The
ANALYST

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of analytical chemistry

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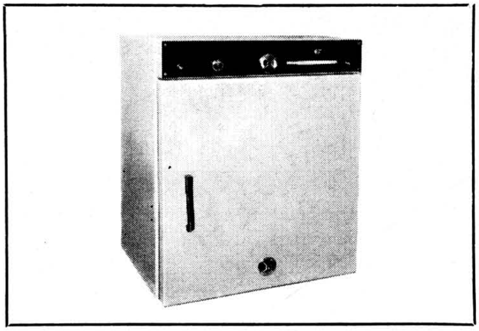

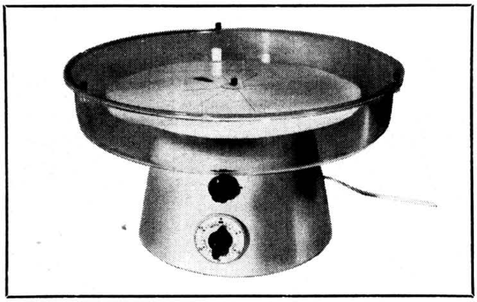

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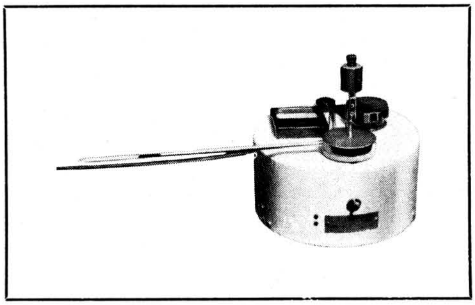

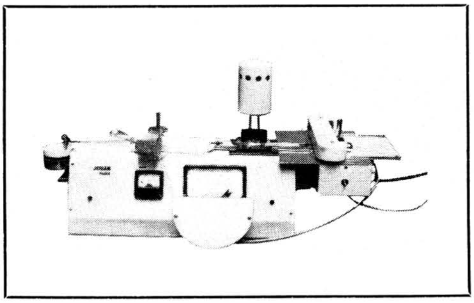

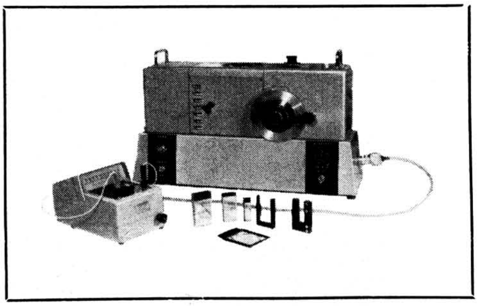

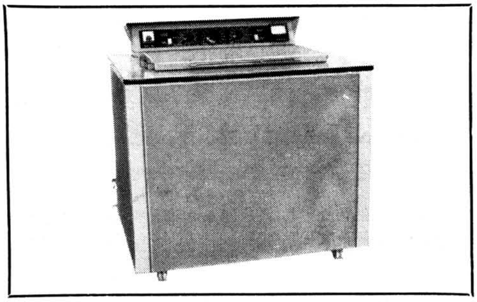

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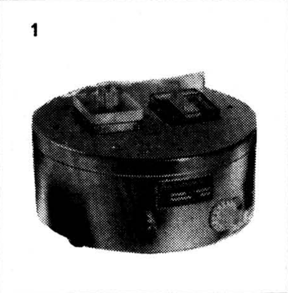

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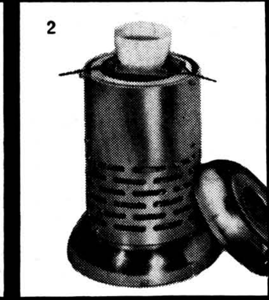

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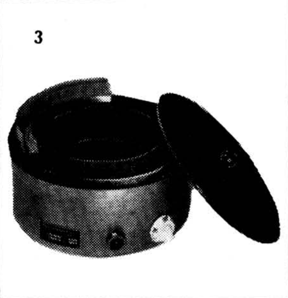

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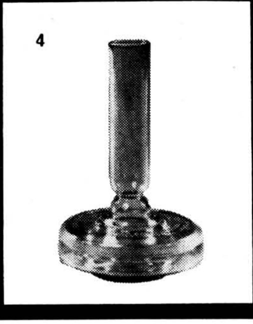

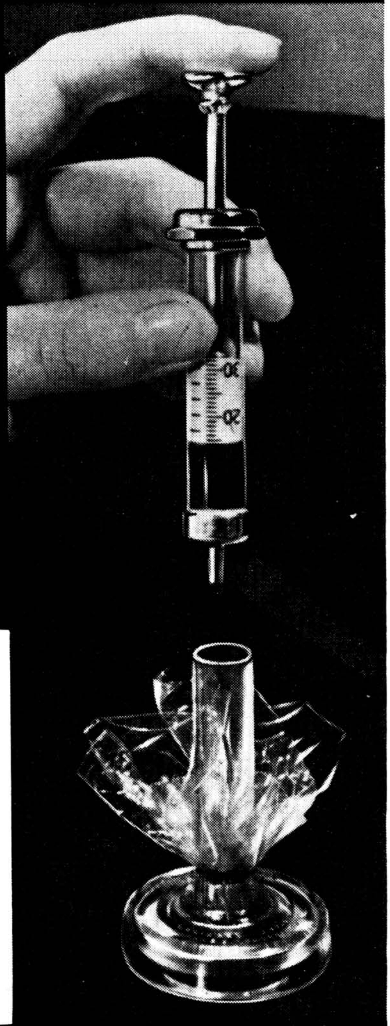

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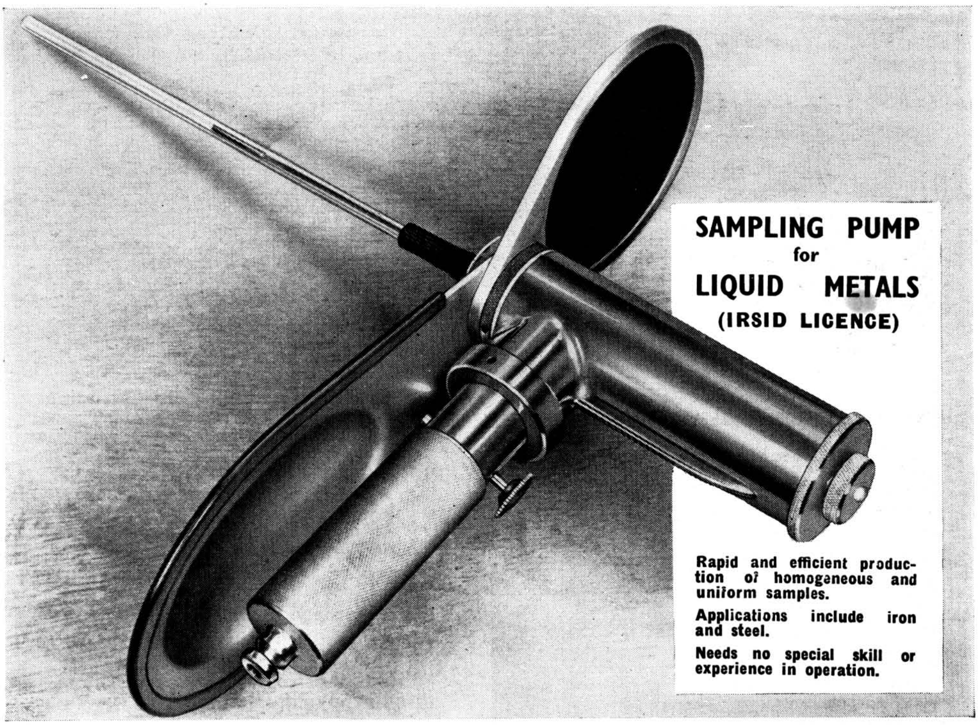

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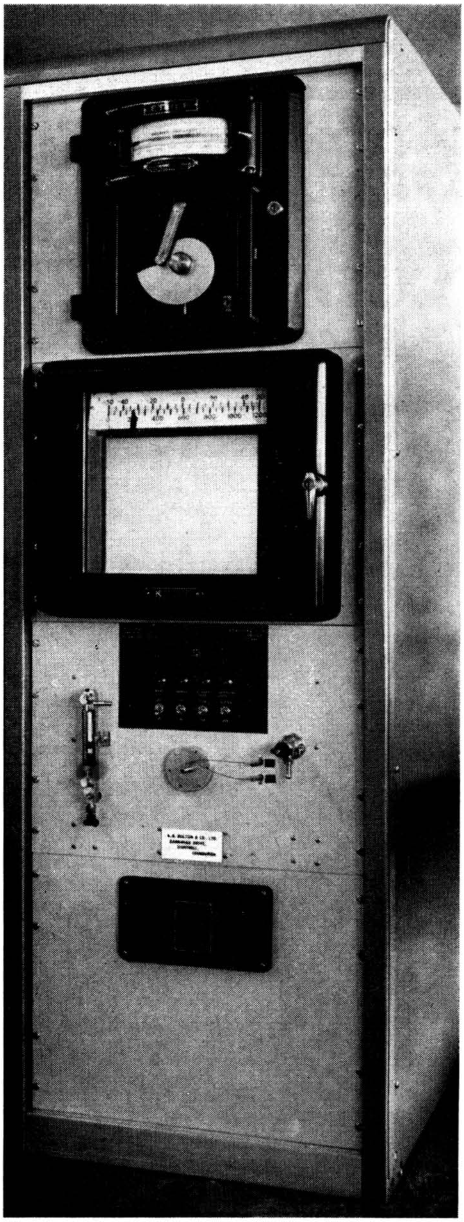

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1. Metcalfe, L. D. and Schmitz, A. A., *Anal. Chem.,* 1961, **33,** 363-4.
2. Mitchell, J., Jnr., Smith, D. M. and Bryant, M. W. D., *J. Amer. Chem. Soc.,* 1940, **62,** 4-6.

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1. Hough, L. and Jones, J. K. N., *J. Chem. Soc.,* 1951, 1122-6.
2. Easterby, D. G., Hough, L. and Jones, J. K. N., *J. Chem. Soc.,* 1951, 3426-8.
3. Bamford, W. R. and Stevens, T. S., *J. Chem. Soc.,* 1952, 4735-40.

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1. Nagakawa, K., Konaka, R. and Nakata, T., *J. Org. Chem.,* 1962, **27,** 1597-1601.

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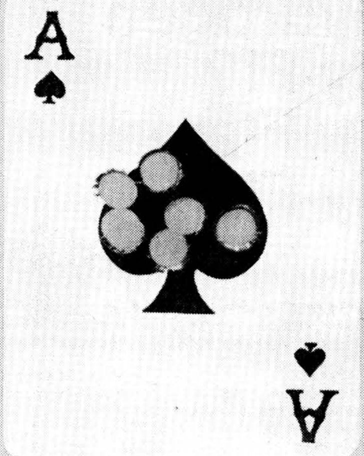

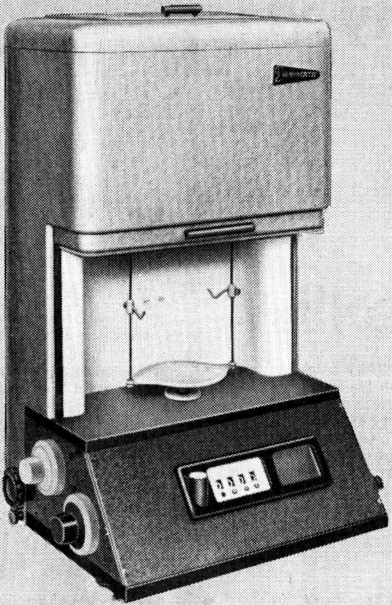

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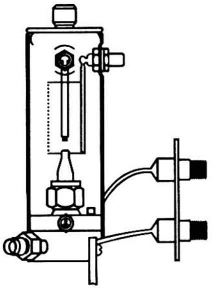

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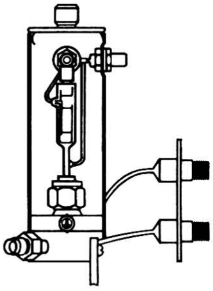

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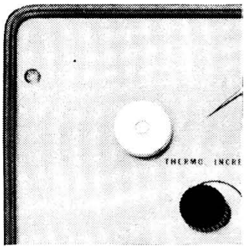

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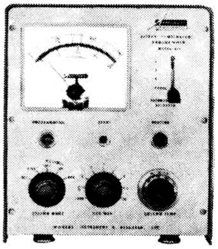

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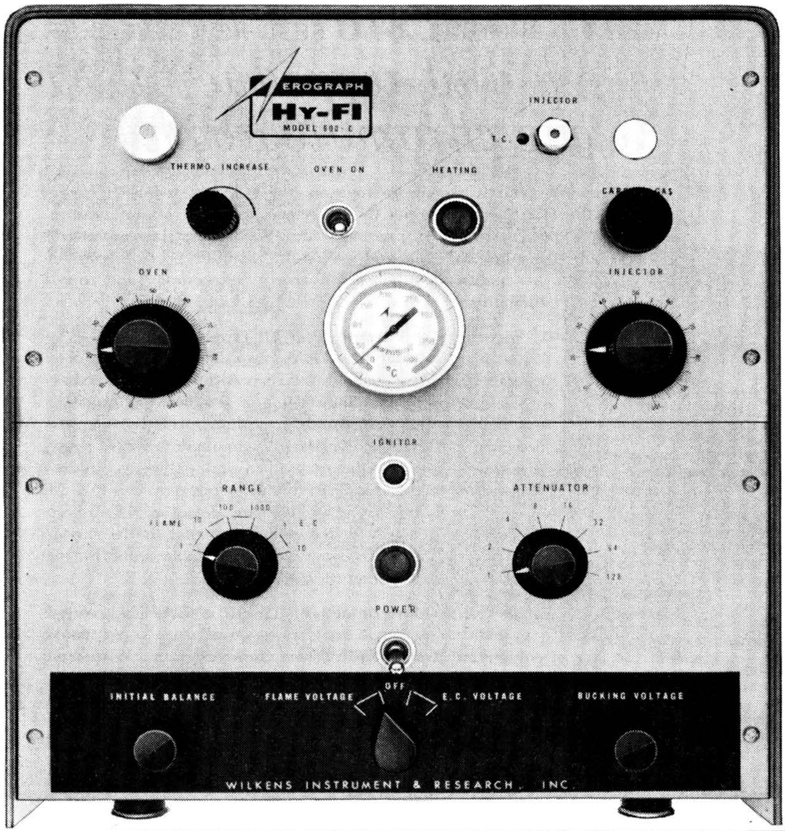
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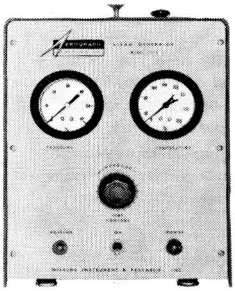

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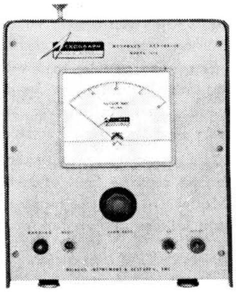

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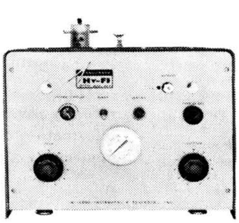

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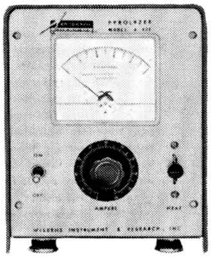

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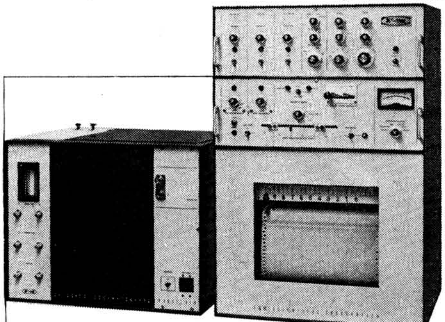

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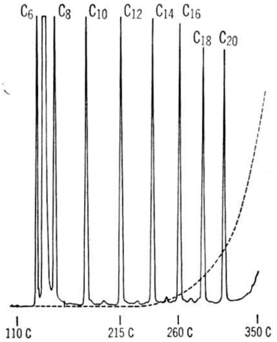

■ Note the stable baseline of this dual-column-compensated chromatogram of a mixture of equal parts of normal C_6 to C_{20} paraffins produced on a Model 810 equipped with dual flame ionization detectors; dashed line represents the drifting baseline obtained during single column operation. Sensitivity of the instrument is indicated by the fact that each peak represents about 2.0 micrograms and the instrument was operated at 1/640 of full sensitivity.

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OCTOBER, 1963 Vol. 88, No. 1051

THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

DEATH

WE record with regret the death of
Edmund Frankel.

SCOTTISH SECTION

A JOINT Meeting of the Scottish Section with the Institute of Chemistry of Ireland was held on Thursday and Friday, September 5th and 6th, 1963, in the Rupert Guinness Hall Dublin. The Company was welcomed by Mr. M. J. Cranley, M.Sc., F.R.I.C., F.I.C.I., President of the Institute of Chemistry of Ireland. The meeting was divided into four sessions, the chairmen being: Dr. A. K. Mills, F.I.C.I.; Mr. A. F. Williams, B.Sc., F.R.I.C.; Mr. J. K. McLellan, M.A., B.Sc., A.R.I.C., Vice-Chairman of the Scottish Section; and Dr. L. Brealey, B.Sc., F.R.I.C.

An apology for absence from Dr. D. C. Garratt, F.R.I.C., President of the Society for Analytical Chemistry, was conveyed to the meeting by Mr. McLellan.

The subject of the meeting was "Modern Aspects of Chromatography" and the following papers were presented and discussed: "Thin-layer Chromatography of Long-chain Amines," by E. S. Lane, B.Sc., Ph.D., F.R.I.C.; "Thin-layer Chromatography and its Applications to Dyestuffs and Plasticisers," by G. R. Jamieson, B.Sc., F.R.I.C.; "Thin-layer Chromatography—Applications to Steroid Chemistry," by P. Oxley, M.A., B.Sc., A.R.I.C.; "Some Applications of Gel Filtration and Ion-exchange Chromatography to the Fractionation of Polysaccharides," by D. M. W. Anderson, B.Sc., Ph.D., F.R.I.C.; "Ion-exchange in the Study of Metal Complexes in Solution," by J. K. Foreman, B.Sc., A.R.I.C.; "Chromatography in the Identification of Plant Products," by D. M. Donnelly, B.Sc., Ph.D., A.R.I.C.; "Some Recent Applications of Paper Chromatography in the Petroleum Industry," by R. B. Delves, A.R.I.C.; "Recent Applications of Gas Chromatography," by B. A. Rose, B.Sc., Ph.D., A.R.C.S., D.I.C., A.R.I.C.; "A Statistical Evaluation of Gas - Liquid Partition Chromatography as a Method of Quantitative Analysis," by C. E. Roland Jones and D. Kinsler; "Determination of Nitro Constituents of Explosives by Gas Chromatography," by A. F. Williams, B.Sc., F.R.I.C.; "The Gas-chromatographic Analysis of Beer," by G. A. F. Harrison, B.A., F.R.I.C., F.I.C.I.; "The Chromatographic Behaviour of Some Nitrophenols on Alumina Impregnated Paper," by L. S. Bark, B.Sc., F.R.I.C., and R. J. T. Graham, M.Sc.; "The Chromatography of *p*-Substituted *p*-Hydroxyazobenzenes on Alumina-impregnated Papers," by R. J. T. Graham, M.Sc., and C. W. Stone, M.Sc., Ph.D., A.R.I.C.

Morning coffee, afternoon tea and lunch were provided each day by Messrs. A. Guinness, Son & Co. (Dublin) Ltd., to whose generous hospitality much of the success of the meeting is due.

On the Thursday evening a bus tour to Glendalough was marred by rain, but nevertheless enjoyed by all who went. The informal dinner on the Friday evening was well attended: the Chair was taken by Professor C. L. Wilson.

MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at **3.30** p.m. on Wednesday, September 18th, **1963**, in the Chemistry Department, The University, Edgbaston, Birmingham 15. The Chair was taken by the Chairman of the Section, Mr. W. H. Stephenson, F.P.S., D.B.A., F.R.I.C.

The theme of the meeting was "Contributions to Analytical Chemistry by Younger Members of the Profession" and the following papers were presented and discussed: "Developments in Periodate Oxidation of Organic Compounds," by G. Dryhurst; "Some Aspects of Cathode-ray Polarography," by M. L. Richardson, A.R.I.C., A.C.T.; "The Gas-chromatographic Determination of Impurities in Dichloran," by J. R. Ellis; "Stereoisomerism of *vic*-Dioximes," by S. Thompson; "Phase-solubility Analysis," by R. E. King, A.R.I.C.; "The Friedel - Crafts Acylation of Cycloalkenes," by E. J. Rudd, A.R.I.C.; "Reduction Methods for the Determination of Trace Quantities of Sulphate," by D. B. Adams, M.A., B.Sc., A.R.I.C.; "Proposals for Modifications to the British Standards Dealing with the Analysis of Raw Copper," by K. H. Denmead.

MICROCHEMISTRY GROUP

A SUMMER Meeting of the Group was held on Wednesday, Thursday and Friday, July 17th, 18th and 19th, **1963**, at the School of Pharmacy, Brunswick Square, London, W.C.1.

The following papers were presented and discussed: "Future Possibilities in Microanalysis," by Dr. A. J. P. Martin, F.R.S.; "Methods of Organic Microanalysis: a Comparative and Critical Study," by Dr. R. Lévy; "Mass Spectrometry and Microanalysis," by A. Quayle, M.Sc., F.R.I.C.; "Infrared and Microchemistry," by D. M. W. Anderson, B.Sc., Ph.D., F.R.I.C; "Some Recent Developments in Functional-group Analysis on the Micro Scale," by Professor S. Veibel; "The Status of Microgram Analysis," by Professor R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F. There were also two discussion meetings. (For a fuller report of this meeting and summaries of the papers, see pages **745** to **750**.)

ATOMIC ABSORPTION SPECTROSCOPY DISCUSSION PANEL

THE fourth meeting of the Atomic Absorption Spectroscopy Discussion Panel of the Physical Methods Group was held at **6.40** p.m. on Tuesday, September 10th, **1963**, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Panel, Mr. W. T. Elwell, F.R.I.C.

The discussion was initiated by Dr. J. B. Willis.

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

A JOINT Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry on Methods for the Analysis of Trade Effluents has been set up under the Chairmanship of Dr. S. G. Burgess. The other members of the Committee are: (representing the Association of British Chemical Manufacturers) Mr. F. G. Broughall, Mr. L. A. Keelan, Mr. J. G. Maltby, Dr. I. S. Wilson; (representing the Society for Analytical Chemistry) Mr. G. E. Eden, Dr. S. H. Jenkins, Mr. J. G. Sherratt and Mr. N. T. Wilkinson.

The Committee has begun work on reviewing "Recommended Methods for the Analysis of Trade Effluents," published in **1958**, with the intention of revision of those methods in need of it. Suggestions for revision from any user of the methods would be welcome, and would assist the Committee by widening the experience on which it can draw; they should be sent to Mr. P. W. Shallis, Secretary of the Analytical Methods Committee, **14** Belgrave Square, London, S.W.1.

Microchemistry Group Summer Meeting, 1963

ONE hundred and eight scientific delegates and fourteen guests attended the Microchemistry Group's three-day Summer Meeting, held in London on July 17th, 18th and 19th, 1963. These dates, immediately following the I.U.P.A.C. Congress, were chosen so that delegates from abroad might be encouraged to attend. In fact, it was gratifying to find that most of the twenty-four overseas visitors, representing the United States of America, Holland, Denmark, Italy, Switzerland, Australia, France, Belgium, Spain and Japan, had come specially for the Summer Meeting. Demand for residential accommodation considerably exceeded the fifty places that had been optimistically reserved in Passfield Hall.

The meeting was centred at the School of Pharmacy, by permission of the Dean, Dr. F. Hartley, who cordially welcomed the Group and its visitors at the initial reception. Dr. R. E. Stuckey, Vice-President of the Society, opened the scientific programme and gave the Society's good wishes for its success.

The object of the meeting was to present accounts of current trends in microchemistry by experts in their fields. As well as the six main lectures, summaries of which are given below, there were two discussion meetings, one on general aspects of microanalysis, introduced by Dr. C. W. Ayres and Mr. R. W. Fennell, and one on instrumental methods of elemental determinations, introduced by Dr. W. Simon, Mr. W. R. Nall and Mr. G. Ingram. Both were stimulating and well supported by brisk discussion from participants.

Delegates were given the opportunity to visit a choice from nine microchemical laboratories in the London area. These visits were much appreciated, and thanks are tendered to the institutions for welcoming their visitors.

A very full programme for scientific delegates included a choice of social events, and there was a varied and enjoyable Ladies' Programme.

At the winding-up Dinner, the President of the Society, Dr. D. C. Garratt, paid tribute to the vigour of the Group and the work of the Sub-Committee that had arranged the meeting.

Future Possibilities in Microanalysis

BY A. J. P. MARTIN

DR. MARTIN suggested that future developments in analytical chemistry must be directed towards reducing the scale of the operations. The processes of chemistry were seldom influenced by the quantity of material, and 1000 molecules could react chemically with the same efficiency as 10^{24} molecules. Man's ability to observe and measure much smaller quantities was limited by the size of his hands, and the apparatus he could manipulate.

The advantages of working on a much smaller scale included speed and economy, the latter being essential in many fields of research work. In gas chromatography and ionisation methods the analyst already has tools sufficiently sensitive to work with 10^{-9} g of material, but he needed first of all a balance capable of weighing such quantities. The present method of applying 1 μg to a capillary column was to weigh 1 mg and by a divider throw the rest away. There should be no difficulty in constructing a suitable balance employing similar principles to the ones used at present, but it must be much smaller. To do this it was essential to overcome the problem of the size of human hands.

Dr. Martin believed he now saw how this should be tackled. It was necessary to make a micromanipulator to replace the hands. It would be crude in comparison with a real hand, but given sufficient degrees of freedom, and fingers for gripping, should not be too difficult to operate. A mechanical system for movement and a pneumatic system for the sensory part would probably be the easiest to make and the most useful to operate. It was impossible completely to reproduce the senses of the hands, but sufficient could be reproduced to begin making one-tenth and one-hundredth scale apparatus.

It was interesting to compare this concept of a micromanipulator with previous ones. Although man had used the microscope for 300 years, the only tools available for making manipulations under it were "stone-age" implements—a "spear" and a "battle-axe," which had only three or four degrees of freedom. (The proposed manipulator would have many more than that.)

The properties of this small world must be considered. The mass of the machine went down as the cube of the scale of reduction, and the increased acceleration varied as the reduction in size. Wear and corrosion would be the same as for a larger machine, but the quantity

แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

of material used was so small that platinum and diamond could be used. Surface tension would be greater and it would be necessary to work in either a completely wet or a completely dry atmosphere. The operator's ability to see would be diminished—at one-tenth he would become very short sighted, at one-hundredth scale almost blind, and at one-thousandth scale would need to use an electron microscope.

If this reduction in our scale of operations could be achieved, it became possible to imagine a micro feeler catching a molecule and "feeling" its composition. Dr. Feynman, of the California Institute of Technology, who had put forward ideas similar to Dr. Martin's own, had suggested that single molecules could be synthesised by pressing the atoms together.

Methods of Organic Microanalysis: a Comparative and Critical Study

BY R. LÉVY

DR. LÉVY reviewed and compared various methods for the micro-determination of elements in organic substances, and included some reference to the effects of a wide range of unusual (hetero-) elements.

For the determination of fluorine, in which the fluoride was measured spectrophotometrically by its bleaching action on iron sulphosalicylate, the oxy-hydrogen flame was the only method he recommended for liquids and volatile compounds, but for other samples the oxygen-flask method could be used, with combustion initiated with a hot silica rod. Use of gelatine capsules always led to low results, but packing in filter-paper with about 15 mg of glucose worked well. The flask combustion had proved itself better for polymers such as Teflon. The spectrophotometric method had a limited precision, and taking 5- to 6-mg sample weights was therefore recommended, standard fluoride solutions being treated at the same time and in an identical manner with the unknowns. Results for phosphorus by the phosphovanadomolybdate colorimetric method were excellent if similar precautions were taken.

For the determination of chlorine, bromine and iodine, five methods of decomposition had been compared. The *oxy-hydrogen flame* had few advantages and required the most skill; iodine could be lost as a solid deposit, and hetero-elements gave more trouble than in other methods. The *Pregl-type bead tube* with detachable absorber was much used without platinum or silica filling, but with at least 100 mm of the combustion tube at over 1000° C. With a series of samples, chlorine or bromine could be determined in 25 minutes. Volatile samples had to be heated with care, but others could be heated automatically. *Oxygen-flask combustion* was cheaper and had little that could break down, such as electric heaters. Generally the bead-tube method was best for routine work and the flask combustion for occasional use, but Dr. Lévy's laboratory had uses for both. Phosphorus, boron, zinc, sodium, manganese and cobalt did not interfere in the determination of chlorine by flask combustion, although some of them interfered in the iodine determination. For similar reasons the *peroxide-fusion* and sulphuric - chromic acid methods were still sometimes used. In the former, fluorine, phosphorus, nickel and zirconium did not interfere, manganese and cobalt could be removed by filtration and tin was the only important element that interfered. The *sulphuric - chromic acid method* (Zacherl and Krainick) was the most widely applicable when hetero-elements were present. It took the most time, but was the easiest to carry out.

Chlorine and bromine were invariably determined by potentiometric argentometry to a pre-determined potential and the condition, *e.g.*, absorbing solutions and volumes, were strictly defined. Iodine was oxidised to iodic acid as in Leipert's method, but by the use of bromine in absence of acetic acid after flask combustion. In presence of chlorine, iodine could be removed by boiling after the addition of more peroxide and sulphuric acid. When chlorine was present together with bromine, the method of correction already published was suitable. This was intended to follow a sodium peroxide fusion, and consequently, when it was used after other methods of decomposition, sodium peroxide had to be added to the solution. Addition of sodium hydroxide and sulphuric acid instead did not give the same results.

For the determination of chloride an electrode of 5- to 6-mm diameter silver rod was used; it was polished daily with fine emery and chamois leather by spinning at 2500 r.p.m. The end-point potential was pre-determined with 5- or 10-ml portions of 0·01 N silver nitrate and 0·01 N potassium chloride (the chloride being added to the nitrate), repeated until results were consistent. Subsequently samples were titrated to this potential by adding excess of silver nitrate and back titrating with potassium chloride.

For bromide the cleaned electrode was stabilised in a silver bromide suspension and its stability was checked by repeated titrations of potassium bromide with 0·002 N solution of silver nitrate; here the back titration was not used.

In conclusion, Dr. Lévy considered the effect of many hetero-elements on the carbon and hydrogen determination using either the Zimmermann filling of copper oxide and silver or the Večeřa filling of cobalt oxide on pumice grains at 750° C. The latter method was shown to have certain advantages.

Mass Spectrometry as a Microanalytical Technique

By A. Quayle

Mr. Quayle said that the first working mass spectrograph had been built by Aston in 1919, and this had set the pattern on which succeeding instruments had been based.

The substance under analysis was excited by an electron beam into giving off streams of positively charged particles. These were focused by passing them through a pair of slits; they were then subjected to electrical and magnetic fields, and the resulting rays focused on some form of detector, either a photographic plate or an ion collector connected to a suitable amplifier. He showed that the amount of deflection of the beam by the magnetic field was proportional to the mass and charge of the particles, by the following mathematical treatment.

The fields deflected the charged particles in an arc. Hence a particle experienced a centrifugal force equal to Mv^2/r. This force was caused by the field H, which was exerting a force HeV. Hence—

$$HeV = \frac{Mv^2}{r} \quad \text{or} \quad r = \frac{Mv}{eH} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \tag{1}$$

But the kinetic energy of the particle after acceleration was the same as its potential energy, *i.e.*—

$$\tfrac{1}{2}Mv^2 = eV \text{ or } v = (2eV/M)^{\frac{1}{2}}.$$

Substituting for v in equation (1)—

$$r = \left(\frac{M^2 2eV}{e^2H^2M}\right)^{\frac{1}{2}} = \left(\frac{2MV}{eH^2}\right)^{\frac{1}{2}},$$

which, when rearranged, gave $M/e = r^2H^2/2V$, and if the fields H and V were constant, $(M/e)^{\frac{1}{2}}$ varied as the deflection (as measured by r). Thus in a beam of ionised particles of equal energy the different masses could be distinguished by the variation in deflection.

In practice the magnetic or electric fields were varied so that ions of different masses were brought in turn to the collector. There were various methods of recording this deflection—focusing the ions on a photographic plate, or measuring the electrical discharge, either by means of a galvanometer spot on photographic paper or by other devices. For qualitative work plane plates could be used, but for accurate quantitative work, concave plates were preferable. When the readings were likely to be indistinct, they could be intensified by making a longer exposure.

