives remarkable quantitative results for copper alloys; he was able to obtain analytical information by a point-to-point exploration over these extremely small areas and to show the variation in composition of a copper - zinc alloy, for example, in a region of diffusion. This kind of information, admittedly at the extreme of my definition of analysis, is nevertheless what the metallurgist ultimately requires.

This leads me to comment on another aspect of microchemistry. As our techniques become more and more sensitive and as it becomes possible to use smaller and smaller samples, there will come a time—indeed it is already with us—when the answers we obtain are not of the kind to which the customer was formerly acclimatised. In one sense we have been deluding ourselves and him all the time. For example, it is possible now to determine 1 microgram of carbon present at a very low concentration in a very small sample, let us say, of titanium. We have found by experience that we can get five results in succession differing appreciably from one another and yet be confident that our apparatus is properly and correctly measuring the amount of carbon present on each occasion. Up to now the metallurgist has been used to receiving one figure, a figure representing the average carbon content of the sample used. The analyst has been used to giving that figure with confidence, because on the size of sample he used he was able to achieve high precision and good agreement on successive samples. "The results of duplicate or triplicate determinations agree" has been a common enough phrase and a common enough criterion in the past in judging the merits of an analytical method. But if we accept, on a purely rational basis, that as the sample gets smaller and smaller so the chances of inhomogeneity must increase, we shall ultimately arrive, and indeed I say we have already arrived, at a point where we can no longer deceive ourselves with average values—we shall give the correct or most probable value for any particular size of sample, and it will be for the metallurgist, for example, to try to make use of this information. Were we indeed able to get this information at the moment in another context, that of semiconductors, the physicist would be only too pleased to have it, for the operation of these devices depends on just these considerations. The concentration of an acceptor or a donor impurity does vary over these extremely small distances and must do so if the devices are to work.

Are we sure that there are not analogies in other fields? In biology, for example, were we able to determine analytically variations in concentration of this or that element or substance over small local areas of concentration, might we not possibly make a contribution to the advancement of knowledge? Is not the history of science, of which we are a part, just this—as our tools become more precise, smaller, sharper, there is revealed to us knowledge and information of which previously we had no conception?

What about the next 30 years? I can only state my conviction that analytical chemistry as we have known it for the last 30 years, and certainly as we have known it since 1874 when the Society began, is bound to change, quite radically. I do not think that even to-day we can continue to talk of chemical analysis and of analytical chemistry and properly identify or describe the activities with which some of us are concerned. Up to a relatively few years ago the art of analysis consisted for the most part in getting our materials chemically separated or prepared in some way so that a measurement could be made, and that measurement was usually one of mass or of volume. To-day we are often prepared to make many other kinds of measurement, often without the need for preliminary separation: we can make some of them without destruction of the sample. We are already at the point where in favourable circumstances we are able to determine the composition of a minute area of a substance by a non-destructive examination of the surface.

These advances arise from two main stimuli—the advances in other technologies, notably electronics, and the need and the resolve of the researcher to obtain information different in character from that offered previously by the analyst, information more scientifically relatable to the qualities with which he is concerned.

I would not like to leave you with the thought that I have deserted my faith in classical analysis or that I have no concern for the commercial or legislative needs of analytical information, including so-called standard methods. But it was my special purpose to discuss that philosophy of what, for want of a better term, we must still call analytical chemistry, which exceeds the everyday repetition of routine analysis. A short paragraph from H. V. Churchill's address[9] on the occasion of his Pittsburgh award so aptly epitomizes what I have to say that I make no excuse for quoting it—

> "At meetings such as this, there is a strong temptation to be reminiscent and to recall the days of the past. But in the field of science, whether it be pure or applied, it is always morning, the beginning of tomorrow. It is a time when dawn stands tiptoe on the misty mountain tops. I yield to no one in my admiration of the great, the near-great, and the unnamed workers who laid the foundation and built the structure that

has brought analytical chemistry to its present high estate and yet analytical chemistry today is but a promise of what is to come."

Let us then enlarge our horizons, to an extent never dreamt of by Voelcker. Let us see ourselves as part of the main stream of scientific research, for in the words of Francis Bacon—

> "The end of our foundation is the knowledge of causes and of the secret of things and of the enlarging of the bounds of human empire to the effecting of all things possible."

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Anniversary Dinner

In the evening following the Annual General Meeting, a Dinner to celebrate the eighty-seventh anniversary of the Society was held, by kind permission of the Prime Warden, Wardens and Court of Assistants of the Worshipful Company of Fishmongers, at Fishmongers' Hall, London Bridge. The members and guests, numbering 153, were received by the President, Mr. R. C. Chirnside, F.R.I.C., and Mrs. Chirnside. The President afterwards took the Chair at the Dinner.

The Guests of the Society and of the President included The Lord Fleck, K.B.E., D.Sc., F.R.I.C., F.R.S. (President of the Society of Chemical Industry); E. Le Q. Herbert, B.Sc., F.H.-W.C., M.I.Chem.E., M.Inst.F., F.Inst.Pet., F.R.I.C. (President of the Royal Institute of Chemistry) and Mrs. Herbert; Sir Harry Jephcott, M.Sc., F.P.S., F.R.I.C., Barrister-at-Law (Chairman of the Council for Scientific and Industrial Research) and Lady Jephcott; Sir Charles F. Goodeve, O.B.E., D.Sc., F.R.I.C., F.R.S. (Director of the British Iron and Steel Research Association) and Lady Goodeve; G. L. Bailey, C.B.E., M.Sc. (Director of the British Non-Ferrous Metals Research Association) and Mrs. Bailey; O. W. Humphreys, C.B.E., B.Sc., F.Inst.P., M.I.E.E., F.R.Ae.S. (Technical Director of The General Electric Company Ltd.) and Mrs. Humphreys; A. T. James, B.Sc., Ph.D. (Chairman of the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum) and Mrs. James; J. H. Hamence, M.Sc., Ph.D., F.R.I.C. (President of the Association of Public Analysts); and F. A. Pester (representing the Worshipful Company of Fishmongers) and Mrs. Pester.

The Loyal Toast was proposed by the President.

Lord Fleck proposed the Toast of the Society, referring to it as one designed to further a real, live, important scientific discipline. He recalled carrying out, at the outset of his career, a complete analysis of a white bearing metal, containing tin, cadmium, bismuth, antimony and lead; a difficult and arduous task. He had also made two complete rock analyses, each taking fully 10 days. By modern rapid methods such analyses took only part of a day. As these improved methods were developed, so the responsibilities of the Society became greater. The sensitivity of modern methods was such that impurities in silicon could be determined down to 10^{-4} parts per million.

He continued by paying tribute to the philosophy of analytical chemistry and the analytical mind. This philosophy had come into the British way of life in the sixteenth century—he had found some reference to analysis as early as 1590. In 1661 Boyle, whom Lord Fleck called the Patron Saint of analytical chemistry, described in "The Sceptical Chymist" analysis by distillation. Analytical chemistry also owed a great debt to the

town of Edinburgh and its citizen Francis Hulme, who described, hidden away in a book of experiments on bleaching, the titration of lyes—in teaspoonfuls.

Analysis was the basis of all scientific work. The Society encouraged the concept of analysis and the work of the analytical mind, which was one of the most valuable assets of British industry. They were very much indebted to the Society for its example and for all it did for science and for analysis in particular. The Toast was coupled with the name of the President.

Mr. Chirnside, replying, recalled that in December, at the Ramsay Dinner, he had had the privilege and pleasure of responding to the Toast of "The Chemical Industry" proposed by Sir Alexander Fleck; now he had the greater pleasure of replying to Baron Fleck of Saltcoats in the County of Ayr. On that occasion one of the other speakers had referred to the Chairmanship of I.C.I. as "a dead-end job with not much in the way of prospects." An alternative more in keeping with Lord Fleck's character was, he thought, "a part-time job allowing many other outlets for his native genius." The way in which he had guided the Fleck Committee's rapid action in producing its report on Coal and also his masterly report on the Fishing Industry should make the country grateful that Lord Fleck had "a part-time job."

He had spoken in warm terms of the Society and its members; it was clear from his early work on the separation of radioisotopes that he had himself been no mean analyst. He had been Chairman of a great Company that believed in analysis and had nurtured in its Divisions some of the most outstanding analysts in the country. The Billingham Division had done much to further the application of gas chromatography. They had also built analytical equipment into the plant and had achieved true automation.

Mr. Chirnside referred briefly to the special meetings that had been held during the past year, first with the Iron and Steel Institute and the Institute of Metals: it gave him particular pleasure to have Sir Charles Goodeve and Mr. Bailey at this Dinner. He had, too, the pleasantest memories of Edinburgh in June at the Gas Chromatography Symposium, revived by seeing Dr. James, the Symposium Chairman, among the guests.

Analysis was a basic tool in all industries. The analyst had to try to make his contribution to all aspects, and his own experience in the research organisation of a great and diversified Company had shown him how wide they were.

Dr. Amos proposed the Toast of The Guests. Lord Fleck was President of the Society of Chemical Industry, with whom our Society was on the most friendly terms, and on whose premises it had its head office. On retiring last year from the Chairmanship of I.C.I., Lord Fleck might well have decided on a period of relaxation, but instead he had taken on both the Presidency of S.C.I. and the Honorary Treasurership of the Royal Society. It was understood that he could also be seen at week-ends felling trees at Billingham. Mr. Herbert would in a few weeks be completing his 2-year term as President of the Royal Institute of Chemistry, and it was clear how wise the Institute had been in its choice in 1959. Although in its early days the Society, which was 2 years older, had shown some hostility towards the Institute, in 1899 a union of the two bodies had been proposed, and cordial relations had existed ever since. There were now over 16,000 chemists in the care of the Institute. Dr. Hamence, a welcome guest as President of the Association of Public Analysts, had himself been principal host 2 years before. This looked like an example of allotropy. Sir Harry Jephcott he particularly welcomed, for last year he had completed 40 years' membership of the Society and was now a life member. He recalled how, in 1915, the Society had taken part in a deputation that had urged the setting up of an organisation to encourage research, which had materialised as the Department of Scientific and Industrial Research, of which Sir Harry was Chairman. Mr. Humphreys, Director of the General Electric Company's Hirst Research Centre, was a physicist, and very much alive to the potentialities and requirements of analytical chemistry. The President had been particularly keen to have metallurgical interests represented, and by inviting the Directors of the relevant Research Associations the Society had as their guests Sir Charles Goodeve, President-elect of the Iron and Steel Institute, and Mr. Bailey, immediate Past President of the Institute of Metals. He was glad to have Dr. James present, as a reminder of the highly successful Symposium held last year. A special guest was Mr. Pester, Clerk to the Worshipful Company of Fishmongers, whom he asked to express to the Court of Assistants the Society's appreciation for being allowed to dine in their beautiful Hall, for which special dispensation had been granted. Finally, he welcomed all the ladies, lending colour and gaiety to the occasion.

Mr. Herbert replied, saying that the association of the Society with the Royal Institute of Chemistry was so close that, as he looked at the list of guests and saw how many Fellows or Associates were present, he began to wonder if he was attending a dinner of his own Institute. Being a President, he said, meant a lot of work and a lot of fun; perhaps the greatest hazard lay in attending dinners, when a President was liable to be called upon to speak.

The President concluded the proceedings by calling upon Dr. Amos, the new President, who had served the Society so well as Honorary Treasurer, and investing him with the Presidential Badge, wishing him a successful term of office. Dr. Amos expressed his pleasure at the honour and presented Mr. Chirnside with a replica of the Society's Badge to wear as a Past President.

Automatic Determination of Penicillin in Fermentation Broth

An Improved Iodimetric Assay

By R. R. GOODALL and ROSEDA DAVIES

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The automatic analytical method described by Ferrari, Russo-Alesi and Kelly for assaying penicillin fermentation broths has been modified in order to overcome certain experimental difficulties and to improve the precision. The method described in this paper requires preliminary manual dilution to bring the concentrations of the reactants (penicilloic acid and iodine) into the linear range of the recorder - colorimeter unit, in which the excess of iodine is measured as its blue complex with starch. It is convenient to include penicillinase in the diluent, so that the automatic stage is confined to iodination, mixing with starch solution and recording the optical density of the residual iodine as its blue complex.

Forty iodine absorptions are recorded hourly. Four of these are standards, and, as the assay of each broth requires both a "blank" to determine iodine-absorbing impurities and a "test" to determine absorption of iodine after conversion by enzyme to penicilloic acid, the net average output of assays is 18 per hour. With the accompanying standards, preparations, etc., the number of samples analysed in a normal working day is 100. The standard deviation of the assay (including both "test" and "blank" iodinations) is from 2 to 2·5 per cent.; this is similar to that of the manual titrimetric method, in which each operator can carry out 25 tests daily. The method has been in routine use for several months.

Three colorimetric reactions of the penicillin nucleus have been adapted for mechanisation. These are (*a*) the formation of a ferric - hydroxamic acid complex, (*b*) conversion to penicilloic acid, which is used to reduce arsenomolybdate to a blue colour and (*c*) conversion to penicilloic acid and then reaction with iodine.

An automatic adaptation of method (*a*) has recently been described by Niedermayer, Russo-Alesi, Lendzian and Kelly.[1] A possible disadvantage of this method is its low intrinsic sensitivity, so that the effect of turbidity present in the sample of broth or arising during the reaction cannot be minimised by dilution; further, under certain conditions of fermentation the "blanks" for broths are of the same order as the "potencies," with consequent loss of precision. This criticism is less likely to apply to the iodimetric assay, as the consumption of iodine by penicilloic acid is exceptionally high (about 9 equivalents per mole). Method (*b*), first described by Pan,[2] has been adapted by Green and Monk[3] to a semi-automatic procedure

involving manually operated units for rapid dispensing, extraction, evaporation, development of colour and measurement with a recording spectrophotometer. Method (*c*) is the most generally accepted procedure as to specificity and precision. Penicillin broth is converted by penicillinase to penicilloic acid, which is then allowed to react with iodine under acid conditions; allowance is made for the iodine absorption of the broth without penicillinase treatment. This method is routinely used in these laboratories without any preliminary treatment of the fermentation broth.[4]

A visit to the Technicon Instrument Corporation's laboratories in New York provided the opportunity for one of us (R.R.G.) to try out the fully automatic adaptation of method (*c*) described by Ferrari, Russo-Alesi and Kelly[5] in 1959. Subsequently, our object has been to improve the sensitivity and precision of the method to the point at which a standard deviation of from 2 to 3 per cent., together with high speed of analysis, can be expected for fermentation broths of potencies greater than 2000 units per ml. Such broths have to be tested in large numbers during a mutant-screening programme.

The iodination of penicilloic acid is not stoicheiometric. Consequently, the problem of achieving the desired accuracy and precision with an automatic method (this applies equally to "blank" and "test," as the results are calculated from the difference between them) to ensure substantial agreement with the well established manual method is probably one of the most difficult applications demanded of the AutoAnalyzer. The nature of these problems is discussed below.

Experimental development

The absorption spectrum of iodine in an excess of potassium iodide solution exhibits a maximum at 360 mμ. The relationship between optical density at 360 mμ and concentration over the range 0 to 1 micro-equivalent of iodine per ml is linear and can be observed as a change in optical density (0·2 cm) of from 0 to 1·8 if a suitable spectrophotometer is used. At this wavelength, however, a Technicon colorimeter fitted with suitable filters does not respond well to changes in concentration of iodine, presumably because of the low photo-activity of selenium cells in the near-ultra-violet region. Ferrari, Russo-Alesi and Kelly[5] measured optical densities at 420 mμ, at the "heel" of the absorption curve, but their published calibration graph does not cover all the available scale and also has an unfavourable slope below a concentration of 2000 units of penicillin per ml, at which the optical density approaches 0·5 (equivalent to 32 per cent. transmission), corresponding to concentrations of about 1 micro-equivalent of iodine per ml.

To attain the requisite precision in an absorptiometric adaptation for penicillin broths, it was necessary to span a large part of the available scale in the determination of total iodine absorption ("test"). About one-third of this must then be deducted to allow for the iodine-absorbing impurities ("blank"). To attain optical densities of the desired order over a range of low concentrations, the colorimetric reaction must be highly sensitive. Iodine absorbs only slightly in the visible spectrum, but for this work an absorption band in the visible region is required so that the AutoAnalyzer can be used to good advantage. Of the alternative methods for determining iodine, one based on the starch - iodine complex seemed to be suitable, as the absorption spectrum of this complex is broad and has a maximum at 600 mμ; further, Beer's law is obeyed for concentrations less than 1 micro-equivalent of iodine per ml. The chosen concentration of soluble starch was just sufficient to develop maximum optical density with 1 micro-equivalent of iodine per ml. Although the peak absorption of this starch - iodine complex is at 600 mμ, our available interference filters had maximum transmission at 526 mμ; our measurements were therefore made below the maximum, and some sensitivity was lost. The absorption peak, however, is not sharp, so that the difference is not critical. The blue complex is stable, provided that high concentrations of electrolyte or acid are avoided. The level of absorption is not affected by changes in room temperature.

The scale of an AutoAnalyzer recorder normally records percentage transmission (T), but a "linearising" device that derives 100 $\times$ the mantissa of log(T, per cent.) and displays the result on a linear scale is also available. The chart is calibrated in equal divisions from 0 to 100, and, within the limits of linear response (about 20 to 99), the transposition to optical density (d) is $(100 - x)/100$, where x is the observed reading; for our purpose d is not required. This scale is about the same length as that of a normal spectrophotometer having logarithmic calibration, but the "linearised" scale can be read more precisely in the region where a

logarithmic form is cramped. This facilitates the precise graphical interpolation of results with the chart reader (see "Apparatus," p. 331). Linearity cannot be maintained below a reading of about 20, so that, for example, the curvature shown in Fig. 1 is due to a decrease in electronic response and not to deviation from Beer's law. Other spectrophotometric measurements on these solutions show that the linear relationship continues up to 0·25 micro-equivalent of iodine per ml.