Gases could readily be handled, and hydrocarbons up to a five-carbon chain had been analysed at room temperature. The size of the sample used was 2 litres at a pressure of 0·1 mm of mercury (approximately 0·3 ml at S.T.P.). Even smaller samples could be used, and analyses had been carried out on 1 cu.mm of gas, *e.g.*, the gas bubbles formed in plate glass during manufacture.

Volatile liquids (having a vapour pressure of more than 30 μ at room temperature) could also be examined, the sample being introduced into the receiver through a tiny orifice. About 1 μl of liquid was required. Samples having a low vapour pressure might have to be heated and so had to be thermally stable.

Solids also had been examined, about 1 mg of sample being introduced into the apparatus, but nine-tenths of the sample was pumped away before analysis.

One method of introduction was to cover a sintered plate with molten gallium and to introduce the sample as a liquid under the metal by a syringe. The sample was then pumped through the sintered plate into the discharge chamber. Thermally unstable or volatile samples could be introduced directly into the chamber through a pipe. Solid samples were introduced into the electron beam as pellets. Samples having molecular weights of up to 800 had been analysed by these techniques.

Mr. Quayle described in detail some of the applications of the technique. He illustrated the analyses of monatomic and diatomic gases by taking fluorine, krypton and nitrogen as examples. Typical spectra such as those given by air and hydrocarbons were discussed in detail, the examples taken being the analyses of methane, ethane, propane and butane. Other materials whose analysis the speaker described were methyl esters, polychloronaphthalenes and alkyl phosphates. The instrument could be used semiquantitatively for the analysis of gas mixtures and was finding increasing application in conjunction with gas chromatography.

Infrared and Microchemistry

By D. M. W. Anderson

Dr. Anderson began by affirming that infrared spectroscopy should be available in every analytical laboratory since it facilitated not only qualitative analysis, but also quantitative analysis and structural determinations on both organic and inorganic molecules. Furthermore, this important modern analytical tool should be of particular interest to microchemists, since analyses could be made on the microgram scale with standard equipment; sub-micro work was possible with the aid of specially designed cells, or auxiliary instrumentation (often comparatively expensive, *e.g.*, beam condensers, scale expansion, microscope attachments), or both, the present useful limit of sensitivity being approximately 10^{-7} g.

After pointing out the extent to which infrared spectroscopy could be used in research, development, and production control in almost every branch of chemical industry, the lecturer indicated that the lecture time would be more profitably spent in considering fundamental principles and experimental techniques, with particular reference to those available for quantitative analysis, rather than discussing an arbitrary selection of recent specialised applications.

Dr. Anderson then outlined very briefly the origins of spectra, interaction of energy with molecules and the requirements for a molecule to absorb in the infrared region. Stressing that modern physical instruments should not be regarded as "black boxes," he described the essential design features of a modern spectrophotometer and discussed the necessity for, and analytical advantages of, double-beam operation. The choice of prism and window materials for operation in the near, normal, and far infrared regions were described, with particular reference to some less common materials and those recently introduced, *e.g.*, "Irtran" glass (four types of which were now available). The analytical advantages of working in the "near" and "far" regions were indicated.

After describing the various techniques for obtaining spectra for solids (organic and inorganic), liquids (aqueous and non-aqueous) and vapours, Dr. Anderson referred to some analytically useful physical applications and then indicated, very briefly, how the qualitative interpretation of a complex spectrum was attempted, stressing that considerable experience was, in general, necessary for success in this type of infrared work.

The remainder of the lecture, which was extensively illustrated with slides, was devoted to a more detailed discussion of methods of quantitative analysis of single components and of complex mixtures. In concluding his lecture, Dr. Anderson drew attention to the recent increased activity in the application of infrared methods to inorganic systems and to aqueous solutions, to the use of polarised radiation, and to the interesting advances that were being made with the aid of the total-attentuated-reflectance technique introduced in 1961.

Some Recent Developments in Functional-group Analysis on the Micro Scale

By Stig Veibel

Professor Veibel stated that micro-elemental analysis permitted the establishment of the empirical, but usually not the structural, formula of an organic compound. For this, functional-group analysis was more important, being the equivalent of the ionic reactions of the elements in inorganic analysis, but it had to be remembered that mutual interference of the different functional groups was much more serious than the mutual influence of the different elements.

Chemical methods had in recent years been supplemented by physical methods such as chromatography (column, paper, gas, thin-layer) and spectroscopy (ultraviolet, infrared, nuclear magnetic resonance, micro-wave, mass), which facilitated the use of micro techniques for the identification of organic compounds.

Three different steps in the identification had to be considered, *viz.*: the *detection* of the presence of a particular functional group, the *characterisation* of the compound through the preparation of a derivative or through determination of a physical constant (m.p., n_D, etc.) and the *determination* of the equivalent weight of the compound with respect to the functional group considered. Commission I of the Division of Analytical Chemistry of I.U.P.A.C. had started work on a Report on Reactions and Reagents useful for these three purposes.

DETECTION OF THE PRESENCE OF A PARTICULAR FUNCTIONAL GROUP—

Feigl's spot tests had been extended to cover many functional groups, but as most of the reactions were colour reactions, they were not sufficiently specific to be fully trusted unless subsequently corroborated by more specific tests. For this the use of reagents such as 2,4-dinitrophenylhydrazine and other hydrazine derivatives, aralkylthiouronium halides, fluoro-2,4-dinitrobenzene, or other classical or new reagents, had been considerably developed in recent years.

CHARACTERISATION OF FUNCTIONAL GROUPS THROUGH DERIVATIVES—

The reagents described above would often permit the preparation of crystalline derivatives under the microscope. Physical constants, such as the melting-point, could then be determined directly under the microscope, but it had to be remembered, *e.g.*, that all hydrazine derivatives of carbonyl compounds were able to exist in *syn* and *anti* forms, which in the neighbourhood of the melting-point easily underwent mutual interconversion, causing a depression of the melting-point. Other derivatives, such as the aralkylthiouronium salts, were easily decomposed at elevated temperatures, and the rate of heating of the bath should therefore be recorded together with the melting-point found.

R_F values (paper or thin-layer chromatography) or retention times (gas chromatography) were, for some derivatives, more useful than melting- or boiling-points. Infrared spectra were also of great value for the characterisation of different compounds containing particular functional groups. Mr. A. Jart had determined the infrared spectra of some 300 benzylthiouronium salts and of some 150 *p*-bromophenyl esters of carboxylic acids. These spectra were to be published in *Acta Polytechnica.*

The latest development was a combination of a gas chromatograph with a mass spectrograph. It was claimed that this method was applicable to samples from 10 g down to 10^{-9} g.

The investigation of the specificity of the various reagents suggested has not always been sufficiently thorough. It is to be hoped that the above-mentioned I.U.P.A.C. report will be critical, especially in this respect.

DETERMINATION OF FUNCTIONAL GROUPS—

Great progress had been made by the introduction of acid - base titrations in non-aqueous solvents, making possible the titration of substances with very weak protolytic activity, *e.g.*, acids with pK_a values up to 10 or 11 and bases with pK_b values up to 11 or 12. The introduction of titration machines, automatically recording the titration curve, had been a great help.

Progress had also been made with redox titrations. Polarography, which until recently had been used mainly in inorganic analysis, had found applications in organic analysis, too, oscillographic polarography being possibly the most useful variant. By a combination of chromatographic and spectrophotometric methods an automatically recorded investigation of, *e.g.*, protein hydrolysates had been made possible. Other instrumental methods included chronopotentiometry, conductometric titrations and electrophoresis.

References to detailed methods could be found in annual or bi-annual progress reports in most of the journals of analytical chemistry and in the "Organic Analysis" series edited by Mitchell, Kolthoff, Proskauer and Weissberger.

The Status of Microgram Analysis

BY R. BELCHER

PROFESSOR BELCHER explained that the submicro procedures developed at the University of Birmingham for the elementary and functional-group analysis of organic compounds used a sample weight of about 30 to 50 μg, but achieved the same order of accuracy as comparable micro techniques. This order of sample weight was chosen because it represented about the lowest level with which it was possible to work without the use of magnification and manipulators. It was not envisaged that these sub-micro procedures would replace existing micro techniques for routine analysis, but rather that they would be employed for those determinations, particularly in biochemistry, where only very small amounts of material were available.

The first method developed had been a sealed-tube digestion for nitrogen-containing compounds, sulphuric acid being used. Ammonia in the digest was eventually oxidised by an excess of hypobromite, the excess being determined iodimetrically. Sealed-tube decomposition with sodium metal was applied to the determination of chlorine, bromine and iodine. The last two elements were conveniently and easily evaluated by amplification titrations (Van der Meulen and Leipert, respectively). Chlorine had proved more troublesome; an indirect amplification procedure based on the use of mercury^{I} iodate had been developed, but the technique was extremely exacting. Fluorine was determined by oxygen-flask combustion, followed by colorimetric determination of fluoride with alizarin complexone and cerium^{III}. A sub-micro Carius digestion was used to determine sulphur. The barium sulphate formed was filtered, then dissolved in an excess of ammoniacal EDTA and the excess of EDTA back-titrated with magnesium solution with Solochrome black 6B as indicator. Although a successful combustion technique had been developed for carbon, it had not proved possible to determine hydrogen at the same time because of losses of water by absorption on the surface of the silica apparatus. The carbon dioxide formed by the combustion was frozen out and eventually determined manometrically. Some procedures had been developed for functional groups, particularly for alkoxyl, alkalimino and carboxyl groups and some non-aqueous titrations had been investigated.

Considerable attention had been focused on the determination of hydrogen, almost every conceivable approach having been tried, even methods that would involve its determination independently from carbon, *e.g.*, the Feigl spot-test reaction for hydrogen by heating the sample with sulphur and evaluation of the resulting hydrogen sulphide. Recent work had shown promise with a combustion procedure in which the water formed was immediately trapped by a desiccant. The carbon dioxide was determined manometrically; then the desiccant was heated, the evolved water passed over heated carbon, the resulting carbon monoxide subjected to the Schutze reaction, and the carbon dioxide from this determined manometrically.

Several successful procedures had been developed for application after a sub-micro oxygen-flask decomposition of the sample. Chloride was evaluated mercurimetrically in an ethanolic medium with diphenylcarbazone as indicator. Bromide and iodide were determined, as before, by amplification titrations. Sulphur, as sulphate, was titrated with barium perchlorate in an ethanolic medium with Thorin as indicator. Previous studies of the determination of phosphorus (and arsenic) by means of a sealed-tube decomposition with nitric acid had indicated substantial losses of phosphorus on the walls of the tube. This effect was also present in the flask combustion, but it had proved possible to eliminate the difficulty. After flask combustion, phosphate was determined *via* a titrimetric quinoline phosphomolybdate procedure or a molybdenum-blue spectrophotometric finish. For arsenic, only a molybdenum-blue finish had proved possible.

Much work was currently being carried out on functional groups. The nitro group was being determined by reduction with excess of titanium^{III} sulphate by using a special sub-micro storage - delivery system for the reagent. Excess of iron^{III} was then added and the excess back-titrated with the titanium^{III}. This procedure had been successfully extended to the determination of the nitroso group, but, as on the micro scale, results had been erratic for azo groups. It had not so far proved possible to differentiate between aldehydic and ketonic carbonyl, but a general procedure for the carbonyl group had been evolved based on an oximation reaction and eventual non-aqueous titration of hydroxylamine. The bromine chloride method was being investigated as a possible general determination of unsaturation. Non-aqueous titration of the thiol group with mercury^{II} perchlorate had shown promise. Remarkable success had been achieved with the Malaprade reaction—periodate titration of glycol groups. On the sub-micro scale it had proved possible to titrate the formaldehyde, formic acid and excess of periodate in a single solution, whereas three aliquots were normally required. A method for determining molecular weight was based on depression of the freezing-point of camphor.

A Review of the Methods Available for the Detection and Determination of Small Amounts of Cyanide*

By L. S. BARK and H. G. HIGSON

(*Department of Chemistry and Applied Chemistry, The Royal College of Advanced Technology, Salford, Lancashire*)

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    Titrimetric methods involving instrumental end-point determination
    Polarographic methods
    The use of gas chromatography
Colorimetric methods
    Methods involving formation of a metal complex
    Other colorimetric methods
    Colorimetric methods based on the König reaction
Conclusion

The detection and determination of small amounts of cyanide ions are important because of the extreme toxicity of cyanide to living matter. Cyanides are used in electroplating, in precious metal refining, in case hardening of steels and in many other processes; in the gas industry, many atmospheres and effluents contain cyanides, *e.g.*, the effluents from coke ovens and other gas-making plant. Hydrogen cyanide is used extensively as a rapid and conveniently applied fumigant for food-storage plants, such as warehouses and the holds of cargo ships.

Because of the extreme toxicity of cyanide, low maximum concentrations are allowed in water (which may be used for drinking purposes) and in atmospheres (where human beings may be working). The World Health Organisation[1] recommends that water containing more than 0·01 p.p.m. of cyanide (as CN^-) should be rejected as unfit for public use (domestic supply); the toxic limit for fish is 0·03 p.p.m. The maximum allowable concentration in atmospheres in the United States of America[2] is 10 p.p.m. (5 mg of HCN per cubic metre of air).

These low limits mean that it is essential to use extremely sensitive tests for detecting and determining cyanide. For several years there has been a steady increase in the extent and variety of the methods available for detecting and determining cyanides, which are found not only as "free cyanides" (from HCN, KCN and NaCN) and unstable cyano-complexes, such as $[Zn(CN)_4]^{2-}$, but also as relatively stable complex cyanides, such as ferrocyanides and cobalticyanides, which, although not showing typical cyanide properties, are still toxic and classified by most health authorities with cyanides.

Most of the methods used for detecting and determining cyanide involve the formation of hydrogen cyanide. Of the suggested procedures for decomposing complex cyanides to give hydrogen cyanide (either for detection or determination), that proposed by Williams,[3] in which the solution of simple and complex cyanides is distilled after addition of an acid solution of cuprous chloride, is recommended by British authorities[4]; and Kruse and Mellon's method,[5] in which the complex cyanides are decomposed by distillation with phosphoric acid in the presence of citric acid and ethylenediaminetetra-acetic acid (EDTA) under partial vacuum, is used by many chemists in the U.S.A. The latter workers[6] also suggested solvent extraction as an isolation method. Serfass, Freeman, Dodge and Zabban[7] used a reflux method with an air current to transfer hydrogen cyanide from the sample to absorption tubes. Decomposition of complex cyanides is hastened by the action of magnesium chloride, mercuric chloride and sulphuric acid, yielding uniform high recoveries of hydrogen cyanide from simple or complex cyanides; boiling under reflux for 1 hour is generally adequate. Complex cyanides of iron, copper or cobalt generally require longer treatment. Schwapowalenko[8] recommended that the hydrogen cyanide be liberated by heating the test solution in the presence of sodium hydrogen carbonate to prevent any interference from volatile oxidising or reducing compounds.

*Reprints of this paper will be available shortly. For details please see p. 822.

The methods used for detecting and determining cyanide can be divided into two main sections, *viz.*, non-colorimetric and colorimetric; these can be further sub-divided, *e.g.*—

Non-colorimetric—

(*a*) Titrimetric methods involving visual end-point indicators.
(*b*) Titrimetric methods involving instrumental methods for determining the end-point.
(*c*) Polarographic methods.
(*d*) Gas-chromatographic methods.

Colorimetric methods—

(*i*) Methods involving formation of metal complexes.
(*ii*) Other methods.

Some methods are applicable only to the detection and some only to the determination of cyanide, but most of the available colorimetric methods are used for both.

NON-COLORIMETRIC METHODS FOR DETECTING OR DETERMINING TRACE AMOUNTS OF CYANIDE

The detection of hydrogen cyanide by smell can be one of the most sensitive tests (0·001 p.p.m. can be detected), but many people are relatively insensitive to the smell.

TITRIMETRIC METHODS INVOLVING VISUAL END-POINT DETECTION—

The earliest reported method for determining cyanide is Liebig's titrimetric method,[9] based on the formation of turbidity due to silver cyanide after all the cyanide has reacted with standard silver nitrate solution. An argenticyano-complex is formed initially, and then a slight excess of silver nitrate produces turbidity due to the formation of silver cyanide. This titration is subject to error in alkaline[10,11] and ammoniacal[12,13] solution. A similar method proposed by Dénigès[14] is based on the turbidity due to silver iodide in the presence of ammonium hydroxide with potassium iodide as indicator; although this method gives high results in the presence of a large excess of ammonia,[12,13,15,16] accurate results are obtained if the concentration of ammonium hydroxide is carefully regulated.[12,13,15,17] Beerstecher[18] modified the Dénigès silver nitrate titration; he used a photo-electric colorimeter or turbidimeter for end-point detection, and delivered 0·001 M silver nitrate solution from a piston microburette. Ryan and Culshaw[19] reported the use of *p*-dimethylaminobenzylidene rhodanine as an indicator in Liebig's method, and this modification was recommended by the American Public Health Association[20] for determining cyanide concentrations of 1 p.p.m. and more. For concentrations greater than 10 to 20 p.p.m., the British recommended method[4] is also the Liebig method, which is therefore still widely used. Ricci[21] published a paper on the inter-relations of the equilibrium constants in aqueous solutions saturated with silver cyanide, and considered mathematically the relation of the point of precipitation of silver cyanide or of silver iodide, as the titration end-point, to the equivalence-point in the argentimetric titration of cyanide. In a second publication[22] he considered the shape of the titration curve, or the graph obtained by plotting a function of the concentration of silver^{I} ion present (p[Ag^+]) against the amount of silver nitrate added, to determine the position of the inflexion-point in the curve and its relation both to the equivalence-point and to the point of first appearance of a precipitate. Two sets of conditions were examined mathematically—

(*i*) the titration of pure aqueous potassium cyanide with silver nitrate, in which the hydrogen ion concentration is variable during the titration, and

(*ii*) the titration of potassium cyanide in presence of excess of ammonia—in this condition the value of the hydrogen ion concentration is practically constant, being fixed mainly by the ammonia.

Under the first conditions the precipitation of silver cyanide would precede the inflexion-point, which would occur only in the supersaturated solution, but the precipitation of silver cyanide, if it should become visible when the solution first becomes theoretically saturated, would give only a negligible (negative) error when taken as the end-point. The inflexion-point occurs before the equivalence-point, but the titration error with the inflexion-point as the end-point would be extremely small. In the presence of excess of ammonia, the inflexion-point occurs at the equivalence-point. Ricci worked out mathematically that the precipitation of silver cyanide (unless the concentration of potassium cyanide was large) occurred after the equivalence-point, leading to a small (positive) error. The precipitation of silver iodide occurred before the inflexion-point. The calculations would suggest that the inflexion-point, without potassium iodide, would be a much better end-point. The importance of this theoretical mathematical treatment is that the best conditions may be selected for titrating different concentrations of cyanide with silver nitrate solution.

Other titrimetric methods involving use of different indicators and titrants have been reported: diphenylcarbazide[23,24] and calcein[25] have been used as indicators in argentimetric titrations; titrations involving the formation of a mercury cyanide have been described by Tanaka and Yamamoto,[26] Gregorowisz and Buhl[27] and Kraljic,[28] who used cupric diethyldithiocarbamate, Variamine Blue and nitrobenzene (with ferrocyanide), respectively, as indicators. It is often necessary before titration to separate the cyanide as hydrogen cyanide by distillation to avoid interference from organic substances and oxidising and reducing agents. Wrónski[29] reported the independent titration of cyanide and sulphide; he used *o*-hydroxymercuribenzoic acid to complex the sulphide and titrated with standard nickel sulphate solution, with murexide as indicator. He also suggested the use of thiofluorescein as an indicator in the argentimetric determination of cyanide; the colour change is, however, not very sharp, and the indicator is not widely used. The use of standard nickel solution in the titration of cyanide was also reported by de Sousa,[30] who determined cyanide in the presence of thiocyanate and chloride by adding a known excess of ammoniacal nickel sulphate solution to the sample and titrating the non-complexed nickel with EDTA, with murexide as indicator.

TITRIMETRIC METHODS INVOLVING INSTRUMENTAL END-POINT DETECTION—

Instrumental methods of analysis are frequently used; the potentiometric titration of cyanide with silver nitrate has been described by Treadwell, Waller and Lauterbach,[31] and Clark.[32] Read and Read[33] suggested bimetallic electrode titration and Gregory and Hughan,[34] using the null-point equivalence potential method proposed by Cavanagh,[35] reported that this method is superior to Liebig's method for determining cyanide in plating solutions.[36] Wick[13] reported that potentiometric titration with mercuric chloride as titrant was an accurate method; Thompson,[17] however, stated that the silver nitrate titration of cyanide to $Ag(CN)_2^-$ was more accurate than the titration with mercuric chloride. Laitinen, Jennings and Parks[37] claimed that the amperometric titration of cyanide with silver nitrate is equal in accuracy and precision to the visual Dénigès method, and is applicable at much higher dilution. Direct amperometry with a rotating silver anode and a stationary platinum cathode has been used by McCloskey,[38] who claims a lower limit of linear response at about 0·01 μg of cyanide in a 7-ml sample and 0·0005 μg of cyanide for a 0·5-μl sample introduced into 10 ml of supporting electrolyte. The electrode response and the sensitivity levels change daily and hence must be frequently checked. A similar system has been operated and patented[39] in this country for electrically determining the concentration of hydrogen cyanide in air (in coal-mines, etc.).

Shinozuka and Stock[40] have described the amperometric titration of low concentrations of cyanide with silver nitrate; they used a rotating platinum electrode and a sodium sulphite medium. A potentiometric method, in which an auxiliary current of 5 to 20 μA per sq. cm is used, has been patented[41] for determining cyanide concentrations in solution (particularly solutions obtained in the refining of gold and silver). Electrometric titrations of cyanide by the dead-stop[42] end-point system with 0·1 N silver nitrate[43] and 0·01 N iodine solution[44] have been reported. Baker and Morrison[45] measured the current from the electrochemical cell Ag/NaOH(0·1 M)/Pt, containing cyanide; the cell operates spontaneously as a measure of one of the reactants in the cell (CN^-)—for 2·6 μg of cyanide, a response current of 17 to 18 μA was reported. The coulometric titrations of cyanide with mercury and silver have been compared by Przybylowicz and Rogers,[46] who showed that mercury was slightly superior to silver for the determination of small amounts of cyanide.

POLAROGRAPHIC METHODS—

Anodic reactions of cyanide at a dropping-mercury electrode have been reported. Jura[47] described the determination of cyanide in flowing alkaline solutions with a shielded dropping-mercury electrode; empirically derived correction factors for the polarographic determination of free cyanide in the presence of sulphide were used by Karchmer and Walker,[48] and Hetman[49] reported a method, depending on a pure reduction wave, in which a base electrolyte consisting of pyridine and potassium nitrate with a mercuric salt was used. The last-named method is uncomplicated and permits the determination of cyanide in concentrations as low as 2 p.p.m. with a comparatively simple polarograph.

THE USE OF GAS CHROMATOGRAPHY—

Gas - liquid chromatography has been used for determining hydrogen cyanide. Woolmington[50] used a method in which water vapour and hydrogen cyanide are separated from oxygen, nitrogen, methane and carbon monoxide by passing the sample (with hydrogen as carrier gas) at 100° to 107° C through a column packed with acid-washed Celite (30 to 60 mesh) impregnated with 20 per cent. w/w of polyoxyethylene glycol (molecular weight 1500). Hydrogen cyanide emerges from the column after 4 to 6 minutes, and its concentration is calculated from peak heights. Schneider and Freund[51] attained sensitivity in their method by a 2000-fold concentration step involving a short column cooled in a mixture of solid carbon dioxide and acetone, and amplification of the thermistor-bridge detector output before recording it on a strip chart.

COLORIMETRIC METHODS

METHODS INVOLVING FORMATION OF A METAL COMPLEX—

Some of these methods, although specific for cyanide and of ample sensitivity, produce unstable colours. The formation of thiocyanate[52,53,54,55] from cyanide (by reaction with ammonium polysulphide) and then ferric ferrithiocyanate (by addition of ferric chloride; producing a blood red colour) is an excellent test for cyanides; however, it is extremely unreliable as a method for determining small amounts of cyanide owing to the instability of the ferric thiocyanate colour. The test is applicable in the presence of sulphide or sulphite; if thiocyanate is originally present, the cyanide must first be isolated before the test is applied (sensitivity, 1 μg of CN^-; concentration limit, 1 in 50,000). Another extremely sensitive test for cyanide depends on the formation of Prussian blue[53,56,57,58,59] ($Fe_4[Fe(CN)_6]_3$). Gettler and Goldbaum[57] found that the sensitivity of the Prussian-blue method could be enhanced by conducting the gas, obtained by aeration of the solution containing hydrogen cyanide (at 90° C), through filter-paper impregnated with ferrous sulphate and dilute alkali (sensitivity, 0·2 μg of CN^-). The cyanide (originally present in the sample) could then be determined by comparing the blue stains produced by immersion of the paper in dilute sulphuric acid with standard stains. Hubach[60] modified this method for detecting cyanides and ferrocyanides in wines. For the detection of cyanide, the aeration of the sample was carried out at room temperature (instead of 90° C). For ferrocyanides, use is made of the fact that hydrogen cyanide is liberated quantitatively from soluble and insoluble ferrocyanides by sulphuric acid in the presence of cuprous chloride at temperatures near 100° C. British authorities[61] recommend Gettler and Goldbaum's method for detecting hydrogen cyanide vapour in air. The copper acetate - benzidine test,[62,63,64] sensitive to 0·25 μg of cyanide (CN^-) in a limit of dilution of 1 in 200,000,[65] is one of the most sensitive and easily applied methods for detecting cyanide. The reaction involves the formation of benzidene blue and is due to the oxidation of benzidine by the removal of copper^{I} from the copper^{II} - copper^{I} system, which raises the oxidation potential of the system and the benzidine is oxidised. It is also probable that copper - benzidine complexes are formed. This test is extremely sensitive for cyanide, provided that oxidising or reducing substances are absent; hence Schwapowalenko's[8] recommendation that hydrogen cyanide be liberated by heating the test solution in the presence of sodium hydrogen carbonate. Cullinane and Chard[66] claimed that a four-fold increase in sensitivity resulted if a substituted benzidine, 2,7-diaminodiphenylene oxide, is used in place of benzidine, but we have not been able to substantiate this claim.

The Weehuizen method,[67,68,69,70] which involves the oxidation of phenolphthalein in alkaline solution to the corresponding red phthalein by copper^{II} ions in the presence of cyanide is a recommended method[4] for determining cyanide. It is an extremely sensitive method, but requires careful control; it is not specific for cyanides because erratic results may be caused by minute amounts of foreign oxidising materials.

A test-tube for detecting hydrogen cyanide in air or other gases has been patented.[71] The tube contains a carrier substance, *e.g.*, silica gel, impregnated with silver chloride, mercurous chloride, lead chloride or a chloride of a metal forming water-insoluble or sparingly soluble cyanides (such as those of copper or palladium), and with an indicator for hydrogen chloride, *e.g.*, bromothymol blue or bromocresol green. The prepared tubes are claimed to be insensitive to oxygen (oxidation) and stable for several years.

The ability of the cyanide ion to form stable complexes and cause de-masking of inner complex-bonded transition metals has also been used by various workers for detecting and determining cyanide. Feigl and Feigl[72] reported a colorimetric procedure in which the de-masking of dimethylglyoxime by the action of cyanide on the palladium dimethylgloximate complex permits nickel ions present to form a red dimethylgloximate. An advantage of this test is that it can be made in alkaline solution, and, in contrast to other methods, does not require the previous liberation and evolution of hydrogen cyanide. Other palladium complexes gave analogous results, and, compared with palladium dimethylgloximate, the palladium salt of 1,2-cyclohexanedione-dioxime[73] gives increased sensitivity. Feigl and Heisig[74] have also reported the detection of 2·5 μg of cyanide by the de-masking of copper from copper^{II} oxinate, which permits aluminium ions present to form the fluorescent aluminium^{III} oxinate.

Brooke[75] selected palladium α-furildioxime as the most sensitive reagent for determining cyanides in "refinery waste water" in the range 0·5 to 3 p.p.m. of cyanide, and Hanker, Gelberg and Witten[76] used the reaction of cyanide with potassium di-(7-iodo-5-sulphooxino)palladium^{II} in alkaline solution. The addition of iron^{III} in acid solution produces a blue colour due to the iron complex with an absorption maximum at 650 mμ. These workers also developed a fluorimetric method depending on the de-masking of 8-hydroxy-5-quinolinesulphonic acid by cyanide from the non-fluorescent potassium di-(5-sulpho-oxino)palladium^{II}. The liberated quinoline derivative then co-ordinates with magnesium ions present to form a fluorescent chelate, which is used for measuring the cyanide concentration. It is claimed that 0·02 μg of cyanide per ml of solution can be determined. Hanker, Gamson and Klapper[77] had earlier developed a method involving the formation of a fluorescent compound by reaction between nicotinamide and cyanogen chloride (formed by the reaction of cyanide and chloramine-T). Although it is rapid, the method is not widely used. Musha, Ito, Yamamoto and Inamori[78] examined the inhibiting action of cyanide ions on the chemiluminescence of luminol (3-aminophthalhydrazide), and determined the cyanide concentration by measurement of the induction period. Yamasaki and Ito[79] indirectly determined cyanide by converting it into a stable nickel complex $[Ni(CN)_4]^{2-}$ at pH 9 to 11 (in presence of an ammonium buffer); the excess of nickel was determined colorimetrically with furil α-dioxime in a suspension at pH 4 containing gelatin, the optical density at 480 mμ being measured.

Several methods involving the de-masking effects of mercury^{II} have been used for detecting and determining cyanide. In one method[80] cyanide is used to liberate 2-hydroxyethyldithiocarbamic acid from its mercury^{II} complex; the liberated acid reacts with copper to form a soluble yellow complex having an absorption maximum at 383 mμ. It is claimed that between 0·2 and 4 p.p.m. of cyanide can be rapidly determined by this method. Some ions interfere, but up to a 60-fold excess of thiocyanate can be tolerated. Tanaka and Yamamoto[81] recently developed a method involving the use of mercuric diphenylcarbazide; paper impregnated with this reagent changes from blue-violet to red in the presence of cyanide (0·25 μg per 0·05 ml) in a neutral or weakly basic solution. With gaseous hydrogen cyanide flowing in a thin glass tube containing a strip of paper, the length of the colour change on the strip of paper is proportional to the amount of cyanide. The sample (approximately 1 ml containing less than 10 μg of cyanide) is heated with sodium hydrogen carbonate in a glass tube. The error is less than 5 per cent., and interference from ferrocyanides is avoided by using cadmium nitrate mixed with the sodium hydrogen carbonate.

Ohlweiler and Meditsch[82] used the colour reaction of mercuric ions with *p*-dimethylaminobenzylidene rhodanine as the basis of an indirect absorptiometric method for determining cyanide, based on the masking of the mercury by reaction with cyanide and measurement of the excess of mercury^{II} by reaction with the organic reagent. These workers also used diphenylcarbazone[83] to react with the mercury not masked by reaction with cyanide, and state that greater sensitivity is thus obtained. Both these methods require the use of a Conway microdiffusion apparatus for preliminary concentration of the cyanide and hence require fairly lengthy test times to obtain results. The methods are not applicable below 0·5 p.p.m. without the use of a differential technique. Hoffman[84] described a similar reaction with diphenylcarbazone; many other ions (iodides, sulphides, etc.) commonly present in effluents interfere.

The ready formation of an argenticyanide complex has been used in a de-masking reaction.[85,86] In the first method,[85] paper impregnated with silver dithizonate is treated with a drop of test solution containing cyanide, and the chromatogram is developed with a mixed water - 0·1 N potassium hydroxide (40 + 1) solution. The area of the white spot (on a violet-pink background) is proportional to the concentration of cyanide. This method is rapid and gives reasonably accurate results; its main advantage is that thiocyanate, chloride and bromide do not interfere. The second method[86] is based on the same principle, but the weakening of the colour of the silver dithizonate in carbon tetrachloride solution is taken as a measure of the amount of cyanide present. When copper, zinc and lead are present in the original solution, they are sequestered with EDTA. For samples containing sulphides or free chloride, the solution is treated with lead nitrate, sodium sulphite or sodium thiosulphate before the addition of EDTA.

Schilt[87] described the spectrophotometric determination of cyanide based on the formation and extraction of the neutral dicyano bis-(1,10-phenanthroline) - iron^{II} complex produced by the exchange reaction between the reagent ferroin and cyanide ions. The method is convenient, relatively free from troublesome interferences and applicable to microgram amounts of cyanide ion and concentrations of the order of microgram per ml (p.p.m.).