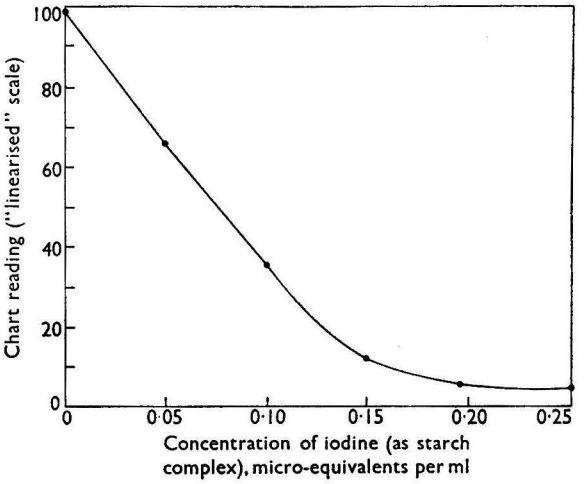

Fig. 1. Relationship between concentration of iodine and chart reading when a 526–12–27 filter and a 10-mm flow cell are used

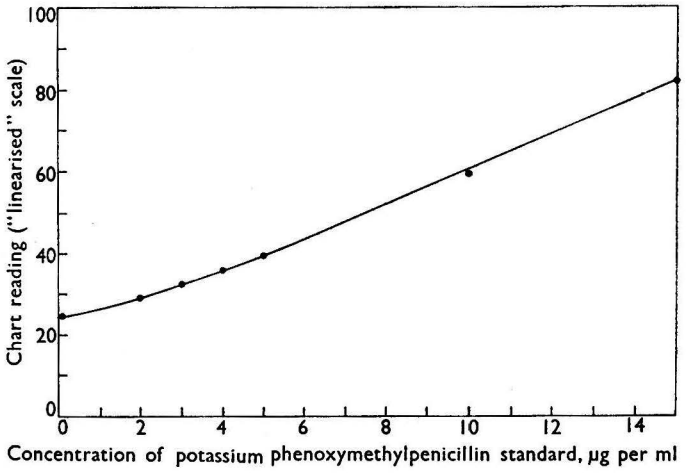

Fig. 2. Relationship between concentration of penicillinase-treated potassium phenoxymethylpenicillin standard and chart reading when a 526–12–27 filter is used

The response curve obtained from a suitable range of potassium phenoxymethylpenicillin standards treated by the method described later is shown in Fig. 2. An increase in the concentration of the penicillin diminishes the concentration of the blue complex and so produces an increase in the chart reading. The "blank" for the broth is determined by using

that part of the curve below a concentration of 5 μg per ml and the "test" on the linear part above this level. The curvature in the 0 to 5 μg per ml region arises in the recorder for the reason already stated.

The development of an assay under these conditions required that the penicillin broth be treated with penicillinase and then diluted to a level at which the iodine consumed was less than the limit shown in Fig. 1 (0·15 micro-equivalent per ml). The use of the dialyser unit for rapid automatic dilution was not as promising as the more orthodox approach finally adopted. After an unsuccessful attempt to operate an automatic three-stage serial dilution of the sample drawn from the sampler plate into a network of pumping circuits, the system suggested by Dr. Holms of these laboratories was put into practice as a preliminary manual operation. This system consists essentially of a pair of self-levelling dilution pipettes (see "Apparatus," p. 331) arranged in series.

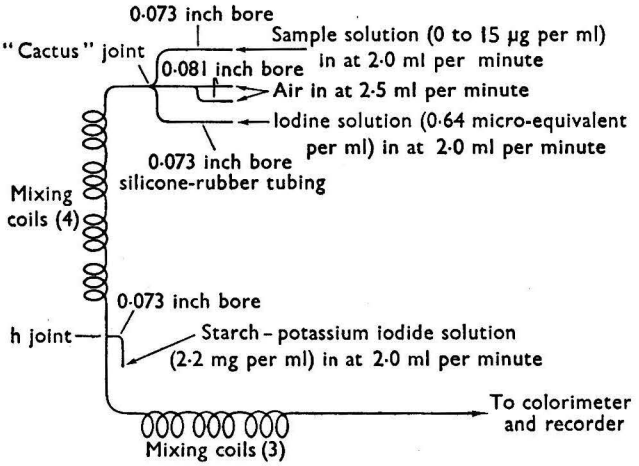

Fig. 3. Flow diagram for iodimetric assay of penicillin

Suitable standard solutions of phenoxymethylpenicillin were prepared and inactivated in 100-ml portions, so that a set of these could be incorporated on each sampling plate. As alkaline or enzymatic inactivation of the standards produced similar results, the former procedure was ultimately adopted to avoid enzymatic contamination of subsequent "blanks." If the standards were inactivated with enzyme, the excess would have to be destroyed; obvious methods, such as boiling or precipitation by protein reagents, were thought to be impracticable. Inactivation of the samples by penicillinase was retained on the grounds of specificity. The mid-point of the acetate buffering range, pH 4·6, was chosen as the final pH for storing solutions before analysis; this was in order to avoid decomposition of the penicillin in the "blank," a complication that could be expected at a lower pH and would result in spuriously high blank values. The necessity for high dilution outside the available AutoAnalyzer units prompted us to incorporate the treatment with enzyme in the dilution stage. The automatic part of the analysis was therefore confined to the iodination and complex-forming stages. There was no dialysis, so that theoretically there should not be much opportunity for background "noise" caused by inter-stage effects.

As can be seen from the flow diagram (Fig. 3), 2 ml per minute of diluted sample are mixed with 2 ml per minute of iodine solution (0·64 micro-equivalent per ml), segmented with 5 ml per minute of air and allowed to react for 2 minutes; no increase in absorption of iodine is obtained by prolonging the reaction. Subsequently, the injection of 2 ml per minute of starch - potassium iodide solution converts all the residual iodine to the blue complex. The fixed parts of the reaction circuit are in glass, with Tygon butt-joints between coils. In the feed- and pump-lines for sample and starch - potassium iodide solutions, Tygon tubing is used. Because of the high solubility of iodine in Tygon, the dilute iodine solution enters via a polythene line into a silicone-rubber pump-tube; the starch - iodine complex also leaves the circuit via a polythene line.

In a normal AutoAnalyzer, a constant flow of the recipient stream passes from the dialyser to the colorimeter; the concentration of solute in this stream alters by diffusion through the cellophane membrane. In our apparatus, there is no separate recipient stream, and the act of sampling increases the throughput per minute of the liquid stream from 4 ml (2 ml each of iodine and starch - potassium iodide solutions) to 6 ml (2 ml each of iodine, starch - potassium iodide and sample solutions). Thus, there is a cyclical increase in flow and in dilution of the reagents by 50 per cent. during the time of sampling, which lasts for 1 minute, with 30-second intervals. The small "blank" peak when buffer is used as sample is a measure of this dilution effect, and the sharp rise at the end of the peaks (see Fig. 4) is attributed to the change in flow rate; this rise can be ignored.

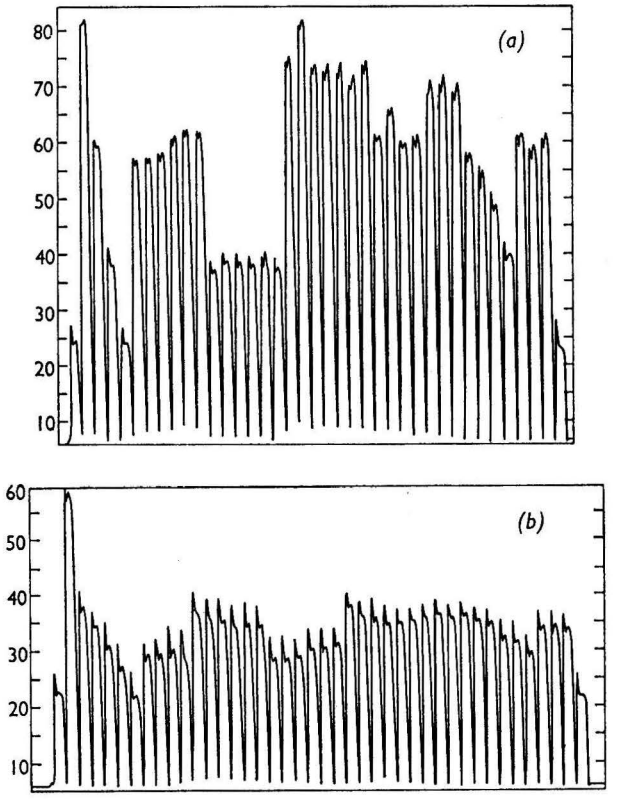

Fig. 4. Typical recordings for penicillin broths: (*a*) "tests"; (*b*) "blanks." Reading from right to left, the peaks in (*a*) are for buffer solution, thirty-three broths, buffer solution, three standards and buffer solution; those in (*b*) are for buffer solution, thirty-four "blanks," buffer solution, five standards and buffer solution. (The "blanks" do not correspond to the "tests")

Several aspects of mixing become apparent when the starch - iodine complex is formed. For example, if the liquid injected into the main segmented stream is of different density, complete mixing requires passage of the segments through approximately three loops of the mixing coil. Removal of air from the stream and passage down a capillary tube cause "drag," so that small inter-sample boundaries become lost. Unwanted mixing and "dead" space occur at the entry to the cuvette.

Precision is dependent on the absence of drift, both in the electrical components and in the concentration of iodine. To avoid drift from the components, the output of the photo-cells has to be matched and must remain so at the working temperature; this is checked by connecting the output from each photo-cell to a potentiometer and tapping off a suitable fraction to a spot galvanometer; one galvanometer is used for each photo-cell.

Loss of iodine into the silicone-rubber pump-tube is greatest during the first 30 minutes; thereafter, slight loss occurs by diffusion through the wall of the tube. The effect on the assay is minimised by interpolating standards at 1-hour intervals or more frequently.

METHOD

APPARATUS—

Compound pipettes for serial dilution—Three pipettes of the type shown in Fig. 5 are required. In operation, capillary C (bore approximately 1·3 mm; volume 0·3356 ml; length approximately 16 cm, depending on volume of joint to stopcock) is filled with sample by suction, and the outside of the jet is wiped dry. Bulb B is filled with diluent, and its contents are then used to displace and dilute the sample in C by turning the stopcocks to deliver as shown. After drainage, a short length of liquid, D, remains in the capillary. If the volumes of bulb B, capillary C and length D are B, C and D, respectively, then the dilution factor is given by the expression $[B + (C - D)]/C$.

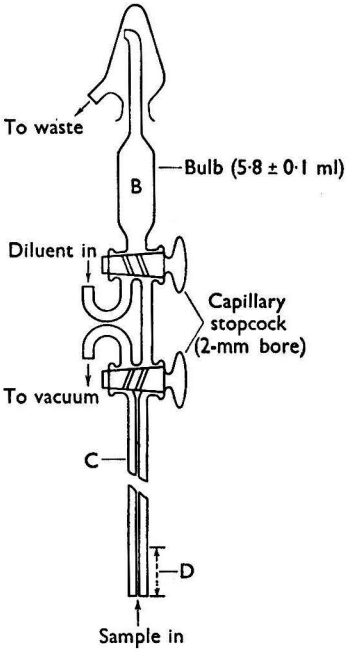

Fig. 5. Compound dilution pipette

To achieve a dilution of 17·5 to 1, bulb B is blown to a capacity of 5·8 ± 0·1 ml and the capillary C (0·016 to 0·017 ml per cm) is made 1 cm longer than the calculated length. The operative dilution factor is determined by diluting N hydrochloric acid. A mark is made 1 cm from the tip of C, and the volume from the mark to the stopcock is filled with the acid by suction. An aliquot of the acid, after dilution as described above, is titrated with 0·1 N sodium hydroxide, nitrazine yellow being used as indicator. The ratio between the normalities of the acid before and after dilution is the effective dilution factor. When the desired value is attained the surplus length of capillary is removed. It is necessary to use a high-quality stopcock, such as DOVC/2/B, obtainable from G. Springham & Co., Harlow New Town, Essex.

Wire racks—To contain thirty-six 6-inch × 1-inch test-tubes.

Test-tubes, 6-inch × 1-inch—Heated to 150° C, after washing, to destroy residual enzyme.

Technicon AutoAnalyzer—This instrument comprises—

(*a*) A sampling plate.

(*b*) A pump and a manifold carrying the sample line (0·073 inch i.d.), two air lines (0·081 inch i.d.) in parallel, an iodine line (approximately 0·073 inch i.d.) of silicone rubber and a starch line (0·073 inch i.d.) arranged as shown in Fig. 3.

(*c*) A glass reaction circuit constructed as shown in Fig. 3.

(*d*) A colorimeter unit having a 10-mm flow cell of modified construction such that the volume of the cuvette is decreased to 1·2 ml. The cuvette is a piece of flattened tube and does not require plane polished windows. A pair of interference filters transmitting in the range 520 to 600 mμ is required. We use 526–12–27 filters; this code signifies maximum transmission (27 per cent.) at 526 mμ and a band width of 12 mμ at half the peak height.

(*e*) A recorder with a "linearised" scale.

Polystyrene sample cups.

Chart reader—A 16-inch × 22-inch Simplon drawing-board having a movable transparent horizontal rule and two clips (obtainable from Messrs. T. Holden, Albert Square, Manchester 2). The rule is engraved, after purchase, in 1- and 0·1-inch divisions over 20 inches.

REAGENTS—

Iodine solution, approximately 0·64 micro-equivalent per ml—Place 1200 ml of distilled water in an amber-glass bottle, add 7·7 ml of a 0·1 N solution of iodine in 2 per cent. w/v potassium iodide solution, and shake.

Starch - potassium iodide solution—Add a suspension of 26·4 g of soluble starch in 200 ml of water to 1800 ml of boiling water; stir during the addition. Dispense 200-ml portions of the solution into ten 20-oz bottles, and sterilise with steam at 5 lb per sq. inch for 30 minutes. Each day, dilute 200 ml of this solution with 1 litre of distilled water, add 1·44 g of potassium iodide, and keep in an amber-glass bottle.

Phosphate buffer solution, 0·5 M (*pH* 6·5)—Dissolve 39 g of anhydrous sodium dihydrogen orthophosphate and 35·5 g of anhydrous disodium hydrogen orthophosphate in water, and dilute to 1 litre.

Phosphate buffer solution, 0·01 M (*pH* 6·5)—Dilute 20 ml of the 0·5 M phosphate buffer solution to 1 litre with distilled water.

Penicillinase solution—Dissolve the contents of one vial of penicillinase (inactivation rate in 20 ml is 20,000 units of penicillin G per minute; obtainable from the Distillers Co. (Biochemicals) Ltd., Speke, Liverpool) in 250 ml of the 0·01 M phosphate buffer solution.

Acetate buffer solution, 0·5 M (*pH* 4·6)—To 500 ml of N acetic acid add 227 ml of N sodium hydroxide, and mix.

Acetate buffer solution, 0·05 M (*pH* 4·6)—Dilute 100 ml of the 0·5 M acetate buffer solution to 1 litre.

Standard phenoxymethylpenicillin solutions—Prepare a standard solution containing 50 mg of potassium penicillin V in 500 ml of distilled water; this solution can be kept for 1 week at 5° C. Each day, prepare standards containing 2, 3, 4, 5, 10 and 15 μg of penicilloic acid per ml as follows. By pipette, place accurately measured 2-, 3-, 4-, 5-, 10- and 15-ml portions of the solution in separate 100-ml calibrated flasks, hydrolyse by adding 3·0 ml of N sodium hydroxide to the contents of each flask, and, after 10 minutes, adjust the pH of each solution to approximately 4·6 by adding 6·0 ml of N acetic acid. Dilute the contents of each flask to the mark. Mix equal volumes of the solutions containing 10 and 15 μg per ml to provide a standard containing 12·5 μg per ml. These solutions comprise the penicilloic acid standards.

ESTABLISHMENT OF BASE LINE—

Begin to pump the iodine and starch solutions, switch on the colorimeter, recorder and chart-drive, and record for about 30 minutes with the sample line empty before beginning the determinations. (The chart reading should be within the limits 6 to 8; if it is not, suitably adjust the concentration of the iodine solution.)

PREPARATION OF "TESTS" AND "BLANKS"—

"Blanks"—Use one of the compound dilution pipettes to take a sample of the broth and to dilute it with 0·01 M phosphate buffer solution; shake the tube used to receive the

diluted solution. Use another compound dilution pipette (A) to sample this solution and to dilute it with 0·05 M acetate buffer solution. Each "blank" so prepared by two serial dilutions is now ready for loading on to the sample plate. Fill the plate with "blanks" as follows. Rinse a polystyrene cup with the diluted sample, fill the cup, insert it in the plate, and suitably mark the aluminium surface beside each sample with washable coloured pencil or ink. Load the plate in this order: buffer solution, standard solutions containing 2, 3, 4 and 5 μg of penicilloic acid per ml, thirty "blanks," buffer solution and, finally, the four standard solutions. (Omit the first set of standards on subsequent plates.) Remove the feed tube from the cuvette, flush the cuvette with water, and check that the recorder reads 100; if it does not, adjust the "100 per cent. T" potentiometer. Replace the feed tube, insert the polythene sampling tube through the crook, and throw the sampling switch to "ON." Prepare as many plates of "blanks" as are required for the day, and record all of them before the "tests" (see below). While the plates of "blanks" are running, at the rate of forty per hour, prepare the "tests" as described below.

"Tests"—Use the third compound dilution pipette to take a sample of broth and to dilute it with the penicillinase solution, shake the receiving tube, and set it aside for at least 30 minutes. Then use pipette A to sample this solution and to dilute it with 0·05 M acetate buffer solution as before. Load the samples and standards on a plate in this order: buffer solution, standard solutions containing 5, 10, 12·5 and 15 μg of penicilloic acid per ml, "tests," buffer solution and, finally, the four standard solutions. (Omit the first set of standards on subsequent plates.)

When the "blank" recordings are complete, remove the plate, and replace it with the plate carrying the "tests." Check the "100 per cent. T" setting as before, and begin to sample the "tests" at the rate of forty per hour.

CLEANING THE SYSTEM—

The object of running all the "blanks" first is to avoid interaction with traces of residual enzyme from the "tests." At the end of the day, or next morning before further "blanks" are recorded, clean the system by pumping water for 5 minutes, N hydrochloric acid for 10 minutes and then water again for 5 minutes through all the liquid-conveying lines.

CALCULATION OF RESULTS—

Clip the chart of the "blank" records on the Simplon drawing-board, align it horizontally, and place the transparent plastic scale over the peaks for the standard solutions. With use of a calibration incorporating the dilution factor and the factor 1·53 (to convert micrograms of potassium phenoxymethylpenicillin to units), construct a graph on the chart paper relating potencies of the standards (in units per millilitre) to mean chart readings. Maintain the scale in horizontal alignment, slide it over each "blank" record until the leading edge covers the top of the peak, and read the appropriate potency at the point where the scale cuts the graph.

When the "tests" have been recorded, use the standards recorded on this chart to construct a graph from which the "test" potencies can be read in a similar manner. Deduct the "blank" from the "test" potency, and record the result as the "net potency" of the sample.

RESULTS AND DISCUSSION OF THE METHOD

Typical test and blank recordings are shown in Fig. 4, the appropriate standards being at the left-hand side of each record; the calibration graphs plotted resemble that in Fig. 2. Results for samples of experimental shaken-flask fermentations for phenoxymethylpenicillin are shown in Tables I and II. Similar results have been obtained for the assay of benzylpenicillin fermentations.

Results by the manual and automatic methods (turntable rate, forty samples per hour) are compared in Table I, which covers a potency range of approximately 2500 to 5000 units per ml. Variation in the amount of iodine absorbed by the "blank" clearly has a significant effect on the net potency; compare, for example, the results for samples Nos. 11 and 18.

To calculate the standard deviation of the method, including dilution, and plate-to-plate variations in standards, "blanks" and "tests," replicate determinations on twenty experimental broths were made, a fresh plate being used for each set. (All these samples were highly turbid, because of dispersed oil; the dilution, however, overcame interference from

TABLE I

COMPARISON OF RESULTS BY AUTOMATIC AND MANUAL METHODS

Sample No.	"Test" potency, units per ml	"Blank" potency, units per ml	Net potency, units per ml	Net potency by manual method, units per ml
1	4430	1280	3150	3120
2	3550	1080	2470	2205
3	4720	1250	3470	3510
4	4920	1420	3500	3450
5	4270	1270	3000	2795
6	5380	1220	4160	4055
7	5020	1040	3980	4085
8	4580	1420	3160	3075
9	5020	1200	3820	3665
10	4260	1470	2790	2685
11	5550	1280	4270	4225
12	3430	1150	2280	2160
13	4500	1360	3140	3090
14	4220	980	3240	3370
15	6260	1300	4960	4705
16	4490	1080	3410	3420
17	4560	1370	3190	3000
18	5560	970	4590	4600
19	5740	1270	4470	4395
20	3840	950	2890	2705
21	4540	1710	2830	2890
22	5640	1150	4490	4410
23	5370	1300	4070	4180
24	4620	1490	3130	2965
25	4150	1260	2890	2795
Mean	4745	1251	3494	3422

this source.) Aliquots from each sample were diluted, and the "blanks" were determined as described above. Fresh aliquots of each sample were diluted with enzyme solution, and, after 1 hour at room temperature, the "test" determinations were made. The total sequence was repeated, and the second plate of "blanks" was analysed before the first plate of "tests" to avoid reaction with any residual enzyme introduced into the lines at the "test" stage.

Table II shows the results and Table III the statistical analysis. The standard deviation of 75 units can be expressed as 2·1 per cent. of the mean net potency of 3558 units per ml.

TABLE II

REPLICATE RESULTS FOR EXPERIMENTAL FERMENTATION BROTHS

Sample No.	Net potency found in— first series of assays (A), units per ml	Net potency found in— second series of assays (B), units per ml	Difference ($B - A$), units per ml
1	3590	3615	25
2	2860	2985	125
3	3360	3480	120
4	3805	3945	140
5	3855	3905	50
6	3685	3760	75
7	3635	3590	−45
8	3220	3095	−125
9	3535	3630	95
10	3565	3595	30
11	3120	3260	140
12	3760	3850	90
13	3995	4060	65
14	3935	3945	10
15	3555	3630	75
16	3570	3780	210
17	2950	2765	−185
18	3890	3870	−20
19	3555	3700	145
20	3215	3215	0

This deviation includes a small bias (51 units between means) on the two sets of repeat determinations, which is the sum of the following deviations. The means of blanks 1 to 20 were (A), 1891 and (B), 1870 and of tests 1 to 20 were (A), 5424 and (B), 5453. This leads to a net positive bias in the (B) series of 21 + 29 = 50 units over the (A) series. Our working experience is that a standard deviation in the range 2 to 2·5 per cent. can be expected in the routine analysis of the type of broth already described. Tests with pure crystalline penicillin V have given results within 1 per cent. of the theoretical.

TABLE III

STATISTICAL ANALYSIS OF RESULTS IN TABLE II

Sum of net potencies found—	
First series of assays, units per ml	70,655
Second series of assays, units per ml	71,675
Sum of differences $(B - A)$, units per ml	1020
Mean net potency found—	
First series of assays, units per ml	3533
Second series of assays, units per ml	3584
Mean for both series, units per ml	3558
Sum of squares of differences, $\Sigma (B - A)^2$	223,350
Variance, $\frac{1 \times 223,350}{40}$	5583·75
Standard deviation, units	74·7
Standard deviation, as percentage of mean net potency for both series	2·1

Preliminary experiments in the same system at the higher rate of sixty per hour also show promise.

We thank Mr. M. Gent, now of the Bradford Institute of Technology, for carrying out the statistical analyses and for helpful discussions.

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The Determination of Small Amounts of Amine in Aqueous Solution

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A colorimetric method for determining small amounts of any amine in acidic aqueous solution has been developed. A complex is formed between the amine and cobalt thiocyanate, and this complex is extracted from aqueous solution at pH 1·4 by a mixed pentyl alcohol - kerosene solvent. The method is accurate to within ±1 per cent. for concentrations down to 5 p.p.m. of amine in the aqueous solution.

VARIOUS long-chain amines are among the most suitable solvents for extracting uranium from aqueous leach liquors, and, in order to decide which of these solvents should be used for a particular extraction, a careful comparison between the properties of the amines is required. One of the most important factors of such a comparison is the assessment of amine loss in the aqueous phase. A method for determining small concentrations of amine in aqueous solution is therefore required; it should be applicable to all amines and sensitive to a concentration of at least 10 p.p.m. Further, to trace losses of solvent during laboratory

experiments, it is desirable to have a method requiring use of only small amounts, about 25 ml, of barren solution *i.e.*, a solution from which the uranium has been extracted. Hershenson and Hume's method,[1] as modified by Audsley, Ryan and Wells[2] and described in a National Chemical Laboratory report,[3] is based on the colour of the amine - cupric chloride complex and has the desired sensitivity, but about 1 litre of barren solution is needed for the recovery and determination of the amine. Ashbrook's method[4] was found to be applicable only to symmetrical tertiary amines. We have devised an alternative procedure, also based on the colour of the amine - cobalt thiocyanate complex; it is applicable to all amines, and only about 25 ml of barren solution are needed for a determination.

Experimental

Solutions of the various primary, secondary and tertiary amines investigated were prepared in 96 per cent. ethanol, with the addition of as much kerosene as was necessary to give complete solution. Aliquots containing 2·5 mg of amine were added to solutions containing known concentrations of cobalt and thiocyanate ions at known pH, and the resulting complex was extracted by shaking with various solvents.

Extraction solvent—

Benzene, kerosene and light petroleum produced no colour when shaken with the amine complex. Chloroform and carbon tetrachloride gave a stable colour only with symmetrical tertiary amines. The methyl propyl ketones, pentyl and higher alcohols and diethyl ether all gave satisfactory colours with the amines tested. Of these solvents, pentyl alcohol was less water-soluble and less volatile than diethyl ether and was more readily available than the ketones; it was therefore chosen as extraction solvent. The optical density of the extracted complex was measured at 625 mμ, which was found to be the optimum wavelength.

Reagent blank—

For accurate determination of low concentrations of amine, it is necessary to obtain the maximum difference in optical density between sample and reagent blank; the colour of the reagent blank should therefore be negligible. Both the amine - cobalt thiocyanate complex and the cobalt - thiocyanate complex are coloured and are extracted from aqueous solution by pentyl alcohol, extraction being due to the formation of ion-association complexes stable in the organic solvent. Variation in the dielectric constant of the solvent, produced by mixing the pentyl alcohol with kerosene, permitted selective extraction of the amine complex and prevented extraction of cobalt thiocyanate; in this way the optical density of the blank was kept to a minimum. With solvent mixtures containing less than 20 per cent. of pentyl alcohol in kerosene, extraction of the amine complex decreased, and with mixtures containing more than 40 per cent. of pentyl alcohol extraction of cobalt thiocyanate was appreciable. Further, it was found that development of the blank colour and its extraction by the solvent were dependent on the pH of the solution. The optimum levels for pH and concentration of pentyl alcohol in kerosene were investigated, and the results are shown in Table I. The best results were obtained by using a solvent mixture containing 20 per cent. v/v of pentyl alcohol at pH 1·4. The pH was varied by using orthophosphoric acid, but maximum absorption again occurred at 625 mμ for the mixed solvent. The optimum concentration of the cobalt thiocyanate solution was found to be 4 per cent. w/v; at a concentration of 2 per cent. w/v, formation of the amine - thiocyanate complex was evidently incomplete, and at 6 per cent. w/v there was a significant blank colour.

Method

Procedure—

Adjust the pH of the sample containing the unknown amount of amine to 1·4 by adding orthophosphoric acid; use a pH meter calibrated in this region with a solution having a standard pH. Add cobaltous nitrate and sodium thiocyanate to give a concentration of 40 g of each salt per litre, and re-adjust the pH to 1·4. Extract the blue complex by shaking the mixture vigorously in a separating funnel for 30 seconds with a 20 per cent. v/v solution of pentyl alcohol in kerosene. Set aside for 10 minutes, separate the aqueous layer, filter the organic layer through a Whatman No. 1 filter-paper, and collect a portion of the filtrate in a 1-cm cell. Measure the optical density against a reagent blank solution at 625 mμ, and calculate the concentration of amine present by reference to a calibration graph.

PREPARATION OF CALIBRATION GRAPH—

Dissolve known amounts of amine in 96 per cent. ethanol, with the addition of as much kerosene as is necessary for complete solution, and add portions of this solution to the cobalt thiocyanate reagent solution to give samples covering the required range of concentrations. Extract the resulting complexes with the pentyl alcohol - kerosene solvent, and measure the optical densities of the extracts at 625 mμ. Beer's law was found to apply over the range of concentrations investigated (5 to 200 p.p.m. of amine), so that only two readings are necessary to define the graph.

TABLE I

VARIATION OF OPTICAL DENSITY WITH pH AND CONCENTRATION OF PENTYL ALCOHOL

In each experiment 50 ml of reagent solution containing 2·5 mg of amine were extracted with 10 ml of pentyl alcohol - kerosene mixture

	Optical density when extraction solvent contained—					
	20% v/v of pentyl alcohol		30% v/v of pentyl alcohol		40% v/v of pentyl alcohol	
pH	Sample	Blank	Sample	Blank	Sample	Blank
1·2	0·267	0·012	0·265	0·032	0·266	0·046
1·3	0·256	0·006	0·257	0·030	0·257	0·040
1·4	0·250	0·000	0·249	0·026	0·250	0·036
1·6	0·236	0·000	0·239	0·022	0·237	0·036
1·7	0·239	0·000	0·238	0·016	0·232	0·032
2·1	0·222	0·000	0·222	0·008	0·220	0·024

TABLE II

OPTICAL DENSITIES FOUND FOR VARIOUS CONCENTRATIONS OF AMINE

Volume of solution extracted, ml	Concentration of amine, p.p.m.	Optical density of— sample solution	Optical density of— blank solution	Optical-density difference
Solution containing 2·5 mg of amine—				
25	100	0·280	0·027	0·253
50	50	0·258	0·007	0·251
75	33	0·254	0·006	0·248
100	25	0·256	0·006	0·250
150	17	0·250	0·000	0·250
200	12·5	0·250	0·002	0·248
250	10	0·248	0·001	0·247
Solution containing 0·5 mg of amine—				
25	20	0·078	0·028	0·050
50	10	0·060	0·008	0·052
75	7·5	0·054	0·004	0·050
100	5	0·052	0·004	0·048
150	3·3	0·047	0·003	0·044
200	2·5	0·035	0·002	0·033

DISCUSSION OF THE METHOD

SENSITIVITY—

To find the limiting concentration of amine in aqueous solution that could be determined by the proposed method, 2·5- and 0·5-mg amounts of amine were diluted to various concentrations, and the resulting solutions were extracted as described above. The optical densities of the extracts are shown in Table II and indicate that the lower limit of concentration is about 5 p.p.m. of amine. The figures in the column headed "optical-density difference," when multiplied by 10, give the amount of amine found, in milligrams. It can be seen that the results are accurate to within about ±1 per cent. when 2·5 mg of amine are present, but only to within about ±5 per cent. for 0·5 mg of amine. By a concentration procedure analogous to that described by Audsley, Ryan and Wells,[2] the sensitivity of the method can be extended to determine 0·2 p.p.m. of amine with an error of less than ±5 per cent.

APPLICABILITY—

In all the work described above, the Rohm and Haas amine XE204 was used. Similar tests were carried out with a variety of primary, secondary and tertiary amines, for which

the method was found to be equally sensitive. It was found that equal amounts of different amines produced slightly different intensities of colour when extracted, so that it was necessary to prepare a separate calibration graph for each amine.

INTERFERENCE BY FERRIC IRON—

Ferric iron, present in uranium leach liquors, interferes with the determination by forming ferric thiocyanate, which is extracted by the pentyl alcohol - kerosene solvent; it must therefore be removed before determination of the amine. Various methods of removal were tried, of which only complexing with phosphate was suitable.

When the sample contained less than 0·5 g of ferric iron per litre, it was necessary to add only slightly more solid sodium dihydrogen orthophosphate than would completely discharge the colour of the ferric thiocyanate before the amine complex was extracted as described above. When the sample contained more than 0·5 g of ferric iron per litre, the procedure described below was used.

> To a 30-ml sample add 5 ml of a 10 per cent. w/v solution of ascorbic acid to reduce ferric iron, and then add 10 ml of a solution containing 20 per cent. w/v each of cobaltous nitrate and sodium thiocyanate. Add at least 10 g of sodium dihydrogen orthophosphate (or more if 10 g is insufficient to discharge the ferric thiocyanate colour), adjust the pH to 2·5 with orthophosphoric acid, and extract with 10 ml of pentyl alcohol - kerosene solvent as before.

The pH is increased to 2·5 before extraction, because it was found that the colour intensity of the iron complex was less at higher pH values and was fairly constant in the pH range 2·3 to 3·5.

Permission to publish this paper has been obtained from the Transvaal and Orange Free State Chamber of Mines.

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Polarographic Determination of Dimethyl and Dibutyl Phthalates in Propellants with use of Zinc Amalgam to Overcome Interference from Nitroglycerine

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Methods for determining phthalates in the presence of nitroglycerine have been investigated, and a satisfactory general procedure has been developed. An extract of the ground propellant in diethyl ether is dissolved in ethanol, and the resulting solution is shaken with zinc amalgam to reduce nitroglycerine. The solution is filtered through a Buchner funnel of the type described by Neal, and, after precipitation of dissolved zinc, a polarogram is recorded; tetramethylammonium bromide solution is used as base electrolyte.

NITROGLYCERINE interferes with the determination of phthalate esters, whether by the classical gravimetric[1] or saponification methods,[2,3,4,5] conventional polarography[6] or ultraviolet spectroscopy.[7] Infra-red spectroscopy can be used to determine phthalates directly in some simple types of propellant, but in the more complex modern propellants, the ether-soluble matter invariably contains at least one substance giving rise to infra-red absorption

bands that coincide with those of the phthalate esters. A method[8] has recently been described for determining dibutyl phthalate directly in the presence of nitroglycerine. This method involves use of a cathode-ray polarograph, which has the advantage over an orthodox polarograph that the presence of greater amounts of a more easily reducible species can be tolerated and so allows direct measurement of the dibutyl phthalate to be made in the presence of nitroglycerine. There seems to be no reason why this method should not be extended to the more difficult determination of dimethyl phthalate. Our work, however, has been carried out by conventional polarography, which necessitates prior chemical reduction of the nitroglycerine to prevent its interference with the phthalate wave.

In our laboratory, dibutyl phthalate has been determined polarographically after reduction of the nitroglycerine by a titanous salt and then extraction of the phthalate ester into light petroleum. However, this method applied to dimethyl phthalate gave results from 10 to 25 per cent. low. The determination of dimethyl phthalate in double-base propellants has, in fact, long remained an intractable analytical problem, as methods successful for the higher alkyl phthalates have given low recoveries when applied to the dimethyl compound.[2,5] These low results have been attributed to the significant solubility of dimethyl phthalate in water and to the readiness with which it can undergo partial hydrolysis during the analytical procedures. An investigation was therefore undertaken to find a satisfactory method for determining dimethyl phthalate and to see if such a method could be applied with advantage to the determination of dibutyl phthalate.