An indirect colorimetric method for determining cyanide (and sulphide) with thiofluorescein has been reported by Wrónski.[88] An alkaline solution of thiofluorescein, decolorised with silver nitrate, becomes blue on the addition of hydrogen cyanide or hydrogen sulphide. The phenomenon is used to determine hydrogen cyanide (1 to 7 μg) and hydrogen sulphide (0·5 to 2 μg). For simultaneous determination, the optical density is measured, then a drop of formaldehyde is added to discharge the colour caused by hydrogen cyanide, and the optical density due to hydrogen sulphide alone is measured after 10 minutes. Gregorowicz, Buhl and Sliwa[89] determined traces of cyanide in alkali sulphides by precipitation of the sulphide ions with zinc ions, and then steam-distillation of hydrogen cyanide from the diluted solution into 0·01 N sodium hydroxide and reaction of the acidified distillate with Variamine Blue solution in the presence of copper sulphate solution. In a second paper[90] the colour reaction of copper^{II} and Variamine Blue with cyanide (0·03 μg per ml), thiocyanate (40 to 200 μg) and iodide (1 to 10 mg) was reported. In the determination of cyanide, a 100-fold excess of sodium, potassium, ammonium, chloride, nitrate and sulphate ions may be present without any ill-effects.

OTHER COLORIMETRIC METHODS—

The use of picric acid[91 to 98] involves simple procedures, easily prepared reagents and a stable developed colour. Although it is not a very sensitive method it has recently been used[99] for determining the residual cyanide in and on apples after fumigation with hydrogen cyanide.

Alkali cyanides and complex cyanides can be detected to a limit of 0·05 μg of cyanide[100] by their catalysis of the benzoin condensation in alkaline solution. The benzoin formed is readily detected by the violet colour obtained on addition of *o*-dinitrobenzene.

COLORIMETRIC METHODS BASED ON THE KÖNIG REACTION—

For the detection and determination of small amounts of cyanide in trade effluents, the method recommended by the Joint Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry[101] is based on the method developed by Aldridge,[102] which is an example of the König[103] synthesis for pyridine dyestuffs, in which cyanogen bromide or chloride reacts with pyridine and an aromatic amine to form a dyestuff. Aldridge's method consists in allowing the cyanide to react with excess of bromine, removing the excess of bromine with arsenious acid solution, and then allowing the cyanogen bromide formed to react with a mixed pyridine - benzidine reagent. An intense orange colour is formed, which changes to red during 6 minutes, according to Aldridge, and is stable for 6 to 24 minutes at 20° C when measured with a Spekker spectrophotometer in 1-cm cells and a 2·303 Ilford blue filter. In his second paper improvements are described, and, by using an Ilford 604 green filter, he claims that an increase in sensitivity of 75 per cent. is obtained with a colour stability of 30 minutes; 0·2 μg of hydrogen cyanide at a concentration of 0·1 μg per ml could be determined with an error of ±2 per cent. by this modified method. Krawczyk[104] reported that the method gives a perceptible orange colour with as little as 0·1 µg of hydrogen cyanide per ml on 100 ml of sample. In the method, cyanide and thiocyanate are determined together, and the thiocyanate is then determined in a separate portion of the acidified and aerated sample; the cyanide is obtained by difference.

Bruce, Howard and Hanzal[105] modified Aldridge's method to determine cyanide and thiocyanate separately, rather than the cyanide by difference. They used three aeration tubes in series; A (air-washing tube) contained 20 per cent. sodium hydroxide solution, B contained 20 per cent. trichloroacetic acid solution and C contained 0·1 N sodium hydroxide solution. The sample containing cyanide and thiocyanate ions was placed by pipette in tube B, and aeration was begun. After 15 minutes' aeration, the cyanide collected in tube C was determined by Aldridge's method. The thiocyanate left in tube B was also determined after aeration.

Saltzman[106] used Aldridge's original procedure and reported that the final colour was unstable, changing in both tint and optical density; the instability of the colour increased with temperature. Colour measurement was made at 510 mµ. Good results were obtained by controlling the temperature and by allowing for the age of the sample colour by means of a set of readings made at various ages of the standards used.

Whereas Aldridge used filters (initially 2·303 Ilford blue, then Ilford 604 green) that transmit light over a relatively broad spectrum region, other workers have used a definite wavelength. These wavelengths have differed rather widely—480, 510, 520 and 532 mµ, which, to some extent, is an indication of the many divergent view-points about this method.

For coloured or turbid samples or samples containing low concentrations of cyanide, Aldridge's method has been modified by Nusbaum and Skupeko[107]; the determination is carried out in the presence of n-butanol, the dye formed is thus extracted with the n-butanol and the sensitivity of the method is extended (0·02 to 0·5 p.p.m.). For samples containing a large excess of sulphide ions, Aldridge's procedure was modified by Baker *et al.* [108] The sulphide ions are oxidised to sulphuric acid with bromine at the same time as cyanide ions are brominated to form cyanogen bromide. This avoids the necessity for prior removal of the sulphide ions from the sample. The method is sensitive to less than 0·5 µg of cyanide in the presence of 2500 µg of sulphide (error ±5 per cent. at a concentration of 10 µg of cyanide).

Russell and Wilkinson[109] have modified Aldridge's method to make possible the determination of cyanide in the presence of thiocyanate, ferrocyanide and ferricyanide, and also in colour solutions. The complex cyanides are "fixed" with zinc acetate solution and the cyanide (as hydrogen cyanide) is distilled from the acidified solution into 0·1 N sodium hydroxide and then determined with a pyridine - benzidine reagent after formation of cyanogen bromide. (The pyridine - benzidine reagent is not the same as that recommended by Aldridge.) Up to 3 p.p.m. of CN^-, present as cyanide ions, can be measured in the presence of up to 25 p.p.m. of CN^-, present as thiocyanate, and up to 5 p.p.m. of CN^-, present as complex ferro- and ferricyanides, in aqueous solutions containing all these substances and also in the presence of sodium and calcium chlorides. The method is accurate to within 0·05 p.p.m. of CN^- at the maximum concentrations of these substances and to within 0·01 p.p.m. of CN^- at lower concentrations. Aldridge's method has been used for a wide range of materials, including the determination of cyanide in biological materials[110] and foodstuffs.[111,112] For biological materials a preliminary distillation step is carried out. For foodstuffs, a modified Conway cell is used to effect a preliminary separation of the cyanide by microdiffusion.

Murty and Viswanathan[113] used barbituric acid in place of benzidine. They used 25 ml of sample (0·01 to 1·5 µg of cyanide per ml), formed cyanogen bromide and incubated the solution at 40° C for 40 minutes to allow colour formation after addition of a mixed pyridine - barbituric acid reagent. This method was claimed to be more satisfactory, since the colour is stable for approximately 3 hours. Kratochvíl[114] oxidised cyanide to cyanogen chloride with chloramine-T solution, and allowed the cyanogen chloride to react with pyridine to form glutaconaldehyde, which reacts with dimedone to produce a violet colour that can be measured, after 30 to 40 minutes, at 580 to 585 mµ. Desmukh and Tatwawadi[115] made use of the fact that cyanides and thiocyanates develop a yellow colour when treated with chloramine-T solution in the presence of pyridine. Schulek, Burger and Fehér[116] reported a method for determining ammonia, cyanide, nitrite and nitrate when present together.

Ammonia and cyanide are distilled off, ammonia is determined by titration of the distillate and the cyanide is then determined by the cyanogen bromide - iodide reaction.

A method similar to Aldridge's method and also based on the König reaction is that proposed by Epstein.[117] Cyanide is oxidised to cyanogen chloride with chloramine-T, the cyanogen chloride is then allowed to react with pyridine containing 3-methyl-1-phenyl-5-pyrazolone and a small amount of bis-(3-methyl-1-phenyl-5-pyrazolone), and the blue colour produced is measured at 630 mμ. The excess of chloramine-T is reduced by the pyrazolone, but since this will also reduce the cyanogen chloride, the pyridine must be added to avoid this. If the "bis-pyrazolone" is not used, a blue colour is still developed, but it is not stable. Epstein's method is sensitive and may be used in acid, neutral or slightly alkaline media; it is recommended by the American Public Health Association.[20] It has been used for determining cyanide in fish tissue[118] and in wines treated with ferrocyanide.[119] Dodge and Zabban[120] and Balla and Bene[44] also described the use of Epstein's method for determining cyanide and a copper - pyridine reagent for thiocyanate. The cyanide was separated from thiocyanate by extraction as hydrogen cyanide from acidic (glacial acetic acid) solution with four 40-ml portions of isopropyl ether. The hydrogen cyanide was re-extracted from the isopropyl ether with three 30-ml portions of 3 per cent. sodium hydroxide solution. The extraction was reported to be over 95 per cent. efficient.

Ludzack, Moore and Ruchhoft[121] considered that three published methods offered the most promise for the determination of cyanide in water and waste samples: (*a*) Aldridge's method as modified by Nusbaum and Skupeko[107]; (*b*) Epstein's method; (*c*) the modified Liebig titration with the use of Ryan and Culshaw's *p*-dimethylaminobenzylidene rhodanine indicator.[19] They concluded that all samples should be treated by acid distillation except when experience had shown that no difference occurs in the results obtained with or without distillation. Certain samples containing interfering substances that could be steam distilled may require solvent extraction before analysis can be attempted. When this is so, 2,2,4-trimethylpentane (iso-octane), hexane or chloroform will remove the soluble interfering substances without extracting more than traces of cyanide. Epstein's method was preferable for cyanide below 1 p.p.m. (Sensitivity could be extended to 5 parts in 10^9 by use of a colour extraction procedure with n-butanol.) When more than 1 p.p.m. of cyanide was to be determined, the silver nitrate titration was recommended.

Other workers who favour Epstein's method are Whiston and Cherry.[122] They discontinued using Aldridge's method owing to the carcinogenic properties of benzidine, and obtained a straight-line calibration graph over the range 0 to 2 p.p.m. with Epstein's method.

CONCLUSION

From the review of methods available for determining small amounts of cyanide ions it is apparent that colorimetric methods are the best for amounts such as 0·1 to 1·0 p.p.m. Sensitivity in this range is evident in the methods involving use of phenolphthalein (or *o*-cresolphthalein) or Prussian blue, or the methods based on the König synthesis, namely Aldridge's method and Epstein's method. Of these methods the phenolphthalein and *o*-cresolphthalein methods are non-specific for cyanides and must usually be applied to samples that have been concentrated by distillation. The Prussian blue method requires the volatilisation of the cyanide and its absorption on treated filter-paper; it is thus subject to similar errors of separation. Small amounts of ferro- or ferricyanides, if present in the sample, tend to break down on distillation, releasing cyanide and causing appreciable errors in the micro-determination of cyanide in the original sample. The two methods based on the König synthesis permit the determination of cyanide directly on the original sample. These two methods are generally considered to be the best for small amounts of cyanide, and in fact both have been selected for use as standard or recommended[20,101] methods. The pyridine - pyrazolone colour development (Epstein) depends on the presence of a small amount of bis-pyrazolone and requires the preparation of a relatively unstable reagent. The pyridine - benzidine reaction with cyanogen halide (Aldridge's procedure) has the necessary sensitivity and stability, but has a distinct disadvantage in that the amine used is a well known active carcinogen. Also, there is some confusion as to the correct wavelength to use when measuring the developed colour in Aldridge's method. The problem is to improve on the existing methods by—

(*i*) the development of a one- or two-stage process that will give a colour with cyanide ions, hence reducing the amount of time necessary for determining cyanide ion, and probably permitting a suitable field method for determining microgram amounts of cyanide to be developed; or

(*ii*) use of a non-carcinogens in the König synthesis, preferably compounds that are more stable and have a greater molecular extinction coefficient than either pyrazolone or benzidine.

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The Analysis of ^{14}CO - $^{14}CO_2$ Mixtures by Gas-chromatographic Separation and Aqueous Solution Counting*

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A method is described for analysing carbon-14 monoxide - carbon-14 dioxide mixtures. Gas-chromatographic separation on a silica-gel column is used to determine both the percentage composition and the activity of each constituent. The carbon monoxide emerging from the column is oxidised to carbon dioxide and then frozen out in a cold trap to which sodium hydroxide solution has been added; the carbon dioxide component is isolated in a second cold trap. The activity of the solution from each trap is directly determined by scintillation counting in a cell containing a layer of plastic phosphor cemented to the inside of its base.

The rapid separation achieved by gas chromatography permits an analysis to be completed in 40 to 60 minutes, depending on counting time.

Results are presented for carbon-14 monoxide - carbon-14 dioxide mixtures covering a range of compositions.

IN connection with tracer studies involving the use of carbon-14, it has been necessary to analyse numerous mixtures of carbon monoxide and carbon dioxide in which both constituents were labelled. For each mixture it has been required to determine the percentage composition and also the amount of activity present in each chemical form, so that the specific activity of each constituent could be calculated.

In our laboratories it has been customary for some years to analyse inactive gas mixtures containing carbon monoxide and dioxide by gas chromatography. For determining minor constituents, including carbon monoxide, in gases containing mainly carbon dioxide, the carbon dioxide has been removed by passage through soda-lime and the minor constituents separated on a molecular-sieve column.[1] When a determination of carbon dioxide has been required, its separation from carbon monoxide has been achieved with a silica-gel column. Such analyses can be completed in a few minutes, a matter of some importance if many samples are to be handled.

On the grounds of familiarity with the technique and the speed of analysis afforded, gas chromatography was adopted as the means of determining the percentage composition of the labelled gas mixtures. In addition, as determination of the individual activities of the carbon monoxide and carbon dioxide also necessitated their separation, it seemed obvious to take advantage of the separation of these constituents achieved in the gas-chromatographic column.

For measuring the activity of the chromatographically separated components, various procedures were available. The activity of the gas from the column could be continuously monitored by a suitable radiation detector, operated in conjunction with a ratemeter and recorder. Alternatively, the active components could be separately trapped out from the gas stream; counting in gas, liquid or solid forms could then be applied as desired. The different techniques employed in the gas-chromatographic separation of radioactive compounds have recently been reviewed by Adloff.[2]

For the work described here, continuous monitoring of the effluent gas would have required additional specialised counting equipment, and this approach was rejected in favour of isolation of the active components. The carbon monoxide, which was the first to emerge from the column, was oxidised to carbon dioxide with heated copper oxide and then frozen out in a cold trap, to which sodium hydroxide solution had initially been added. The carbon dioxide component was later isolated in a similar trap. After the traps had been warmed to room temperature, the activity of the solution in each trap was determined by a direct counting method.

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This procedure has proved satisfactory in use over 2 years. The speed of the gas-chromatographic separation is of particular advantage, and an analysis can be completed in 40 to 60 minutes, depending on the time required for counting.

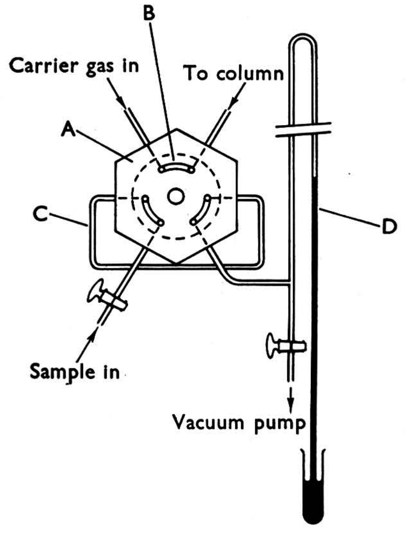
The development of this procedure involved investigations into the gas chromatography of active mixtures and into the counting of aqueous solutions containing carbon-14. These investigations are described below, preceded by an account of the apparatus and of the analytical procedure finally evolved.

APPARATUS

GAS-CHROMATOGRAPHIC APPARATUS—

The gas-chromatographic apparatus used was made in our laboratories and was similar to that previously described.[1] The analytical column was a 6-foot length of ¼-inch internal diameter stainless-steel tubing of 20 s.w.g. wall thickness, packed with 36- to 52-mesh silica gel that had been heated *in vacuo* before being packed into the column. A second packed column was used to obtain a parallel flow of carrier gas to serve as a reference gas for the detector. The columns were maintained at 100° C by an electrically heated steam-jacket. The carrier gas was argon, supplied from a cylinder and dried by passage over pellets of molecular sieve (Linde type 5A); the flow rate through each column was 30 ml per minute. The detector was a katharometer, made as previously described,[1] in which the sensitive elements were tungsten filaments. The signal from the katharometer, after attentuation by known factors, if required, was fed to a potentiometric recorder so that the heights of recorded chromatographic peaks could be measured. In addition, an attachment was made to the recorder so that the mechanical movement of the recorder pen produced, from a slide wire, a voltage proportional to the pen deflection; application of the voltage produced to an indicating integrating motor (Electromethods Ltd., Stevenage) permitted automatic reading of the "areas" of chromatographic peaks.

The gas-sampling system, incorporating a valve of the type previously described,[1] is shown in Fig. 1. With the valve in the position shown, the carrier gas passed directly to the column; at the same time the sample inlet was connected to a detachable sample loop of known volume and thence to a mercury manometer and to a vacuum pump. The sample loop was evacuated, and then the sample gas was admitted to the desired pressure. Rotation of the valve through 60° then allowed carrier gas to pass through the loop and sweep the sample on to the column, with minimal interruption in the flow of carrier gas.



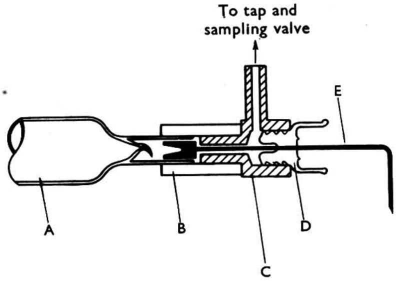
A = Sampling valve body
B = Groove in rotating valve head
C = Detachable loop
D = Manometer

Fig. 1. Gas-sampling system, showing valve in sampling position

The gas samples to be analysed were usually in silica bulbs provided with a break-seal. To permit portions of the gas to be withdrawn without admitting air, the break-seal end of a bulb was connected by pressure tubing to a sampling head of the type shown in Fig. 2. The sampling head had a side-arm connected via a tap to the gas-sampling system described above. The end of the sampling head was closed with a rubber serum cap through which passed a steel wire with a shaped end-piece. In operation, the sampling head was evacuated simultaneously with the sample loop, and the tap between the sampling head and the gas-sampling valve was then closed. The steel wire was twisted to break the break-seal, and gas was admitted to the sample loop as required.

TRAPPING SYSTEM—

A two-way tap was fitted at the point where the gas stream from the analytical column emerged from the katharometer block. With the tap in one position, the gas passed directly to a trap cooled in liquid oxygen, to freeze out the carbon dioxide component. (Liquid nitrogen, if used, would condense the argon used as carrier gas.) With the tap in the other position, the gas passed over copper oxide at 500° C, to oxidise carbon monoxide to carbon dioxide, and thence to a second cold trap to isolate the carbon monoxide component. The copper oxide was in the form of a roll of copper gauze, oxidised by prior heating in oxygen and contained in a length of silica tubing of 3 mm internal diameter that was heated over a length of 4 inches by an external winding of Nichrome wire. To facilitate control of the apparatus, the volumes of tubing (glass and poly(vinyl chloride)) between the katharometer block and the traps were kept small, so that only a few seconds would elapse between emergence of a constituent from the column (as detected by the katharometer) and its arrival in the appropriate trap.



A = Bulb
B = Pressure tubing
C = Brass fitting
D = Rubber serum cap
E = Steel wire with shaped end-piece

Fig. 2. Sampling head used with sealed bulbs

The traps, of borosilicate glass, were of the type shown in Fig. 3; their design was based on that of traps used to freeze out small amounts of carbon dioxide in the determination of carbon in steel by the "low pressure" method.[3] Sodium hydroxide solution was added to each trap before connection to the apparatus, so that the trapped active component was finally obtained as an alkaline aqueous solution. In use the traps were immersed in liquid oxygen up to the bottom of the joint. A vacuum grease was used on the joint of each trap, and, in addition, the joint was held in place with springs (not shown in Fig. 3). There was thus no risk of loosening the joint when the traps were held by the inlet and exit tubes for the purpose of manipulating the traps in and out of the liquid oxygen.

COUNTING CELL AND COUNTING EQUIPMENT—

The active aqueous solutions obtained in the traps on re-warming to room temperature were counted in a specially constructed cell, which is shown in Fig. 4. The main body of the cell was turned from 2-inch diameter Perspex rod. The base consisted of a disc of NE102 plastic phosphor, 0·005 inch thick (Nuclear Enterprises Ltd.), cemented to a $\frac{1}{16}$-inch thick Perspex disc; amyl acetate was used as the cementing solvent. The base was in turn cemented to the main body of the cell. The dimensions of the cell were chosen to permit use in an Ekco

N664 scintillation counter, operated in conjunction with an Ekco N530 scaler. It was found appropriate to use the same instrumental settings as used for scintillation counting of carbon-14 in toluene-2,5-diphenyloxazole solutions, namely: E.H.T., 1100 volts; gain, 1000 ×; discriminator setting, 17 volts.

METHOD FOR ANALYSING ^{14}CO - ^{14}CO$_2$ MIXTURES

PROCEDURE—

The bulb containing the gas sample to be analysed was connected to the sampling head (see Fig. 2), and the sample loop and sampling head were evacuated with the vacuum pump. The tap between the pump and the sampling system was then turned off and the system allowed to remain evacuated for several minutes to check for possible leaks.

Meanwhile, 5 ml of 0·1 N sodium hydroxide were placed by pipette into each of two dry traps, the traps were re-assembled and their taps closed. Each trap was dipped for a few seconds into liquid oxygen, removed and swirled, and the process was repeated until the sodium hydroxide solution had frozen in a thin layer on the wall of the trap tube. (Freezing in this manner avoided cracking the tubes.) The two traps were connected to the gas-chromatographic apparatus, immersed up to the bottom of the joint in liquid oxygen, and in turn purged of air with the flow of carrier gas from the column. The taps of the carbon dioxide

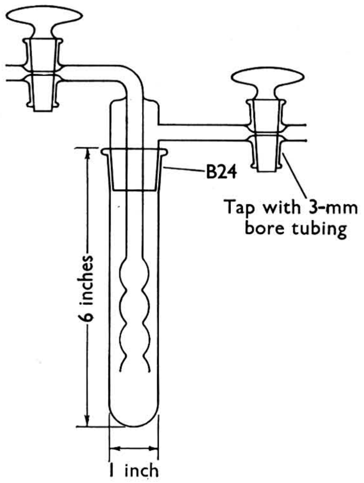

B24
Tap with 3-mm bore tubing
6 inches
1 inch

Fig. 3. Trap for freezing out carbon dioxide

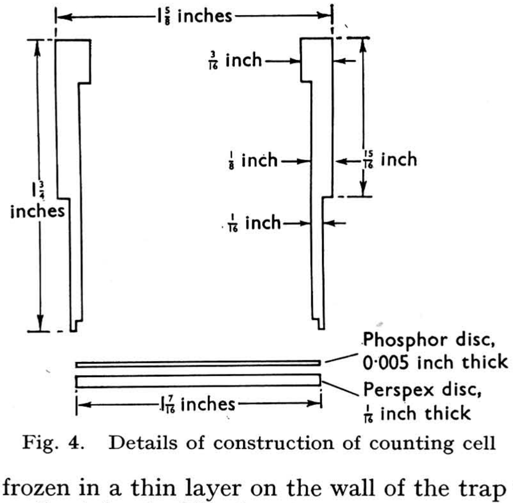

1$\frac{5}{8}$ inches
$\frac{3}{16}$ inch
$\frac{1}{8}$ inch
$\frac{15}{16}$ inch
1$\frac{3}{4}$ inches
$\frac{1}{16}$ inch
Phosphor disc, 0·005 inch thick
Perspex disc, $\frac{1}{16}$ inch thick
1$\frac{7}{16}$ inches

Fig. 4. Details of construction of counting cell

trap were then closed, and carrier gas was allowed to continue flowing through the carbon monoxide trap.

The break-seal of the sample bulb was then broken, and gas was admitted to the sample loop to the required pressure as shown on the manometer. (With a sample loop of volume about 1·5 c.c., sample pressures of about 200 mm of mercury were generally used, if sufficient sample was available). The sample gas in the loop was then injected into the column by operating the gas-sampling valve. The air temperature near the sample loop, assumed to be the same as that of the sample, was noted at this point.

Any carbon monoxide present in the sample was shown by a peak on the recorder chart occurring 1¼ minutes after injection of the sample. After a further 2 minutes, *i.e.*, 3 to 3½ minutes after injection, the taps were operated to divert the effluent gas from the column to the carbon dioxide trap, and the taps of the carbon monoxide trap were closed. The carbon dioxide peak was recorded about 4½ minutes after injection, and the gas stream was allowed to flow through the carbon dioxide trap for a further 2 minutes after the peak had been recorded.

While the carbon dioxide was being eluted, the exit tube of the carbon monoxide trap was connected to the vacuum pump via a capillary "leak." The exit tap of this trap was opened for a brief period, then closed and the vacuum connection removed. (It was necessary to remove most of the argon present in the trap, so that undue pressure would not result on subsequent re-warming of the trap to room temperature; the capillary leak restricted the flow of gas, so that small particles of solid carbon dioxide would not be blown out of the trap.) The trap was removed from the liquid oxygen and re-warmed to room temperature by immersion for a few minutes in warm water. Finally, the trap was shaken mechanically for 5 minutes to dissolve any carbon dioxide that was now in the gaseous form. The same series of operations was applied to the carbon dioxide trap.

For counting, most of the solution from a trap was transferred to the counting cell by means of a dry pipette (quantitative transfer is unnecessary, but dilution must be avoided). Fifty milligrams of a dye, Naphthalene Leather Carbon G.S. (Imperial Chemical Industries Ltd.), were added to the cell, and the solution was swirled to dissolve the dye. The cell was then transferred to the scintillation counter and the solution counted. Each count was corrected for the background count of the cell, determined by counting 5 ml of 0·1 N sodium hydroxide with 50 mg of dye in the cell. The background count was measured for each series of determinations, usually during the preliminary preparations of the chromatographic apparatus.

At least two, usually three, analyses were made on each gas sample. By having traps available, replicate analyses could be performed in rapid succession, the solutions from one analysis being counted during the chromatographic stage of the subsequent analysis. After use, the traps were well washed with water, then with acetone, and dried by drawing air through them. After each count the counting cell was washed well with water and dried with tissues; the cell was then ready for re-use.

CALCULATION OF RESULTS AND CALIBRATION—

The percentage of the minor constituent (usually carbon monoxide) was obtained by correcting the observed peak heights, peak areas, or both, to a standard sample pressure and temperature, then reading off the percentage from a calibration graph prepared by chromatographic separation of inactive gas mixtures of known composition. The percentage of the major constituent was usually obtained by difference. (Traces of nitrogen and hydrogen were sometimes present, but invariably in insignificant amounts.)

As discussed later, the counting technique used was such that the observed count rate, corrected for background, was proportional to the concentration of carbon-14 in the solution, regardless of the volume of solution added to the cell. The cell factor f (the net count rate given by a carbon-14 concentration of 1 μC per ml) was determined by counting a solution of sodium ^{14}C-carbonate of certified activity (nominally 1 μC per g) obtained from the Radiochemical Centre, Amersham.

If the solution from a trap gave a count rate r (corrected for background), then the total activity (in μC) in the trap was 5r/f, the total volume of the trap solution being 5 ml. The specific activity of a constituent, in μC per standard c.c., was then given by the expression—

$$\frac{5\mathrm{r}}{\mathrm{f}} \times \frac{760\,(273 + t)}{V \times p \times 273} \times \frac{100}{\mathrm{P}},$$

where P was the percentage of the constituent, and V in c.c., p in mm of mercury and t in degrees C were, respectively, the volume, pressure and temperature of the gas sample. Of these quantities, V was kept constant by using the same sample loop throughout the work.

COUNTING OF CARBON-14 IN AQUEOUS SOLUTION

Isolation of the active constituents as aqueous solutions was adopted because direct counting of the solutions appeared to offer the minimum amount of manipulation compared with counting in gas or solid form. The counting technique used was essentially that proposed by Jenkinson[4] and which appeared particularly appropriate to the work described here.

In the counting cell made by Jenkinson and in the cell used in this work, the scintillations detected by the counter occur in the thin layer of plastic phosphor that forms the inner side of the base of the cell. Because of the short range in water (< 1 mm) of the soft beta radiation of carbon-14, only the activity present in a thin layer of solution adjacent to the phosphor contributes to the observed count rate. This resembles the condition of "infinite thickness" in solid counting, from which it might be expected that the count rate would be proportional to the concentration of activity in the solution and be independent of the volume. However, Jenkinson observed some variation of count rate with different volumes of the same solution. He attributed this to variations in the extent to which light emitted upwards by the phosphor layer was re-directed to the counter by internal reflection in the solution. Jenkinson therefore added a dye to eliminate transmission of light through the solution; the count rate was then proportional to the specific activity of the solution and independent of the volume counted.

This property is an advantage in our work. The shape of the inner member of each trap, designed to give a large cold surface, was such that quantitative transfer of a solution from a trap would inevitably result in considerable dilution due to the addition of washings. By using Jenkinson's counting technique, any indefinite volume of the trap solution could be transferred to the cell for counting, provided, of course, that sufficient solution were added to cover the base of the cell.

Some experiments on this counting technique, relevant to the analysis of carbon-14 monoxide - carbon-14 dioxide mixtures, are described below.

PRELIMINARY EXPERIMENTS—

The first experiments were directed toward establishing the conditions under which consistent count rates could be obtained for a solution, independent of the volume counted. For this purpose, different volumes of sodium ^{14}C-carbonate solution, with and without dye, were counted. As recommended by Jenkinson,[4] the dye used was Naphthalene Leather Carbon G.S.

The results obtained (see Table I) confirmed Jenkinson's observations[4] that count rate varied with volume in the absence of dye, and that count rates independent of volume were obtained with 0·1 per cent. w/v of dye, this concentration not being critical. It was apparent that use of the dye only slightly reduced the counting efficiency.

TABLE I

PRELIMINARY EXPERIMENTS ON COUNTING OF $Na_2{}^{14}CO_3$ SOLUTION

Volume of solution counted, ml	Concentration of dye, % w/v	Count rate, c.p.s.
3	0	187·2
5	0	183·9
10	0	180·1
3	0·05	176·0
3	0·1	178·0
3	0·15	177·7
5	0·1	177·2
7·5	0·1	177·2
10	0·1	176·7

EFFECT OF CONCENTRATION OF ALKALI—

Jenkinson[4] reported that increased concentrations of inactive solute caused some reduction in count rate, presumably by a self-absorption effect. In the work described in this paper, the effect on count rate of different concentrations of alkali was investigated. A dilute solution of sodium ^{14}C-carbonate was counted after various amounts of inactive sodium hydroxide or carbonate solution had been added, the observed count rates being corrected for the resulting dilutions; the concentration of dye was 0·1 per cent. w/v in all solutions counted. The results in Table II showed a progressive reduction in corrected count rate with increasing concentration of alkali. It was however apparent that if 0·1 N solutions were used, appreciable relative variations in concentration would have negligible effect on count rate. For absorption of the carbon dioxide from the size of gas sample customarily used (1·5 c.c. at 200 mm pressure), 5 ml of 0·1 N sodium hydroxide would provide a substantial excess, and 0·1 N sodium hydroxide was adopted as the medium for counting.

TABLE II

EFFECT OF INACTIVE ALKALI CONCENTRATION ON COUNT RATE OF AN $Na_2{}^{14}CO_3$ SOLUTION

Alkali added	Concentration of added alkali in solution counted, N	Count rate, % of count rate without added alkali
Sodium hydroxide ..	0·10	99·8
	0·17	99·2
	0·27	98·8
	0·50	98·8
	1·0	97·8
Sodium carbonate ..	0·10	99·8
	0·18	99·4
	0·33	98·9
	0·67	97·5
	1·0	96·9

CALIBRATION AND COUNTING EFFICIENCY—

Calibration of the cell has been effected, as described on p. 765, by counting a sodium ^{14}C-carbonate solution of certified activity. The first cell used in this work gave, on first calibration, a cell factor of 330 c.p.s. (the count rate for 1 μC of carbon-14 per ml). A second cell gave a similar factor. As the same count rate is obtained with different volumes of the same solution, the counting efficiency achieved depends on the volume of solution counted. With 5 ml of solution, the cell factor quoted above corresponds to a counting efficiency of 0·2 per cent. This relatively low efficiency was no disadvantage in the work described here, the main virtue being the simplicity of the counting technique. The gas samples to be analysed contained several μC of carbon-14 per standard c.c., so that sizable count rates, *e.g.*, of the order of 100 c.p.s. for the main constituent, were usually obtained.

With a cell in almost daily use, it has been found that the base tends in time to become slightly opaque, possibly owing to weakening of the adhesion between the plastic phosphor layer and the underlying Perspex. Possibly for this reason the counting efficiency of a cell decreases in time, and it is advisable to re-calibrate a cell every few months.

Jenkinson stated that high background count rates with his cell could arise either from undue exposure of the cell to light or from use with neutral or acid solutions, hence his recommendation that all solutions be made alkaline with sodium hydroxide before counting.[4] In one cell used by us, the latter effect was observed in attempting to count a solution containing carbon-14 labelled sucrose. The former effect has not been observed; handling of the cell in daylight or normal lighting conditions has invariably given background counts indistinguishable from that of the scintillation counter with no sample present (0·5 to 0·6 c.p.s.) The precaution has, however, been taken of storing the cell in the dark when not in use.