Experimental

A modified reduction process, involving use of a buffered titanous solution at room temperature, and subsequent extraction with light petroleum from a saturated solution of sodium chloride still led to an approximately 10 per cent. loss of dimethyl phthalate, which was found to occur mainly at the extraction stage. As a further approach to the problem, the reduction of nitroglycerine with metal reductors in neutral ethanolic solution was considered, for it seemed possible that this treatment would prevent hydrolysis of dimethyl phthalate; further, subsequent solvent extraction would not be necessary, as the ethanolic solution would readily lend itself to polarography. After unsuccessful attempts with unamalgamated zinc, it was decided to try liquid zinc amalgam, and this was prepared as described by Kolthoff and Belcher.[9]

Initial tests were carried out by shaking solutions of nitroglycerine in ethanol with different amounts of amalgam for different times and then checking the extent of reduction polarographically. These tests indicated that the amount of amalgam used and the time and vigour of shaking all affected reduction of the nitroglycerine. It was established that 500 mg of nitroglycerine in 25 ml of ethanol were completely reduced when shaken with 6 ml of zinc amalgam for 1 hour at the rate of approximately 300 cycles per minute, the flask being clamped horizontally in a shaking machine having a horizontal movement. These conditions always gave satisfactory reduction.

However, when this procedure was applied to mixtures of dimethyl phthalate and nitroglycerine, zinc ions resulting from the reduction caused interference similar to that of nitroglycerine; they produced a large polarographic step preceding that of the phthalate. This secondary interference was overcome by precipitating the zinc as hydroxide with tetramethylammonium hydroxide solution, but it was found that the presence of an amount of base in excess of that required for precipitating the zinc diminished the height of the phthalate step. It was therefore necessary to control the pH of the solution, and this was satisfactorily accomplished by adding tetramethylammonium hydroxide solution until the change-point of cresol red - thymol blue indicator was reached. The change in colour of this indicator was sufficiently apparent even in the dark-brown solutions produced by some propellant compositions, and the indicator itself did not interfere with the phthalate polarogram, which was reproducible and remained of constant height for prepared solutions that had been set aside for 2 hours.

Alone, dimethyl phthalate in a supporting electrolyte of tetramethylammonium bromide gives two steps at half-wave potentials of $-1{\cdot}65$ and $-1{\cdot}85$ volts against a mercury-pool anode. In the presence of reduced nitroglycerine, only the first step can be recorded, the second step being apparently merged with a larger reduction step (presumably produced by nitrite). This causes the top of the first phthalate step to slope upwards, whereas, in the absence of reduced nitroglycerine, the top is flat. In the preparation of a standard,

therefore, phthalate was added to an amount of reduced nitroglycerine equal to that resulting from treatment of the sample. Further, at the concentrations of nitroglycerine used, formation of the nitrite step is just beginning at −1·60 volts and so slightly enhances the first phthalate step. To correct for this, the applied potential corresponding to the top of the phthalate step as measured was noted, and the increase in current corresponding to this potential was read from a polarogram given by this same concentration of reduced nitroglycerine. This reading was subtracted from the heights of the steps for both sample and standard.

The phthalate step produced under these conditions is characterised by a slight kink. This is apparently produced by zinc ions, as addition of a zinc salt to a phthalate solution in the absence of reduced nitroglycerine and then precipitation of the zinc affects the phthalate polarogram in this way. The relationship between the height of the whole step and the concentration of phthalate ester was, however, shown to be linear.

After reduction, the residual sludge of zinc amalgam was separated by filtration. For this purpose, a Buchner funnel of the type described by Neal[10] was found to be preferable to filter-paper. This funnel is designed for direct filtration under vacuum into narrow-necked flasks and consists of a standard ground-glass joint, with a side-arm for connection to the pump, annularly fused to the stem of a sintered-glass filter funnel. The filter funnels and 100-ml calibrated flasks were fitted with B19 cones and sockets, respectively, for convenience of operation.

The method was then applied to the determination of dimethyl phthalate in propellant compositions and gave good results. As the procedure is easier to operate than that involving reduction by a titanous solution, dibutyl phthalate in propellants was also determined with liquid zinc amalgam as reductant; the results were again satisfactory.

Method

Reagents—

Diethyl ether, peroxide-free.

Ethanol, 95 per cent.

Zinc amalgam—Heat about 3 g of pure zinc with about 100 g of mercury and 5 ml of dilute sulphuric acid (1 + 4) on a bath of hot water until the pieces of zinc have dissolved in the mercury. (This operation should be carried out in a fume chamber because of the toxic effects of mercury vapour.) Cool, transfer to a separating funnel, and run off the amalgam to separate it from any solid material. Wash the amalgam with successive portions of water until the washings are free from acid, separate from the water, and store for use. When this stock has been used, prepare fresh amalgam by using in place of mercury the amalgam residues retained on the filter during determinations.

Tetramethylammonium hydroxide, approximately 0·5 N, aqueous.

Tetramethylammonium bromide solution, 20 per cent. w/v, aqueous.

Indicator solution—Mix ethanolic 0·1 per cent. w/v solutions of cresol red (1 volume) and thymol blue (3 volumes).

Gelatin solution, 0·5 per cent. w/v, aqueous.

Reduced nitroglycerine solution—Reduce 1·25 g of nitroglycerine in 50 ml of ethanol with about 15 ml of zinc amalgam as described under "Procedure." Separate the amalgam by filtration, dilute the filtrate to 100 ml with ethanol, and mix well.

Standard dimethyl phthalate solution—Transfer an accurately weighed amount (about 0·2 g) of dimethyl phthalate to a 200-ml calibrated flask, dissolve in ethanol, and dilute to the mark at 20° C.

Standard dibutyl phthalate solution—Transfer an accurately weighed amount (about 0·2 g) of dibutyl phthalate to a 200-ml calibrated flask, dissolve in ethanol, and dilute to the mark at 20° C.

Procedure—

Extract an amount of sample ground to pass through a No. 21 s.w.g. sieve and containing about 500 mg of nitroglycerine with diethyl ether for 7 hours in a Soxhlet apparatus; use a 250-ml conical flask fitted with a ground-glass joint. Remove the ether, and dissolve the extract in 25 ml of ethanol. Add 6 ml of amalgam, insert a stopper, place the flask on its

side in a horizontal shaking machine, and shake for 1 hour at approximately 300 cycles per minute. Remove the flask from the shaker, and filter the contents through a Buchner funnel of the type described by Neal[10]; the funnel should be of porosity No. 4, fitted with a B19 cone and inserted in a B19 socket attached to the neck of a 100-ml calibrated flask. Apply moderate suction, wash the residual amalgam and the sinter well with successive portions of ethanol, dilute the contents of the 100-ml flask to the mark with ethanol at 20° C, and mix well.

By pipette, place a 25-ml portion of the solution in a 50-ml calibrated flask, add 10 ml of tetramethylammonium bromide solution, 0·5 ml of indicator solution and then tetramethylammonium hydroxide solution, dropwise, until a permanent change in colour occurs. Add 1 ml of gelatin solution, and dilute to the mark with ethanol at 20° C. Mix well, and filter sufficient of the solution through a dry Whatman No. 41 filter-paper into a polarographic cell.

Bubble nitrogen through the solution for 10 minutes, having first passed it through a wash-bottle containing some of the same solution or an exactly similar solution to equilibrate the nitrogen with ethanol and water vapours. Use a bell-shaped dome and water seal to prevent re-solution of oxygen during polarography, and, at a suitable sensitivity, record a polarogram from −1·4 to −1·8 volts against the mercury-pool anode.

TABLE I

DIMETHYL PHTHALATE FOUND IN PROPELLANTS

Sample	Dimethyl phthalate added, %	Dimethyl phthalate found, %
Synthetic propellant, type 1*	1·89	1·90
	1·98	1·98, 1·98
	2·19	2·18, 2·19
	2·39	2·38, 2·42
	2·44	2·46
Manufactured propellant, type 1	Nil	2·23, 2·29
	Nil	2·26
Manufactured propellant, type 2†	Nil	Nil
Dimethyl phthalate *plus* ether-soluble matter from manufactured propellant, type 2	2·95	2·95, 2·94

* Sample contained nitrocellulose, nitroglycerine, triacetin, 2-nitrodiphenylamine, dimethyl phthalate and other additives.
† Sample contained the same ingredients as did type 1, but no dimethyl phthalate was present.

TABLE II

DIBUTYL PHTHALATE FOUND IN PROPELLANTS

Sample	Dibutyl phthalate added, %	Dibutyl phthalate found by— proposed method, %	Dibutyl phthalate found by— method involving titanous reduction, %
Synthetic propellant*	6·49	6·49, 6·49	—
	6·95	6·97, 6·95	—
Manufactured propellant*	Nil	7·16, 7·25, 7·15	7·21†

* Sample contained nitrocellulose, nitroglycerine, carbamite, dibutyl phthalate and other additives.
† Mean of several determinations.

According to which ester is being determined, prepare a standard by adding a suitable amount of standard dimethyl or dibutyl phthalate solution to 10 ml of the reduced nitroglycerine solution. Treat this solution exactly as described above for the 25-ml portion of reduced sample solution, and record a polarogram under the same conditions. Also record a polarogram for a similarly treated 10-ml portion of the reduced nitroglycerine solution. Subtract the small contribution that this makes to the height of the phthalate step from the step heights for both sample and standard, and thus evaluate the phthalate ester content of the sample.

RESULTS

When the proposed method was tested on a prepared mixture of 500 mg of nitroglycerine and 59·0 mg of dimethyl phthalate, the amounts of dimethyl phthalate found were 59·0 and

58·8 mg. The results obtained when the method was applied to various types of propellant are shown in Tables I and II.

Zinc amalgam reduces the aromatic nitro-compounds that occur in some propellants and so overcomes any polarographic interference likely to arise from these ingredients. None of the other substances present in propellants containing dimethyl or dibutyl phthalates was found to interfere with the procedure. The method is proposed, in particular, as an accurate and facile means of determining dimethyl and dibutyl phthalates in double-base propellants. Reduction by liquid zinc amalgam is also recommended as a technique that might advantageously be applied to other problems in the analysis of propellants when interference from nitroglycerine or aromatic nitro-compounds has to be overcome.

We thank Mr. G. Watts, who assisted in the early stages of the investigation, and the Head of the Naval Ordnance Inspection Laboratory for permission to publish this paper.

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The Determination of ^{14}C and ^{32}P in Animal Tissue and Blood Fractions by the Liquid-scintillation Method

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A liquid-scintillation method for determining ^{14}C and ^{32}P in tissues, blood sera and their fractions is described. The influence of the volumes of scintillator, sample and Hyamine 10-X solution on the efficiency of counting water-soluble sources of ^{32}P has been studied. Investigation of the use of *p*-dioxan to achieve miscibility between scintillator and lipid extracts from fresh tissues and blood sera has shown that this substance has no effect on the efficiency of counting. The optimum volumes of scintillator, *p*-dioxan and Hyamine 10-X solution for maximum efficiency are summarised.

Efficiencies of counting for the various types of extract from blood sera and oviduct protein were reproducible, so that the absolute activities in the fractions could be calculated; the sum of these activities was equal to the activity in the whole-blood sera and protein determined independently.

The liquid-scintillation method and its applications have been reviewed by Davidson and Fiegelson[1] and Bell and Hayes.[2] We have described[3] methods for the radioassay of ^{14}C-labelled tissues, proteins and amino acids and have investigated the experimental variables affecting the counting and the reproducibility of these methods. This paper describes the radioassay of ^{14}C and ^{32}P in tissue and blood fractions separated by chemical techniques.

In biological experiments involving the uptake of tracer substances, it is of advantage to determine the absolute levels of uptake into individual fractions, and such results can only be obtained when the efficiency of counting is known. In view of the high cost of tracer substances and the low concentration of some of the more important cellular fractions, a high efficiency of counting is essential. Factors influencing the efficiency of counting for ^{32}P have therefore been examined, with a view also to avoiding the use of internal standards.

We have found that organic-solvent extracts of fresh biological materials are not usually completely miscible with the scintillator, owing to an inherent content of water. Systems containing traces of water have been blended with scintillators by using alcohols,[4,5] and *p*-dioxan has been used by several investigators for counting tritiated water.[6] This compound is a scintillation solvent,[7] and we have studied its use for blending lipid extracts containing small amounts of water.

p-Dioxan is incapable of blending aqueous solutions with scintillator, and we have used 2-methyl-4-(1,1,3,3-tetramethylbutyl)phenoxyethoxyethyldimethylbenzylammonium chloride monohydrate (Hyamine 10-X, obtainable from C. Lennig and Co. (G.B.) Ltd., London, W.C.1) for this purpose, as described previously for ^{14}C sources.[3] The use of this compound for counting sources of ^{32}P is described.

Experimental

The NE8301 liquid-scintillation assembly (obtainable from Nuclear Enterprises (G.B.) Ltd., Edinburgh 11) described previously[3] was used. The NE213 scintillator (Nuclear Enterprises Ltd.) was based on xylene and contained naphthalene and 1,4-bis-2-(5-phenyloxazolyl)benzene as spectrum shifter. A 1 M solution of Hyamine 10-X (molecular weight 480·11) in analytical-reagent grade methanol was used, and [^{14}C]benzoic acid, 1-[^{14}C]stearic acid and [^{32}P]orthophosphate in isotonic saline, pH 7, were obtained from the Radiochemical Centre, Amersham, Bucks.

Preparation of blood and tissue extracts—

Twelve hours before they were killed, some oestrogen-treated pullets were injected intraperitoneally with 270 μc of ^{32}P and others with 45 μc of 1-[^{14}C]stearic acid. The oviduct tissue was removed immediately after slaughter, and blood was obtained by allowing free bleeding from the jugular vein. Determinations of moisture in blood and oviduct tissue were made by drying *in vacuo* over phosphorus pentoxide. Inorganic fractions were extracted from the oviduct tissues by Schmidt and Thannhauser's method for phosphorus,[8] and lipids were extracted by Schneider's method.[9] Nucleic acid and phosphoprotein-phosphorus fractions were separated from the residues by Schmidt and Thannhauser's technique.

The inorganic-phosphorus fractions of the blood serum from the ^{32}P-treated birds were obtained by Fiske and Subba Row's method,[10] the lipid-phosphorus fractions by Youngburg and Youngburg's method[11] and the vitellin fractions by Laskowski's technique.[12] Similar extractions were carried out on the ^{14}C-labelled blood serum. The ^{14}C- and ^{32}P-labelled tissues and blood sera were dissolved and counted as previously described.[3]

Discussion of results

Effect of volume of scintillator on efficiency of counting for ^{32}P—

Aqueous solutions—Previous investigations[3] of counting for ^{14}C had shown the beneficial effect of using small volumes of aqueous sample and an optimum volume of scintillator for obtaining high efficiencies. A 0·1-ml sample was used to determine the optimum volume of scintillator for counting ^{32}P, and a 1·3-ml portion of a 1 M solution of Hyamine 10-X in methanol was used to blend the aqueous sample with increasing volumes of scintillator in the counting vessel. The effect of Hyamine 10-X on the efficiency of counting is considered below. Maximum efficiency (81 per cent.) for an aqueous source of ^{32}P was achieved with 3 ml of scintillator, compared with a maximum efficiency of 65 per cent. with 8 ml of scintillator for ^{14}C.[3] Further addition of scintillator up to 12 ml did not increase the efficiency above 81 per cent. This efficiency has been attained with several independent sources of [^{32}P]orthophosphate and is probably attributable to the higher energy of the β-emissions from ^{32}P as compared with ^{14}C.

Lipid sources—An ether extract of oviduct tissue containing ^{32}P-labelled lipid material was used to investigate the effect of the volume of scintillator on the count rate of such a

source, since a standard source of ^{32}P soluble in the scintillator was not available. A 0·1-ml portion of this solution was blended with 0·25 ml of *p*-dioxan to produce a clear solution with the scintillator (*p*-dioxan was necessary because of the traces of water derived from the tissue, and results presented later show that its presence had no quenching effect). The fact that the volume of scintillator used had no marked effect on count rate is shown by the results below.

Volume of scintillator, ml	0·1	0·25	0·50	1·0	2·0	4·0	8·0
Counts per minute for 0·1 ml of source *plus* 0·25 ml of *p*-dioxan	747	720	746	748	771	754	770

This finding differs greatly from those obtained by Stitch[13] and ourselves[3] for sources of ^{14}C soluble in scintillator. The background count for the aqueous solutions was 40 counts per minute and that for solutions soluble in the scintillator was 50 counts per minute.

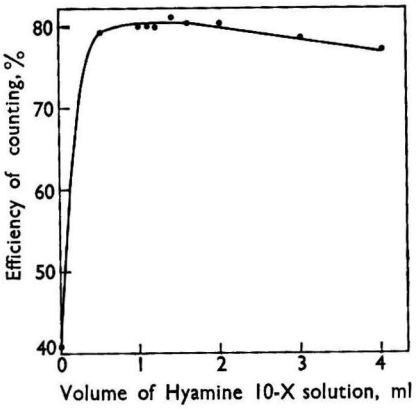

Fig. 1. Effect of volume of Hyamine 10-X solution on efficiency of counting a 0·1-ml sample of aqueous solution containing 16·647 mμc of activity (^{32}P); 4 ml of scintillator were used

TABLE I

EFFECT ON COUNT RATES OF VOLUME OF *p*-DIOXAN USED FOR BLENDING

The volumes of scintillator and sample used were 4 and 0·1 ml, respectively

1-[^{14}C]stearic acid		^{14}C-labelled lipid extract		^{32}P-labelled lipid extract	
Volume of *p*-dioxan used, ml	Activity, counts per minute	Volume of *p*-dioxan used, ml	Activity, counts per minute	Volume of *p*-dioxan used, ml	Activity, counts per minute
0·0	4006	0·05	670	0·10	604
0·1	4016	0·10	686	0·20	650
0·2	4010	0·15	653	0·60	637
0·5	4005	0·20	700	1·60	604
1·0	4120	0·25	688	2·60	628
2·0	4005	0·50	674	3·60	639
3·0	3914				
4·0	3902				

EFFECT OF VOLUME OF HYAMINE 10-X SOLUTION ON EFFICIENCY OF COUNTING FOR ^{32}P—

The effect of the volume of Hyamine 10-X solution on the efficiency of counting is shown in Fig. 1. To obtain a clear solution of a 0·1-ml portion of sample in 4 ml of scintillator, 1·3 ml of Hyamine 10-X solution were required, and this volume was used in counting all aqueous 0·1-ml samples containing ^{32}P. Maximum efficiency, however, was attained over a wide range of volumes of Hyamine 10-X solution (0·5 to 3·0 ml). This is in contrast to

the curves obtained for ^{14}C in aqueous solution; such a curve had a sharp peak at the volume of Hyamine 10-X required to give a clear solution.[3] With large volumes of sample, for which greater volumes of Hyamine 10-X are required to produce a clear solution, some decrease in efficiency has been experienced, *e.g.*, with a 0·4-ml sample the efficiency was decreased by 1·5 per cent.

In subsequent work with aqueous solutions of ^{32}P-labelled substances, 0·1-ml samples were used and were blended with scintillator by using 1·3 ml of Hyamine 10-X solution. It was found by the use of internal standards that, with this small volume of sample, the inorganic, nucleic acid and phosphoprotein-phosphorus fractions of tissues could be counted with an efficiency of 81 per cent.

EFFECT OF VOLUME OF *p*-DIOXAN ON COUNT RATE—

The effect of the volume of *p*-dioxan used for blending on the count rate of a source of 1-[^{14}C]stearic acid dissolved in scintillator was investigated; the results are shown in Table I and indicate that up to 4 ml of *p*-dioxan had no effect. Although there is some indication of a decrease in count rate in the presence of more than 2 ml of *p*-dioxan, the lower figures are within the limits of statistical variation. Some experiments with extracts of ^{14}C- and ^{32}P-labelled oviduct-lipid material showed that 0·1-ml portions of these extracts were completely miscible with scintillator when 0·25 ml of *p*-dioxan was added. The results of these experiments are also shown in Table I and indicate that the *p*-dioxan again had no significant effect on the count rate. This is in accordance with Davidson's results for *p*-dioxan as a scintillation solvent.[7] Lipid extracts from dried tissues and dried blood sera are directly miscible with scintillator, as no water is present.

DETERMINATION OF EFFICIENCY OF COUNTING FOR LIPID EXTRACTS—

As no standard organic source of ^{32}P was available for determining the absolute efficiency of counting ^{32}P-labelled lipid extracts, 0·1-ml aliquots of extracts were counted, and the count rates were compared with those for aliquots of the same extract that had been converted to inorganic phosphorus by dry ashing with excess of magnesium acetate and dissolved in 2 N hydrochloric acid before counting. The efficiency of counting a solution in hydrochloric acid was found to be the same as that for [^{32}P]orthophosphate in water. The efficiency of counting the ^{32}P-lipid extract was calculated to be 99 per cent., which is similar to that obtained for ^{32}P by Guinn.[14]

TABLE II

RECOVERY OF ADDED RADIOACTIVITY FROM OVIDUCT LIPID EXTRACTS

Activity was added as 1-[^{14}C]stearic acid; the volumes of scintillator and *p*-dioxan used were 4 and 0·25 ml, respectively, and the scintillator was not de-oxygenated with nitrogen; the efficiency of counting 1-[^{14}C]stearic acid alone with scintillator and *p*-dioxan was 87·3 per cent.

Activity added to 0·1 ml of sample, mμc	Activity measured, counts per minute (corrected for blank)	Efficiency of counting, %
0·25	475	85·6
	488	87·9
0·50	971	87·5
	951	85·7
0·75	1482	89·0
	1424	85·5

The efficiency of counting ^{14}C-lipid extracts of oviduct tissue was determined by the recovery of activity, added as 1-[^{14}C]stearic acid, from these extracts. The results in Table II show that 0·1-ml samples of lipid extract have no measurable quenching effects and may therefore be assumed to be counted at the same efficiency as the standard 1-[^{14}C]stearic acid source, *i.e.*, 87 per cent. Similar results have been obtained for the recovery of [^{14}C]benzoic acid from extracts of blood lipids.

Although 0·1-ml aliquots of lipid extracts of fresh oviduct tissue and blood serum can be counted at the same efficiency as can [^{14}C]benzoic acid, an increase in the volume of lipid

sample causes a decrease in the efficiency of counting. This is shown by the results in Table III, from which it can be seen that 0·05- and 0·1-ml samples can be counted without significant quenching. Samples of greater volume, however, show self-quenching effects, with a decrease in the recovery of added [^{14}C]benzoic acid. It is of advantage here to summarise the experimental conditions used to count the various types of sample investigated and to indicate the efficiency of counting; the volumes of acid and blending agents used are shown in Table IV.

Table III

Effect of volume of lipid extract sample on count rate of extract and recovery of added radioactivity

The volumes of scintillator and *p*-dioxan used were 4 and 1·0 ml, respectively; the efficiency of counting the [^{14}C]benzoic acid source was 87·9 per cent.

Volume of sample, ml	Activity present,* counts per minute	Activity measured, counts per minute	Recovery of 2 mμc of added [^{14}C]benzoic acid, %
0·05	167	167	98·4
0·10	334	332	97·8
0·20	668	595	96·2
0·30	1002	852	93·6
0·40	1336	1172	93·0

*Calculated by multiplication of the measured value for 0·05 ml of sample.

Table IV

Volumes of reagents in counting vessel for various types of sample

The volumes of scintillator and sample used were 4 and 0·1 ml, respectively

Description of sample	Volume of 2 N hydrochloric acid added, ml	Volume of 1 M Hyamine 10-X in methanol used, ml	Volume of *p*-dioxan used, ml	Efficiency of counting for— ^{14}C, %	Efficiency of counting for— ^{32}P, %
Lipid extract from fresh tissue (trace of water present) ..	Nil	Nil	0·25	88	99
Lipid extract from dry tissue ..	Nil	Nil	Nil	88	99
Acid aqueous extract	Nil	1·3	Nil	59	81
Alkaline aqueous extract	0·05	1·8	Nil	55	81
Solutions of blood sera and tissue, 1 N potassium hydroxide and Hyamine 10-X solution ..	0·05	1·15	Nil	59	81

Table V

Balance study of incorporation of 1-[^{14}C]stearic acid and ^{32}P (as orthophosphate) into blood-serum fractions and whole blood serum

Sample	1-[^{14}C]stearic acid: Activity measured, counts per minute	1-[^{14}C]stearic acid: Efficiency of counting, %	1-[^{14}C]stearic acid: Calculated activity, disintegrations per minute	[^{32}P]orthophosphate: Activity measured, counts per minute	[^{32}P]orthophosphate: Efficiency of counting, %	[^{32}P]orthophosphate: Calculated activity, disintegrations per minute
Whole blood serum (dried) ..	50,096	59	84,909	322,066	81	397,612
Inorganic fraction	3039	59	5150	90,396	81	111,000
Lipid fraction	67,056	88	76,200	181,170	99	183,000
Protein fraction	1959	59	3320	86,476	81	106,760
Sum of counts in fractions			84,670			401,330
Recovery (percentage of disintegrations in whole blood)			99·7			100·9

INCORPORATION OF ^{32}P AND ^{14}C INTO TISSUE AND BLOOD FRACTIONS—

The efficiency of counting, and hence the specific activity in absolute units, often has to be determined for whole tissues or blood sera and their fractions in order to obtain maximum information in metabolic experiments involving uptake of tracer substances. When the specific activities are expressed in absolute units, confirmation of the accuracy of the counting methods is provided when the sum of the activities of the fractions is equal to the activity of the whole tissue or blood serum determined independently.

The results in Tables V and VI show that, when the techniques described above are used, the sum of the activities of the fractions (calculated for the same weight of tissue or blood serum) is equal to the total activity of the tissue or blood serum; in computing these results, the efficiencies shown in Table IV for the various types of solution were used.

TABLE VI

BALANCE STUDY OF INCORPORATION OF ^{32}P (AS ORTHOPHOSPHATE) INTO FRACTIONS OF OVIDUCT TISSUE, PROTEIN AND NUCLEIC ACIDS

Sample	Activity, disintegrations per minute
Total protein and nucleic acid in potassium hydroxide solution ..	494,455
Ribonucleic acid phosphorus	318,382
Deoxyribonucleic acid phosphorus	47,223
Phosphoprotein	139,103
Sum of counts in fractions	504,708
Recovery (percentage of total activity)	102·1

When results such as those in Tables V and VI are coupled with chemical data for the content of the element in each fraction, precise information on relative uptake into the fractions can be obtained. The recoveries of activity (99·7 to 102·1 per cent.) are within the acceptable limits of error for such biochemical separations and give further proof of the accuracy of the efficiencies of counting used.

We thank Professor J. Houston for his interest and advice during this work and acknowledge the receipt of a grant from the British Egg Marketing Board for puchasing part of the equipment used; we also thank C. Lennig & Co. Ltd. for a gift of Hyamine 10-X. One of us (H.G.B.) is indebted to the British Egg Marketing Board for a Research Studentship.

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The Detection of Organic Peroxides

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The limits of detection of a number of alkyl hydroperoxides, per-esters and dialkyl, diacyl and ketone peroxides by potassium iodide, titanic sulphate and 4,4′-tetramethyldiaminodiphenylmethane have been determined, and the utility of iron salts in extending the range of application of the last-named reagent has been noted.

Procedures based on the liberation of iodine from potassium iodide under suitable conditions of solvent, temperature, acidity, etc., are widely used for determining organic peroxides, and, when carried out as described below, this reaction will detect hydroperoxides and acyl and ketone peroxides. The peroxide contents of oils and fats can be determined by reaction with titanic sulphate and measurement of the intensity of the resulting orange-yellow colour.[1] In the work described here, hydroperoxides and ketone peroxides were found to be the only types that reacted with titanic sulphate. Small amounts of benzoyl peroxide can readily be detected by reaction with 4,4′-tetramethyldiaminodiphenylmethane (tetramethyl base) to give a blue colour.[2] Other acyl peroxides and per-esters have also been found to react with this reagent under the same conditions. Ferrous salts catalyse the decomposition of organic peroxides,[3] and application of this fact to the reaction with tetramethyl base extended the utility of the test; ferric salts had a similar catalytic effect. Leucomalachite green, di-(*p*-dimethylaminophenyl)phenylmethane, was oxidised to malachite green by benzoyl peroxide, and ferrous salts exhibited the catalytic effect noted with tetramethyl base; however, owing to aerial oxidation, the reaction was not so convenient. This factor is inappreciable when tetramethyl base is used.

Method

Reagents—

When possible, materials should be of analytical-reagent grade.

Potassium iodide solution—Dissolve 15 g of potassium iodide in 10 ml of air-free distilled water, and add 100 ml of air-free methanol and 1 ml of glacial acetic acid; store the solution under an atmosphere of nitrogen. (The preparation of this reagent is adapted from that described by Matthews and Patchan.[4])

Titanic sulphate solution—Fuse 0·1 g of titanium dioxide with 7·5 g of potassium pyrosulphate, and dissolve the mixture in 100 ml of 10 per cent. v/v sulphuric acid.

Tetramethyl base solution, 5 per cent. w/v, in benzene—4,4′-Tetramethyldiaminodiphenylmethane obtained from the British Drug Houses Ltd. was used.

Ammonium ferrous sulphate solution, 5 per cent. w/v, aqueous.

Ammonium ferric sulphate solution, 1 per cent. w/v, aqueous.

Benzene.

Organic peroxides—Commercially available materials obtained from Novadel Ltd., London, S.W.18, and Laporte Chemicals Ltd., Luton, Beds., were used.

Procedure—

Test A—Apply 1 drop (0·01 ml) of a solution of the peroxide in benzene to a piece of filter-paper, allow to dry, and then apply 1 drop of potassium iodide solution or titanic sulphate solution. The former reagent produces a yellow-brown stain of iodine in the presence of hydroperoxides or aryl or ketone peroxides; the latter gives an orange colour with hydroperoxides and ketone peroxides only. The sensitivity of the test with potassium iodide solution can be increased by the use of starch.

Test B—Apply 1 drop of tetramethyl base solution to a piece of filter-paper, allow to dry, apply 1 drop (0·01 ml) of a solution of the peroxide in benzene, and again allow to dry. A blue colour is obtained in the presence of acyl peroxides and per-esters. (Alternatively, the peroxide solution may be applied to the filter-paper before the tetramethyl base solution.)

Test C—Carry out test B on filter-paper previously soaked in a solution of ammonium ferrous or ferric sulphate and then dried. Alternatively the iron salt solution can be applied to the colourless spot left as a negative result by test B. The range of peroxides detected with tetramethyl base solution is extended by this modification to include hydroperoxides, ketone peroxides and, when ammonium ferric sulphate solution is used, some dialkyl peroxides.

Results

The limits of detection found when the proposed tests were applied to twenty-two organic peroxides of various types are shown in Table I. Hydrogen peroxide reacts in tests A and C, but not in test B. The proposed tests will be of use in locating and identifying peroxides after chromatographic separations.

Table I

Limits of detection for organic peroxides

Compound	Limit of detection with—		Limit of detection with tetramethyl base solution		
	potassium iodide reagent solution, μg per 0·01 ml	titanic sulphate solution, μg per 0·01 ml	Alone, μg per 0·01 ml	On paper treated with ferrous salt, μg per 0·01 ml	On paper treated with ferric salt, μg per 0·01 ml
t-Butyl hydroperoxide	100	>100	>100	10	5
Cumene hydroperoxide	20	10	>100	1	2
p-Menthane hydroperoxide	>100	>100	>100	2	2
Di-isopropylbenzene hydroperoxide	10	100	100	5	5
Di-t-butyl peroxide	>100	>100	>100	>100	>50
Dicumyl peroxide					>50
Cumyl-t-butyl peroxide					50
2,2-bis(t-Butylperoxy)butane					>50
Acetyl peroxide	20	>100	100	5	10
Octanoyl peroxide	100	>100	10	5	10
Lauroyl peroxide	>100	>100	100	10	5
Benzoyl peroxide	2	>100	1	10	1
p-Chlorobenzoyl peroxide	20	>100	2	10	5
2,4-Dichlorobenzoyl peroxide	20	>100	10	10	5
t-Butyl perbenzoate	>100	>100	100	2	5
t-Butyl peracetate				5	5
Di-t-butyl perphthalate				2	10
Ethyl methyl ketone peroxide	1	10	>100	2	2
Isobutyl methyl ketone peroxide				2	2
Methyl pentyl ketone peroxide				5	5
Cyclohexanone peroxide				2	5
Dibenzal diperoxide	>100	>100	>100	>100	50

I thank the directors of Sterling Moulding Materials Ltd. for permission to publish this paper.

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The Determination of Impurities in Chlorine Gas by Gas Chromatography

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A rapid, accurate and precise gas-chromatographic method for determining up to 1·5 per cent. v/v each of hydrogen, nitrogen, oxygen and carbon dioxide in chlorine gas is described. Separation of the components is effected by using two chromatographic columns in series. The first column contains silica gel and is used for separating carbon dioxide and chlorine from each other and from the permanent gases. The second column, packed with a molecular sieve, separates hydrogen, oxygen and nitrogen.

Small amounts of oxygen, nitrogen, hydrogen and carbon dioxide are usually present as impurities in commercially produced chlorine gas. The method normally used for determining these impurities involves passing a known volume of the gas slowly through a solution of ferrous sulphate or potassium iodide to remove the chlorine and analysing the residual mixture of gases by the conventional Orsat procedure. The method is lengthy and unsuitable for routine work; further, it is not accurate. Gas-chromatographic methods, on the other hand, are rapid, accurate and ideally suited to routine operation.

Mixtures of permanent gases can be separated by using certain solid adsorbents or combinations of solid adsorbents, such as activated charcoal,[1,2] silica gel[3,4] and molecular sieves,[5,6] in accordance with well known techniques. Ellis and Iveson[7] have used gas - liquid partition chromatography with polytrifluoromonochloroethylene as stationary phase for separating volatile halogen and interhalogen compounds. No single solid adsorbent, however, is capable of resolving a mixture containing chlorine, hydrogen, oxygen, nitrogen and carbon dioxide into its five components. Carbon dioxide and chlorine are irreversibly adsorbed by molecular sieves, whereas oxygen and nitrogen can only be conveniently separated on these materials. Ellis and Iveson's method can be used to separate chlorine from the other components, but gas - liquid partition chromatography is not capable of separating any of the permanent gases or carbon dioxide. It has been found, however, that chlorine is eluted from silica gel within a reasonable time at temperatures greater than 50° C and is well separated from carbon dioxide and the other gases.

It was therefore considered that the best method for determining impurities in chlorine gas would be to use an arrangement consisting of a column containing silica gel for separating carbon dioxide and chlorine in series with a column containing a molecular sieve for separating oxygen, hydrogen and nitrogen. Since chlorine is irreversibly adsorbed by molecular sieves, thereby causing them to lose their resolving powers, its removal from the gas stream would be necessary before the stream entered the second column.