GAS CHROMATOGRAPHY OF THE LABELLED GAS MIXTURES

In developing the gas-chromatographic part of the procedure described, particular attention was directed to assessing the efficiency of the trapping system, to examining the possibility of "trailing" of active constituents from the column and to determining the precise volume of gas sample analysed. These points are discussed below.

EFFICIENCY OF THE TRAPPING SYSTEM—

The efficiency of the cold traps for freezing out carbon dioxide was tested by putting samples of carbon-14 dioxide through the gas-chromatographic procedure, two traps in series being used. In two runs on slightly different amounts of sample, count rates of 48·3 and 45·5 c.p.s. were obtained for the solutions from the first trap, corresponding, respectively, to

2·56 and 2·57 μC per standard c.c. for the specific activity of the gas; in each test the second trap yielded no detectable activity ($< 0·1$ c.p.s.).

These and other results showed that a single cold trap gave quantitative removal of carbon dioxide from the steam of carrier gas. However, to ensure complete removal of the carbon monoxide component, it was also necessary to achieve its complete oxidation to the dioxide on passage through the heated copper oxide. The efficiency of the oxidation process was checked by putting samples of inactive carbon monoxide through the gas-chromatographic process and collecting the carrier gas emerging from the copper oxide tube during the period when the carbon monoxide was being eluted from the column. Analysis of the collected gas showed that quantitative oxidation of the carbon monoxide was being obtained.

EXAMINATION FOR TRAILING EFFECTS—

Under the conditions employed in the method, the peaks of carbon monoxide and dioxide occurred, respectively, at 1¼ and 4½ minutes after injection of the sample. For the first 3 or 3½ minutes after injection, the gas from the column was passing into the carbon monoxide trap; thereafter, until 2 minutes after the end of the carbon dioxide peak (as observed on the recorder chart) the gas was passing into the carbon dioxide trap.

With this system, any trailing, *i.e.*, the slow release of a constituent from the column after the main peak had passed, could result in incomplete recovery of the activity. In addition, trailing of the carbon dioxide could result in activity from this constituent being included in the carbon monoxide fraction of a succeeding analysis. It was therefore important to ascertain whether or not trailing occurred to any significant extent.

With a comparatively new column being used, a sample of carbon-14 dioxide was passed through the gas-chromatographic apparatus, the carbon dioxide trap being replaced at intervals after the peak had been recorded. Only an extremely small amount of activity, negligible when compared with the total amount present, was recovered after the normal period of collection (see Table III). A similar test with carbon-14 monoxide, though less sensitive because of the smaller amount of activity used, showed no evidence of trailing (see Table III).

It was apparent from these results that trailing was unlikely to be a significant source of error when a fairly new column was used. It is, however, well known that trailing may become more evident with continued use of a column. In this and related work it has been found that trailing and other adverse effects may necessitate renewal of the columns after about 6 months. (The life of a column appears to be largely a function of time, rather than of frequency of use, possibly because of our practice of maintaining a slow flow of carrier gas through a column when it is not in use.) It may be of interest to note that chromatography of active gases can be made an extremely sensitive means of detecting trailing.

TABLE III

EXAMINATION FOR TRAILING EFFECTS

Sample used	Period of collection of active constituent	Count rate of trap solution corrected for background, c.p.s.
Carbon-14 monoxide ..	Up to 2 minutes after CO peak	13·4
	2 to 5 minutes after CO peak	<0·1
	5 to 10 minutes after CO peak	<0·1
Carbon-14 dioxide ..	Up to 2 minutes after CO_2 peak	159
	2 to 5 minutes after CO_2 peak	0·2
	5 to 10 minutes after CO_2 peak	<0·1

DETERMINATION OF SAMPLE VOLUME—

The same sample loop, of measured volume 1·42 c.c., was used for all determinations. However, this volume did not represent the total volume of gas sample analysed, a small additional amount of gas being present in the connections inside the gas sampling valve (see Fig. 1). This additional volume was known, from the construction of the valve, to be about 0·15 c.c. For determining the percentage composition of gases, the presence of this additional volume of sample was irrelevant, as the same total volume of gas would be used both in analysis and in calibration with gases of known composition. However, to permit calculation of the specific activity of constituents, in μC per standard c.c., it was essential to know the precise volume of gas sample analysed.

The additional volume of gas in the valve was determined indirectly. Samples of active and of inactive carbon dioxide were submitted to the chromatographic process, with the use of both the normal sample loop and a small loop of volume (0·253 c.c.) similar to that in the valve. At a given sample pressure, the ratios of peak areas and of amounts of activity found were assumed to be proportional to the ratio of sample volumes used, *i.e.* $(1·42 + x)/(0·253 + x)$, from which x, the volume of gas in the valve, could be calculated. Four such determinations gave values of 0·15, 0·15, 0·18 and 0·19, the mean value of 0·17 c.c. being taken. This value was consistent with the expected volume of about 0·15 c.c.

With the normal loop, of volume 1·42 c.c., the total sample volume was therefore taken to be 1·59 c.c. This value was thought to be accurate to within about 1 per cent. Because of the expected accuracy of the activity measurements, a much greater accuracy in measuring the precise sample volume would have been superfluous.

RESULTS

The results obtained on a sample of carbon-14 dioxide are shown in some detail in Table IV, in which sample pressures and temperatures and also the observed count rates are listed.

TABLE IV

RESULTS ON A SAMPLE OF $^{14}CO_2$

Sample pressure, mm of Hg	Temperature, °C	Count rate of trap solution, c.p.s.	Count rate corrected for background, c.p.s.	Specific activity of CO_2, µC per standard c.c.
151	30	48·9	48·3	2·56
142	30	46·1	45·5	2·57
92	31	28·8	28·2	2·46
135	26	44·2	43·6	2·55
101·5	31·5	32·6	32·0	2·54

This particular sample was of lower specific activity than normally used, giving rise to lower count rates than normally observed. The sample, in which no carbon monoxide was detected, was subjected to the analytical process primarily to assess the precision obtainable in that part of the process involving the trapping of the carbon dioxide and the measurement of activity.

To illustrate the precision obtained in the analysis of mixtures, in which an additional possible source of error arises from the determination of percentage composition, the results of analyses of a typical series of samples are shown in Table V. Each figure quoted for the

TABLE V

RESULTS FOR A TYPICAL SERIES OF ^{14}CO - $^{14}CO_2$ MIXTURES

Sample number	Carbon monoxide present, %	Specific activity of CO (A), µC per standard c.c.	Specific activity of CO_2 (B), µC per standard c.c.	Ratio of specific activities B/A
1555	$\left.\begin{matrix}30·5\\31·3\end{matrix}\right\}30·9$	$\left.\begin{matrix}5·2\\5·2\end{matrix}\right\}5·2$	$\left.\begin{matrix}5·29\\5·31\end{matrix}\right\}5·3$	1·02
1552	$\left.\begin{matrix}14·0\\13·7\\13·8\end{matrix}\right\}13·8$	$\left.\begin{matrix}5·65\\5·85\\5·75\end{matrix}\right\}5·75$	$\left.\begin{matrix}6·05\\6·03\\5·96\end{matrix}\right\}6·0$	1·04
1553	$\left.\begin{matrix}10·1\\9·9\\10·0\end{matrix}\right\}10·0$	$\left.\begin{matrix}5·95\\5·9\\5·75\end{matrix}\right\}5·85$	$\left.\begin{matrix}6·14\\6·19\\6·10\end{matrix}\right\}6·15$	1·05
1547	$\left.\begin{matrix}7·9\\7·75\\7·8\end{matrix}\right\}7·8$	$\left.\begin{matrix}5·9\\6·25\\6·3\end{matrix}\right\}6·15$	$\left.\begin{matrix}6·21\\6·25\\6·38\end{matrix}\right\}6·3$	1·02
1549	$\left.\begin{matrix}7·1\\7·2\\7·15\end{matrix}\right\}7·15$	$\left.\begin{matrix}5·85\\5·95\\6·0\end{matrix}\right\}5·95$	$\left.\begin{matrix}6·31\\6·13\\6·16\end{matrix}\right\}6·2$	1·04
1546	$\left.\begin{matrix}6·6\\6·65\\6·65\end{matrix}\right\}6·65$	$\left.\begin{matrix}5·8\\6·1\\6·2\end{matrix}\right\}6·05$	$\left.\begin{matrix}6·28\\6·30\\6·19\end{matrix}\right\}6·25$	1·03
1548	$\left.\begin{matrix}5·65\\5·55\end{matrix}\right\}5·6$	$\left.\begin{matrix}6·0\\6·0\end{matrix}\right\}6·0$	$\left.\begin{matrix}6·50\\6·41\end{matrix}\right\}6·45$	1·07

percentage carbon monoxide was the mean of the two values deduced from the height and from the area of the peak; for calculating the specific activity of the carbon dioxide, the percentage of carbon dioxide was taken by difference.

The gas samples referred to in Table V were from reactor-irradiated bulbs that had originally contained only graphite and labelled carbon dioxide, the carbon monoxide found being a product of the radiation-induced reaction between graphite and carbon dioxide. The carbon monoxide, being partly derived from the carbon of the unlabelled graphite, would be produced at a specific activity lower than that of the carbon dioxide; in addition, interchange of activity between the two gaseous constituents would arise from the radiation-induced exchange reaction—$^{14}CO_2 + CO \rightleftharpoons {}^{14}CO + CO_2$. At equilibrium, the ratio of specific activities of the two constituents is equal to the equilibrium constant for the exchange reaction. The results in Table V show essentially constant values for the ratio of specific activities of carbon dioxide and carbon monoxide, the mean ratio being **1·04**. This figure is in excellent agreement with the value of **1·03** ± 0·008 for the equilibrium constant of the exchange reaction, reported by Stranks.[5]

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The Determination of Oxygen in Vacuum-melted Steels, Molybdenum and Single-crystal Silicon by Vacuum Fusion

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The equipment and techniques used for determining oxygen in vacuum-melted steels, molybdenum and single-crystal silicon by vacuum fusion, at levels down to less than 1 p.p.m., are described.

The oxygen content of steels at levels of 115 p.p.m. and 6 p.p.m. has been determined with coefficients of variation of 2·3 and 5·2 per cent., respectively. Results on sintered and arc-cast molybdenum with oxygen levels of 42 p.p.m. and 2 p.p.m. showed coefficients of variation of 2 and 8 per cent., respectively.

Experiments with zone-refined molybdenum indicated that the oxygen content consisted of a residual surface contamination of 0·8 μg per sq. cm with an internal oxygen content of less than 0·2 p.p.m. With vacuum grown single-crystal silicon a coefficient of variation of 10 per cent. at a level of 17 p.p.m. was obtained on a limited sample weight of 0·5 g.

A COMPREHENSIVE account of the vacuum fusion method of analysis and its applications has been given by Sloman.[1 to 7] In recent years developments of the technique have been concentrated chiefly along two lines of research, *viz.*, analyses of the rarer metals (beryllium, molybdenum, tantalum, titanium, tungsten, etc.) and greater accuracy and precision in determining low levels of oxygen content. Progress in the latter field, however, still lags behind metallurgical requirements, and dissatisfaction has been expressed[8,9] at the lack of precision and accuracy obtainable at low levels of oxygen content (0 to 20 p.p.m.) in the vacuum-fusion analysis of steel and molybdenum.

Little evidence is available in the literature for reproducibilities of determinations of oxygen of below 100 p.p.m. Lassner and Wölfel[10] have obtained a coefficient of variation of 6·1 per cent. on six samples of sintered molybdenum with a mean value of 30 p.p.m., and Mallet and Griffith[11] have demonstrated the internal consistency of the method below 40 p.p.m. to within ±1 p.p.m. on samples of molybdenum spiked with molybdenum powder. McDonald and Fagel[12] have determined oxygen in molybdenum by vacuum extraction at 2000° C and by vacuum fusion in a tin - iron bath. By vacuum extraction they obtained a mean of 7·6 p.p.m. on eleven samples with a coefficient of variation of 36 per cent.; by vacuum fusion the coefficient of variation was 21 per cent. on a mean of 7·3 p.p.m. on four samples of the same material.

Many of the results quoted indicated that the method was reliable for steel, although, recently, Pearce and Masson[13] working on the method of isotopic dilution have produced evidence suggesting that the results obtained by vacuum fusion analysis of steels were seriously in error below 200 p.p.m. owing to adsorption of the evolved gases on the cooler parts of the apparatus. However, their experiments do not appear to be conclusive, and their conclusions conflict with the main body of evidence[6,7,14,15] and our experience. Recent work by Coleman[16] on fast neutron-activation analysis has also confirmed the reliability of vacuum-fusion analysis on two of the samples quoted by Pearce and Masson.

The object of the work described here was to develop the technique for determining oxygen in vacuum-melted steels, sintered, arc-cast and zone-refined molybdenum and single-crystal silicon, all with an oxygen content below 100 p.p.m. It was considered that, to meet the needs of the metallurgist, a method having a coefficient of variation of not more than 10 per cent. was required at levels down to 1 p.p.m.

APPARATUS

GENERAL—

The vacuum fusion apparatus (see Fig. 1) was similar in its basic design to that described by Gray and Davis.[17] Use was made of Sloman's design of crucible and furnace assembly and the principles of Ransley's low pressure analysis system.[18,19] The measuring system has been described previously by Bacon[20] and was designed to measure volumes of gas from 0·005 to 2·0 ml with a precision of ±1 per cent. by using a McLeod gauge and a series of expansion volumes that permitted the pressure to be kept within that of the maximum precision of the McLeod gauge by varying the capacity of the collecting volume.

MEASURING AND ANALYTICAL SYSTEMS—

The minimum collecting volume normally used was 917 ml, although the smaller volume of 692 ml could be used by excluding the McLeod gauge and using the Pirani for pressure measurements. This was done for determining the blank rate or for analysing small samples (below 2 g) with extremely low contents of gas (below 2 p.p.m.). The collecting volume could be increased to 21 litres in steps, increasing each time by a factor of approximately 2, by means of expansion volumes. The collecting volumes were calibrated volumetrically by adding water and checked by means of expansion ratios. The results agreed to within 1 per cent.

Two pressure gauges were used, a McLeod for making accurate measurements and a Pirani for making rapid measurements, determining precise pressure ratios and registering the gas evolution and so following the course of the reaction. The McLeod gauge had two pressure ranges, 0 to 70 $\times 10^{-3}$ to r and 0 to 300 $\times 10^{-3}$ torr. The fine scale had both linear and square-law calibration. The linear range, which was based on a compression ratio of 2000 to 1, had 1-mm graduations corresponding to 0·5 $\times 10^{-3}$ torr pressure increments. Repeated observations of the pressure with this scale showed the reading error to be no more than 0·5 mm (0·25 $\times 10^{-3}$ torr). Used in the range 25 to 70 $\times 10^{-3}$ torr the gauge had, therefore, a maximum reading error of 1 per cent.

The Pirani gauge had a normal G.E.C. gauge head and was operated with a potential of 4 volts across the bridge. The out-of-balance current was recorded on a milliammeter with 1 mA full-scale deflection and an eye sensitivity of 1 μA. Three pressure ranges were provided by means of shunts. The first two were linear over their full ranges, which were 0 to 7 $\times 10^{-3}$ torr and 0 to 35 $\times 10^{-3}$ torr, and the third scale, which was non-linear, was used merely as a guide for pressure in excess of 35 $\times 10^{-3}$ torr. Pressure ratios, obtained by readings of near full-scale deflection on the linear scales, had a theoretical reproducibility of 0·1 per cent., and results close to this were obtained in practice. For readings less than full scale, correspondingly larger percentage variations were of course obtained. In practice, the coarser scale (0 to 35 $\times 10^{-3}$ torr) was preferred, as slight pressure changes due to adsorption and mechanical disturbances had less effect at the higher pressures.

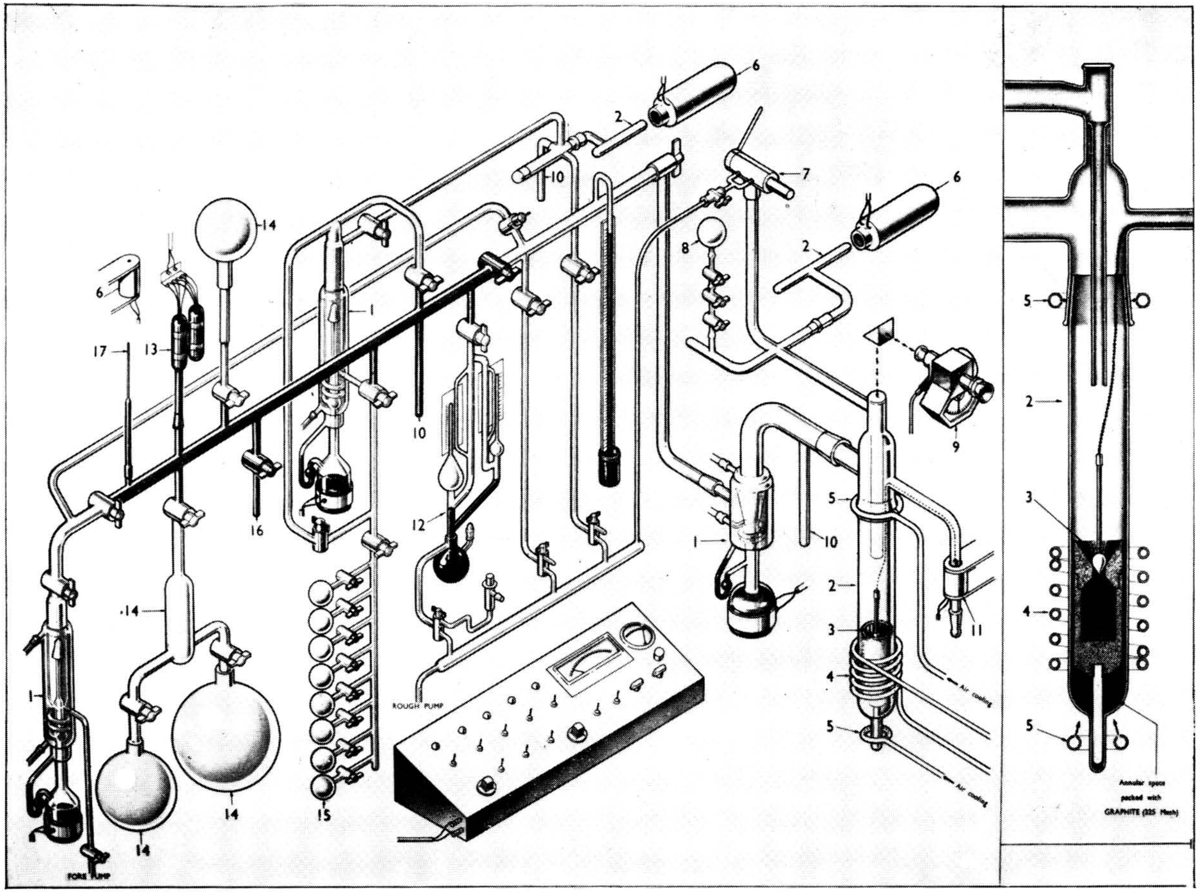
NEW FEATURES AND IMPROVEMENT OF TECHNIQUE AND DESIGN—

A summary is given below of the new features introduced and modifications in technique and design.

(*a*) The furnace head was re-designed in Pyrex glass and a fast mercury diffusion pump (rated at 30 litres per second) joined into the head with wide bore tubing (greater than 45 mm internal diameter) to allow rapid removal of the gases from the furnace tube. A positive means of guiding samples into the crucible was provided, and the optical flat was largely screened from the crucible to avoid blackening by carbon and metallic films.

(*b*) An ultra-pure grade of graphite was used (208 spectrographic, obtainable from Le Carbone (Gt. Britain) Ltd., 64 Finsbury Pavement, London, E.C.2). This allowed more rapid de-gassing and lower ultimate blank rates than could be obtained with normal "pure" graphite.

(*c*) A vacuum lock was incorporated to replace the mercury lift used in earlier work. This provided a rapid and convenient means of introducing all types of samples directly into the high-vacuum system. The lock was a scaled-up version of that described by Parker,[21] with the addition of vacuum connections to the gaps between the


6
2
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17
13
1
10
16
12
1
5
10
2
3
4
5
11
Air cooling
Air cooling
ROUGH PUMP
FORE PUMP
14
14
14
15
5
2
3
4
5
Annular space packed with GRAPHITE (325 Mesh)

1. Two-stage mercury diffusion pump
2. Silica furnace tubes
3. Graphite crucible assembly
4. Induction heating coil
5. Air cooling
6. Resistance furnaces
7. Vacuum lock
8. Gas sample bulb
9. Optical pyrometer
10. Cold fingers
11. Stopper-raising coil
12. McLeod gauge
13. Pirani gauge head
14. Expansion volumes
15. Gas storage bulbs
16. Hopcalite bulb
17. Palladium thimble

Fig. 1. Schematic diagram of vacuum fusion apparatus

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O-rings. Little air entered the system with the samples, and no change was detected in the furnace blank rate after the lock had been used.

(*d*) A silica furnace tube in which samples could be heated to 1000° C was attached to the sample storage arm. Pre-heating removed much of the surface contamination and also greatly reduced the hydrogen content of samples. This allowed a more precise and accurate determination of the oxygen content, particularly on samples containing relatively large amounts of hydrogen or having an extremely low oxygen content.

(*e*) A gas "doser" was connected to the system to introduce different amounts of a gas of known composition into the apparatus to study gettering problems. This apparatus consisted of a 180-ml glass bulb connected to two smaller bulbs of 0·71- and 0·18-ml capacity, by good quality vacuum taps. The secondary volumes were so arranged that either 1/1000 or 4/1000 of the content of the main bulb could be fractionated into the vacuum-fusion system.

(*f*) A series of eight storage bulbs, each of about 110-ml capacity, was connected to the gas-collection system through a mercury diffusion pump. Gas samples could thus be stored during a run and analysed at a more convenient time. A silica furnace tube was also connected to this diffusion pump so that the equipment could be used for determining hydrogen by vacuum extraction.

(*g*) The vacuum-fusion furnace tube was air cooled. This system replaced the water cooling that had been used previously. Little difference was noticed between the two methods, but it seemed preferable to allow the walls of the furnace tube to reach the higher temperatures attained by air cooling as they would be less likely to absorb gases.

(*h*) Two types of induction heater were used; one of 8 kW operating at a nominal frequency of 750 kc/s and the other of 17 kW at a nominal frequency of 5 kc/s. The latter unit was preferred as the lower frequency induced a stirring action in the melt giving a more rapid evolution of gas. Low blank rates were obtained more consistently with this lower frequency as there was no tendency for the graphite powder to pick up induced currents as occurred with the higher frequency, which at times gave rise to "hot spots" and consequent higher blank rates.

(*i*) High-vacuum taps of good quality were used throughout the system in preference to mercury cut-offs. A liquid nitrogen trap was kept on the analytical system while the apparatus was in use, and this served to remove grease vapours, water, carbon dioxide and other condensable substances from the system.

(*j*) A series of four expansion volumes as from 0·7 to 11 litres was incorporated into the collecting system so that the volume could be adjusted to bring the pressure measurements within the region of linearity of the Pirani gauge and close to the pressure of maximum precision of the McLeod gauge.

EXPERIMENTAL

DE-GASSING—

The method of packing the graphite powder and the initial application of heat to the crucible were found to be critical operations, on which the successful de-gassing and the final blank rate were dependent.

Graphite powder (less than 325 mesh) was first compacted in the narrow extension of the furnace tube, to a depth of 0·5 inch. The crucible assembly was then placed in position and held centrally in the tube by means of a jig that fitted into the throat of the crucible. Graphite powder was packed around the crucible as loosely as possible. The furnace tube was then sealed into the head with vacuum wax, the induction heater and air cooling system were switched on, and the crucible was heated to approximately 1400° C. (All temperatures were measured with a disappearing filament optical pyrometer and are uncorrected.) The pressure in the furnace was then reduced by means of the "rough" vacuum pump at a rate of 3 cm per minute to a pressure of 10^{-1} torr, after which the furnace diffusion pump was switched on and the pumping routed through the analytical system. The temperature of the crucible was then raised to 2200° C and the apparatus allowed to de-gas for 3 hours.

BLANK RATES—

The procedures outlined above gave a final blank rate of approximately 1 μl per minute at 2200° C. When the temperature was dropped to 1750° C the blank rate fell to 0·3 μl per minute. Lower blank rates could be obtained by a more prolonged de-gassing period, but were difficult to maintain during a "run." A blank rate of 0·3 to 1 μl per minute was therefore accepted as a working level and was usually maintained if the samples added were of low gas content.

The "blank" gas was fairly constant in quantity and composition, and the results were corrected for this additional gas if it amounted to more than 1 per cent. of the total gas collected from the sample. A typical analysis of "blank" gas gave 75 per cent. of carbon monoxide, 7 per cent. of hydrogen and 18 per cent. of nitrogen.

GAS ANALYSIS—

A sample of the gas to be analysed was isolated in the smallest volume (the analytical section) at a pressure of 25 to 30 × 10^{-3} torr (*i.e.*, nearly full-scale deflection on the coarse Pirani scale). To obtain this reading the pressure of the gas sample could be either reduced by appropriate expansion or increased by pumping the gas from the volumes in which it was contained into the gas storage bulbs and then back into the analytical section. Small adjustments were made by varying the level of the mercury in the McLeod gauge.

The first stage of the analysis was carried out by exposing the gas to Hopcalite reagent contained in the small bulb attached to the analytical system. This oxidised the carbon monoxide to carbon dioxide, which was then removed from the system by condensation in the cold finger (−196° C). The palladium thimble was then heated to 450° C and the hydrogen allowed to diffuse out. The gas remaining was assumed to be nitrogen. The percentages of the three gases present were calculated from the pressure changes on the Pirani gauge. For this calculation the recorded decrease in pressure due to hydrogen was multiplied by a factor of 0·65, since the Pirani has a higher sensitivity for hydrogen than for carbon monoxide and nitrogen, which have similar sensitivities.

A volume of 0·010 ml at S.T.P. was taken for each analysis, 2 minutes were allowed for removal of carbon monoxide and 1·5 minutes for hydrogen diffusion. The time taken for a complete analysis was 4 minutes.

The precision of the analytical system was tested in practice on gas mixtures of known composition, and the over-all coefficient of variation for oxygen was found to be less than 1 per cent. when carbon monoxide formed more than 50 per cent. of the gas collected.

USE OF TIN AS AN "ANTI-GETTER"—

The use of tin as a flux or to overcome gettering is well known, and our experience has confirmed the efficacy of this technique.

The addition of tin (0·1 g) at intervals has been found to overcome the effect of gettering during vacuum fusion analysis, even with steels containing relatively large amounts of manganese, copper, vanadium and other alloy additions, possibly by blanketing the deposited films. Other theories have been advanced,[22] but the mechanism is still somewhat obscure.

ASSESSMENT OF ACCURACY

Direct tests of the accuracy of the method at low levels of oxygen, which were of interest, by preparing and analysing samples of known oxygen content were not considered feasible. Spiking samples with known weights of oxide, although not simulating exactly the conditions encountered in the analysis of a sample, gave an assessment of other stages of the process and was some indication of the accuracy to be expected. In this method the choice of a suitably prepared metal envelope having a low oxygen content, to contain the additions, minimised the objections to this type of evaluation.

EXPERIMENTS ON SAMPLES WITH KNOWN AMOUNTS OF OXIDE ADDED—

Two series of experiments were carried out, one with a steel capsule as a container for silica and the other with nickel foil to contain additions of tantalum oxide. The mean oxygen content of the capsules and the nickel foil was determined by carrying out ten determinations on each material.

Small fragments of drawn silica filament were used for the first series of experiments, and tantalum oxide, prepared from pure tantalum wire ignited at 1000° C in air under conditions in which the form of the wire was retained, was employed for the second series. The increase in weight of the tantalum was found to be that required by the reaction $Ta \rightarrow Ta_2O_5$. The results of these experiments are shown in Table I.

TABLE I

RESULTS

Oxide added	Amount of oxide added, µg	Oxide content determined by vacuum fusion, µg	Equivalent to oxygen in metal on 10-g sample, p.p.m.	Error, %
Silica	92	99	4·9	+7·6
	159	156	8·5	−1·9
	146	153	7·8	+4·8
	194	180	10·4	−7·2
Tantalum oxide ..	260	294	4·7	−13·1
	163	173	2·95	+6·2
	325	316	5·9	−2·7
	280	254	5·1	−9·3
	296	315	5·35	+6·4
	190	215	3·45	+13·1
	220	197	4·0	−10·4
	315	331	5·7	+5·1
	243	263	4·4	+8·3

With the exception of two results the recovery of oxygen from the samples was within about ±10 per cent. of the amount added. The gas evolved from samples of approximately 27 µg of tantalum oxide and 94 µg of silica would be equivalent to that evolved by a 10-g sample of metal containing approximately 5 p.p.m. of oxygen.

OTHER INDICATIONS OF ACCURACY—

The considerations listed below, although not constituting any proof of accuracy, do serve to give added confidence in the validity of the results obtained.

1. At low oxygen levels samples were analysed at two sample weights, usually 10 g and 1·5 g. Agreement between the results indicated satisfactory sample preparation and absence of interference by surface oxide.
2. Similar results were obtained under widely different conditions, for example, molybdenum fused in an iron bath at 1750° C and without a bath at 2200° C (see Table V).
3. Single-crystal silicon gives an absorption band in the infrared at 9 µ due to the oxygen content. The ratio of the mean oxygen contents of the vacuum fusion results for the two silicon samples (see Table VI) was 1·39. This compared reasonably well with the ratio of 1·47 obtained from infrared measurements of the 9-µ band in the two samples.

The results of the experiments detailed above constituted reasonable grounds for considering that the vacuum-fusion process gives results for low levels of oxygen in metals which are accurate within the limits of the standard deviations obtained.

SOURCES OF ERROR IN VACUUM-FUSION ANALYSIS

Consideration was given to possible sources of error in vacuum fusion analysis, and for this purpose the procedure was broken down and examined in four categories.

SAMPLE PREPARATION—

Two possible sources of error were apparent in this procedure, namely errors due to oxide film remaining on the samples, and errors due to removal of internal oxygen by outward diffusion as carbon monoxide during the pre-heating.

Although the possibility of outward diffusion of oxygen had to be considered, it was not thought that this was likely to occur to any great extent under the pre-heating conditions used, and this was shown to be true.

A collection of the gas evolved during the pre-heating period showed that approximately 1·5 µg of oxygen per sq. cm was given off from the samples. Most of this gas was collected during the first 5 to 10 minutes, and heating for more prolonged periods (up to 1 hour) did not produce any appreciable increase in the amount of carbon monoxide collected. Some results obtained on steel and molybdenum are shown in Table II.

TABLE II

EFFECT OF DIFFERENT PRE-HEATING TIMES

Material	Pre-heating time, minutes	Number of determinations	Mean oxygen content, p.p.m.	Standard deviation, p.p.m.	Weight of sample taken, g	Surface area of sample, sq. cm	Approximate amount of oxygen removed from surface, µg per sq. cm
Steel	0	6	6·7	0·25	2	2·2	1·2
	10	6	5·4	0·17	2	2·2	1·2
Molybdenum ..	0	5	4·6	1·2	1·5	1·5	1·9
	10	6	2·7	0·6	1·5	1·5	1·9

The extent of any remaining oxide should be shown up by differences in results obtained on large and small samples of the same material, but the simplicity of results obtained on vacuum-melted steel at the lowest level available (see Table IV), showed that this was not significant. For molybdenum, however, there was evidence (see Table V) of a remaining oxide contamination of about 0·8 µg per sq. cm.

FUSION AND GAS EVOLUTION—

Thermodynamic considerations[6,23] have shown that the solubility of oxygen in an iron bath saturated with carbon at temperatures above 1650° C and in contact with a pressure of carbon monoxide below 10^{-3} torr, is negligible. The similarity of results obtained under different conditions (see Table V) would seem to confirm this conclusion, which has been accepted as the basis of all vacuum-fusion work.

GAS COLLECTION AND ANALYSIS—

The completeness of the gas recovery was checked by using the gas "doser" filled with carbon monoxide to a pressure of 15 cm. This was attached to the sample entry system as shown in Fig. 1. The results are shown in Table III.

TABLE III

RECOVERY OF CARBON MONOXIDE UNDER DIFFERENT CONDITIONS

The gas was collected for 1 minute

Amount of iron as charge in crucible, g	Temperature, °C	Carbon monoxide added, ml	Tin added, g	Carbon monoxide recovered, ml
0	1950	$0{\cdot}067_1$	0·0	$0{\cdot}067_0$
20	1950*	$0{\cdot}067_0$	0·0	$0{\cdot}049_4$
20	1950†	$0{\cdot}067_0$	0·1	$0{\cdot}066_7$

* Temperature maintained for 2 hours.
† Temperature maintained for 2 hours 20 minutes.