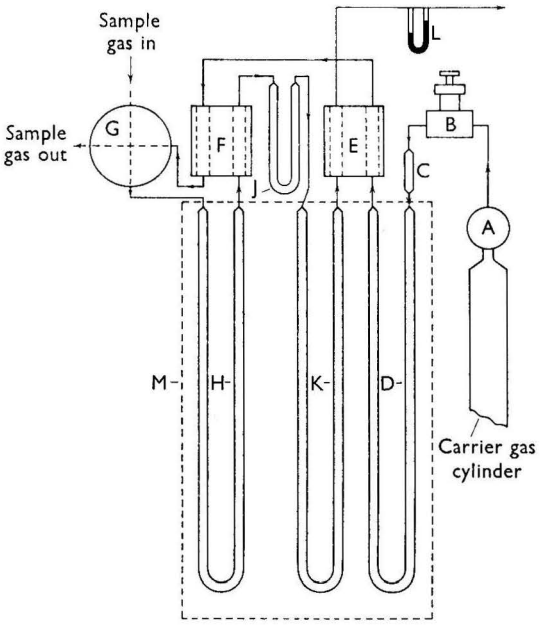
Experimental

Chromatographic apparatus—

The apparatus used is shown diagrammatically in Fig. 1. The rate of flow of carrier gas (argon or helium) through the apparatus was controlled by means of an Edwards V.P.C. pressure controller and measured with a calibrated capillary flow-meter. Detection was by means of a Veco thermistor-bead cell at the end of the first column and a Griffin and George thermal-conductivity cell at the end of the second column. Each detector was incorporated in a separate Wheatstone-bridge circuit and operated by a 6-volt accumulator. Peaks were recorded on a Leeds and Northrup 5- or 10-mV recorder having facilities for switching from one bridge circuit to the other. Samples (25 ml) of gas at atmospheric pressure and temperature were introduced into the stream of carrier gas by means of an all-glass sampling device similar to that described by Harvey and Chalkley.[8]

Chlorine and water vapour were removed from the gas stream after the first detector by means of a glass U-tube (41 cm long, 6 mm i.d.), the first limb of which was packed with 30- to 60-mesh Celite impregnated with saturated potassium iodide solution containing a

little starch. This packing was prepared by adding the Celite to the iodide solution until a free-flowing material was obtained. The second limb contained 30- to 60-mesh self-indicating silica gel to remove water vapour arising from the iodide solution. Each U-tube could remove approximately 500 ml of chlorine, which corresponded to twenty analyses. The progress of chlorine removal could be followed by observing the advance of the leading edge of a sharply defined yellow band in the Celite - potassium iodide packing.



A = Reducing valve
B = Edwards V.P.C. pressure controller
C = Drying tube
D = Pre-heating column
E = Thermal-conductivity detector
F = Thermistor-bead detector
G = All-glass sampling device
H = Silica gel column
J = Tube for chlorine removal
K = Molecular sieve column
L = Calibrated capillary flow-meter
M = Heated column

Fig. 1. Schematic diagram of chromatographic apparatus

The first column consisted of 114 cm of 6 mm i.d. glass tubing packed with 40- to 60-mesh silica gel that had previously been dried at 110° C for 24 hours. The second column consisted of 198 cm of similar tubing packed with 30- to 44-mesh Linde 5A molecular sieve that had been activated by drying at 350° C for 5 hours. The two columns, together with a tube for pre-heating the carrier gas, were controlled at any desired temperature up to 100° C by placing them in an electrically heated column (6 cm i.d.); the temperature was kept sufficiently constant (to within ± 1° C) by controlling the power input to the heater by means of a 0- to 240-volt Variac transformer. The two detectors were lagged and kept at room temperature, as normal variations in room temperature had no appreciable effect on their sensitivities.

APPARATUS FOR PREPARING STANDARD MIXTURES OF GASES—

Standard mixtures of gases were prepared by using the apparatus shown in Fig. 2. Impure chlorine gas from a cylinder was flushed through vessel A and sampling device B, with taps C, D, E, F, G and H open. The Dewar flask was half filled with a mixture of acetone and dry ice, and about 30 ml of liquid chlorine were collected in vessel P. The

supply of chlorine was then turned off and tap C was closed. The mixture of acetone and dry ice was removed from around vessel P, and chlorine gas was flushed through the system. Tap F was opened and closed periodically to remove traces of air from the limb of manometer K (containing sulphuric acid). The chlorine flushing through the system was then tested for traces of hydrogen, oxygen, nitrogen and carbon dioxide by turning taps G, H and J, so introducing a sample of gas into the chromatograph. When the gas was found to be completely free from these impurities, tap F was closed and the pressure in vessel A was allowed to build up until there was a difference of approximately 130 cm between the two levels of sulphuric acid in the manometer. Tap D was then closed and the chlorine was re-cooled. The known volume of chlorine gas in vessel A was then corrected to atmospheric pressure from the density of concentrated sulphuric acid. With tap E closed, known amounts of oxygen, nitrogen, carbon dioxide and hydrogen were injected into the chlorine through the self-sealing serum cap L by means of a hypodermic syringe. The volume of the vessel and the total pressure were such that an injection of 1 ml of impurity was equivalent to a concentration of 0·21 per cent. v/v in the chlorine gas. After 5 minutes, complete mixing of the gases had occurred; this was shown by replicate determinations on the same mixture after various periods of time.

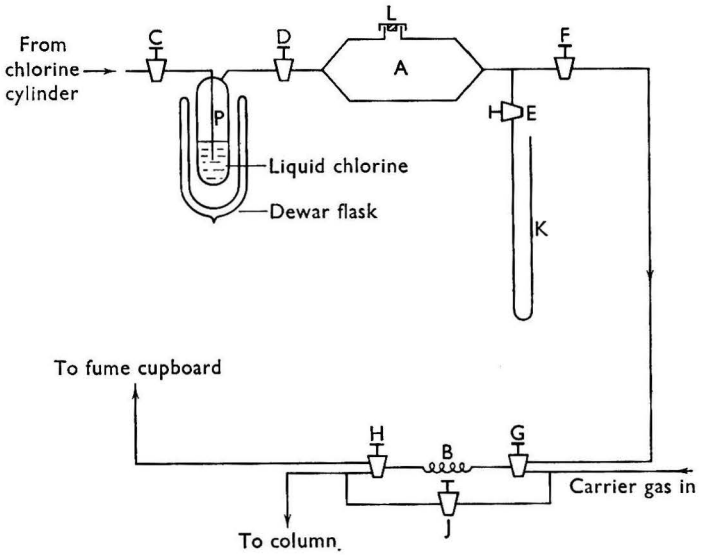


Fig. 2. Diagram of apparatus used for preparing standard mixtures of gases

The gas-sampling device was flushed out with the mixture by opening tap F. This tap was then closed, allowing the mixture in the 25-ml sample loop, B, to attain atmospheric pressure, and, by turning taps G, H and J, the sample was introduced into the chromatograph. The gas-mixing vessel, sampling device and connecting tubes were darkened to prevent the light-initiated reaction between hydrogen and chlorine.

Results

The results in Table I were obtained by using the apparatus described above, but with a 198-cm column of silica gel maintained at 100° C and a 114-cm column of molecular sieve placed outside the heating jacket at room temperature. Under these conditions, the retention times were: hydrogen, 1 minute; oxygen, 3·5 minutes; carbon dioxide (through column of silica gel only), 4·5 minutes; nitrogen, 7·5 minutes. Each result in Table I was obtained from a different standard mixture of gases. Precision was good for hydrogen, oxygen and nitrogen, but results for carbon dioxide were less precise because of the similarity between the thermal conductivities of argon and carbon dioxide and hence the low sensitivity of detection; better results for carbon dioxide were obtained by using helium as carrier gas, as described later.

The regression equations for the four impurities were—

Hydrogen content, % v/v = $0{\cdot}009639h - 0{\cdot}039$
(Standard error = 0·014 % v/v of hydrogen)

Oxygen content, % v/v = $0{\cdot}01058h + 0{\cdot}005$
(Standard error = 0·022 % v/v of oxygen)

Nitrogen content, % v/v = $0{\cdot}02689h + 0{\cdot}009$
(Standard error = 0·018 % v/v of nitrogen)

Carbon dioxide content, % v/v = $0{\cdot}06101h - 0{\cdot}017$
(Standard error = 0·039 % v/v of carbon dioxide)

in which h is the height of the appropriate peak.

TABLE I

PEAK HEIGHTS RECORDED WITH EACH COLUMN AT A DIFFERENT TEMPERATURE

Length of silica gel column, 198 cm
Length of molecular sieve column, 114 cm
Temperature of silica gel column, 100° C
Temperature of molecular sieve column, 20° C
Argon flow rate, 43·5 ml per minute

Concentration of impurity, % v/v	Peak height for— hydrogen, mm	oxygen, mm	nitrogen, mm	carbon dioxide, mm
0·21	24·0	19·0	7·5	3·5
	—	19·0	8·0	3·5
	—	21·0	8·0	—
0·42	47·5	39·5	15·5	7·0
	—	37·0	15·0	7·0
	—	37·0	15·0	—
0·63	72·0	60·0	23·0	11·0
	—	60·0	22·0	12·0
	—	61·0	22·0	—
0·84	92·0	79·0	31·0	14·0
	—	78·5	32·0	—
	—	82·0	32·0	—
1·05	112·5	100·0	38·0	17·0
	—	93·5	39·0	17·0
	—	—	38·5	—
1·26	134·0	—	—	—
1·47	156·0	—	—	—

The column lengths and temperatures used in obtaining the results in Table I had certain practical disadvantages. A decrease in the activity of the column of molecular sieve resulted in interference between the peaks for carbon dioxide and nitrogen. A small peak was obtained from the second detector as chlorine was desorbed from the first column and re-absorbed by the potassium iodide, presumably as a result of pressure changes in the system; this peak was also prone to interfere with the peak for nitrogen. The results in Table II were obtained by using the more satisfactory arrangement with both columns maintained at 60° C. Carbon dioxide and chlorine emerged from the first column after the hydrogen, oxygen and nitrogen had emerged from the second column; in this way, interference between peaks was impossible. The retention times were: hydrogen, 1·5 minutes; oxygen, 3 minutes; nitrogen, 4·5 minutes; carbon dioxide (through column of silica gel only), 8 minutes; chlorine (through column of silica gel only), 16 minutes. A typical chromatogram is shown in Fig. 3.

Under these conditions, the regression equations were—

Hydrogen content, % v/v = $0{\cdot}006188h - 0{\cdot}023$
(Standard error = 0·016 % v/v of hydrogen)

Oxygen content, % v/v = $0{\cdot}005446h - 0{\cdot}006$
(Standard error = 0·004 % v/v of oxygen)

Nitrogen content, % v/v = 0·009609h − 0·001
(Standard error = 0·003 % v/v of nitrogen)

Carbon dioxide content, % v/v = 0·06249h − 0·011
(Standard error = 0·039 % v/v of carbon dioxide)

It can be seen that the results for oxygen and nitrogen in Table II are more precise than those in Table I. This is probably because elution of oxygen and nitrogen from the molecular sieve was more rapid at 60° C, so giving greater sensitivity and producing sharper peaks.

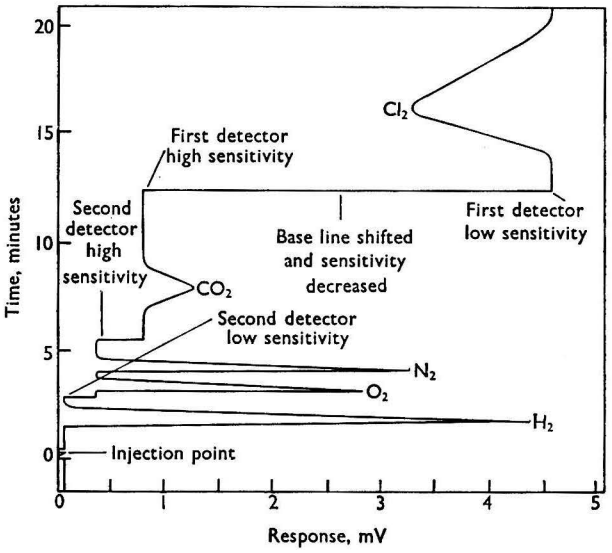


Fig. 3. Typical chromatogram recorded with both columns at 60° C. (Base-line shifts are indicated to show changes in sensitivity for the various peaks)

Table II

Peak heights recorded with both columns at 60° C

Length of silica gel column, 114 cm
Length of molecular sieve column, 198 cm
Argon flow rate, 43·5 ml per minute

Concentration of impurity, % v/v	Peak height for— hydrogen, mm	oxygen, mm	nitrogen, mm	carbon dioxide, mm
0·126	—	—	—	2·5
0·210	36·0	40·0	22·5	3·0
0·336	58·0	63·0	36·0	5·0
0·420	74·0	78·0	45·0	6·5
0·546	—	101·0	57·0	9·0
0·630	109·5	117·0	66·0	11·5
0·756	123·0	140·0	—	12·5
0·756	126·0	—	—	—
0·840	141·5	156·0	88·0	14·0
0·966	—	177·0	100·5	15·0
0·966	—	—	103·0	—
1·050	173·0	195·0	109·5	16·0
1·260	203·0	—	—	—

Although the results for carbon dioxide were sufficiently precise for most control purposes, much greater accuracy and precision were attained with the same apparatus when helium was used as carrier gas. With a 114-cm column of silica gel at 75° C and a flow rate of

35 ml of helium per minute, the peak heights for concentrations up to 0·42 per cent. v/v of carbon dioxide in chlorine gas were—

Carbon dioxide present, % v/v	0·084	0·130	0·170	0·210	0·250	0·294	0·340	0·380	0·420
Peak height, mm	41·0	63·5	86·0	110·5	127·0	142·5	160·5	181·0	208·0

The regression equation was—

$$\text{Carbon dioxide content, \% v/v} = 0{\cdot}002086h - 0{\cdot}0064$$
$$\text{(Standard error} = 0{\cdot}009 \text{ \% v/v of carbon dioxide)}$$

The apparatus can be calibrated by using one standard mixture of gases containing known concentrations of all the impurities at about the 1 per cent. v/v level. A standard homogeneous mixture of the impurities in chlorine cannot be prepared at high pressure and kept in a cylinder because of the low vapour pressure of liquid chlorine and its reactivity towards hydrogen. The preparation of a standard mixture of the impurities in an inert gas, *e.g.*, argon, to be stored under pressure in a cylinder was therefore considered. However, there was a marked difference in the response of the apparatus to a given amount of impurity when argon was substituted for chlorine (see Table III).

TABLE III

PEAK HEIGHTS FOR VARIOUS IMPURITIES IN ARGON AND CHLORINE

Impurity	Peak height for 1·05% v/v of impurity in— chlorine, mm	argon, mm
Oxygen	55·0, 55·5	20·5, 19·5
Nitrogen	23·0, 23·0	9·0, 9·0
Carbon dioxide	10·0, 10·0	3·5, 3·0

The higher peaks for the samples containing chlorine are believed to be due to the strong adsorption of chlorine by the silica gel, which results in concentration of the impurities in the carrier gas as the sample enters the column. The occupation by chlorine of otherwise active sites in the silica gel may also play a part.

CONCLUSIONS

Small concentrations of hydrogen, nitrogen, oxygen and carbon dioxide in chlorine gas can be determined accurately and precisely with the chromatographic apparatus described. Calibration graphs of impurity content against peak height are linear and pass close to the origin. For calibration purposes, it is essential to use gaseous mixtures containing chlorine as the major constituent. The method is simple and ideally suitable for the routine determination of impurities in chlorine gas. A complete analysis can be made in about 10 minutes.

We thank Mr. N. H. Stilwell, who carried out most of the experimental work, and African Explosives and Chemical Industries Ltd. for permission to publish the results.

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Notes

THE SEMI-MICRO DETERMINATION OF FLUORINE AND CHLORINE IN ORGANIC COMPOUNDS

PART IV.* THE DETERMINATION OF HALOGENS IN GASES AND VOLATILE LIQUIDS

IN Part III[1] of this series the determination of the halogens in fluoro-, chlorofluoro- and bromofluoro-compounds was described. The method consisted in decomposition in di-isopropyl ether solution by the diphenyl - sodium - dimethoxyethane complex, subsequent passage of the aqueous extract of the product through a cation-exchange resin and then titration of the resulting hydrogen, chloride or bromide ions.

The method has proved highly successful for non-volatile compounds, and even liquids having fairly low boiling-points, such as fluorobenzene, can be decomposed quantitatively if weighed in a gelatin capsule, but for these compounds there is a limiting vapour pressure above which this technique cannot be used. As the only other method available for determining organically bound fluorine in gaseous compounds[2] requires fairly elaborate apparatus and involves a difficult technique, we thought it worth-while to develop our method for this purpose, and we have devised a procedure for decomposing gases and volatile liquids having boiling-points up to 80° or 90° C.

As the gases have to be weighed in a glass bulb of capacity about 100 ml, it has been necessary to use an ordinary analytical balance that can be read to four decimal places. Consequently, rather larger weights of sample (40 to 60 mg) must be taken in order that the error in the weighing shall not cause too great an error in the determination. If a bulb of accurately known volume is used, the same weighings can be used to calculate the molecular weights of the samples.

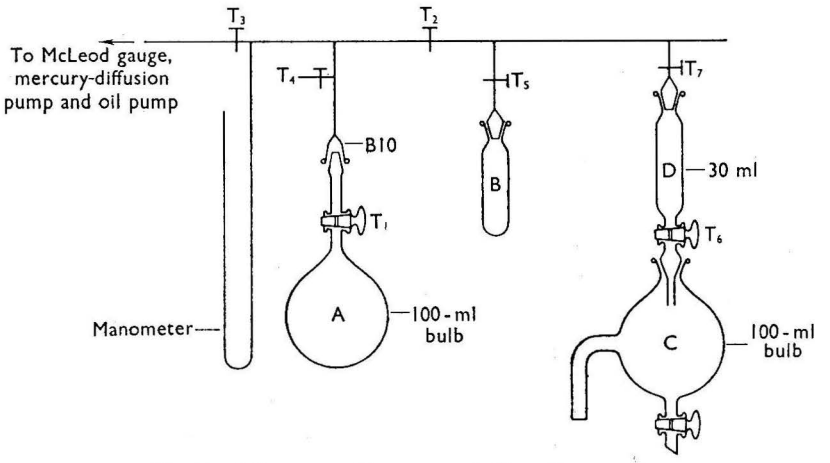

Fig. 1. Diagrammatic representation of apparatus

METHOD

PROCEDURE—

Carefully lubricate the tap and cone of bulb A with Apiezon L grease (avoid use of an excess of grease), and evacuate the bulb on the apparatus shown in Fig. 1 to a "sticking" vacuum. Close taps T_1, T_2 and T_3, open tap T_4, and remove bulb A from the vacuum line. Carefully wipe the grease from the cone (use a cloth moistened with carbon tetrachloride), and polish the bulb, tap and neck with chamois leather. Leave the bulb in the balance case for 15 minutes, and then weigh it to the nearest 0·1 mg. Re-attach the bulb to the vacuum line, and, with vessel B (containing the sample to be analysed) cooled in liquid air and taps T_1, T_2, T_3 and T_5 open, again evacuate to a "sticking" vacuum. Close tap T_3, and allow vessel B to warm slowly until the pressure in the system is such as to introduce 40 to 60 mg of sample into bulb A. Close tap T_1, and find the weight of sample taken by removing, cleaning and weighing bulb A as before. Again

* For details of Part III of this series, see reference list, p. 357.

attach bulb A to the vacuum line, evacuate with taps T_2, T_3, T_6 and T_7 open, and transfer the sample to bulb C by closing tap T_3, opening tap T_1 and cooling the side-arm of bulb C in liquid air. Close tap T_6, release the vacuum by opening tap T_4, and detach the unit comprised of bulb C and vessel D.

Allow the sample to attain room temperature and expand in bulb C. Add 10 ml of the diphenyl - sodium - dimethoxyethane complex via vessel D, and then add 25 ml of di-isopropyl ether; take care to leave the bore of tap T_6 full of liquid in order to maintain a partial vacuum in bulb C. Shake bulb C carefully for 4 minutes to convert all the halogens to sodium halides, extract these with water, and analyse the solution as described previously.[1] Determine chlorine, bromine and iodine by the oxycyanide method.

Results

The results obtained when the proposed method was applied to a series of gases and volatile liquids are shown in Table I.

Table I

Halogen contents found in various compounds

Compound	Boiling-point, °C	Weight taken, g	Fluorine content— present, %	Fluorine content— found, %	Chlorine content— present, %	Chlorine content— found, %	Bromine content— present, %	Bromine content— found, %	Iodine content— present, %	Iodine content— found, %	Molecular weight— calculated	Molecular weight— found
CFCl:CFCl ..	22	0·0570	28·6	28·1	53·3	53·4	—	—	—	—	132·9	132
$(CF_3)_2CF{\cdot}CF(CF_3)_2$	60	0·0456	78·7	78·4	—	—	—	—	—	—	338·1	337·5
$CCl_2F{\cdot}CF_3$	−2	0·0625	44·5	44·4	41·5	41·3	—	—	—	—	171	171
$CF_2Cl{\cdot}CF_2I$ ..	56	0·0480	29·0	29·5	—	—	—	—	—	—	—	—
$CF_2Cl{\cdot}CF_2Br$ ..	22	0·0562	35·3	34·9	—	—	—	—	—	—	215·4	216
C_2F_5I	13	0·0546	38·6	38·2	—	—	—	—	51·6	51·8	245·9	245·3
C_2F_5Br	−20	0·0600	47·8	47·4	—	—	40·2	39·5	—	—	—	—
$(CF_3)_2CFI$	39	0·0579	44·9	44·6	—	—	—	—	42·9	42·8	—	—
$(CF_3)_2CFBr$ ..	12	0·0584	53·4	53·7	—	—	32·1	32·2	—	—	248·9	248
CF_3Br	−60	0·0529	38·3	37·9	—	—	53·7	53·9	—	—	—	—
CF_2:CFCl	−27	0·0620	48·9	48·6	30·4	30·9	—	—	—	—	—	—
C_6F_6	81	0·0572	61·2	61·0	—	—	—	—	—	—	—	—

One of us (J.S.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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Note—Reference 1 is to Part III of this series.

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USE OF INDUCTION HEATING IN DETERMINATIONS OF CARBON AND HYDROGEN

Currently, there is considerable interest in the synthesis of compounds and polymeric materials that are thermally stable. In our experience the analysis of such substances presents unusual difficulties, which lead to erratic results when the usual combustion procedures are applied. This is particularly so for certain organo-boron compounds, the formation of boron carbide or boron trioxide, or both, presumably being the main cause of trouble.

In this laboratory, carbon and hydrogen contents are normally determined by Belcher and Ingram's "empty-tube" method,[1] a bunsen burner being used for the initial volatilisation of the sample. However, when this method was applied to a typical organo-boron compound (compound X in Table I), only a small percentage of the sample was volatilised, thereby giving low results for carbon; these results were not greatly improved when the time of heating was increased. Results were somewhat better when higher temperatures of combustion were used, and evidence was obtained suggesting that volatilisation of the sample would be complete if a temperature of about 1300° C could be maintained for, say, 15 minutes. As the heat necessary to attain this

temperature could not be applied externally without risk of reaching the softening-point of the silica combustion tube, the use of induction heating was investigated. Bobránski,[2] in a Pregl-type determination, used this form of heating in conjunction with a manometric device so that the combustion could be automatically controlled.

Exploratory experiments were carried out with a 14-kW 350-kcs high-frequency generator in conjunction with a single-turn water-cooled copper coil. The coil was placed round the silica combustion tube about 1·5 inches from the main furnace, and a platinum boat mounted on a ceramic base was placed in the centre of the coil. The bunsen burner already built into the apparatus was left in a position just after the oxygen inlet and was utilised to pre-heat the incoming oxygen. This prevents any condensation of the decomposition products should a "back-pressure" develop. A standard compound was then weighed into the boat, sample and boat were inserted as described above, the flow of oxygen was adjusted to 50 ml per minute, and the bunsen burner was then lit. The induction furnace was switched on, and the current induced in the platinum boat was gradually increased until the temperature, as determined by an optical pyrometer, reached 1300° C, the over-all time of combustion being 10 minutes. A further 10 minutes was allowed for sweeping out the apparatus, and the determination was then completed in the normal manner. Several determinations were made in this way, acetanilide being used as standard compound, but the results for carbon were always low by about 3 per cent.

It was then realised that condensation of the products of decomposition was taking place on the cold part of the silica tube between the coil and the main oxidation furnace, but it was not possible to move the coil any closer without inducing a current in the metal casing of the furnace. This difficulty was overcome by dispensing with the ceramic base of the platinum boat and placing the boat inside a roll of platinum foil, 3 inches long, which reached from the coil into the main furnace. The foil was wound with platinum wire, which allowed for spot contact between the foil and the silica tube, so that, when the boat was heated, the roll of platinum became red hot and some of its heat was transferred to the combustion tube, in this way preventing condensation. The boat containing the sample was again placed at the centre of the coil. With this arrangement, satisfactory results, *i.e.*, within $\pm 0{\cdot}3$ per cent. of the theoretical values, were obtained for standard compounds (see Table I).

TABLE I

CARBON AND HYDROGEN CONTENTS FOUND FOR VARIOUS COMPOUNDS

Sample	Carbon content found, %	Hydrogen content found, %	Theoretical carbon content, %	Theoretical hydrogen content, %
Acetanilide	71·02, 71·11, 71·07 70·95, 71·22, 70·99	6·99, 6·95, 7·00 6·54, 6·87, 6·79	71·10	6·70
Phenyl boronic anhydride ..	68·92, 69·41	4·62, 4·84	69·36	4·82
Trimethylamine - boron trichloride (1 + 1 adduct) ..	20·57, 20·63	5·04, 4·98	20·42	5·10
Sodium tetraphenyl borate ..	84·50, 84·41	5·75, 5·73	84·26	5·85
Compound X (containing C, H, N, B and O)	68·56, 68·44, 68·80	4·31, 4·70, 4·65	—	—

In order to standardise the procedure, the combustion of all samples was carried out at about 1300° C, even when it was known that their combustion presented no difficulties under normal conditions, *e.g.*, the first four compounds listed in Table I. The results seem to indicate that the method is fundamentally sound, and further work is in progress based on this assumption.

A 1-kW induction heater is now being used with a saddle-type coil, which seems to be more flexible in its use than the full-circle copper coil. During further use, we hope that any deleterious effect on the apparatus arising from operation at this high temperature will become apparent. No such effect has so far been observed, and the blank values are stable at 0·050 mg for carbon dioxide and 0·250 mg for water. It is hoped that further results will be communicated later.

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COMPENSATION FOR TEMPERATURE VARIATIONS WITHIN THE CELL OF A DISSOLVED-OXYGEN INDICATOR/RECORDER INCORPORATING A WIDE-BORE DROPPING-MERCURY ELECTRODE

THE concentration of oxygen dissolved in water can be measured by a polarographic method, described fully by Briggs, Dyke and Knowles.[1] A dropping-mercury electrode is maintained at a constant negative potential against a zinc electrode in a cell through which the water flows at a constant rate; the cell current is a measure of the concentration of dissolved oxygen in the water. It is necessary, however, to compensate for variations in current produced in the measuring cell by changes in temperature, and this is achieved by incorporating a batch of thermistors, R_t, in the cell, as shown in Fig. 1. The values of the shunt and series resistances, R_2 and R_3, respectively, were determined by experiment.

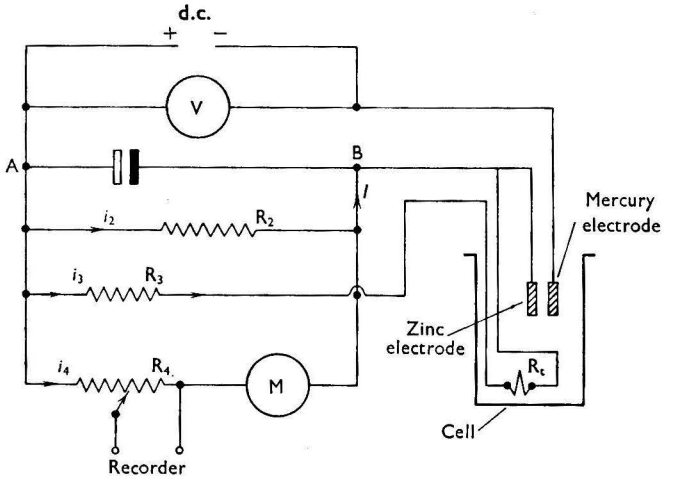

Fig. 1. Circuit for dissolved-oxygen indicator and recorder with compensation for temperature

It has now been found possible to calculate the values of these resistances by using formulae derived from the considerations below.

Let it be assumed that unit increase in temperature of the cell results in an increase, δI, in the cell current and a decrease, $-\delta R_t$, in the resistance of the thermistors. If V is the voltage between A and B (see Fig. 1) then—

$$V = i_2R_2 = i_3(R_3 + R_t) = i_4(R_4 + R_m) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

in which R_2, R_3, R_4, R_m and R_t are the resistances of R_2, R_3, R_4, meter M and the thermistors, respectively.

For compensation, i_4 must remain unchanged; hence δi_4 must be zero. From equation (1), therefore, $\delta V = 0$, $\delta i_2 = 0$ and

$$\frac{\delta i_3}{i_3} + \frac{\delta R_t}{R_3 + R_t} = 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The cell current, I, is given by the equation—

$$I = i_2 + i_3 + i_4 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

and therefore $\delta I = \delta i_3$.

Suppose that $x = -\delta R_t/R_t$ is the gradient of the temperature characteristic of the thermistor at the appropriate temperature, $k = \delta I/I$ is the gradient of the temperature characteristic of the cell and $\phi = i_4/I$ is the meter factor or current ratio, it can then be shown from the above equations that

$$R_3 = \sqrt{\frac{x\phi}{k} \times R_t(R_4 + R_m)} - R_t \quad .. \quad .. \quad .. \quad .. \quad (4)$$

and that

$$\frac{1}{R_2} = \left(\frac{1-\phi}{\phi} \times \frac{1}{R_4 + R_m}\right) - \frac{1}{R_3 + R_t} \quad .. \quad .. \quad .. \quad .. \quad (5)$$

The value of x can be determined experimentally for the thermistor or batch of thermistors with a Wheatstone bridge, and values of k have been quoted by Briggs, Dyke and Knowles, *e.g.*, 0·0163 per °C at 15° C.

Values for R_2 and R_3 can be calculated from equations (4) and (5). For positive values of R_2 and R_3, restrictions are imposed, *viz.*

$$R_3 + R_t > \frac{\phi}{1-\phi} \times (R_4 + R_m) > R_t\left[\frac{k}{x(1-\phi)}\right] \quad .. \quad .. \quad .. \quad .. \quad (6)$$

and, as R_t occurs on both sides of this inequality, care must be taken in the choice of thermistor and meter.

The values of x and R_t depend on the choice of thermistor, but, by using more than one in series or in parallel, the value of R_t can be increased or decreased with no significant effect on the value of x; expression (6) suggests a value for R_t as low as space and economics will allow. The choice of meter affects the values of R_m and ϕ; a sensitive meter has a high value for R_m and a low one for ϕ, but the effective value of R_m can be increased by means of R_4 independently of the value of ϕ.

In practice, resistors R_2, R_3 and R_4 should be wound in manganin, which has a temperature coefficient of 0·00001 per °C, and a microammeter can be obtained with a coefficient of 0·0002 per °C. These resistors and the meter are not usually subjected to the same changes in temperature as occur in the measuring cell, but, according to circumstances, consideration must be given to any possible inaccuracies that might result from changes in the ambient temperature.

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THE DETERMINATION OF SMALL AMOUNTS OF ARSENIC IN ORGANIC MATTER

In the report of the Analytical Methods Committee[1] it is stated (p. 631) that "The Sub-Committee agreed that a wet-oxidation procedure must be specified, as no method of dry oxidation could be relied on to give complete recovery of arsenic." It has been pointed out to the Sub-Committee that small amounts of arsenic in coal have been determined satisfactorily after a process of dry ignition.[2,3,4] There are, of course, other specific instances where a particular method of dry ignition has been established as satisfactory for a given material. The quoted passage was intended to mean that methods of dry oxidation could not be applied generally to the extremely wide variety of types of sample envisaged in the report without risk of arsenic being lost in some instances.

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Book Reviews

CHROMATOGRAPHIC AND ELECTROPHORETIC TECHNIQUES. Volume I. CHROMATOGRAPHY. Edited by IVOR SMITH, B.Sc., Ph.D., F.R.I.C. Second Edition. Pp. xviii + 617. London: William Heinemann Medical Books Ltd. 1960. Price 65s.

The first edition of this book was written only about two and a half years ago, and in the intervening period there has been one reprint. It is not surprising that a second edition of this very practical book has now been called for; in this, the purpose of the first edition has been maintained, *i.e.*, to bring together in precise form tried and tested paper-chromatographic methods of value to clinical and other biochemists.

Dr. Smith has prevailed upon other workers of first-class experience to describe, in the new edition, methods for the chromatography of radioactive substances and to provide up-to-date information about ion-exchange celluloses. Wherever practicable, the opportunity has been taken to bring the subject matter of the first edition up to date, and accurate information is provided on the paper chromatography of such varied compounds as amino acids and their derivatives, indoles, imidazoles, guanidines, purines, sugars, phenolic acids, keto acids etc., plant phenols, cholesterol derivatives, phospholipids, barbiturates, alkaloids, glutarimides, steroids and even inorganic ions.

The methods are based on the use of a universal apparatus, and, with this equipment in his possession, the clinical biochemist should find no difficulty in carrying out the chromatographic separations described in this second edition.

Analytical chemists in other fields owe a great deal to the work of biochemists in the chromatographic field, and they will be well advised to examine some of the procedures so clearly described in this well written book.

J. HASLAM

CHROMATOGRAPHIC AND ELECTROPHORETIC TECHNIQUES. Volume II. ZONE ELECTROPHORESIS. Edited by IVOR SMITH, B.Sc., Ph.D., F.R.I.C. Pp. viii + 215. London: William Heinemann Medical Books Ltd. 1960. Price 30s.

Zone electrophoresis is the name conventionally adopted for techniques involving a stabilising medium such as paper, cellulose powder, agar, starch gel, etc., being thus distinct from the classical moving-boundary method. In the reviewer's opinion, the terms "stabilised electrophoresis" and "free electrophoresis" would be more convenient and appropriate.

The purpose of the book is to present in a concise way well tried and tested procedures that can be applied without further experimentation to routine work in clinical and biochemical laboratories. The theoretical part and the literature are deliberately limited to an extent just sufficient to make the subject matter interesting and intelligible, yet to avoid time-consuming literature searches. In this the editor and his specialist contributors have succeeded admirably.

After a short but useful introduction to theory, technique of and equipment for low-voltage paper electrophoresis, practical procedures are described for the separation of human serum proteins, lipoproteins, glycoproteins, cholesterol and phosphate. The quantitative determination of proteins is treated, justifiably, with a certain amount of scepticism, but the clinical interpretation of the results is given in a clear and expert way.