These results gave a strong indication that, provided the crucible was not allowed to run for prolonged periods without additions of tin being made, carbon monoxide was recovered quantitatively from the region of the crucible.

So far it has been tacitly assumed that any oxygen present in the samples would be converted to carbon monoxide. This was a reasonable assumption, as the monoxide is by far the most stable oxide of carbon under the conditions of fusion. To confirm that the dioxide was absent, the gas evolved from samples of steel was collected with a solid carbon dioxide - acetone cold trap in position in place of liquid nitrogen. After the gas had been collected this trap was replaced by liquid nitrogen, when in all instances a pressure drop not exceeding 1 per cent. of the total pressure was recorded. Part of this decrease was due to the temperature effect of the liquid nitrogen, but the experiment indicated that, if carbon dioxide was present, it consisted of less than 1 per cent. of the total gas collected (80 per cent. of carbon monoxide). This agrees with the conclusion of other workers[24] who have found that carbon monoxide, nitrogen and hydrogen form at least 99 per cent. of the gas evolved.

HOMOGENEITY OF SAMPLE—

To determine the effect of possible variations in the method it was necessary to have homogeneous samples. Several secondary steel standards were available from the British Iron and Steel Research Association and covered the higher part of the range 40 to 150 p.p.m.; the results obtained on these agreed closely with those of other analysts. However, an investigation of the oxygen distribution in one such sample (B.B.L.) showed a considerable concentration gradient of oxygen from the centre to the outside of the bar, and for this reason sections taken from ingots were preferred for determining the standard deviation of the method. Sections 2 inches × 2 inches × 1 inch were taken from near the centre of the ingot, the 1-inch dimension being along the longitudinal axis. Non-uniformity in the sample would of course increase the standard deviation obtained, but the similarity of the coefficient of variation for the different sample weights of A437 suggested that this was not a factor, for this sample at least. An independent check of homogeneity was possible only with the samples of silicon, when the coefficient of variation determined by infrared methods was less than 3 per cent. Arc-cast molybdenum samples were taken from near the centre of the ingots, but for sintered and zone-refined material $\frac{5}{8}$-inch bar was used.

METHOD

PROCEDURE FOR STEEL—

Various types of steels were analysed successfully, including alloys containing 20 per cent. of manganese. The steels for which the apparatus was developed, however, were vacuum-melted R.A.R.D.E. high tensile steels, usually having an oxygen content between 5 and 15 p.p.m. and containing various alloying elements such as copper, manganese and vanadium in amounts up to 3 per cent. of each element.

Samples were usually received in cubes of side 1 inch taken from near the centre of the ingot. For analysis these were fabricated into right cylinders with hemispherical ends 1 cm in diameter, 2 cm in length and weighing 10 g. An alternative type of sample was a cube of side 6 to 7 mm weighing 1·5 to 2 g. The cylindrical samples were polished with carborundum cloth; the surfaces of the cubes were cleaned with a fine file. When clean, the samples were weighed immediately and introduced into the high vacuum by means of the vacuum lock. Usually the smaller type of sample was used; they were easier to prepare and clean, and more samples could be analysed in one run.

When they had been placed in the sample loading compartment, the samples were moved magnetically into the silica pre-heating furnace tube which held 5 of the large or 15 of the small samples. When the samples were in position, the resistance furnace was moved over the silica tube and the temperature of the samples raised to 1000° C. Fifteen minutes were allowed for the 10-g samples to reach this temperature and 10 minutes for the small samples.

Before the samples were fused, a 10-g slug of vacuum-melted steel was placed, together with 0·1 g of tin, in the previously de-gassed crucible. The steel added with the tin prevented spluttering of the latter and also assisted the rapid melting of the subsequent samples. Analysis was then begun.

The gas evolved from each sample was collected for 2 minutes. This was found to be sufficient time, since the main evolution of gas, as shown on the Pirani gauge, occurred within the first 30 seconds, and at the end of 2 minutes the evolution of gas had usually dropped to the level of the blank rate. The gas collected was measured and analysed. After the analysis of every third sample, 0·1 g of tin was added to prevent gettering. Samples were analysed at the rate of one every 10 minutes, which included the time required for blank determinations.

PROCEDURE FOR MOLYBDENUM—

Samples of molybdenum were received as sections of vacuum arc-melted ingots or as sintered or zone-refined rods of approximately 1 cm diameter. These were usually machined into right cylinders of length 2 cm and diameter 1 cm with hemispherical ends (weight 13 g). The dimensions were varied occasionally to give samples of lower weight (10 g).

The samples were cleaned by anodic etching for 3 minutes in a (1 + 7) mixture of sulphuric acid, sp.gr. 1·84, and methanol, a nickel cathode and a current of 1·5 amps being used. The samples were washed with three successive portions of methanol, dried with paper tissue, weighed and loaded into the apparatus as rapidly as possible. The samples were pre-heated in batches of five for 15 minutes at 1000° C.

Molybdenum samples were fused under two different sets of conditions; in an iron - tin bath at 1750° to 1800° C or directly in the graphite crucible at 2200° C.

The iron - tin bath was prepared initially by placing 20 g of vacuum-melted steel and 0·1 g of tin in the crucible; when this had been de-gassed and the furnace blank rate had fallen to 1 µl per minute, usually after 5 minutes, a sample of molybdenum was added. Before each subsequent addition of molybdenum, a further 10 g of steel and 0·1 g of tin were added to the contents of the bath. It was found essential to add the samples of molybdenum within 15 minutes of adding the steel. If the interval was more prolonged the bath became viscous and the evolution of gas from the molybdenum was slow and often incomplete. By using this technique a maximum of nine 10-g samples could be analysed per run.

The direct-melting technique was comparatively simple. Samples of molybdenum were added to the contents of the crucible at 2200° C, and the gas was collected for 1 minute, measured and analysed. The samples melted rapidly under these conditions owing, possibly, to the formation of a carbon - molybdenum eutectic. By this technique a maximum of twenty 10-g samples could be analysed during one run. This method was preferred to the iron-bath technique since it was simpler, more rapid and more reliable, particularly on samples having a low gas content. After additions of sample the furnace blank rate rapidly returned to its previous level. During the run the blank rate tended to decrease slightly whereas with the iron-bath technique it usually tended to increase slightly.

PROCEDURE FOR SILICON—

The samples of silicon for analysis were taken from vacuum- and argon-grown single crystals of approximate diameter 1 cm. These had been cut into slices 3 mm thick and optically polished for infrared examination; the slices had then been cut diametrically, and one half of each (weight 0·4 to 0·5 g) was used for the analysis.

The samples were weighed and then cleaned by etching for 15 seconds in a 10-ml polythene beaker with 5 ml of a (1 + 1) mixture of nitric acid, sp.gr. 1·42, and hydrofluoric acid, sp.gr. 1·15. The beaker rested in a large 8-inch diameter evaporating basin, and when etching was complete the beaker and contents were swamped with 200 ml of de-ionised water. The silicon was removed with platinum-tipped forceps, washed in fresh de-ionised water and then transferred to the vacuum lock as quickly as possible. Most of the adhering water was shaken off and the rest was removed in the first vacuum stage of the lock. It was found by experiment that 35 mg of sample were removed during the etching process, and, therefore, this amount was subtracted from the recorded weight. When in the vacuum system, the samples were pre-heated at 1000° C for 5 minutes before analysis.

An iron bath was used for the analysis since molten silicon attacks carbon rather vigorously. The crucible was maintained at 1700° C, which gave a furnace blank rate 0·3 to 0·5 µl per minute. Vacuum-melted steel (10 g) and 0·1 g of tin were used for the initial bath, and after every three analyses a further 10 g of steel and 0·1 g of tin were added.

PROCEDURE FOR OTHER METALS AND POWDERS—

The apparatus was also used successfully for samples of thorium in an iron bath at 1950° C and for chromium and copper at 1700° C. Samples of iron, ferro-silicon, ferro-molybdenum and ferro-aluminium powders were also analysed by wrapping them in nickel foil and fusing in an iron bath.

RESULTS

The mean results and standard deviations obtained on a series of typical vacuum-melted steels are shown in Table IV; the corresponding results obtained on sintered, arc-cast and zone-refined molybdenum are shown in Table V. Results obtained on two samples of single-crystal silicon grown under a partial pressure of argon (sample A) and in vacuum (sample B) are shown in Table VI.

TABLE IV

RESULTS OBTAINED ON VACUUM-MELTED STEELS

Sample number	Approximate weight of sample, g	Number of determinations	Mean, p.p.m.	Standard deviation, p.p.m.	Coefficient of variation, %
A379*	1·5	11	115	2·7	2·3
A329†	1·5	12	12·0	0·59	4·9
A437(b)‡.. ..	1·5	12	6·37	0·40	6·3
	10·0	6	6·35	0·33	5·2

* Vacuum-melted Swedish iron, containing less than 0·1 per cent. of total impurity.

† Vacuum-melted R.A.R.D.E. steel containing 1 per cent. of carbon, 1·8 per cent. of silicon, 1·4 per cent. of manganese, 1·3 per cent. of molybdenum, 0·6 per cent. of vanadium and 1·5 per cent. of copper.

‡ Vacuum-melted steel containing 0·6 per cent. of carbon with less than 0·1 per cent. of minor constituents.

TABLE V

RESULTS OBTAINED ON DIFFERENT TYPES OF MOLYBDENUM

Type of molybdenum	Approximate weight of sample, g	Conditions of fusion	Number of determinations	Temperature, °C	Mean oxygen content, p.p.m.	Standard deivation (1σ), p.p.m.	Coefficient of variation, %
Sintered bar X..	14	Iron - tin bath	8	1750	57·0	1·3	2·3
	14	No bath	7	2200	57·4	1·4	2·4
	2	No bath	13	2200	54·9	1·7	3·1
Sintered bar Y..	13	No bath	11	2200	42·5	0·8	1·9
	2	No bath	11	2200	42·8	1·1	2·5
	10	Iron - tin bath	20	1750	1·32	0·40	30·0
Arc cast.. ..	10	No bath	12	2200	1·97	0·16	7·9
	1·5	No bath	6	2200	2·66	0·63	24·0
Zone refined ..	10	No bath	4	2200	0·35	0·07	20·0
	1·5	No bath	4	2200	0·85	0·16	19·0

There was a significant difference between the means of the results on the large and small samples for the first sintered molybdenum bar (X) in which the samples were taken from different positions in the bar. A second bar (Y) was therefore analysed at different weights, and this time the large and small samples were taken from alternate positions along the bar; there was little difference in the means of these results.

With arc-cast ingots the mean value of the results obtained on the 10-g samples by using an iron bath was lower than that obtained by direct melting. The spread of the results obtained by the former method was 0·76 to 2·40 p.p.m. compared with 1·73 to 2·31 p.p.m. obtained by direct melting. In fact, the higher results on the iron - tin bath series corresponded to the results obtained by the direct-melting technique, which suggests that, for some samples, alloying with the bath metal was slow and evolution of gas incomplete. More consistent results might have been obtained with a higher ratio of iron to molybdenum in the bath, but this would have limited the number of determinations per run still further. The advantages of the direct-melting technique were thus apparent as twenty samples could be analysed per run with greater precision.

With zone-refined samples, there was a difference of 0·5 p.p.m. between results at different sample weights, which can be explained as being due to residual surface contamination. The results agree at both weights if a surface contamination of 0·8 μg per sq. cm is assumed.

The small samples were discs 8 mm in diameter and 2 mm thick with a total surface area of 1·5 sq. cm. A correction of 0·8 p.p.m. could be applied to the results for the small samples and 0·4 p.p.m. to those for the large samples (surface area 5·0 sq. cm). When these corrections were applied, the figure suggested that the oxygen content of the zone-refined molybdenum was less than 0·2 p.p.m.

TABLE VI

RESULTS OBTAINED ON 2 TYPES OF SINGLE-CRYSTAL SILICON

Type of single-crystal silicon	Number of determinations	Mean oxygen content, p.p.m.	Standard deviation (1σ), p.p.m.	Coefficient of variation, %
Argon grown	6	12·3	1·6	13
Vacuum grown	8	17·1	1·4	8·3

The ratio of 1·39 obtained on the results of the samples of silicon analysed by vacuum fusion compares favourably with the 1·47 from infrared measurements. Closer agreement would probably be obtained if the surface contamination of the silicon was determined and the results were corrected accordingly.

CONCLUSIONS

The vacuum-fusion technique has been developed successfully and applied to the analysis of steel, molybdenum and silicon at low levels of oxygen (less than 1 p.p.m. in molybdenum).

With samples of steel the coefficients of variation obtained were much less than 10 per cent., and no bias due to remaining oxide films was observed. There was good indication that the method was accurate down to 6 p.p.m., the lowest level encountered.

Coefficients of variation of less than 10 per cent. were obtained on the determination of oxygen in molybdenum down to 2 p.p.m., but at this lowest level there was a positive bias due to residual surface contamination. Analysis of zone-refined material suggested that most of the oxygen evolved came from the residual surface contamination and that the oxygen content of the material was in the range 0 to 0·2 p.p.m.

Analysis of 0·5-g samples of single-crystal silicon gave a coefficient of variation of 10 per cent. at the level of 17 p.p.m. of oxygen. The ratio between the levels of oxygen obtained on the two different series of samples agrees fairly well with the same ratio obtained by infrared examination at 9 μ.

We acknowledge the work done by the late Mr. A. Bacon who made a significant contribution to the progress of this work and thank Mr. R. J. Loneragan who carried out the infrared analyses and was responsible for some early work in the field.[25] Acknowledgment is also made to Mr. B. R. Watson-Adams, who carried out many of the analyses, for helpful suggestions and practical assistance.

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The Quantitative Determination of Active Hydrogen by a Modification of the Zerewitinoff Method

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The gasometric method for determining active hydrogen in organic compounds by using methyl magnesium iodide has been modified and made more accurate and precise. The sources and magnitudes of the errors in the determination are considered, and a method of correction is given. The method was developed for determining hydroxyl groups in silanols, but has been found applicable to a range of compounds containing active hydrogen. The effects of solvents and of impurities associated with silanols have also been studied. The accuracy of the method has been shown to be ±1·5 per cent. of the theoretical value, and it is possible to determine –OH percentages down to 0·04 per cent.

A METHOD for determining the hydroxyl content of silanols was required, which could be used for the routine control of the quality of silicone intermediates and resin solutions. Titration of the silanol group with Karl Fischer reagent has been studied by Gilman and Miller[1] and Grubb,[2] but our preliminary investigation of this method showed it to be of limited application, and it was decided to investigate the reaction between Grignard reagent and silanols.

The use of Grignard reagents for the quantitative determination of active hydrogen was first suggested by Tschugaeff,[3] and it was extensively studied by Zerewitinoff[4] and later modified by Roth.[5] Sudborough and Hibbert,[6] in studying the determination of amines by the Zerewitinoff technique, found that the methane generated during reaction was partly soluble in the reaction mixture, and they devised a method of correcting for this effect. Hibbert[7] apparently overlooked methane solubility as a cause of the low results obtained on the lower aliphatic alcohols, and, instead, he suggested that an equilibrium was attained. The introduction by Kohler and Richtmeyer[8] of an apparatus, in which the Grignard reagent was contained under an inert atmosphere of dry nitrogen, was an important development, and the first widely adopted procedure was that of Soltys,[9] who modified the Kohler apparatus. Hollyday and Cottle,[10] working with the lower aliphatic alcohols and using a modified Kohler apparatus, concluded that close control of the relative concentrations of reactants was necessary for quantitative results. However, they overlooked methane solubility as a possible cause of low results.

Several workers[6,11,12,13,14] have pointed out that methane solubility can affect the result of a determination, and various correction techniques have been developed, the simplest of which is to use pure methane as the inert gas in the apparatus; this has been successfully adopted by Lehmann and Basch,[11] Brown and Hafliger[12] and Guenther.[13] Villars[14] derived a factor that, when multiplied by the observed volume of methane, corrected for methane solubility; however, no mention was made of a correction for the vapour pressure effect of the reaction mixture. Many methods[15,16,17] involving the use of special apparatus have been developed, which give reasonable results without the necessity of correcting for methane solubility; but it was felt that none of these methods was suitable for routine use. The choice of solvent for the sample is important and has often been stressed.[4,8,10,18] The formation of insoluble products usually leads to low results,[19] presumably because of occlusion of unreacted sample. Heating the reaction mixture has, in some instances, increased the result.[4,20] Constant temperature control of the gases inside the apparatus during determinations is extremely important, and several papers refer to this point,[10,11,13,16] although few have rigidly applied it in practice.

In a review, Olleman[21] states "Although several investigators have reported results within 1 to 2 per cent. of the theoretical values, in general reproducibility and accuracy are probably ±3 to 5 per cent."

As a result of our study of the literature, preliminary experiments were carried out, and the conclusions listed below were reached—

(*a*) The solvent for the sample should be easily dried and purified, possess a relatively low vapour pressure at the temperature of the determinations, and be completely miscible with Grignard reagent. Xylene fulfils these requirements.

(*b*) The use of pure methane as the inert gas in the apparatus is to be preferred, since it will completely eliminate errors due to methane solubility, because both the reagent and the solvent for the sample can be saturated with methane before reaction. Unfortunately, there is no ready supply of methane of 99·9 per cent. purity in this country. Nitrogen was chosen as the inert gas because a pure grade is readily available, and it has been extensively used by previous workers. However, its use does introduce the need for solubility corrections, which are discussed below.

(*c*) The methane generated by the sample on reaction with the Grignard reagent is partly soluble in the reaction mixture, the exact volume dissolved depending on the partial pressure of the methane and on the temperature.

(*d*) The experimental procedure for a determination is such that, before reaction, both the solvent for the sample and the Grignard reagent are saturated with nitrogen. After reaction, because of the methane generated, there is a decrease in the partial pressure of the nitrogen and some of the dissolved nitrogen is liberated from the reaction mixture.

(*e*) Because of the solubility effects discussed in (*c*) and (*d*), the volume of solvent for the sample, the volume of Grignard reagent added and the volume of nitrogen in the system before reaction must be kept constant for all determinations.

(*f*) The blank value, which is the increase in volume observed on mixing solvent and Grignard reagent alone, is the sum of two values: (*i*) the volume of methane generated by traces of active hydrogen (if any) in the solvent, and (*ii*) the volume of vapour produced by the reaction mixture in the presence of a constant volume of nitrogen.

(*g*) After reaction of a sample the total volume of the system increases, and there is a corresponding increase in the volume of vapour produced by the reaction mixture.

(*h*) The volume of the system and all the effects discussed above are temperature dependent, and the temperature of the system must be accurately controlled. A working temperature of 25° ± 0·1° C was chosen as convenient.

Hence, corrections must be applied for the solubility of the methane, the change in solubility of the nitrogen and the volume change due to the vapour pressure of the reaction mixture.

An equation was derived that related the theoretical volume of methane to the observed volume, the blank value and the correction terms for the solubility and vapour pressure effects referred to above. However, to obtain values for these correction terms, the coefficients of solubility of pure methane and of nitrogen in the reaction mixture and also the vapour pressure of the reaction mixture were required. Since these values were unknown the equation was simplified and the correction terms were represented by a single term, V_c, as shown in the equation below.

$$V_t - (V_o - B) = V_c \quad \ldots \quad (1)$$

where V_t = the theoretical volume of methane generated by the sample,
V_o = the observed volume increase after reaction and
B = the blank volume.

(Equation 1 applies to a system at constant temperature and pressure and containing a constant volume of nitrogen gas and a reaction mixture of constant volume and composition.)

For a known weight of a pure standard substance, if the reaction is assumed to be stoicheiometric, V_t can be calculated; from the value of $(V_o - B)$, obtained experimentally, the corresponding value of the correction V_c can be calculated by using equation 1. Thus by varying the weight of standard substance a series of values of $(V_o - B)$ and V_c can be obtained and a graph plotted of $(V_o - B)$ against V_c.

Hence, from the value of $(V_o - B)$ obtained for a sample the corresponding correction V_c may be obtained from the graph. Then V_t for the sample is given by—

$$V_t = (V_o - B) + V_c \quad \ldots \quad (2)$$

The experimental work described consisted in investigating the accuracy and precision of this proposed graphical correction procedure for several silanols. It was extended to include the determination of active hydrogen in alcohols, phenols, carboxylic acids and amines, and the effects of solvents and siloxanes on the method were studied.

Because water is formed by the condensation of silanols to siloxanes, there is a possibility that water may be present as an impurity in silanol samples, either in solution or as free water droplets. Hamelin[22] suggests that water reacts quantitatively with Grignard reagent, and so the effects of water both as a dilute solution in toluene and as free water droplets were examined. The solution of water in toluene was prepared by shaking together water and toluene at a temperature below room temperature, and, after separation, the toluene was decanted off. This solution remained clear and bright at room temperature, and the water concentration was found by titrating with Karl Fischer reagent.

β-Naphthol was chosen as the standard substance for the preparation of the calibration graph because it is readily available, easily purified by recrystallisation and stable if stored in a dark bottle. A working temperature of 25° ± 0·1° C was used, and all volumes were corrected to standard pressure.

METHOD

REAGENTS—

Magnesium metal, granular—Dry laboratory-reagent grade magnesium for 3 hours in an oven at 135° C immediately before use.

n-Dibutyl ether—Boil under reflux with sodium metal for 1 hour; then distil, and reject the first 50 ml of distillate.

Methyl iodide—Laboratory-reagent grade is satisfactory.

Nitrogen, dry—Pass nitrogen from the cylinder over a mercury safety bottle into a column containing soda lime, to remove traces of carbon dioxide, and then through activated alumina and molecular sieves to remove water. Finally, pass the nitrogen through a 125-ml Dreschel bottle, containing silicone fluid MS200/350cS to a depth of about 6 cm, so that the bubble rate can be observed and controlled.

Solvent xylene—Boil xylene under reflux for 1 hour with sodium metal, and then distil. Reject the first 50 ml of distillate, but collect a suitable fraction in a clean dry bottle. The dry xylene from this bottle should be transferred as required into a 10-oz bottle fitted with a glass stopper. To this xylene add small pieces of sodium metal, set aside until effervescence ceases, and then stopper securely. Always replace the stopper tightly after use.

Grignard reagent—Prepare a 0·75 M solution of methyl magnesium iodide in n-dibutyl ether.[17] This solution, when stored under nitrogen in a well-stoppered bottle, is stable for several months.

APPARATUS—

Constant temperature water-bath and external circulating pump—A constant temperature water-bath capable of controlling the temperature of the water passing through the apparatus at 25° ± 0·1° C is required. A suitable water-bath is manufactured by Townson and Mercer, catalogue number E.270. Water from the bath is forced through the apparatus by a pump capable of supporting a water-head of about 4 feet. Water passes through the circuit in the direction shown in Fig. 1 and overflows from the side-arm of the beaker back to the water-bath.

Reaction flasks—Flat-bottomed 25-ml flasks (tolerance ±2 ml) fitted with B19 ground-glass joints and glass lugs. Dry in an oven at 135° C for at least 1 hour before use, and cool in a desiccator.

Syringe—All-glass 2-ml syringe fitted with a No. 17 stainless-steel hypodermic needle. When not in use, store the syringe in a desiccator.

Reaction apparatus—This is essentially that described by Soltys.[9] Assemble as shown in Fig. 1, in such a way that it is pivoted to allow the contents of the reaction flask to be shaken during a determination. Thoroughly dry the apparatus in an oven at 150° C before assembling, and flush with dry nitrogen at a flow rate of 3 bubbles per second for half an hour, with a dry flask attached and the taps in position A (see Fig. 2). Do not stopper the reservoir. When the apparatus has been flushed, turn the taps to position B (see Fig. 2), and fill the reservoir two-thirds full with Grignard reagent; clean and grease the joint with Vaseline, and stopper securely.

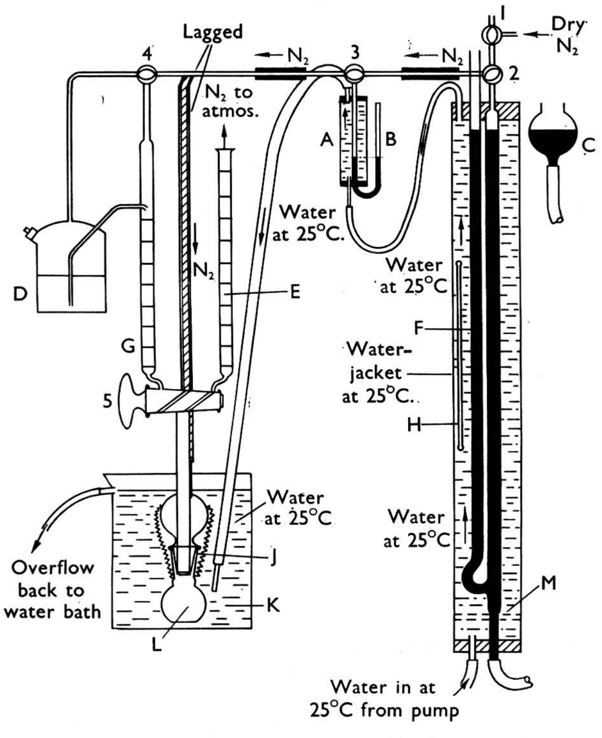
DETERMINATION OF THE BLANK VALUE—

All tap positions referred to in the method are shown in Fig. 2.

With the syringe place 2 ml of the dry xylene in a reaction flask, taking care not to include any sediment from the xylene bottle. Grease the upper half of the B19 cone joint with Vaseline, and attach the flask, securing it by means of springs. Totally immerse the flask and the glass bulb above the joint in the water, at 25° ± 0·1° C, contained in the special beaker. The water temperature in the jacket and beaker must be maintained at 25° ± 0·1° C throughout all determinations.

Turn taps 1, 2, 3, 4 and 5 (see Fig. 1) to position B, and flush the apparatus for 15 minutes with dry nitrogen. Then fill the reagent burette to the zero mark with Grignard reagent as described below.

Turn taps 1 to 5 to position C. In this position the nitrogen pressure builds up and excess of nitrogen vents off through the mercury safety bottle. Lower the mercury reservoir slowly to draw the reagent over into the burette. When the burette is full to the zero mark rapidly raise the mercury reservoir, and approximately equilibrate the mercury levels in the gas burette. This raising of the reservoir when the reagent reaches the zero mark in the reagent burette is necessary to prevent reagent being drawn into the connecting tubes between the apparatus and gas burette. With the mercury levels approximately equal in the gas burette, return the taps to position B for a few seconds. Now turn the taps, in numerical order, to position D.



A = Water-jacket
B = Dibutyl phthalate manometer
C = Mercury reservoir
D = Reagent reservoir
E = Side-arm
F = 50-ml gas burette
G = 10-ml reagent burette
H = Thermometer
J = B19 cone
K = Special beaker
L = Reaction flask
M = Cork (for support)

Fig. 1. Constant-temperature apparatus for determining active hydrogen by a modification of the Zerewitinoff method

Check that the system is gas-tight by lowering the mercury reservoir by about 20 cm. Set aside for 2 minutes, noting whether or not the mercury levels remain steady. If a leak is detected, raise the reservoir, clean and re-grease taps 1, 2, 3 and 4, and then repeat the procedure for testing for leaks. When the system is gas-tight, raise the mercury reservoir and turn the taps to position E. Adjust the level of the mercury in the gas burette, and note the reading.

N.B.—Always return the mercury to the same level in the burette before proceeding with a determination.

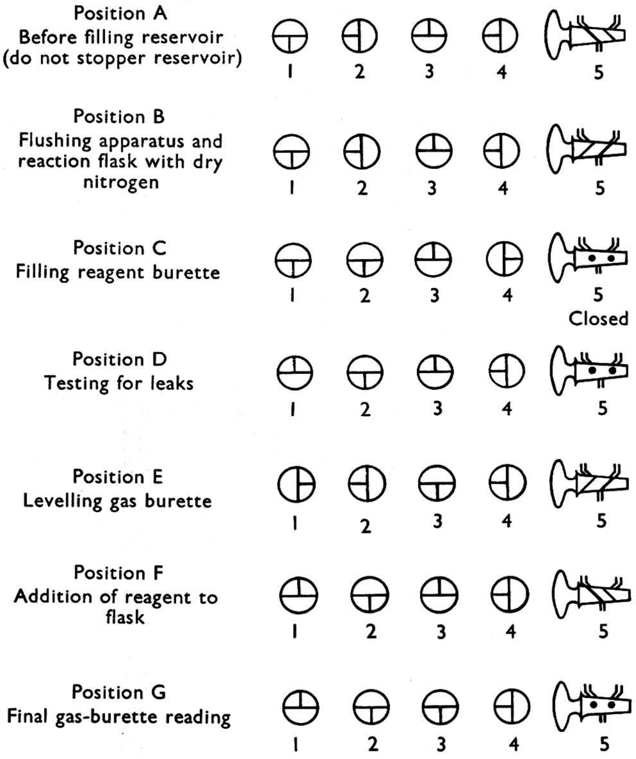

Position A
Before filling reservoir
(do not stopper reservoir)
1
2
3
4
5
Position B
Flushing apparatus and
reaction flask with dry
nitrogen
1
2
3
4
5
Position C
Filling reagent burette
1
2
3
4
5
Closed
Position D
Testing for leaks
1
2
3
4
5
Position E
Levelling gas burette
1
2
3
4
5
Position F
Addition of reagent to
flask
1
2
3
4
5
Position G
Final gas-burette reading
1
2
3
4
5

Fig. 2. Diagram of tap positions

Note the reading in the reagent burette, and return the taps to position D. Lower the mercury reservoir to create a small partial vacuum in the reaction flask, and while maintaining this small vacuum turn only tap 5 to position F until 5 ± 0·1 ml of reagent is drawn from the burette into the flask. Close tap 5, and approximately equilibrate the mercury levels in the gas burette. Shake the flask and contents for 2 minutes, keeping the mercury levels in the gas burette equal during the evolution of any gases. After the evolution of gas has ceased, set the flask aside for a further 3 minutes with occasional shaking. Adjust the mercury levels in the gas burette until they are approximately equal. Now turn tap 3 to position G thus bringing the dibutyl phthalate manometer into the system, and adjust the mercury reservoir so that the pressure in the system equals atmospheric pressure. Note the reading in the gas burette.

Calculate the volume occupied by the blank from the recorded increase in volume, after subtracting the volume of Grignard reagent added to the flask.

Check the blank value daily before proceeding with an analysis.

CLEANING THE APPARATUS—

Turn the taps to position E. Clean the flask, the joint and reagent delivery tube with dilute hydrochloric acid, water, acetone and finally with diethyl ether. Dry the flask in an oven, and wipe the inside and outside of the joint with a clean dry cloth. Attach an empty reaction flask to the joint, and flush with dry nitrogen for 3 minutes with the taps turned to position B.

COMPOUNDS ANALYSED—

Table I shows the purification procedure and constants of these compounds.

TABLE I

PURIFICATION PROCEDURES AND CONSTANTS OF COMPOUNDS ANALYSED

	Melting-point		
Compound	Cited in literature, °C	Found, °C	Notes
Tetramethyldisiloxane-1,3-diol	67 to 68[25]	68·5	Recrystallised twice from light petroleum
Diphenylsilanediol	—	165	—
Diphenyldimethyldisiloxane-1,3-diol	—	115·5	—
Triphenylsilanol	150·5 to 151·5[25]	151	Recrystallised twice from benzene
Tetraphenyldisiloxane-1,3-diol	108 to 109[13]	109	—
β-Naphthol	122[26]	122	AnalaR grade, recrystallised twice from carbon tetrachloride and stored in a dark bottle in a desiccator. Used to prepare calibration graph
α-Naphthol	96[26]	95	Recrystallised from carbon tetrachloride
Resorcinol	110[26]	110	Recrystallised twice from benzene and stored in a dark bottle
Phenol	41[26]	41	AnalaR grade
Thymol	51·5[26]	50·5	B.D.H. laboratory-reagent grade
Salicylaldehyde	196·5[26] (boiling-point)	196 (boiling-point)	G.P.R. grade, redistilled and mid-cut collected
Vanillin	82[26]	82	Micro-analytical-reagent grade
Benzoic acid	122[26]	122	Micro-analytical-reagent grade, ground to powder
Glacial acetic acid	—	—	AnalaR grade, 97·6 per cent. pure
n-Butanol	—	—	AnalaR grade
Octan-2-ol (capryl alcohol)	—	—	Micro-analytical-reagent grade
Aniline	184·4[26] (boiling-point)	184 (boiling-point)	AnalaR grade, freshly redistilled and mid-cut collected
Cyclohexylamine	134[26] (boiling-point)	134 (boiling-point)	Hopkin & Williams fine-chemicals grade, freshly redistilled and mid-cut collected
Di-n-propylamine	110·7[26] (boiling-point)	110 (boiling-point)	B.D.H. laboratory-reagent grade, freshly redistilled and mid-cut collected

PREPARATION OF THE CALIBRATION GRAPH—

NOTE—A calibration graph refers only to the apparatus with which it has been prepared. If the apparatus suffers a change in volume exceeding 5 ml, a new calibration graph must be prepared.

Into a clean dry flask weigh accurately between 0·03 and 0·19 g of β-naphthol, and with the syringe add 2 ± 0·1 ml of sodium-dried xylene. Attach the reaction flask to the apparatus, and proceed exactly as described for the blank determination.

Record the final total volume in the gas burette, and calculate the volume collected to the nearest 0·1 ml. Record the corrected barometric pressure at the time of the determination, *i.e.*, mm of mercury at 0° C.[23] Correct the volume collected to the standard pressure to obtain V_0; subtract the blank value to obtain $(V_0 - B)$.

Calculate the theoretical volume of methane evolved by the known weight of sample at standard pressure and 25° C, from the equation—

$$V_t = \frac{W}{144{\cdot}2} \times 24{,}470 \text{ ml}$$

where W = the weight of β-naphthol taken, in grams. Then the correction, V_c, in millilitres,

$$= V_t - (V_o - B).$$

Repeat the procedure on weights of β-naphthol, such that the range of gas volumes collected is between 5 and 30 ml. Plot a graph of V_c against $(V_o - B)$. A typical calibration graph is shown in Fig. 3.

SAMPLE ANALYSIS—

Weigh accurately into a clean dry flask a suitable amount of the sample to produce about 25 ml of methane. From the syringe carefully add $2 \pm 0{\cdot}1$ ml of the dry xylene. Now proceed exactly as described for the blank determination. The time required for complete evolution of gas depends on the reactivity of the sample, but after the evolution of gas has ceased the flask must be set aside for a further 3 minutes, with occasional shaking, to attain equilibrium conditions before making the final adjustments to the manometer.

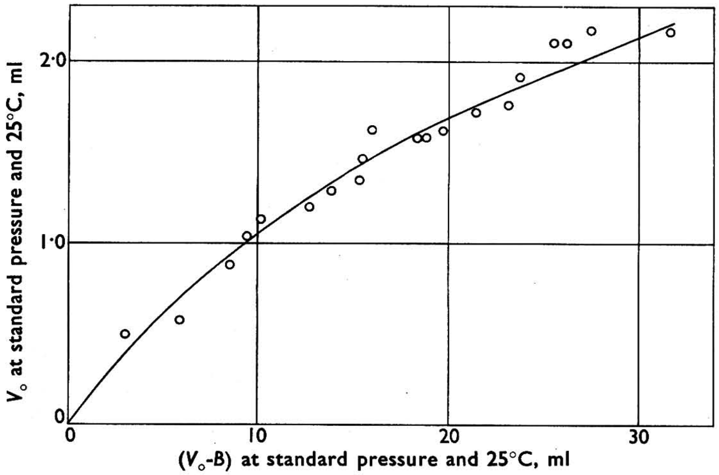


Fig. 3. Typical calibration graph

Correct the volume collected to standard pressure, subtract the blank volume, and by reference to the calibration graph read off the corresponding correction volume, V_c, to the nearest 0·1 ml.

ADD the correction to the value of $(V_o - B)$ to give the true volume, V_t, of methane evolved by the known weight of sample.

$$V_t, \text{ ml} = (V_o - B) + V_c, \text{ at S.P. and } 25^\circ \text{ C}.$$

Then

$$\text{–OH per cent. w/w} = \frac{V_t \times 1{\cdot}7}{\text{Sample weight} \times 24{\cdot}47}$$

DISCUSSION OF RESULTS

The statistical treatment of the results obtained on four pure silanols having –OH percentages from 6·1 to 20·5 per cent. are shown in Table II. No bias was found, and the application of Bartlett's variance ratio test[24] showed that the apparent difference in the variances is non-significant.

The results shown in Table III, for the analysis of another silanol and some alcohols, phenols, carboxylic acids and amines, indicate that the method is applicable to a wide range of compounds containing active hydrogen. The reaction time for the compounds listed was less than 5 minutes, with the exception of cyclohexylamine and di-n-propylamine. The low results obtained with vanillin and glacial acetic acid may be due to occlusion of unreacted sample in the precipitates that both substances formed on reacting with the Grignard reagent.

The results for the reaction of water in droplet form and in toluene solution were less than half the theoretical value, if it is assumed that there is only one active hydrogen atom per mole of water. When water droplets were present the reaction was slow and the droplets became coated with a white precipitate until reaction eventually ceased. Heating the reaction mixture during the determination had no effect on the result. Similarly, water in toluene solution did not react completely, and a faint white precipitate was observed each time.

Presumably these low results were caused either by occlusion of unreacted water by the precipitate or by the formation of hydrated magnesium salts. This problem has been discussed by Hamelin,[22] but our experimental results do not agree with his conclusions.

No significant effect was observed on the result of a standard β-naphthol analysis when amounts of up to 2 ml of dry xylene, toluene or benzene were added to the 2 ml of xylene used as solvent in the proposed method. Presumably, as the methane solubility increases, the volume of nitrogen liberated from the reaction mixture also increases, and the net volume change does not cause a significant error. However, the addition of 2 ml of light petroleum caused interference, and low results were obtained.

Table II

STATISTICAL TREATMENT OF THE RESULTS OBTAINED ON PURE SILANOLS

Compound	Number of determinations	Mean purity found, % w/w	Variance	Standard deviation
Tetramethyldisiloxane-1,3-diol	20	99·9	0·41	0·64
Diphenylsilanediol	20	100·0	0·58	0·76
Diphenyldimethyldisiloxane-1,3-diol	9	100·1	0·33	0·58
Triphenylsilanol	5	99·8	0·77	0·88

Table III

RESULTS OBTAINED FOR VARIOUS COMPOUNDS

Compound	Found, –OH % w/w	Mean of results	Theory, –OH % w/w
Tetraphenyldisiloxane-1,3-diol	8·3, 8·2	8·25	8·21
α-Naphthol	12·0, 11·9	12·0	11·8
Resorcinol	31·0, 30·6	30·8	30·88
Phenol	18·3, 18·3	18·3	18·1
Thymol	11·4, 11·4	11·4	11·32
Salicylaldehyde	13·9, 13·8	13·9	13·92
Vanillin*	4·8, 7·4, 7·7†	—	11·17
Benzoic acid	13·9, 14·2, 14·0, 14·2	14·0	13·93
Glacial acetic acid*	26·7, 26·9	26·8	29·82
n-Butanol	22·9, 22·6, 23·2	22·9	23·07
Octan-2-ol (capryl alcohol)	13·1, 13·1, 13·0	13·1	13·06
Aniline	16·2, 16·1‡	16·2	16·12
Cyclohexylamine§	15·5, 15·3‡	15·4	15·14
Di-n-propylamine‖	14·8, 14·7‡	14·8	14·83

* Precipitate formed on reaction.
† After heating reaction mixture at 100° C for 5 minutes.
‡ Results expressed as –NH per cent. w/w.
§ Reaction time 15 minutes.
‖ Reaction time 60 minutes.

Low results were also obtained on standard β-naphthol when small amounts of acetone were added, but in this instance an insoluble product was formed between the acetone and the Grignard reagent.

Because silanols can contain various siloxanes as impurities, mixtures of equal weights of siloxane and standard β-naphthol were analysed to ascertain whether or not the siloxanes interfered in the determination. No interference was observed from—(*a*) hexamethylcyclotrisiloxane, (*b*) octamethylcyclotetrasiloxane, (*c*) decamethylcyclopentasiloxane, (*d*) a mixture of dimethylcyclopolysiloxanes, (*e*) linear dimethylpolysiloxanes trimethylsilyl endblocked

(MS 200 fluids), (*f*) a mixture of phenylmethylcyclopolysiloxanes, (*g*) 2,4,6,8-tetramethylcyclotetrasiloxane or (*h*) a mixture of linear methylhydrogenpolysiloxanes trimethylsilyl endblocked (MS 1107 fluid).

CONCLUSIONS

The method is applicable to a wide range of compounds, and, with the exceptions of acetone and light petroleum, no interference with the substances tested has been encountered.

A low result is obtained if a precipitate is formed when the substance reacts with Grignard reagent. For samples containing water, it is essential that the water be removed before determining active hydrogen, because water does react with Grignard reagent although the reaction is not quantitative.

The method has been improved, and the accuracy of the graphical correction procedure is ± 1·5 per cent. of the theoretical value. It is possible to determine –OH percentages down to 0·04 per cent.

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The Micro-determination of Sulphur in Organic Compounds by Fusion with Sodium Peroxide and Titration of the Sulphate with Barium Perchlorate

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The method described by Inglis for the volumetric micro-determination of sulphur in organic compounds has been critically examined. The method involves fusion of the sample with sodium peroxide in a metal bomb, removal of sodium from the aqueous extract of the fusion product by means of a cation-exchange resin and titration of the sulphate ion with barium perchlorate. Each of these operations has been investigated, and modifications have been introduced to improve the method. This modified procedure is described, and results are given to illustrate the accuracy and precision achieved in the analysis of several organic sulphur compounds, including some containing nitrogen, chlorine or fluorine as additional elements.

ALTHOUGH the oxygen-flask combustion technique[1] combined with the barium perchlorate titration procedure[2] is a well established method for determining sulphur in organic compounds, it is necessary on occasion to use an alternative technique, such as fusion with sodium peroxide in a micro-bomb, for the decomposition of the sample. A serious disadvantage of this fusion procedure is that the large amount of sodium in the extract of the fusion product interferes in the subsequent titration with barium perchlorate. In an attractive method devised by Inglis[3] this defect is overcome by the use of a cation-exchange resin for the removal of sodium. Investigations carried out in this laboratory have confirmed that the method is basically satisfactory, and have suggested some modifications for the improvement of its convenience and reliability.

EXPERIMENTAL

TITRATION OF SULPHURIC ACID WITH BARIUM PERCHLORATE—

Since we were interested in the analysis of organic sulphur compounds containing chlorine, fluorine or nitrogen, the effect of these elements on the titration of sulphuric acid was examined. A series of equal portions of 0·025 N sulphuric acid, each corresponding to 0·875 mg of sulphur, were measured in a content pipette and diluted to 10 ml. Each solution was titrated with aqueous 0·01 N barium perchlorate after the addition of 70 ml of ethanol, 0·1 ml of 0·5 per cent. thorin solution, 0·1 ml of 0·03 per cent. methylene blue solution and different amounts of hydrochloric acid, hydrofluoric acid or nitric acid. The solutions were stirred magnetically throughout the titrations, and the appearance of a pink colour, persisting for at least 20 seconds, was taken as the end-point. In these and all subsequent titrations the mixed indicator recommended by Wagner[4] was used in preference to thorin alone, and, for reasons given elsewhere,[5] the aqueous barium perchlorate was preferred to the alcoholic solution proposed by Fritz and Yamamura.[2] The results obtained in this series of experiments (see Table I) show that, when an error of about 1 per cent. is acceptable, amounts of chlorine, fluorine or nitrate up to about 2 mg can be tolerated, and that the effect of larger amounts of fluorine can be suppressed by adding boric acid.[6] Some impairment of the end-point was observed if the amount of boric acid used was much in excess of 30 mg.

Two precautions taken in the use of barium perchlorate may be mentioned here. Standardisation of the titrant and all subsequent titrations of sample solutions were always carried out by the same operator, and care was taken to ensure that the correct proportion of methylene blue to thorin was used. The significance of the second precaution was established by the result of an experiment in which six equal volumes of 0·025 N sulphuric acid, each corresponding to 0·875 mg of sulphur, were measured in a content pipette and diluted to 25 ml.

Each solution was then titrated with barium perchlorate after the addition of 100 ml of ethanol, 0·1 ml of 0·5 per cent. thorin solution and different amounts of 0·03 per cent. methylene blue solution. Satisfactory end-points were obtained with 0·1 to 0·14 ml of methylene blue, but the titration values tended to increase over the range. With still larger volumes of methylene blue, the titration values continued to rise and the end-points became difficult or even impossible to detect. The results are shown in Table II.

TABLE I

TITRATION OF SULPHURIC ACID (≡ 0·875 mg OF SULPHUR) IN THE PRESENCE OF CHLORIDE, FLUORIDE OR NITRATE

	Sulphur found in presence of		
Weight of additional element, mg	chloride, mg	fluoride, mg	nitrate, mg
0·0	0·878	0·877	0·873
0·5	0·881	—	0·876
1·0	0·881	0·879	0·880
2·0	0·885	0·884	0·881
3·0	0·887	0·902	0·886
4·0	0·888	0·962	—
4·0 (+ boric acid)	—	0·875	—

TABLE II

TITRATION OF SULPHURIC ACID (≡ 0·875 mg OF SULPHUR) IN THE PRESENCE OF DIFFERENT AMOUNTS OF 0·03 per cent. METHYLENE BLUE SOLUTION

Volume of methylene blue solution, ml	Sulphur found, mg
0·1	0·876
0·12	0·879
0·14	0·886
0·16	0·891
0·18	0·908
0·20	> 0·908

REMOVAL OF SODIUM BY MEANS OF CATION-EXCHANGE RESIN—

In the procedure described by Inglis[3] the aqueous extract of the sodium peroxide fusion product is diluted to 50 ml, and about 15 ml of this solution was used to rinse about 30 g of moist cation-exchange resin. The remainder of the solution is then stirred with the resin for several minutes, and decanted. A 25-ml portion of the solution is titrated with alcoholic barium perchlorate after the addition of 100 ml of ethanol and a few drops of 0·2 per cent. thorin indicator solution.

In order to conserve the sample solution an attempt was made to modify this procedure in a manner such that a 25-ml portion of the solution could be added directly to the moist resin and the resulting sulphuric acid quantitatively recovered for titration. The recovery of the sulphuric acid by rinsing the resin with water was not investigated, since the final volume of solution to be titrated after the addition of the appropriate amount of ethanol would have been excessive. Satisfactory recovery of sulphuric acid was obtained by the use of ethanol in a series of experiments with solutions of sodium sulphate containing the equivalent of 0·999 mg of sulphur per 25 ml. For these tests a quantity of Amberlite IR-120(H) was washed with hydrochloric acid, water, ethanol, water, sodium hydroxide and water, in that order, as described under "Method," p. 795. About 30 g of the moist resin were shaken in a stoppered conical flask with about 20 ml of ethanol to remove some of the water. The solution was decanted, and the resin shaken for 5 minutes with 25 ml of the sodium sulphate solution. This solution was then decanted, and the resin washed with four successive 25-ml portions of ethanol. The combined solutions were titrated with barium perchlorate in the usual manner. Since this procedure was required for use with the aqueous extracts of the sodium peroxide fusion products of organic sulphur compounds, these tests were repeated with a series of solutions each containing 0·4 g of sodium hydroxide in addition to sodium sulphate equivalent to 1·012 mg of sulphur. The amount of sodium hydroxide was chosen to approximate to the amount expected in the extracts of sodium peroxide fusion products. The satisfactory results obtained in both series of tests are shown in Table III.

TABLE III

DETERMINATION OF SULPHUR IN SODIUM SULPHATE SOLUTIONS AFTER REMOVAL OF SODIUM BY MEANS OF A CATION-EXCHANGE RESIN

Test solution	Sulphur found, mg	Mean, mg	Precision (standard deviation)
Sodium sulphate (≡0·999 mg of sulphur)	1·00, 1·01, 1·00, 1·01, 1·01, 1·01, 1·02, 1·02, 1·01, 1·01, 1·00, 1·01	1·01	±0·007
Sodium sulphate (≡1·012 mg of sulphur) + 0·4 g of sodium hydroxide	1·01, 1·02, 1·02, 1·01, 1·01, 1·01, 1·03, 1·02, 1·03, 1·00, 1·04, 1·02, 1·02, 1·02	1·02	±0·01

At this stage of the work the exchange capacity of the resin was determined on two 32-g portions of moist resin containing about 31 per cent. of water, as determined by the loss in weight of a separate portion of resin after it had been dried in air for about 4 hours. One portion was washed with ethanol and then shaken for 5 minutes with successive 25-ml portions of 0·5 N sodium hydroxide. After each addition the resin was washed with ethanol. Exhaustion of the resin, as shown by the presence of alkali in the decanted solution, occurred with the seventh portion of test solution. The weight of sodium quantitatively exchanged was therefore about 1·7 g. The second portion of resin was first washed with water and then shaken with successive 25-ml portions of the test solution as before, except that the resin was washed with water in place of ethanol after each addition of the test solution. The weight of sodium exchanged before exhaustion of the resin was again about 1·7 g.

DECOMPOSITION OF THE SAMPLE BY FUSION WITH SODIUM PEROXIDE—

In the interests of speed and convenience, an attempt was first made to carry out the sodium peroxide fusion procedure in an electrically fired stainless-steel micro-bomb[7] instead of in the gas-heated nickel bomb used by Inglis.[3] The organic sample, mixed with about 1 g of sodium peroxide and 60 mg of starch, was decomposed in the electrically fired bomb, and the aqueous extract of the fusion product was diluted to 50 ml. A 25-ml aliquot of this solution was shaken with cation-exchange resin, and the decanted solution titrated with barium perchlorate in the presence of ethanol. The results obtained with sulphonal (sulphur calculated = 28·09 per cent.) ranged from 21·0 to 27·8 per cent. of sulphur, and the titration end-points were unsatisfactory.

In a further series of analyses with benzyl disulphide (sulphur calculated = 26·03 per cent.) as the test substance, the results ranged from 25·2 to 25·9 per cent. of sulphur, the end-points were again unsatisfactory, and no improvement was effected by the use of glycol[3] in place of starch. An attempt was next made to carry out the fusion procedure in a gas-heated Parr micro-bomb constructed from the alloy "Ilium," but the results obtained were erratic and the titration end-points abnormal. The cause of the unsatisfactory end-points was subsequently traced to the presence of chromium in the fusion products. The chromium derived from the stainless-steel bomb and from the Ilium alloy was present as chromate in the extracts of the fusion products. In this form, chromium is not removed by a cation-exchange resin, and is known to interfere in the barium perchlorate titration. In addition to this source of error, the extremely low values obtained with the electrically fired bomb were probably caused by incomplete decomposition of the sample during the very short fusion period. Much improved results were obtained in a series of analyses in which the samples were fused with sodium peroxide and glycol in a nickel bomb as described by Inglis,[3] but occasional unsatisfactory values suggested the need for closer control of the fusion process.

In a series of experiments carried out with a nickel bomb of the type designed for use in the potassium fusion of fluorine compounds,[8] the samples were heated with sodium peroxide and glycol at various temperatures and for different times. Excellent results were obtained by heating for 2 to 3 minutes at 650° C in a muffle furnace. In all tests the fusion product extracts contained only small amounts of insoluble matter, but if heating was prolonged to above about 3 minutes considerable amounts of insoluble matter were produced by chemical attack on the bomb. Since the addition of glycol to the sodium peroxide was thought to be unnecessary, a further series of tests was carried out with sodium peroxide alone. In these tests the samples were mixed with about 1 g of sodium peroxide and heated for 2·5 minutes at 650° C. The fusion products were extracted with water, the extracts diluted to 50 ml, and a 25-ml aliquot was treated with cation-exchange resin before titration with barium perchlorate. The results obtained with a variety of sulphur compounds, including some containing nitrogen, fluorine or chlorine as additional elements, are shown in Table IV.

TABLE IV

DETERMINATION OF SULPHUR IN VARIOUS COMPOUNDS

Compound	Sulphur present, %	Sulphur found, %	Mean, %	Precision (standard deviation)
Benzyl disulphide	26·03	26·05, 26·1 26·10, 26·15 26·05, 25·80 25·80, 25·75 26·10, 26·20 25·70, 26·20	26·0	±0·18
Sulphonal	28·08	28·30, 28·20 28·30	28·27	—
Sulphanilic acid	18·51	18·40, 18·70 18·60, 18·40	18·52	—
Sodium dodecylsulphate ..	11·09	11·10, 11·20 11·00	11·10	—
S-Benzyl thiuronium chloride	15·80	15·90, 15·80 15·70, 16·00 15·70, 15·80 15·90, 15·90 15·70, 15·70	15·81	±0·11
Benzyl disulphide + *m*-dinitrobenzene ..	26·03	26·20, 26·10 26·10, 26·20 25·90, 26·10 26·20, 26·20 25·90, 26·20 25·90, 26·10	26·10	±0·12
Benzyl disulphide + fluorobenzoic acid ..	26·03	26·00, 25·80 26·10	25·97	—

TABLE V

FORMATION OF NITRATE BY FUSION OF NITROGENOUS ORGANIC COMPOUNDS WITH SODIUM PEROXIDE

Compound	Weight taken, mg	Nitrogen present, mg	Nitrogen, expressed as nitrate, mg	Nitrate found, mg
S-Benzyl thiuronium chloride ..	10·158	1·400	6·197	0·275
	10·026	1·385	6·138	0·285
	9·650	1·333	5·900	0·270
Benzyl disulphide + *m*-dinitrobenzene	7·480 + 8·436	1·406	6·224	0·500
	7·360 + 8·330	1·389	6·148	0·540

In the analyses of mixtures of benzyl disulphide and fluorobenzoic acid the amounts of the fluorine compound present were in each test equivalent to about 2 mg of fluorine. Interference by fluoride ion was suppressed by the addition of about 30 mg of boric acid to the solutions immediately before titration. This procedure was preferred to the addition of a controlled amount of sodium hydroxide recommended by Inglis.[3] Before the analysis of the nitrogenous sulphur compounds was attempted, the amount of nitrate produced by the fusion of such compounds with sodium peroxide was determined, *S*-benzyl thiuronium chloride and a mixture of benzyl disulphide with *m*-dinitrobenzene being used as the test substances. The weighed samples were fused with sodium peroxide at 650° C in a nickel bomb, and the aqueous extracts of the fusion products were diluted to 50 ml in each test. The nitrate contents of the solutions were then determined by a colorimetric method; the results are shown in Table V.

The amounts of nitrate found in all these tests were less than the amount (2·0 mg) known to interfere significantly in the barium perchlorate titration. With *S*-benzyl thiuronium chloride the conversion of nitrogen to nitrate was about 4·5 per cent. compared with about 8·5 per cent. for the mixtures of benzyl disulphide and dinitrobenzene. In contrast to the reported formation of nitrite in the decomposition of nitrogenous compounds by the oxygen-flask combustion technique,[9] no nitrite was found in any of the tests described above.

METHOD

APPARATUS—

Nickel "fluorine bomb," capacity 2 *ml*—Obtainable from Charles W. Cook and Sons Limited, 97 Walsall Road, Perry Barr, Birmingham.

Conical flask with ground-glass stopper, capacity 150 *or* 200 *ml*—The type described by Haslam and Moses[10] is recommended.

Magnetic stirrer.

Microburette, capacity 10 *ml*—Conforming to B.S. 1428.[11]

REAGENTS—

Sodium peroxide—M.A.R. grade.

Ethanol, absolute.

Barium perchlorate, 0·01 N, *aqueous*—Adjust to about pH 3·0 by adding perchloric acid.

Thorin indicator solution—Dissolve 25 mg of thorin in 5 ml of distilled water.

Methylene blue indicator solution—Dissolve 15 mg of methylene blue in 50 ml of water.

Cation-exchange resin, Amberlite IR-120(*H*)—Suitable pre-treatment of the resin has been described elsewhere,[5] but is given here for the convenience of the user. By the column method, wash about 400 g of the analytical-grade resin with about 700 ml of 3·0 N hydrochloric acid and then with 4 or 5 litres of water. Transfer the resin to a 1-litre flask, remove most of the water by decantation, and shake the resin thoroughly for several minutes with three successive 100-ml portions of ethanol. Remove the residual ethanol by repeated washing with water, and shake the resin vigorously with 400 ml of 0·5 N sodium hydroxide for about 10 minutes. Decant the slightly turbid solution, wash the resin with water until all suspended fine particles have been removed, and filter on a Buchner funnel. Press the resin between filter-papers, and store it in a glass stoppered bottle sealed with adhesive tape.

PROCEDURE—

Fusion of the sample with sodium peroxide—Place in the dry bomb 0·5 g of powdered sodium peroxide, a suitable weighed amount of the sample (5 to 15 mg) and a further 0·5 g of sodium peroxide. Close the bomb, and mix the contents by rotation. Heat the bomb in a muffle furnace for 3 minutes at 650° C. Cool the bomb, remove the lid, and extract the fusion product by placing the bomb in a small beaker containing 10 to 15 ml of water and warming until effervescence ceases. Remove the bomb, rinse it with water and then rinse the lid. Transfer the combined solutions quantitatively to a 50-ml calibrated flask, and dilute to the mark.

Removal of sodium from the fusion-product extract, and titration of the sulphate ion—Place about 30 g of the cation-exchange resin in a conical flask. Add about 25 ml of ethanol, shake the stoppered flask for about 1 minute, remove the ethanol by decantation, and repeat the operation with a further 20 ml of ethanol. Transfer 25 ml of the fusion-product extract to the resin, shake for about 5 minutes, and decant the solution into a suitable conical titration flask containing a magnetic stirrer bar. Rinse the resin with four successive 25-ml portions of ethanol; add all washings to the contents of the titration flask. Add 0·1 ml each of thorin and methylene blue indicator solutions, and titrate with 0·01 N barium perchlorate to a pink end-point colour persisting for about 20 seconds. Carry out a blank determination in the same manner, omitting only the sample. The blank value should lie between 0·1 and 0·2 ml.

PRECAUTIONS—

1. When the sodium peroxide fusion is carried out as described, only a small amount of insoluble matter should be found in the aqueous extract of the fusion product, but this material can interfere with the detection of the end-point of the titration. For the best results the extract should be set aside overnight, so that a clear portion can be withdrawn for titration.

2. End-points in the barium perchlorate titration may be unsatisfactory if the ethanol-washed resin is set aside for more than about 2 hours before use. If such a delay is unavoidable, the resin should be washed once more with about 20 ml of ethanol immediately before use.

3. With some batches of resin it has been observed that, after pre-treatment in the prescribed manner, unsatisfactory end-points are obtained in the titration of the resin-treated sample solution. If this defect is found with any portion of a given batch of resin, it is recommended that all subsequent portions should be vigorously shaken with about 25 ml of 0·5 N sodium hydroxide for about 10 minutes, and then washed with water and ethanol in succession before use.

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Automatic Thermometric Titration*

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The usefulness and applications of thermometric methods of chemical analysis are discussed, with particular reference to automated routine volumetric analysis. Titrations have been performed with a constant-delivery-rate syringe burette, and the temperature change of the titrand has been followed by means of a thermistor bridge feeding a recording millivoltmeter. The method is widely applicable and can be made sufficiently rapid to make strict ambient temperature control unnecessary. Consecutive end-points of different components of mixtures may be detected in one titration by using single- or two-component titrants.

It is well known that, when a chemical reaction occurs, energy changes take place resulting in the evolution of heat into, or the absorption of heat from, the surrounding medium. Thus, for example, when an acid is neutralised by adding alkali, heat is evolved equivalent to the heat of formation of water, and the temperature of the solution rises.

Similarly, during the chelation of aluminium or magnesium ions with tetrasodium ethylenediaminetetra-acetate heat is absorbed and the temperature of the mixture falls. The energy changes occurring in such reactions are, of course, proportional to the amount of substance formed, and so might be used as a measure of this amount. Until recently little use appears to have been made of this parameter for analytical work,[1] the main reason, no doubt, being the availability of other more practical methods for determining the end-points of reactions, for example, by the use of coloured indicators or by changes in electrode potentials. The advent of the thermistor, a semi-conductor device having a high negative temperature coefficient of resistance, has, within the last decade, made it possible to measure rapidly, accurately and conveniently small changes in temperature, and thus to record the course of rapid chemical reactions. Several workers in America[2,3,4,5,6] have suggested that this principle of measuring heat changes or "thermometric titration" could be of great value, since the end-point of a reaction followed in this way would not be obscured by other effects, such as colour of solution or poisoning of electrodes, etc. If suitable precautions were taken, side effects due to dilution or stirring could be eliminated, since these would be included in the standardisation process.

An apparatus based on a circuit published by Jordan and Alleman[4] was constructed in this laboratory, and the results obtained with it were encouraging. For example, it was found possible to follow on a recording millivoltmeter the temperature changes occurring in many different types of reaction, including acid - alkali, oxidation - reduction, chelatometric and precipitation titrations.

INSTRUMENTATION

The earlier workers in the field of thermometric titration (or enthalpy titration as it is sometimes called) used a syringe burette driven by a synchronous motor which delivered titrant at a constant rate up to about 0·6 ml per minute. The reaction vessel was thermally insulated by being contained in a Dewar flask, and stirring was by means of a 600 r.p.m. glass stirrer. The molar concentration of the titrant was usually about 100 times that of the titrand to minimise volume changes and the effect of slight differences in temperature of the two solutions. (Under these conditions ±0·3° C difference could be tolerated.) Titration times of about 2 minutes were used, and the temperature changes were followed on a recording millivoltmeter fed from a bridge circuit incorporating a thermistor. The curve obtained showed a temperature ordinate and a titre abscissa. Tangents to the curve were drawn to simplify measurement of the length of the chart between the initial and equivalence-points. This method eliminated recorder-response time lags and other variables, since they were self-compensating.

Zenchelsky and Segatto in their paper on derivative thermometric titrations[3] pointed out that an increase in the rate of addition of titrant would be advantageous, since this would increase the rate of rise of temperature and thus permit the first or second differential of the temperature - time curve to be used to obtain sharper end-point determination. They

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* Communication No. 2349H from the Kodak Research Laboratory.

suggested, however, that a limit to such an increase in rate of titrant addition would be set by problems of heat transfer and gave 2 ml per minute as their estimate of the limit as applied to a volume of about 25 ml of titrand solution. During some earlier work in this laboratory, when high-speed mixing was required, it had been found that a vibrator, driving a Perspex paddle drilled obliquely with several holes, was much more effective and convenient than other methods tried. Accordingly, this method (see Fig. 1) was adopted in our work on thermometric titration, the thermistor being made the support for the paddle and thus also vibrating in the titrand solution during the reaction. Under these conditions, it has in fact been found that the efficiency of stirring allows a titrant addition rate of up to 10 ml per minute. This means that a complete titration may be carried out in less than 20 seconds, and, in consequence, heat losses or gains due to ambient temperature changes or small differences between temperatures of titrant and titrand are insufficient to interfere with end-point detection. The use of a Dewar flask to protect the reaction vessel is no longer necessary, and construction of the apparatus is simplified. In the first experiments a Metrohm syringe burette giving a titrant addition rate of 10 ml per minute was used. This was unsuitable for modification to meet our requirements in other respects, and it was later decided to construct an automatic syringe burette specifically designed for the type of titration envisaged.[7] This accommodated a standard 5-ml glass syringe giving a delivery rate of 7·0 ml per minute. The temperature changes and titration times (which were proportional to volume of titrant added) were followed on a recording millivoltmeter in a similar manner to that used by earlier workers, though at a later stage in our work it was found more convenient to replace the normal bridge circuit by one giving constant sensitivity over a temperature range of 15 to 30° C.[8] The chart speed used by Jordan and Alleman was 1 inch per minute, and a titration was usually of about 2 minutes duration, so that the accuracy depended on careful measurement of about 2 inches of record. In our work, the titrations being of only 10 to 20 seconds duration, a much greater chart speed was necessary, and speeds of up to 30 inches per minute were used. Thus up to 10 inches of record were obtained per titration, and this allowed an accuracy of about $\pm 0{\cdot}5$ per cent. in measurement of titre. For convenience of illustration in this paper, chart speeds of 6 inches per minute were used giving results similar to those of Jordan and Alleman[4] (on the curves, 1 ml of titrant is equivalent to approximately 8·6 seconds). The time involved in obtaining quantitative results from the recorder charts is, however, out of proportion to that taken by the titration itself and, although this is relatively unimportant in investigative work, it would greatly detract from the value of the method for routine operation. For this reason it was considered necessary to develop apparatus that would permit results to be obtained in digital form. Details of the construction of a prototype automatic digital thermometric titrator, which is simple to operate and maintain, have already been given.[7]

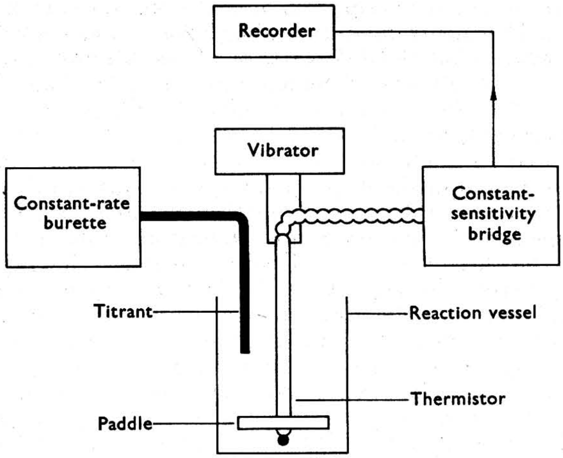

Fig. 1. Titration apparatus

ANALYTICAL APPLICATIONS

Turning now to various aspects of the analytical applications for which thermometric titration might be suitable, we may first make a general classification according to the rate of chemical reaction involved. Thus, in order to carry out direct titrations by this method, the rate of addition of titrant must be slow enough to allow it to be used up as it is added; otherwise the concentration would build up during a titration, and an incorrect end-point would be obtained. Fortunately, most inorganic reactions are ionic in character and, at the dilutions in which we are interested, take place almost instantaneously, subject to the limitations imposed by mixing. However, should a slow reaction be involved it will usually be possible to determine the concentration of a reactant by adding an excess of the titrant, allowing time for the reaction to be completed (if necessary accelerating this by heating) and then back-titrating with a suitable rapidly-reacting reagent. Back titration may also be of value when the excess of a reactant giving low-energy change may be determined by titration with another reactant giving a much greater energy change. Subject to this restriction then, the only other limitation to the use of the method for any reaction appears to be the amount of the energy change involved. For the prototype digital thermo-titrator this limitation was found to correspond to a rate of temperature change of 0·01° C per second. By using a sensitive recording millivoltmeter, qualitative results have been obtained for energy changes of about the same order. If suitable concentrations of reactant are selected, all the well-known types of inorganic reaction are included in this range, although there may be some individual ones for which our instrument is not sufficiently sensitive. It must be stated that the medium in which reactions are carried out is unimportant provided it does not attack the glass protective coating of the thermistor. Thus a wide field of non-aqueous reactions[1] is opened for study, and this procedure may prove invaluable for organic chemical assay. Some typical reactions, which are illustrated in Figs. 2 to 7, will now be considered.