The same cannot be said about the chapter dealing with amino acids, restricted, as it is, to only a few applications in urine tests. The following contribution gives a very brief but good description of the usefulness of electrophoresis for the separation of nucleotides and nucleoside monophosphates.

The chapter on haemoglobins is of outstanding quality, amply illustrated and referenced, and exhaustive with regard to detailed working procedures. The same impression is gained of the contribution on cellulose acetate electrophoresis, immuno-electrophoresis and other immuno-diffusion methods. Here, the advantages of cellulose acetate as a stabilising medium over paper are clearly set out, and many helpful practical hints are given. Overlapping to some extent with this is the following chapter, devoted to techniques involving stabilising media such as agar gel, starch block, starch gel and sponge rubber. The account of results obtainable by the cellulose acetate technique when different makes of commercially available apparatus are used seems to be superfluous in a book meant to be concise. However, immuno-electrophoresis in agar gel is treated with the utmost skill, detailed instructions being given for avoiding pitfalls in the preparation of samples and in staining procedures. Gel-diffusion methods, particularly the Ouchterlony technique,

and Smithies's starch-gel technique are well described. Numerous practical hints are offered for the correct preparation of the starch gel, on which so much of the success of the method depends.

A good case is made out in the next chapter for the usefulness of high-voltage paper electrophoresis in clinical practice, especially for amino acids, indoles, purines, pyrimidines and phenolic acids in urine, plasma and cerebrospinal fluid. It is a pity that the quality of the contribution is marred by certain inaccurate statements. For instance, the design of the apparatus principally illustrated and described is not an improvement of the apparatus described by Werner and Westphal (1955), but one developed independently by the reviewer since 1953. The fundamental difference between the two designs is that one is a double-cooled, compressed sandwich type, whereas the other (Werner and Westphal) is a bottom-cooled "moist-chamber" type.

Further, glucose can be cleanly separated from galactose and fructose in borate buffer of pH 9·2, and even the slow-moving organic acids can be efficiently separated at pH 2·0, particularly when the sample is applied as a thin band instead of a spot. The statement on mobility measurements is out-dated, and the frequent confusion of references could easily have been avoided.

A short final chapter deals with some applications of continuous (curtain) electrophoresis to serum proteins, including glycoproteins and haptoglobins. The many variables plaguing the technique and means for their control are clearly pointed out, and a return to the use of a comparatively simple apparatus is strongly advocated.

The well printed, well illustrated book is a worthy companion of Volume I and as such should find a rightful place on the shelves of clinical chemists and biochemists dealing with similar or related problems.

D. Gross

Laboratory Handbook of Toxic Agents. Editor-in-Chief: C. H. Gray, D.Sc., M.D., F.R.C.P., A.R.C.S., F.R.I.C. Pp. viii + 170. London: The Royal Institute of Chemistry. 1960. Price 20s.

From time to time, the Royal Institute of Chemistry has recorded in its Journal reports of explosions and other laboratory accidents; the present book is an extension of this activity. The analyst is exposed to the danger of toxic substances no less than his colleague in other branches of chemical work; indeed, in some circumstances the danger may be greater, for he may not be aware of it until his work is at least partially completed.

The opening chapters deal with general principles, precautions and preventions and first aid. The main body of the work consists of about two hundred monographs on poisonous and corrosive gases, reagents and solvents in fairly general use, giving a brief description of the products, their particular hazards, their effects, acute and chronic, and appropriate first aid. In general, inorganic compounds lend themselves to grouping, *e.g.*, vanadium compounds (*cf. Analyst*, 1960, **85**, 851), but organic compounds call for more individual treatment. Common solvents whose main hazard is flammability are not included. The book concludes with an account of precautions against radiations.

B. A. Ellis

Medicine, Science and the Law. Vol. I, No. 1, October, 1960. Editor: Francis E. Camps, M.D., D.T.M. & H. Pp. iv + 132. London: Sweet & Maxwell Ltd. Annual Subscription (4 parts per year) 63s.; $10.00. Single numbers 17s. 6d.

This new publication is sponsored by the British Academy of Forensic Sciences and takes its name from the three sections of the Academy. The contents are stated to be directed to anaesthetists, biochemists, biologists, chemists, coroners, members of forensic science laboratories, lawyers, pathologists, police officers, police surgeons, prison medical officers, psychiatrists and zoologists, amongst many others. These contents will be classified under the headings of editorials, articles, famous forensic scientists, law for the scientist, abstracts and references, books and publications, current research projects and courses, learned societies, glossary and index. The law for the scientist and abstracts and references sections will be arranged under 66 headings ranging alphabetically from Abortion, Accidents, Adoption and Agriculture to Therapeutic Substances, Therapy, Toxicology and Treatment of Offenders. Most of these subjects deal with medical jurisprudence, but non-medical forensic science has not been neglected, *e.g.*, Arson, Ballistics and Explosives, Fibres, Questioned Documents. There will thus be some overlap with the *Journal of the Forensic Science Society* (reviewed in *Analyst*, 1961, **86**, 141), but this is unavoidable in modern times when there is no clear demarcation between specialised sciences.

The non-medical forensic scientist will be more at home with the *Journal of the Forensic Science Society*, but he will find much of interest in *Medicine, Science and the Law*.

J. R. Nicholls

GAS CHROMATOGRAPHY 1960. Edited by R. P. W. SCOTT. Pp. xviii + 466. London: Butterworths Publications Ltd. 1960. Price 95s.

This book comprises a complete account of the proceedings of the third symposium, organised jointly by the Society for Analytical Chemistry and the Gas Chromatography Discussion Group of the Institute of Petroleum, held at the Assembly Rooms, Edinburgh, 8th–10th June, 1960. It contains twenty-nine papers, all read at the symposium, and verbatim reports of the discussions thereon. The papers are classified in three sections.

Section I deals with apparatus and technique, and the first half is devoted to a comparison of the β-ray and flame-ionisation detectors—probably the most widely used and certainly the most widely discussed ionisation detectors at the present time. There is also a paper showing how an ionisation detector can be used to produce either a differential or an integral chromatogram and discussing the advantages of each type. In the second half of the section there is an interesting example of the use of a low-pressure discharge detector as an instrument for gas analysis apart from gas chromatography. There is also a technique described as "vapour flow chromatography," which is in effect a modification of frontal analysis in an attempt to eliminate some of the disadvantages normally attending this method. The last two papers deal with automation and high-speed routine analysis.

Section II deals with the theory of gas chromatography and the application of theoretical considerations to practical ends. There is the usual emphasis on column efficiency, with special reference this time to capillary and to large-bore preparative columns. Other papers deal with some unusual fixed phases—including one that can separate isomers according to their molecular shapes—and with the temperature limitations of stationary phases. The latter paper gives some useful data and a salutary warning against taking apparently "obviously" non-volatile liquids for granted. An interesting paper in this section describes the use of diazomethane to insert a methylene group at the end of a hydrocarbon chain, so permitting commercially unavailable hydrocarbons to be produced from lower members of the series and their retention characteristics to be determined.

Section III deals with some new analytical applications of gas chromatography, four papers being devoted to its use in inorganic analysis. Inorganic samples tend to be rather more reactive —sometimes corrosive—than most organic samples; consequently, some new problems of apparatus design and choice of stationary phase are considered in these papers. A paper on the application of gas chromatography to anaesthetic research describes a technique by which the output from an anaesthetic machine or the patient's expired breath can be continuously monitored. A useful technique for the identification of non-volatile substances, *e.g.*, polymers, by gas chromatography of their pyrolysis products is also given. A pyrolysis unit is inserted into the injection system of a gas chromatograph and is provided with an electronic time-switch circuit by which the conditions of pyrolysis of the injected sample are made reproducible. A paper on the separation of unsaturated compounds also contains useful data on high-temperature stationary phases.

Each paper has it own literature references, and there is a useful summing-up of the symposium by Mr. C. S. G. Phillips. The recommendations on nomenclature and presentation of data given in "Gas Chromatography 1958" are here clarified and expanded. Mr. R. P. W. Scott, the editor, is to be congratulated on the vast collection of information he has packed into such a compact and readable book. Any analyst who uses gas chromatography should have it. He is bound to find something helpful—not least the thought-provoking suggestions thrown out in the introductory lectures to each section. The book is, in fact, a worthy successor to its "ancestors" of 1956 and 1958.

B. A. ROSE

NAME INDEX OF ORGANIC REACTIONS. By J. E. GOWAN, Ph.D., and T. S. WHEELER, B.Sc., M.R.I.A. Second Edition. Pp. viii + 293. London: Longmans, Green & Co. Ltd. 1960. Price 50s.

The use of names to designate chemical reactions is a useful form of shorthand—in moderation. The student will doubtless know those associated with Cannizaro, Griess, Friedel - Crafts, Grignard, Fischer - Speier, Skraup, Sandmeyer, Schotten - Baumann. Later, according to circumstances, will come the Baeyer - Drewson route to indigo and the Bohn indanthrone synthesis or the Bergmann peptide procedure involving benzyloxycarbonyl derivatives or Oppenauer oxidation and Birch reduction. All these and over seven hundred more are here collected together; this number is

double that given in the Merck Index (1960) and seven times that in Surrey's "Name Reactions," which also gives some biographical details.

The monographs are short and give general outlines of the reactions, graphic formulae and literature references, including in particular recent papers and standard works; there are cross-references to allied reactions, if "named." The alphabetical arrangement forms its own index, as the title indicates, but is supplemented by two others, one listing the reactions by type and the other a general index of chemicals, individually and by classes.

Colour reactions, which are even more numerous, are not considered here. The book will be very useful both to refresh the memory and to learn speedily about strangers. At a venture, will the name Hafner appear in the next edition? B. A. ELLIS

Publications Received

POLAROMETRICKÉ TITRACE. By Doc. RNDr. JAN DOLEŽAL, C.Sc., and Doc. RNDr. PhMr. JAROSLAV ZÝKA, C.Sc. Pp. 150. Prague: Státní Nakladatelství Technické Literatury. 1961. Price 11.60 Kcs.

THE RADIOCHEMISTRY OF MANGANESE. By G. W. LEDDICOTTE. Pp. vi + 23. Washington, D.C.: National Academy of Sciences—National Research Council. 1960. Price 50 cents. *Nuclear Science Series: NAS—NS-3018.*

PAPER ELECTROPHORESIS: A REVIEW OF METHODS AND RESULTS. By L. P. RIBEIRO, E. MITIDIERI and O. R. AFFONSO. Pp. xii + 463. Amsterdam, London, New York and Princeton: Elsevier Publishing Company; London: D. Van Nostrand Co. Ltd. 1961. Price 72s.

THE MECHANISM OF HETEROGENEOUS CATALYSIS. Proceedings of the Symposium held in Amsterdam, November 12th–13th, 1959. Edited by J. H. DE BOER *et al.* Pp. x + 180. Amsterdam, London, New York and Princeton: Elsevier Publishing Company; London: D. Van Nostrand Co. Ltd. 1961. Price 15s.

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MICROANALYSIS BY THE RING OVEN TECHNIQUE. By HERBERT WEISZ. Pp. 112. Oxford, London, New York and Paris: Pergamon Press. 1961. Price 30s.

TREATISE ON ANALYTICAL CHEMISTRY. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. Part II. Analytical Chemistry of the Elements. Vol. 3. Pp. xviii + 380. New York and London: Interscience Publishers Inc. 1961. Price (single volume) $13.25; 100s.: (subscribers to whole series) $12.00; 90s.

X-RAY ANALYSIS OF ORGANIC STRUCTURES. By S. C. NYBURG. Pp. xiv + 434. New York and London: Academic Press Inc. 1961. Price $13.00; 93s.

THE SOCIETY FOR ANALYTICAL CHEMISTRY

FORMERLY THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

FOUNDED 1874. INCORPORATED 1907.

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry by holding periodical meetings, by promoting lectures, discussions and conferences, and by the publication of a journal devoted to all branches of analytical chemistry; to study questions relating to the analysis, nature and composition of natural and manufactured materials generally; and to promote, or assist to promote, the efficiency and the proper administration of the laws relating to the control and composition of such materials.

The Society includes members of the following classes:—(*a*) Ordinary Members who are persons of not less than 21 years of age and who are or have been engaged in analytical consulting or professional chemistry; (*b*) Junior Members who are persons between the ages of 18 and 27 years who are or have been engaged in analytical, consulting or professional chemistry or *bona fide* full-time or part-time students of chemistry. Each candidate for election must be proposed by three Ordinary Members of the Society who shall provide written testimony of their personal knowledge as to his scientific and professional fitness. If the Council in their discretion think fit, such testimony may be dispensed with in the case of a candidate not residing in the United Kingdom. Every application is placed before the Council and the Council have the power in their absolute discretion to elect candidates or to suspend or reject any application. Subject to the approval of Council, any Junior Member above the age of 21 may become an Ordinary Member if he so wishes. A member ceases to be a Junior Member on the 31st day of December in the year in which he attains the age of 27 years. Junior Members may attend all meetings, but are not entitled to vote.

The Entrance Fee for Ordinary Members is £1 1s. and the Annual Subscription is £3 3s. Junior Members are not required to pay an Entrance Fee and their Annual Subscription is £1 1s. No Entrance Fee is payable by a Junior Member on transferring to Ordinary Membership. The Entrance Fee (where applicable) and first year's Subscription must accompany the completed Form of Application for Membership. Subscriptions are due on January 1st of each year.

Scientific Meetings of the Society are usually held on the first Wednesday in October, November, December, February, April and May, in London, but from time to time meetings are arranged in other parts of the country. The Annual General Meeting is usually held in London on the first Friday in March. Notices of all meetings are sent to members by post.

All members of the Society have the privilege of using the Library of The Chemical Society. Full details about this facility can be obtained from the Librarian, The Chemical Society, Burlington House, Piccadilly, London, W.1.

The Analyst, the official organ of the Society, is issued monthly, to all Ordinary and Junior Members, and contains reports of the proceedings of the Society, original papers and notes, information about analytical methods, Government reports and reviews of books. In addition, all Ordinary Members receive *Analytical Abstracts*, providing a reliable index to the analytical literature of the world.

Forms of application for membership of the Society may be obtained from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1.

LOCAL SECTIONS AND SUBJECT GROUPS

THE North of England, Scottish, Western and Midlands Sections were formed to promote the aims and interests of the Society among the members in those areas. The Microchemistry, Physical Methods and Biological Methods Groups have been formed within the Society to further the study of the application of microchemical, physical and biological methods of analysis. All members of the Society are eligible for membership of the Groups.

The Sections and Groups hold their own meetings from time to time in different places. There is no extra subscription for membership of a Section or Group. Application for registration as a member should be made to the Secretary.

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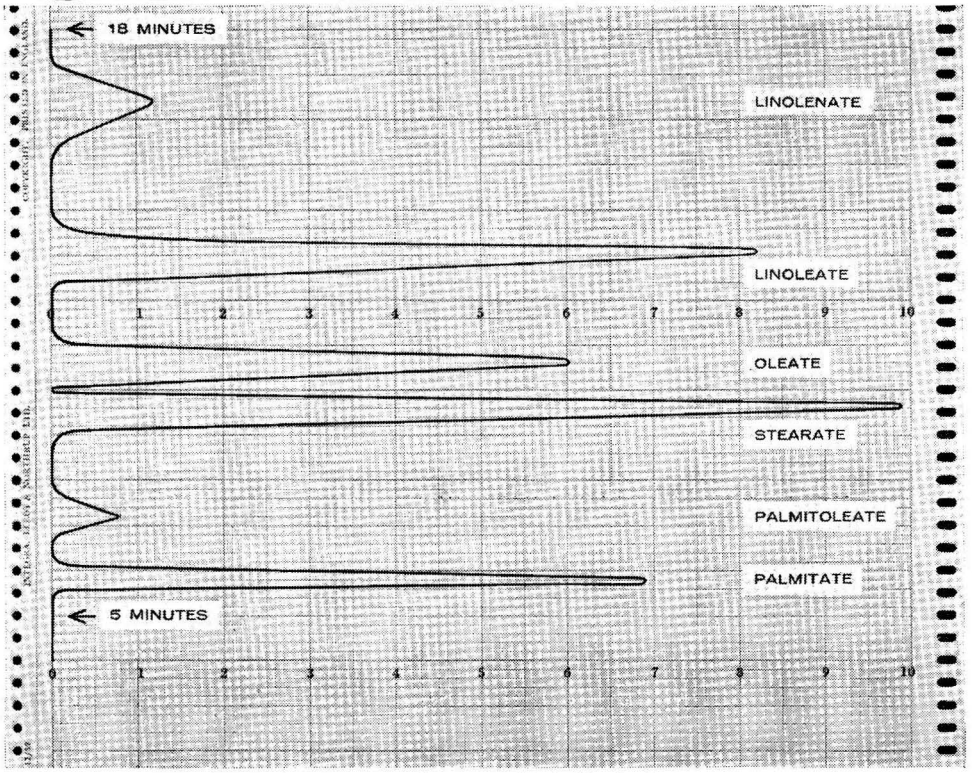

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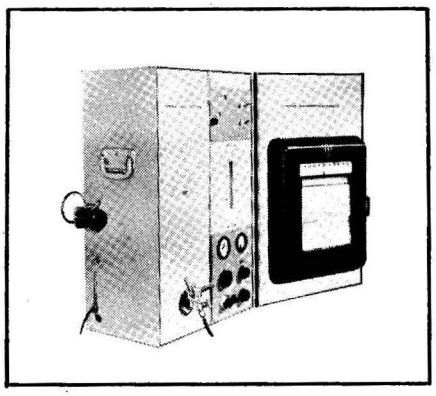

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