For convenience of discussion these may be classified into groups.

1. NEUTRALISATION OF ACID BY ALKALI—

The neutralisation of a strong acid by a strong alkali is typified by curve B of Fig. 2. For a dibasic alkali, curve C, there are two equivalence-points, the first (a) corresponding to neutralisation of one equivalent of acid, *i.e.*, the formation of the acid salt, in this instance the hydrogen carbonate, and the second (*b*) to complete neutralisation, *i.e.*, the formation of the neutral salt. For a strong acid and weak alkali titration, the equivalence-point is less distinct, as shown in curve D.

2. PRECIPITATION (DOUBLE DECOMPOSITION)—

Curve A of Fig. 2 illustrates the exothermic reaction between hydrochloric acid and silver nitrate. It will be seen that the heat produced in this reaction is greater than that due to neutralisation of an equivalent amount of hydrochloric acid. Further examples are shown in Fig. 7, and these will be dealt with under "Mixed Titrants."

3. OXIDATION - REDUCTION—

Curves A, B and C of Fig. 3 are typical of oxidation - reduction titrations and show the reaction of 0·05 M potassium permanganate with sodium sulphite, acidified potassium iodide and acidified ammonium ferrous sulphate solutions, respectively. This type of reaction gives the greatest observed heat change, which for sodium sulphite is about 6 times that for an equivalent neutralisation reaction.

4. CHELATION—

Probably the most widely exploited chemical in inorganic analysis in recent times is the tetrasodium salt of ethylenediaminetetra-acetic acid, Na_4Y, and this has been chosen to illustrate some of the interesting possibilities of the thermometric method in this field. Thus, in Fig. 4, curve B illustrates the reaction of Na_4Y with barium nitrate. This is a straightforward exothermic reaction giving a well-defined end-point corresponding to the formation of $Na_2[BaY]$. Curve A, for the reaction with silver nitrate, shows three equivalence-points (c), (d) and (e), corresponding to $Na[Ag_3Y]$, $Na_2[Ag_2Y]$ and $Na_3[AgY]$. This reaction is also an exothermic one, but, as has been pointed out by earlier workers, many cations give an endothermic reaction with Na_4Y, *e.g.*, magnesium and aluminium. It has also been shown that, on adding Na_4Y to a mixture of such cations as calcium and magnesium, the whole of the calcium is chelated before the magnesium starts to react, giving a thermometric titration curve showing a rise in temperature due to the first reaction and then a fall due to the second. We have found experimentally that, as perhaps might be expected, the sequence of reaction with Na_4Y in any mixture of cations corresponds to the sequence of the stability constants of the chelates concerned. The sequence we have found is listed in Table I, the most reactive metal ion (mercuric) being placed at the top and the least reactive (potassium) at the bottom. It will be noticed, however, that there is no obvious relation between sequence of reaction and direction of energy change. Whereas the majority of the reactions are exothermic, others are endothermic and these can, therefore, be used to separate the titration of metals on either side of them in the list. For example, mixtures of ferric iron, aluminium, calcium, magnesium and barium have been separated in a single titration as shown in Fig. 4, curve D. The equivalence-points (h), (j), (k), (l) and (m), do not, however, correspond exactly to the expected values, since, under the experimental conditions used, interactions occur. These interactions may be due to different rates of reaction or ionisation, which would lead to substitution in the manner described under "Substitution Reactions."

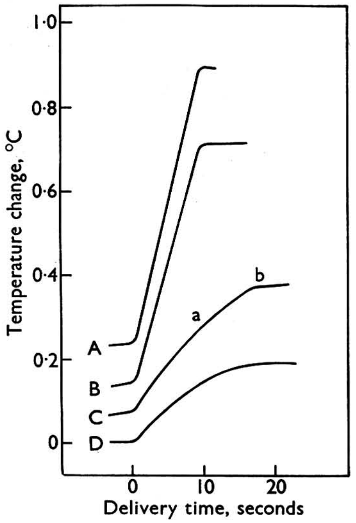

Fig. 2. Titrations with M hydrochloric acid of 20 ml of titrand containing 1 mmole of reactant: curve A, silver nitrate; curve B, sodium hydroxide; curve C, sodium carbonate; curve D, sodium tetraborate

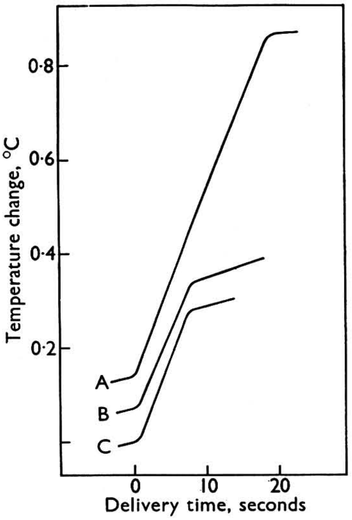

Fig. 3. Titrations with 0·05 M potassium permanganate of 20 ml of titrand containing 0·2 mmole of reactant: curve A, sodium sulphite; curve B, potassium iodide + sulphuric acid; curve C, ammonium ferrous sulphate + sulphuric acid

Some Na_4Y reactions do not give a sharp turn-over at the end-point, and it is often possible (by adding a second constituent to the titrand solution, whose heat of reaction is of opposite sign and which reacts after the solution being determined) to increase the rate of heat change at the end-point and so to achieve sharper detection. Curve C of Fig. 4 demonstrates the improved barium end-point (f) (compare curve B) obtained by adding ammonium nitrate solution, which itself gives an extremely poor end-point (g).

5. SUBSTITUTION REACTIONS—

It can be seen from the experimental results shown in Table I, indicating the relation between sequence of reaction and stability constants for EDTA chelates, that the metal ion in a solution of any chelate may be displaced by any other metal ion higher in the Table. It will further be seen that there are four possible combinations of substitution reactions of chelates which can occur. Thus, the metal ion in either an exothermally or endothermally formed chelate may be replaced by either an endothermally or exothermally reactive metal ion. Examples of these reactions are shown in Figs. 5 and 6.

The formation of calcium chelate is an exothermic reaction, so that when the chelate breaks down during substitution this heat appears in an endothermic form, while simultaneously the copper chelate is being formed in an exothermic reaction. Since curve B in Fig. 5 shows a rise in temperature, the conclusion is drawn that the heat of formation of the copper chelate is greater than that of the calcium chelate, although the types of reaction are similar.

On the other hand, replacement of calcium by aluminium, as illustrated in curve B of Fig. 6, gives an endothermic reaction with a greater heat change than that associated with the direct chelation of aluminium, although a poor end-point (o) is obtained.

TABLE I

SEQUENCE OF REACTION OF CATIONS WITH EDTA TETRASODIUM SALT AND PUBLISHED VALUES FOR STABILITY CONSTANTS (Log K_a)

Cation	Thermal change	Stability constants
Mercuric	Exothermic	21·8
Stannic	Exothermic	—
Ferric	Exothermic	25·1
Cupric	Exothermic	18·3
Nickelic	Exothermic	18·6
Plumbous	Exothermic	18·0
Cadmium	Exothermic	16·5
Zinc	Exothermic	16·3
Cobaltous	Exothermic	16·1
Ceric	Exothermic	—
Aluminium	Endothermic	16·1
Ferrous	Exothermic	14·4
Uranyl	Endothermic	—
Manganous	Exothermic	14·0
Calcium	Exothermic	10·6
Beryllium	Endothermic	—
Magnesium	Endothermic	8·7
Chromic	Endothermic	—
Strontium	Exothermic	8·6
Barium	Exothermic	7·7
Silver	Exothermic	7·3
Ammonium	Endothermic	—
Lithium	Endothermic	2·8
Potassium	Endothermic	—

The formation of magnesium chelate is an endothermic reaction, and replacement by copper results in a much greater heat change, as shown in curve A of Fig. 5, than that associated with the direct chelation of copper. In this reaction a good end-point is obtained. On the other hand, replacement of magnesium by aluminium, as shown in curve A of Fig. 6, gives a smaller heat change than for the direct chelation of aluminium. It may be concluded that the heat of formation of the aluminium chelate is greater than that of magnesium chelate. Once again a poor end-point (n) is obtained.

It is obvious that this method could be extended to facilitate analyses in which the heat of formation of the chelate is of low order, since, by suitable choice of the metal cation being displaced, much greater temperature changes can be observed.

6. MIXED TITRANTS—

Under "Chelation," the simultaneous determination of several components of a mixture of metal cations by titration with a single titrant was discussed. Similar results can be obtained for anions; for example, a mixture of iodide, bromide and chloride titrated with silver nitrate shows equivalence-points in that order, as would be expected. In some reactions, it is possible to make use of an extension to such a scheme of analysis by using a mixed titrant. An example of this is shown in Fig. 7, where a mixture of silver and thorium nitrates has been used to titrate all four halides, both separately and in a mixture. It will be seen from curve A that, at the start of the titration, fluoride and iodide react simultaneously to produce a rate of temperature rise equivalent to the sum of the separate reactions. When all the fluoride has been used up, equivalence-point (p), the iodide continues to react until it is used up at (q), followed by the bromide (r) and chloride (s).

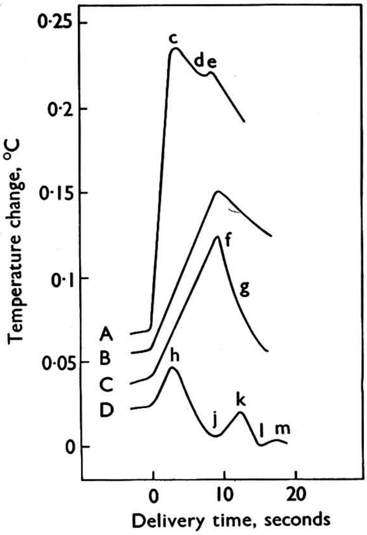

Fig. 4. Titrations with M tetrasodium EDTA of 20 ml of titrand containing: curve A, 1·0 mmole of silver; curve B, 1·0 mmole of barium; curve C, 1·0 mmole of barium + 1·0 mmole of ammonium; curve D, 0·3 mmole of iron^{III} + 0·3 mmole of aluminium + 0·8 mmole of calcium + 0·25 mmole of magnesium + 0·15 mmole of barium

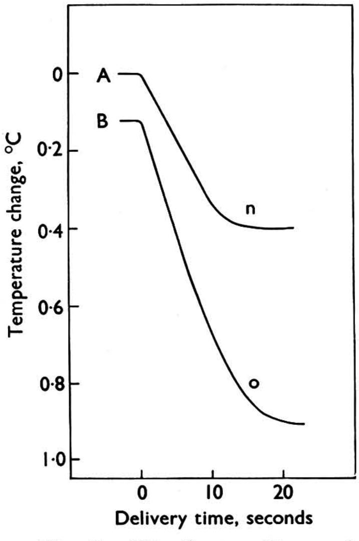

Fig. 6. Titrations with M aluminium nitrate of 20 ml of titrand containing 1 mmole of reactant: curve A, disodium magnesium - EDTA complex; curve B, disodium calcium - EDTA complex

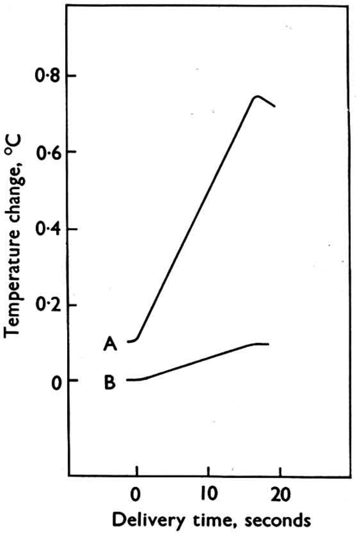

Fig. 5. Titrations with M cupric nitrate of 20 ml of titrand containing 2 mmole of reactant: curve A, disodium magnesium - EDTA complex; curve B, disodium calcium - EDTA complex

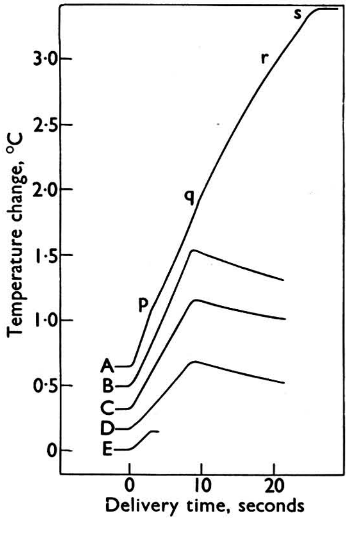

Fig. 7. Titrations with M thorium nitrate + silver nitrate of 20 ml of titrand containing 1 mmole of reactant: curve A, sodium fluoride + sodium chloride + sodium bromide + sodium iodide + nitric acid; curve B, sodium iodide; curve C, sodium bromide; curve D, sodium chloride; curve E, sodium fluoride + nitric acid

QUANTITATIVE DATA—

Although quantitative results can usually be more simply and rapidly obtained by using the automatic digital titrator, it is obviously desirable to make some reference to the method involving the use of a recorder to plot the thermal changes occurring during a titration. The conditions of experiment with respect to rate of addition of titrant, stirring and temperature sensing were the same as for the digital method. It follows that the quantitative data obtained by the latter method may also be taken as representative of the accuracy and reproducibility of the recorder method, provided that the actual recorder used has suitable sensitivity, rapid response and a sufficiently fast chart speed to permit accurate measurements to be taken on the curves obtained. It should be noted that the sharpness or otherwise of the curve of the record at the end-point of a reaction does not unduly influence the precision with which it may be located, provided that the straight line portions are long enough to permit tangents to be drawn accurately. This is a limitation for mixtures containing only a small proportion of one component, but the fact that such a minor component would usually be detected might nevertheless be an advantage and allow the analyst to use an alternative method of determination.

The results obtained when a chart speed of 8 inches per minute and a titrant delivery rate of 6·92 ml per minute were used are shown in Table II.

TABLE II

PRECISION OF TITRATION

Titrand	Titrant	Replicates	Mean titre, mm	Standard deviation, %
20 ml of 0·1 M $Cu(NO_3)_2$	M EDTA (Na_4)	11	60·28	±0·3
20 ml of 0·1 M NaOH	M HCl	11	57·06	±0·4
10 ml of 0·2 M $AgNO_3$	M HCl	11	58·39	±0·6
20 ml of 0·1 M I_2(in KI)	M $Na_2S_2O_3$	12	62·22	±1·3

CONCLUSIONS

It is apparent from the foregoing that the method is widely applicable. Thus, whereas most of the well-known volumetric methods can be carried out thermometrically, most of the determinations that are normally performed gravimetrically are also possible. In some instances several components can be determined by a single titration, thus avoiding the separation process that might otherwise be necessary. Alternatively, an extra component may sometimes be added to a mixture to provide end-point discrimination between two other components, again avoiding the necessity of making a physical separation. The saving in the time taken for analysis by precipitation reactions as compared with the gravimetric method will be obvious, but it is also considerable when compared with straightforward volumetric analysis with the use of indicators.

In comparison with potentiometric titrations, the thermometric method is simpler in that one thermistor takes the place of a series of different types of electrode. It must, however, be emphasised that, at this stage of instrumentation, it is not possible to work with such low concentrations as are possible with the former method.

It has been shown that the sequence of reaction of EDTA with a mixture of cations corresponds to the sequence of the stability constants of the chelates concerned. Similarly, for precipitation reactions in which there is a common ion, the sequence corresponds to that of the solubility products of the precipitates. It is therefore possible, in most instances, to predict from available data whether or not a thermometric titration method will be suitable for any given analytical problem. In this way, reagents that are not usually even considered for titrimetric work may be found to be suitable for particular applications. For example, magnesium chloride might be used for determining carbonate in a mixture of carbonate and hydrogen carbonate since magnesium hydrogen carbonate is sufficiently soluble not to interfere with the carbonate end-point. This titrant could also be used to back-titrate most cations, after adding the tetrasodium salt of EDTA, since the magnesium - EDTA complex has a fairly low stability constant and would not displace cations with higher stability constants.

Finally, as a result of the work described here and elsewhere, it is our belief that thermometric titration will play an important part in the future development of analytical methods, not only in the inorganic but also in the organic field.

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Determination of Specific Surface Area by Air-permeation at Low Porosities

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The average particle diameter of a powder can be determined with the Fisher sub-sieve sizer, as normally operated, at porosities within the range 0·80 to 0·40. The resulting figure for this diameter varies with the porosity of the powder bed, inadequate compression of the sample yielding a high result. A similar variation occurs with other air-permeation methods. Certain samples probably require compression to porosities below 0·40 to achieve uniform porosity and a consistent result. A simple method for extending the porosity range of the Fisher instrument below 0·40 is described.

MANY authors[1,2,3,4] have observed that the average particle diameter of powders, determined by air-permeation, varies with the porosity of the sample bed, lower values for this diameter being obtained at low porosities. We have confirmed, for several samples of griseofulvin and other antibiotics, that this phenomenon also occurs with the air-permeation apparatus described by Gooden and Smith[5] and available commercially as the Fisher sub-sieve sizer (Fisher Scientific Company, Pittsburg, Pa., U.S.A.; Kek Ltd., Ancoats, Manchester 12).

It is therefore evident that air-permeation does not yield a unique value for the average particle diameter of a powder. To overcome this difficulty, we prefer to test the sample at various porosities and to record as the diameter of the sample the minimum value found. For this purpose the Fisher sub-sieve sizer is more convenient than other types of apparatus, because it incorporates a device for compressing the sample to successively lower porosities and a chart from which the porosity and average particle diameter can be read directly.

Some samples, however, can readily be compressed to porosities lower than the minimum, 0·40, provided for on the Fisher chart. The main purpose of this paper is, therefore, to describe means whereby such samples can be tested at lower porosities with the existing chart.

METHOD

The instrument is assumed to obey the Gooden and Smith[5] equation, which can be expressed as—

$$d_{\mathrm{vs}} = \frac{\mathrm{c}LX}{(\mathrm{A}L - X)^{3/2}} \cdot \sqrt{\frac{F}{\mathrm{P} - F}} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where d_{vs} is the average particle diameter (volume-surface mean diameter) in microns, c is the instrument constant (3·80), L is the height of the compressed bed of powder (cm), X is the volume of the sample excluding bed porosity (c.c.), A is the cross-sectional area of the sample tube (1·267 sq. cm), F is the pressure difference across the flowmeter resistance (g per sq. cm), and P is the instrument air pressure (50 g per sq. cm).

The instrument chart, however, is designed to be used with a standard sample volume, X, of 1 c.c. It is, therefore, calibrated according to the equation—

$$d_{\mathrm{vs}}' = \frac{\mathrm{c}L}{(\mathrm{A}L - 1)^{3/2}} \cdot \sqrt{\frac{F}{\mathrm{P} - F}} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where d_{vs}' is the diameter indicated on the chart and corresponds to the average particle diameter only when the instrument is used as intended, *i.e.*, when $X = 1$.

The chart also indicates the bed porosity, ϵ', in accordance with the equation—

$$\epsilon' = 1 - 1/\mathrm{A}L \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

This equation also is correct only when $X = 1$ since, in general, the bed porosity, ϵ, is given by—

$$\epsilon = 1 - X/\mathrm{A}L \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

If a different sample volume is used, so that X is not unity, the average particle diameter can nevertheless be calculated from the diameter indicated on the chart. Comparison of equations (1) and (2) shows that the average particle diameter, d_{VS}, will be given by—

$$d_{\text{VS}} = X\left(\frac{1 - 1/\text{A}L}{1 - X/\text{A}L}\right)^{3/2} d_{\text{VS}}' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5)$$

and hence, after substitution of equations (3) and (4) in equation (5), by—

$$d_{\text{VS}} = X(\epsilon'/\epsilon)^{3/2} d_{\text{VS}}' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (6)$$

Similarly, the bed porosity, ϵ, can be calculated from the indicated porosity, ϵ', by means of the equation—

$$\epsilon = 1 - X(1 - \epsilon') \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (7)$$

We have found that the value of X must lie between about 1·2 and 1·3 to extend the range of ϵ down to the minimum porosities attainable with some samples we have used. If ϵ' is set at intervals of 0·04 and X is 1·25 c.c., ϵ will form a series at intervals of 0·05, as shown in Table I. This has the advantage that no interpolation is necessary when setting ϵ' on the instrument chart or plotting ϵ on a graph of the results.

The weight of sample required to give a volume of X c.c. is $X\rho$ g, where ρ is the density of the particles. For smooth particles containing no internal pores, ρ is the density of the solid material comprising the particles. Since, in general, the air flows around each particle but not through internal pores, the appropriate density of a porous particle is equal to its weight divided by its volume including internal pores.

The powders with which we have worked consisted of simple crystals, or fragments of crystals, with no internal faults or pores visible under a microscope. We have assumed, therefore, that the appropriate particle density is that measured by displacement of liquid in a specific-gravity bottle.

PROCEDURE—

Take a weight (in grams) of sample equal to the density × 1·25. Compress the weighed sample to the sample height curve of the Fisher chart at a high value of indicated porosity from Table I. Read the indicated diameter on the chart, and multiply the result by the corresponding diameter factor from the Table. Compress the sample to successively lower porosities until the corrected diameter reaches a minimum.

TABLE I

DIAMETER CORRECTION FACTORS AND THE CORRESPONDING VALUES OF INDICATED AND CORRECTED POROSITY

The sample volume, X, = 1·25 c.c.

Indicated porosity, ϵ'	Corrected porosity, ϵ	Diameter factor, $X(\epsilon'/\epsilon)^{3/2}$
0·80	0·75	1·377
0·76	0·70	1·414
0·72	0·65	1·457
0·68	0·60	1·508
0·64	0·55	1·569
0·60	0·50	1·643
0·56	0·45	1·735
0·52	0·40	1·853
0·48	0·35	2·008
0·44	0·30	2·220
0·40	0·25	2·530

EXPERIMENTAL

The Fisher instrument was calibrated to conform with equation (1) by checking the accuracy of the constants c, A and P and the variables L and F. Details of the calibration method, which involves the use of a capillary tube of accurately known dimensions, are contained in a paper being prepared for publication.

The validity of the correction method (equation (6)) was demonstrated by testing a sample of griseofulvin at the normal sample weight level and at the × 1·25 level.

The normal weight sample was compressed to successively lower porosities over the range 0·65 to 0·40, and corresponding readings of average diameter were obtained. The over-weight sample was similarly tested over the range 0·68 to 0·41 indicated porosity, corresponding to 0·60 to 0·26 bed porosity. Light compression in a screw clamp was necessary to attain porosities below 0·35; because this might have crushed some of the particles and altered the average diameter, the compressed plug was removed from the tube at the end of the run, broken up through a 40-mesh sieve and re-tested on the instrument at the × 1·25 level.

RESULTS

The values for average particle diameter for the three determinations were plotted against porosity (see Fig. 1). The various points obtained from the two levels of sample weight lie close to a single curve and thus confirm the validity of the method. The points resulting from the repeat determination on the previously compressed plug also fall close to the original curve at the low porosities. This demonstrates that the slope of the curve is not due to the particles being crushed by compression.

The shape of curve shown in Fig. 1 is typical of our results in testing many samples of griseofulvin and other antibiotics. The average diameter falls more or less rapidly at first and then levels out to a minimum when tight compression has been achieved. Doubtless, this effect is due, at least in part, to the tendency of fine powders to form lumpy aggregates, as discussed below. Rigden[6] has stated that determinations of air-permeation on such powders will be in error at high porosities if the bed of powder contains aggregates of lower porosity than the matrix in which they are embedded. Until the bed is compressed to a uniform porosity equal to that of the aggregates, air will pass more readily around than through the aggregates. Thus the instrument reading will reflect the diameter of the aggregates rather than that of the individual particles.

Carman and Malherbe[4] found a similar tendency for the diameter of fine powders to become constant at low porosities. For each sample there was a different "normal" porosity range within which the powder was compressed uniformly enough to give a constant result. They found a normal porosity range of about 0·5 to 0·4 for samples of uniform particle size, but concluded that for non-uniform samples, in which small particles fit into the voids between large ones, normal porosity could well be 0·3 or less.

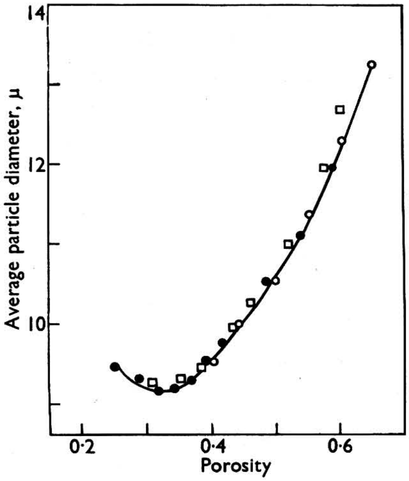

Fig. 1. Average particle diameter of a sample of griseofulvin as determined in the Fisher sub-sieve sampler: ○, on normal weight of sample; ●, on over-weight sample, results corrected as shown in Table I; □, compressed plug, from previous determination at porosity 0·26, broken up through sieve and re-tested

This accords well with our experience of griseofulvin samples. We have found normal porosities as high as 0·53 for samples of uniform particle size and as low as 0·25 for non-uniform material.

With further reduction of porosity, our curves usually show a slight rise in diameter after the minimum has been reached. This feature is absent from the results of Carman and Malherbe; because their samples were finer than ours, it is possible that they had greater difficulty in achieving a sufficiently tight compression.

This means that normal porosity is not to be regarded as a range within which the diameter is a constant, but as a point at which the diameter is a minimum. In this connection, as Carman and Malherbe have observed, there is a scatter of experimental points about a mean value of diameter at each porosity, so that results over a limited porosity range may give the impression that diameter is independent of porosity. In our work, experimental scatter was reduced by attention to the details of calibration mentioned above.

The question of which point on such curves corresponds to the true diameter raises complex issues, not only about uniformity of porosity but also about validity of the porosity function in the equation and the theory of air flow.[3] Discussion of these problems is beyond the scope of this paper, but further work on them is described in detail in a paper being prepared.

Meanwhile, for purposes of analytical control, there is a need to define a technique that will give a unique value for the average particle diameter of a powder. The American Society for Testing Materials' method for cement[7] meets this need by standardising the porosity of the compressed sample at 0·500. This is satisfactory, because cement is free-flowing and non-cohesive; the range of porosities that can be achieved with cement is limited.

With more cohesive powders, such as griseofulvin, it is possible to achieve a wider range of porosities, and the variation of average particle diameter with porosity is greater. Defining the average diameter as the minimum on the diameter - porosity curve not only provides the unique value required for analytical control, but avoids possible error due to channelling of air through an inadequately compressed bed when the sample has an unusually low normal porosity.

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The Quantitative Determination of Nitroglycerin by the Schultze - Tiemann Method

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The Schultze - Tiemann method for determining nitrogen content has been used for quantitatively determining nitroglycerin in powders and dynamites. The method is simple, rapid and gives accurate results; the presence of diphenylamine, diethyldiphenylurea, dimethyldiphenylurea, dipentylphthalate, dinitrotoluene or paraffin oil does not interfere.

In the analysis of explosives it is frequently necessary to determine the nitroglycerin content of powders and dynamites. Different procedures for the quantitative determination of nitroglycerin have been proposed; some depend on the preferential solvent action of carbon disulphide on the true nitro-compounds and similarly that of aqueous acetic acid (about 75 per cent.) on glycerol trinitrate,[1,2,3] the two liquids being nearly immiscible. Methods are used in which nitroglycerin is destroyed so that other compounds, such as nitro-compounds present in the mixture, can be subsequently extracted and determined; the loss in weight can be calculated as the amount of nitroglycerin.[4] This has been effected by reduction with ferrous chloride in concentrated hydrochloric acid[5] and also with ammonium sulphide.[4]

It has long been known that the percentage of nitroglycerin in admixture with other compounds can be deduced from the nitrogen content. This method will be applicable only if no substance is present that will evolve nitrogen in the determination, or if the amount of nitrogen due to other nitric esters or nitrates is known.[3] Several methods for determining the nitrogen content have been suggested.[6,7,8,9,10] The methods proposed by Silberaad, Phillips and Merriman[11] and Muraour[10] rely on the reduction of the nitrate groups of nitroglycerin by suitable reagents and then the determination of the nitrogen as ammonia. Excellent results were obtained by Muraour's method, but, because of the time required for a determination, it was not suitable for control analysis.[6]

The ferrous - titanous titration procedure proposed by Knecht and Hibbert[12] for analysing potassium nitrate was applied by Becker to glycerin trinitrate.[6] Becker's volumetric method for the quantitative determination of nitroglycerin consists in dissolving the extracted ingredients from the powder sample in acetic acid, adding an excess of ferrous chloride and hydrochloric acid, boiling the solution, and then titrating the resulting ferric iron with standard titanous chloride solution, ammonium thiocyanate being used as indicator. An atmosphere of carbon dioxide is maintained in the titration flask during the entire period. Although a somewhat complicated piece of apparatus is required, this method is the one most widely used in control and research laboratories[8]; small amounts of diethyldiphenylurea, diphenylamine or both do not interfere in the determination.

Other methods for determining nitrogen content have been proposed; *e.g.*, the nitrometer method[3] and the Schultze - Tiemann method[9] were early suggested as methods for the quantitative determination of nitroglycerin. These methods were neglected when it was found that certain compounds, *e.g.*, diphenylamine, diethyldiphenylurea and mononitrotoluenes, present in admixture with nitroglycerin could interfere in the determination and cause low results.[3,6]

During this investigation, trials have been made to determine the nitroglycerin content of powders and dynamites by the Schultze - Tiemann method, but low results were consistently obtained. The causes of these low results were thoroughly investigated and the official Schultze - Tiemann method was slightly modified; satisfactory results have subsequently been obtained. The procedure was simplified so as to be suitable for the control determination of the nitroglycerin content of powders and dynamites.

METHOD

APPARATUS—

The apparatus (see Fig. 1) consists of a long-necked Kjeldahl flask, A, of capacity about 200 ml connected to a one-way valve, B, and a delivery tube, C. The Kjeldahl flask is tightly fitted with a rubber stopper carrying a funnel, D, with a stopcock, E. The nitric oxide is collected over approximately 33 per cent. sodium hydroxide solution in a graduated burette, F, with a zero mark beginning from the stopcock, G.

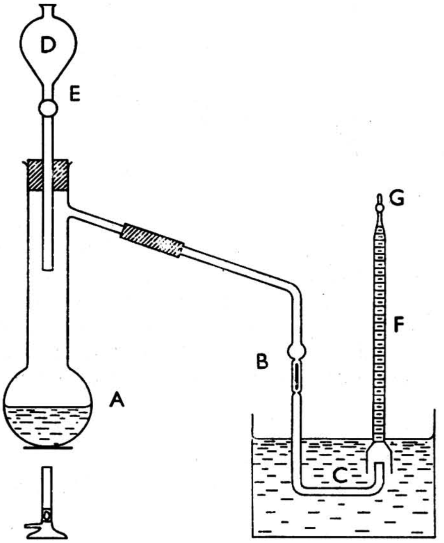

Fig. 1. Apparatus for determining the nitrogen content of explosives

REAGENTS—

Sodium hydroxide solution, approximately 33 *per cent.*

Ferrous chloride solution—Dissolve 120 g of powdered iron in 373 ml of hydrochloric acid, sp.gr. 1·19, and 227 ml of distilled water.

PROCEDURE—

Extract a weighed amount of the finely ground powder with diethyl ether in a Soxhlet apparatus for 24 hours.[4,8] Allow the ether in the extraction flask to evaporate, and dry the ether extract at 45° to 50° C for about 16 hours to constant weight. Cool, weigh, and calculate the ether extract as a percentage.

In a small weighing bottle weigh a sample of the ether extract (about 100 mg). Transfer a 20- to 30-mg sample (weighed by difference) to the flask. Introduce 30 ml of distilled water into the flask, and then add 10 ml of 0·1 N potassium permanganate. Tightly seal the flask by means of the rubber stopper carrying the funnel D. Open stopcock E and gently heat the flask with a bunsen burner. When the solution boils, close the stopcock E, and expel all air from the flask through valve B by continuing to boil the solution. To ensure that all the air is expelled, cool the apparatus, and introduce a small amount of water into the flask through stopcock E (care should be taken not to admit any air); then boil the solution again until no air collects over the sodium hydroxide in the burette.

After all the air has been expelled, introduce, successively, 20-ml portions of ferrous chloride solution and of diluted hydrochloric acid (1 + 1) into the flask from funnel D through stopcock E; take care not to admit any air into the reaction flask. Heat the flask, and collect the liberated nitric oxide over sodium hydroxide solution in the graduated burette F. After all nitric oxide has been expelled, repeat the process two or three times with 10-ml portions of ferrous chloride solution and of dilute hydrochloric acid and finally with distilled water until no further nitric oxide is liberated. Then transfer the burette to a cylinder filled with water, and, after 10 to 15 minutes, read off the volume, V, barometric pressure, P, and temperature, t; calculate the percentage by weight, G, of nitrogen in the sample from the expression—

$$G = \frac{V \times 100 \times 14{\cdot}01 \times (P - b) \times 273}{W \times 22389{\cdot}6 \times 760 \times (273 + t)},$$

where W = weight of sample taken and
b = water vapour pressure at t° C.

Hence calculate the nitroglycerin content of the sample from the expression—

$$\text{Nitroglycerin, \%} = \frac{\text{Percentage by weight of ether extract} \times G}{\text{Nitrogen content of nitroglycerin}}$$

NOTE—Blank experiments for determining the nitrogen content of nitroglycerin should be carried out in the same apparatus as used above. Before each set of determinations triplicate samples of commercial nitroglycerin should be analysed and the mean value taken as the nitrogen content; this value should accord with the theoretical (about 18·4 per cent.[13]). The Schultze - Tiemann apparatus should be checked periodically by testing with pure potassium nitrate as the sample.

RESULTS AND DISCUSSION OF THE METHOD

The Schultze - Tiemann method has been recommended by different workers for determining nitrate nitrogen.[7,15,16,17,18] It was once considered more suitable than the nitrometer method for analysing cellulose nitrate, particularly when the samples to be tested are in a physical condition such that they do not easily dissolve in sulphuric acid.[7,15] Results obtained by the nitrometer and Schultze - Tiemann methods were found to be in close agreement.[3,7,17,18]

During the investigation described here, formulated mixtures containing different amounts of nitroglycerol, dinitrotoluene, diethyldiphenylurea (Centralite I), dimethyldiphenylurea (Centralite II), dipentylphthalate (amylol) and paraffin oil were prepared as shown in Table I. The quantitative determination of nitroglycerin present in these formulated mixtures (see Table I), as well as certain types of powders and dynamites of known chemical compositions (see Table II), was carried out by means of the proposed method.

In the official Schultze - Tiemann method air is expelled from the decomposition flask by boiling water. After all the air has been expelled, ferrous chloride solution and dilute hydrochloric acid are added, and the reaction mixture is then boiled until all the nitric oxide has been liberated.

$$HNO_3 + 3FeCl_2 + 3HCl = 3FeCl_3 + 2H_2O + NO$$
$$KNO_3 + 3FeCl_2 + 4HCl = 3FeCl_3 + 2H_2O + KCl + NO$$

It is significant that when commercial nitroglycerin and the formulated mixtures (see Table I) were analysed by the procedure described in the official test, the results obtained were consistently lower than the theoretical. The nitrogen content of nitroglycerin was found to be about 16·5 per cent., whereas, when a sample was analysed by the nitrometer method, it was found to contain 18·35 per cent. of nitrogen. The percentages of nitroglycerin present in the formulated mixtures (see Table I) were also found to be 3 to 5 per cent. low; the nitrometer method also gave low results (by 3 to 4 per cent.).

On the other hand, when 10 ml of 0·1 N potassium permanganate were added to the distilled water present in the decomposition flask, before air is expelled from the flask, the results obtained were found to be satisfactory. Commercial nitroglycerin (when permanganate solution was added) was found to contain 18·4 to 18·45 per cent. nitrogen; a value that accords with the theoretical.[13] Further, it is apparent that the glycerin found by analysis in the formulated mixtures closely corresponds with the true value. When the method was applied to some types of powders and dynamites of known chemical compositions, the results were found to be satisfactory (see Table II).

The nitrogen contents of cellulose nitrate and of pure potassium nitrate were determined by means of the official Schultze - Tiemann method (without addition of permanganate) and the results (13·76 and 12·23 per cent. of nitrogen, respectively) were found to be in close agreement with the nitrometer values (13·81 and 12·26 per cent., respectively); this was not so when nitroglycerin was analysed. This may be related to the fact that glycerin trinitrate has an appreciable vapour pressure at 100° C[19,20] and part of the loss during the determination of nitrogen by the Schultze - Tiemann method (without addition of permanganate) may have been caused by steam distillation of the ester during the displacement of air from the decomposition flask. When potassium permanganate is added it oxidises glycerin trinitrate to nitric acid,[12]

$$C_3H_5(NO_3)_3 + 3\tfrac{1}{2}O_2 \longrightarrow 3HNO_3 + 3CO_2 + H_2O$$

and thereby minimises the vaporisation of nitroglycerin when the air is expelled from the flask.

TABLE I

DETERMINATION OF NITROGLYCERIN IN FORMULATED MIXTURES

Composition of mixture, %	Nitroglycerin found, %	Mean, %	Error, %
Nitroglycerin, 71·06; diphenylamine, 3·24; Centralite I*, 6·70; Amylol†, 19·0	71·08, 71·09, 71·05, 71·13	71·09	+0·03
Nitroglycerin, 59·02; dinitrotoluene, 30·00; diphenylamine, 5·40; Centralite I*, 5·58	59·02, 59·03, 59·07, 59·04	59·04	+0·02
Nitroglycerin, 51·78; diphenylamine, 20·00; Centralite II‡, 10·00; Amylol†, 18·22	51·84, 51·80, 51·77, 51·82	51·81	+0·03
Nitroglycerin, 79·8; diphenylamine, 7·0; Centralite I*, 4·5; Centralite II‡, 2·0; Amylol†, 6·7	79·86, 79·85, 79·76, 79·90	79·84	+0·04
Nitroglycerin, 32·97; diphenylamine, 4·00; Centralite II‡, 4·00; dinitrotoluene, 34·03; Amylol†, 15·00; paraffin oil, 10·00	33·05, 33·02, 33·01, 32·95	33·01	+0·04

* Diethyldiphenylurea.
† Dipentylphthalate.
‡ Dimethyldiphenylurea.

TABLE II

DETERMINATION OF NITROGLYCERIN IN POWDERS AND DYNAMITES

	Nitroglycerin found by—		
Specified composition of sample, %	Nitrometer method, %	Modification of Muraour's method,[4] %	Schultze - Tiemann method, %
Nitroglycerin powder I—			
Nitroglycerin, 27·1 ± 0·5; nitrocellulose, 64·0 ± 1·0; diphenylamine, 1·0 ± 0·2; Centralite I*, 2·0 ± 0·2; Amylol†, 4·65 ± 0·2; petroleum jelly, 1·45 ± 0·2	24·3, 23·9, 23·5 (Mean 23·9)	27·09, 27·23, 27·40 (Mean 27·24)	27·30, 27·32, 27·32 (Mean 27·31)
Nitroglycerin powder II—			
Nitroglycerin, 26·0 ± 0·5; nitrocellulose, 68·8 ± 1·0; diphenylamine, 1·2 ± 0·2; Centralite I*, 0·5 ± 0·2; Amylol†, 3·5 ± 0·5	23·0, 23·3, 22·92 (Mean 23·07)	26·05, 26·10, 26·15 (Mean, 26·10)	26·10, 26·15, 26·18 (Mean, 26·14)
Nitroglycerin powder III—			
Nitroglycerin, 29·6 ± 0·5; nitrocellulose, 66·0 ± 1·0; diphenylamine, 1·0 ± 0·2; Centralite I*, 1·0 ± 0·2; Amylol†, 1·0 ± 0·2; petroleum jelly, 1·4 ± 0·2	26·6, 25·9 (Mean 26·25)	29·86, 29·80, 29·70 (Mean, 29·79)	29·72, 29·75, 29·80 (Mean, 29·76)
Extra dynamite I, ether extract—			
Nitroglycerin, 20 ± 2; trioil, 12 ± 2	19·70, 19·68 (Mean, 19·69)	—	19·80, 19·85 (Mean, 19·83)
Extra dynamite II, ether extract—			
Nitroglycerin, 22 ± 1; trioil, 11 ± 1	21·90, 21·92 (Mean, 21·91)	—	22·02, 22·04 (Mean, 22·03)

* Diethyldiphenylurea.
† Dipentylphthalate.

The results in Tables I and II clearly indicate that different percentages of diphenylamine, dinitrotoluene, diethyldiphenylurea, dimethyldiphenylurea, dipentylphthalate and paraffin oil do not interfere in the quantitative determination of nitroglycerin present in admixture with these compounds by the Schultze - Tiemann method. Further, this method of analysis is simple and rapid, and gives accurate results.

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SHORT PAPERS

A Method for determining Orthophosphate in Water

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The methods currently recommended[1,2,3] for determining phosphate in water involve the reduction of molybdophosphoric acid, the blue colour so obtained being proportional to the amount of phosphorus present. In all of these methods close control of acidity is necessary, different acid concentrations giving rise to "blue" of various spectral properties.[4] Control of reaction temperature is important for reproducible results, and the colour formed is subject to fading. Stannous chloride is the reductant favoured when greatest sensitivity is required, but this reagent is unstable and must be freshly prepared. Variation in the amount of stannous chloride reagent used has also been found to have an effect on the final optical density produced by a known amount of phosphorus.

The vanadium phosphomolybdate method developed by Kitson and Mellon[5] appeared to be free from most of these disadvantages. A simpler version of their procedure, proposed by Hanson,[6] has recently been adopted as the official spectrophotometric method[7] for determining phosphoric acid in fertilisers and feeding stuffs. This method has now been investigated as applied to the determination of the phosphate content of water, and a rapid simple procedure has been evolved.

Experimental

Hanson's[6] procedure requires the addition of 25 ml of a vanadium molybdate reagent for 5 to 6·2 mg of phosphoric acid (as P_2O_5) in a final volume of 100 ml. Optical-density measurements of the resulting yellow colour are made at 420 mμ against a reference solution containing 5·0 mg of phosphoric acid similarly treated. The amounts of phosphate (as PO_4) to be found in water usually lie in the range 0 to 5 mg per litre. Hence, experiments have been performed to discover the minimum amount of vanadium molybdate to be used, the maximum permissible acid strength of the reagent and the wavelength for optical-density measurement best suited to the sensitivity required.

The proposed reagent contains one-half of the amounts of ammonium vanadate and ammonium molybdate suggested by Hanson.[6] One millilitre of this reagent is sufficient to determine up to 100 μg of phosphorus (as P). Because of the proposed decreased volume of reagent, it has been necessary to increase the nitric acid content somewhat. Further increase in acidity results in a decrease in sensitivity, but the method is insensitive to decrease in acidity owing to the alkalinity of most waters. To ensure the required sensitivity, optical-density measurements are made at 370 mμ in 4-cm cuvettes against distilled water. By using these reduced amounts of reagent the blank has been found to have the acceptable value of about 0·025. The reagent is stable for at least 3 months.

The rate of colour development is temperature dependent, but the maximum optical density is attained, in all reactions, within 10 minutes after adding the reagent. This maximum value is independent of temperature in the range 0° to 30° C and is stable for at least 2 hours.

Interference caused by the colour of some natural waters, whose absorption can be appreciable at 370 mμ, is avoided by determining the optical density of a second portion of the sample to which only dilute nitric acid has been added. Subtraction of this value from that obtained by the proposed procedure then gives a corrected figure related to the phosphate content of the water.

In a litre of water, up to at least 5000 mg of chloride, 20 mg of fluoride, 2000 mg of alkalinity (as calcium carbonate), 200 mg of silicate (as SiO_2) and 2 mg of ferric iron have been shown not to interfere in the proposed procedure. Polyphosphates (*e.g.*, hexametaphosphate and pyrophosphate) are not usually present in natural waters, but may occur in treated waters. They do not interfere in this method provided that the optical-density readings are taken not more than 30 minutes after adding the reagent. Polyphosphates are very slowly hydrolysed by the acidic reagent, the rate of hydrolysis appearing to increase with time.

The proposed method gives a reproducible and accurate determination of the soluble orthophosphate content (as PO_4) in the range 0·02 to 4 mg per litre of a water. The results obtained are similar to those obtained by the standard stannous chloride - molybdenum blue procedure, but they are achieved more simply and with greater certainty.

METHOD

REAGENTS—

All reagents should be of recognised analytical grade; solutions should be prepared in distilled or de-ionised water.

Vanadium molybdate solution—Dissolve 0·50 g of ammonium vanadate in warm water, cool, and add 125 ml of nitric acid, sp.gr. 1·42. Add a solution of 10·0 g of ammonium molybdate in water, and dilute to 1 litre.

Nitric acid, 2·0 N, *approximately.*

Standard phosphate solution—Dissolve 0·716 g of potassium dihydrogen phosphate (dried at 150° C) in water, and dilute to 1 litre. Dilute 20 ml to 1 litre as required.

$$1 \text{ ml} \equiv 10\ \mu\text{g of phosphate as } PO_4$$

PREPARATION OF STANDARD GRAPH—

Dilute to 50 ml appropriate volumes of the standard phosphate solution to the range 0 to 200 µg of phosphate as PO_4. To each add 1 ml of vanadium molybdate solution, mix well, and set aside at room temperature for 10 minutes. Measure the optical density of each test solution in 4-cm cuvettes against distilled water with a suitable spectrophotometer at 370 mµ. Plot a graph relating optical density to phosphate content; this should be linear.

PROCEDURE FOR COLOURLESS SAMPLES—

Take 50 ml of sample and proceed as described under "Preparation of Standard Graph" at ". . . add 1 ml of vanadium molybdate solution. . . ." Determine the orthophosphate content of the sample by referring the optical density so determined to the previously prepared standard graph.

PROCEDURE FOR COLOURED SAMPLES—

Proceed as described for colourless samples.

To 50 ml of sample add 1 ml of 2 N nitric acid, and determine the optical density of this solution as described above.

Determine the orthophosphate content of the sample by referring the difference in the optical densities obtained to the standard graph.

Turbid samples should be filtered, preferably through sintered-glass, before examination.

RESULTS

All optical-density measurements were made with a Unicam SP600 spectrophotometer.

RECOVERY OF ADDED PHOSPHATE—

The recovery of orthophosphate added to several waters of various sources and degrees of hardness has been determined by the proposed method; the results are shown in Table I.

TABLE I

RECOVERY OF ORTHOPHOSPHATE ADDED TO WATER

Source of water	Hardness as $CaCO_3$, mg per litre	Phosphate present, mg of PO_4 per litre	Phosphate added, mg of PO_4 per litre	Phosphate found, mg of PO_4 per litre
River	260	1·9	0·30	2·2
River	255	1·9	1·2	3·1
Borehole	290	0·15	0·60	0·72
River	330	0·85	3·0	3·9
Lake*	70	0·09	0·60	0·70

* This sample was coloured, Hazen 125.

REPRODUCIBILITY OF THE MEHOD—

The excellent reproducibility of the method is illustrated by the optical densities tabulated below obtained by repeated treatment of different waters.

Optical density due to water No. 1	0·532, 0·532, 0·532, 0·533, 0·532, 0·532
Optical density due to water No. 2	0·323, 0·322, 0·321, 0·322, 0·323

COMPARISON OF METHODS—

Determinations have been made by the proposed method and by a stannous chloride - molybdenum blue method[2] on several drinking and boiler-feed waters. The results obtained are shown in Table II.

TABLE II

COMPARISON OF METHODS

Results are expressed as mg of PO_4 per litre

	Orthophosphate found by—	
Sample	Proposed method	Molybdenum blue method
Drinking water No. 1	0·93	0·95
Drinking water No. 2	0·01	Nil
Drinking water No. 3	0·55	0·55
Drinking water No. 4	0·12	0·12
Drinking water No. 5	0·09	0·12
Drinking water No. 6	1·9	1·9
Boiler-feed water No. 1*	0·21	0·19
Boiler-feed water No. 2*	0·15	0·16
Boiler-feed water No. 3*	0·36	0·34

* These samples also contained about 1·5 mg of sodium hexametaphosphate (as PO_4) per litre.

Permission to publish this paper has been given by the Government Chemist, Department of Scientific and Industrial Research.

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The Rapid Micro-determination of Carbon and Hydrogen with Magnesium Oxide-Catalyst Oxide Mixture

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THE use of magnesium oxide in slow combustion methods for determining carbon and hydrogen in the presence of fluorine has been advocated by several authors,[1,2] the tube filling consisting of separate layers of magnesium oxide and copper oxide. Campbell and Macdonald[3] first suggested the use of magnesium oxide on its own, especially for fluorinated materials, an oxygen flow rate of 12 ml per minute being maintained.

We have applied a single intimate mixture of magnesium oxide - catalyst oxide powders at temperatures between 900° to 1000° C and at an oxygen flow rate of 100 ml per minute with horizontal and vertical (Coleman) trains being used; the time required for combustion and sweeping is only 12 minutes. The proposed method has been tested on a wide range of organic compounds containing fluorine, chlorine, bromine, iodine, sulphur, nitrogen, phosphorus, arsenic, silicon, germanium and boron.

We have used mixtures of magnesium oxide with copper oxide, cobalt oxide, nickel oxide, vanadium pentoxide and platinum and have found the system magnesium oxide - copper oxide to be the best under the conditions described in this paper. Chlorine- and bromine-containing compounds were burnt with a mixture of magnesium oxide, copper oxide and silver.

Since most end-products of oxidative pyrolysis of organic compounds are acidic, basic conditions will accelerate the attainment of equilibrium, and this is most likely the function of magnesium oxide in the proposed mixture. When using copper oxide without magnesium oxide we obtained poor results under rapid conditions; conversely, magnesium oxide alone also proved inadequate, yielding low values for carbon.

The performance of the horizontal train was, in general, more uniform than that of the Coleman train.

METHOD

APPARATUS—

Horizontal train—The quartz tube (see Fig. 1) is 55 to 60 cm long and 11 mm in diameter. The rear portion of the tube (25 cm) is empty and serves for the insertion of the sample in a platinum boat; it is heated by a movable furnace of the split type, adjusted to approximately 950 °C. The remaining portion of the tube is filled permanently and is heated by furnaces A and B. The lengths of the furnaces and the sequences of the layers surrounded by them are: A, 20 cm long, filled with granules of the magnesium oxide - catalyst oxide mixture; B, 7 cm long, filled with M.A.R. grade silver-wool, which occupies most of the gap between A and B. The "beak" of the combustion tube is packed with M.A.R. grade silver-wool. The temperatures of furnaces A and B are adjusted to 950° and 180° C, respectively.

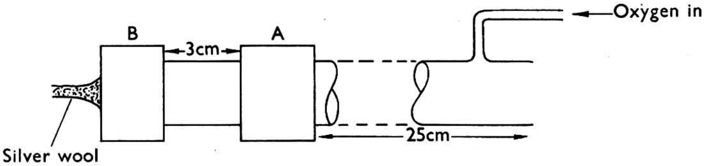

Fig. 1. Combustion tube and heating units

The pre-heater, pre-treat absorption tube, Rotameter, nitrogen oxide absorption tube and Flaschenträger-type absorption tubes are of conventional type.[4] The water-absorption tube is filled with M.A.R. grade anhydrone. The carbon dioxide absorption tube contains three layers: "carbabsorb" soda-lime (self-indicating granules, 15 to 20 mesh), ascarite and anhydrone. The use of ascarite alone may result in blocking of the carbon dioxide absorption tube under rapid conditions, and low values for carbon are obtained.

Vertical train, Coleman Model 33: *carbon - hydrogen analyser*—A detailed description of this automatic train is given in a pamphlet issued by the manufacturers.[5] We shall therefore restrict ourselves to listing the modifications introduced by us—

(*i*) The quartz combustion tube, which is 34·5 cm long and 10 mm in diameter, has an empty portion of 12·5 cm at the top end (for the insertion of the sample); this is followed by a layer of magnesium oxide - catalyst oxide mixture (12·5 cm) and finally by a roll of 40-mesh silver gauze (7·5 cm).

(*ii*) Carbon dioxide and pre-treat absorption tubes contain 15- to 20-mesh "carbabsorb" soda-lime.

(*iii*) The temperature of the final section of the metal tubing inside the apparatus is maintained at approximately 100° C. This eliminates fluctuations of the hydrogen values with changes in room temperature.

MAGNESIUM OXIDE - CATALYST OXIDE MIXTURE—

The materials may be of laboratory-reagent grade. The procedure described below was adopted for preparing the mixture. Equal amounts, by weight, of magnesium oxide and catalyst oxide powders* are cautiously mixed with water, until a thick uniformly coloured paste is obtained. After being dried at 120° C, the cake is ignited for 1 hour at 850° C in a muffle furnace.

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* Copper oxide in wire form is also satisfactory, except for compounds that are difficult to burn, *e.g.*, bispentafluorophenyl mercury, when copper oxide powder proved superior.

PROCEDURE—

In general, the procedure follows the pattern established for the rapid technique.[6,7] The platinum boat containing between 5 and 15 mg of sample is inserted in the combustion tube approximately 5 cm from furnace A, and the mouth of the combustion tube is closed. The operations listed in Table I require careful timing with a stopwatch.

TABLE I

DETAILS AND SEQUENCE OF OPERATIONS

Operation	Operating time, seconds	Flow rate, ml per minute	Position of furnace
Purge	50	100	Platinum boat halfway between furnace A and movable furnace
Pre-heat	120	0	Movable furnace pulled into position around the combustion tube
Slow combustion	120	4	Movable furnace brought up to the platinum boat
Fast combustion	120	100	Movable furnace brought up to furnace A
Final sweep	300	100	Position as for "Fast Combustion"

After the final sweeping, the absorption tubes are weighed within 2 minutes for the Coleman train and 3 minutes for the horizontal train. Thus, an over-all time for weighing plus determination is 16 minutes for the Coleman and 18 minutes for the horizontal train.

Some typical results for over 600 analyses are shown in Table II. With the horizontal train, about 200 analyses have been performed without the tube filling being changed.

TABLE II

TYPICAL RESULTS

Sample	Carbon found, %	Carbon calculated, %	Hydrogen found, %	Hydrogen calculated, %
Benzoic acid (M.A.S.)	68·92	68·84	5·05	4·95
Phenylthiourea (M.A.S.)	55·02	55·24	5·35	5·30
p-Chlorobenzoic acid (M.A.S.)	53·72	53·69	3·39	3·22
p-Bromobenzoic acid (M.A.S.)	41·70	41·82	2·62	2·51
o-Iodobenzoic acid (M.A.S.)	34·00	33·90	2·06	2·03
Trifluoroacetanilide (M.A.S.)	50·71	50·80	3·29	3·20
m-Trifluoromethylbenzoic acid (M.A.S.)	50·55	50·54	2·67	2·65
Biphenylsulphone	65·75	65·99	4·84	4·62
Triphenylphosphine (M.A.S.)	82·39	82·42	5·96	5·77
2-Aminoethoxydiphenylborane	74·8	74·7	7·4	7·1
sym-Tetraphenyldimethyldisilane	79·2	79·1	6·6	6·6
Manganese tricarbonyl-di-triphenylphosphine hydride	70·5	70·5	4·55	4·7
Phenyl manganese tetracarbonyltriphenylarsine	61·2	61·0	3·6	3·6
Hexaphenyldigermane	71·1	71·2	4·9	4·94

We thank Mr. P. Woodbridge for carrying out various analytical determinations.

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Book Reviews

RESIDUE REVIEWS: RESIDUES OF PESTICIDES AND OTHER FOREIGN CHEMICALS IN FOODS AND FEEDS. Volume 2. Edited by FRANCIS A. GUNTHER. Pp. iv + 156. Berlin, Göttingen and Heidelberg: Springer-Verlag. 1963. Price DM 22.

The second volume of "Residue Reviews" is essentially similar in scope to the first (see *Analyst*, 1963, **88**, 486). All the chapters deal with pesticide residues and, with one exception, all are presented in English. Polarographic methods for the determination of insecticide and fungicide residues are reviewed, in French, by P. H. Martens and P. Nangniot (pp. 25); and, incidentally, this imparts a bilingual atmosphere to the subject index at the end of the volume. The applicability of the method to copper, mercuric, arsenic, selenium and organo-tin compounds, to phosphides and to products containing elemental sulphur are briefly considered, followed by specific accounts of the use of polarography for nicotine, the pyrethrins and a full review of the work on various synthetic organic pesticide residue determinations in soils, seeds, fruit and vegetables.

The volume begins with a short account by A. L. Taylor (U.S. Department of Agriculture) on nematocide residues in plants (pp. 8, including three pages of summaries and references), about which there appears to be little published information. C. H. van Middelem writes on the nature, incidence and effects of parathion residues on leafy crops (pp. 22), the amount of published and unpublished information on which (he remarks) is exceeded only by that for DDT. This is a useful summary of the whole subject; chemistry, mode of action, toxicology, translocation and decomposition, residue determination and results, together with the implications of the latter in the United States. J. W. Mitchell and P. J. Linder write on the movements of plant growth regulating substances (pp. 26). The accumulation of residues is influenced by translocation and exudation mechanisms; by external factors such as those arising from the choice of wetting agent, dispersion solvent and the pH condition of the preparation applied; and other environmental factors.

Melvin E. Getz reviews published work on the determination of organophosphate pesticides and their residues by paper chromatography (pp. 17), emphasising the difficulties arising from the need to characterise not only the pure (or commercial) pesticides themselves, but also any toxic break-down products. The positive identification of individual constituent compounds still requires further attention. This is a straightforward review of published chromatographic systems, including clean-up methods and chromogenic agents. The longest chapter (pp. 54), by R. C. Blinn and the Editor, is on the use of infrared and ultraviolet spectrophotometric methods of residue analysis. This is a useful summary. It opens with a brief introduction to the theoretical basis for the spectra and the consideration of such practical details as the radiation sources and optical materials. Considerable use is made of tabulation in the presentation of the review of infrared work (5 Figs. and 7 Tables in all) and there are some hundred classified references to the use of the method in residue and formulation analysis and in metabolic studies. There is less to say of ultraviolet methods, but again a tabular summary of published methods for pesticide residues is provided. The authors remark, somewhat quaintly, that in the United States the field of residue chemistry has recently emerged from its gestation period; perhaps the same could be said of "Residue Reviews," although it remains to be seen what will be the eventual width of scope of the publication and how broad will be the shoulders of this lusty infant. H. EGAN

LINE INTERFERENCE IN EMISSION SPECTROGRAPHIC ANALYSIS: A GENERAL EMISSION SPECTROGRAPHIC METHOD INCLUDING SENSITIVITIES OF ANALYTICAL LINES AND INTERFERING LINES. By J. KROONEN and D. VADER. Pp. viii + 213. Amsterdam, London and New York: Elsevier Publishing Company. 1963. Price D.fl. 30; 60s.; DM 33.50.

This publication is the outcome of several years experience in the authors' laboratory with a general emission spectrographic method for the analysis of miscellaneous powdered samples. The sample is diluted with a lithium carbonate - graphite mixture, which acts as an internal standard and buffer, and this is excited in a d.c. arc.

The authors have studied the characteristics of 38 of the more common elements and most of the book (190 pages, in fact) is taken up with tables giving data on their analytical lines. For each analytical line is given its wavelength, excitation potential (where known), sensitivity, useful concentration range and a list of interfering lines within the interval ±0·65 Å. The sensitivities of interfering lines and differences in wavelength from the analytical line are also included. Over

500 lines are listed with about 8500 interfering lines, of which nearly 1000 are recorded for the first time. Full details of the method used are given in the early pages of the book.

Two basic shortcomings are almost inevitable in any book of this kind: the incomplete coverage of the elements that are detectable by emission spectrography, and the fact that the information it contains does not necessarily apply when alternative methods of excitation are used. For instance, no information is given on any of the metals of the rare-earth or platinum groups (with the exception of platinum itself). The sensitivities quoted both for analytical and interfering lines apply only when the recommended method, or a method giving a similar arc temperature (about 5500° K), is used. For example, the authors recognise that their tabulated lists of sensitivities are different from those published by the N.B.S. based on a copper arc.

In laboratories where semi-quantitative spectrographic methods differ from those described, little value will be gained from this book, because the recorded sensitivities are not applicable and most of the interfering lines will be found in the more extensive M.I.T. wavelength tables.

When, however, the recommended method is, or can be, used and particularly where the development of a general spectrographic method of analysis is intended, the book will be invaluable.

The size of the book (12 inches × 8½ inches) is rather large for many book cases, but the layout and the printing make the tables easy to read. J. A. F. GIDLEY

MICROCHEMICAL TECHNIQUES. Edited by NICHOLAS D. CHERONIS. Microchemical Journal Symposium Series. Volume II. Pp. xviii + 1181. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1962. Price £15.

This book contains the proceedings of the 1961 International Symposium on Microchemical Techniques organised by the Metropolitan Microchemical Society at the Pennsylvania State University, U.S.A. The contents are divided into Introduction (Welcoming Addresses and 2 "historical" papers), Plenary Lectures (4), Microscopical Techniques (10 papers), Techniques of Inorganic Elemental Analysis (7 papers), Techniques of Organic Elemental Analysis (17 papers), Techniques of General Organic and Functional Group Analysis (8 papers), Chromatographic Techniques (8 papers), Titrimetric, Polarographic, Electrochemical and Radiochemical Techniques (19 papers), Microchemical Implements and Techniques for the Determination of Molecular Weight and Physical Properties (13 papers), Micro and Semimicro Methods in Teaching (6 papers) and Round Table Discussions (5 topics). The discussion is reported for several of the papers; an author and subject index complete the book.

The Section of Analytical Chemistry of the International Union of Pure and Applied Chemistry extended its sponsorship to the Symposium, a clear indication of the high quality of the papers. The book itself maintains the standard of production set by Volume I of the Series (see *Analyst*, 1962, **87**, 415). It is a credit both to the publisher and to the editor, whose unfortunate death occurred before the publication was completed. Although the price places it well outside the pocket of the individual purchaser, the book seems certain to become a valuable library reference work.

A point of some concern to myself, and no doubt to others, is the time lag that often elapses before symposium proceedings are finally published. In the present instance, I was particularly interested in some of the papers in mid 1962, by which time only the paging of the text had been reached. Although it is virtually impossible to get all of some 100 authors to submit their manuscripts by any agreed date and the volume of editorial work is large, surely something can be done to hasten publication. One possible solution is that successfully adopted in connection with the International Gas Chromatographic Symposium held at Houston, Texas, U.S.A., in January, 1963. It was stipulated that all of the papers must deal with original material and be submitted to *Analytical Chemistry* for review before the meeting. The few papers not meeting the deadline were reviewed during the symposium itself. In this way it was possible to publish the 23 symposium papers in the April issue of *Analytical Chemistry*. M. WILLIAMS

ROCK-FORMING MINERALS. Volume 4. FRAMEWORK SILICATES. By W. A. DEER, M.Sc., Ph.D., F.R.S., R. A. HOWIE, M.A., Ph.D., F.G.S., and J. ZUSSMAN, M.A., Ph.D., F.Inst.P. Pp. x + 435. London: Longmans, Green & Co. Ltd., 1963. Price 95s.

The publication of Volume 4 sees the completion of this work on the rock-forming minerals, selected as they are on the basis of their presence or absence determining or modifying the name of a rock.

This volume deals with the so-called framework silicates, *viz.*, the felspars, the zeolites, the silica minerals quartz, tridymite, and cristobalite, the sodalite and nepheline groups, and the single minerals petalite, leucite, cancrinite, scapolite and analcite, on the lines used in the volumes published earlier (see *Analyst*, 1963 **88**, 246).

The 1620 chemical analyses spread throughout the five volumes are the main feature for the analyst; but there is, besides these plenty that is of wider chemical interest in this work, which presents an up-to-date account of modern views on the many important minerals that have been selected for consideration.

The printing and the diagrams are well done, as, indeed, they should be at the price charged for each volume.

L. S. THEOBALD

PROBLEMS IN INORGANIC CHEMISTRY. By HOWARD NECHAMKIN. Pp. x + 171. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Company Inc. 1963. Price 30s.

The problems set and illustrated in this book are designed to illuminate the general range of topics covered by an up-to-date course on Inorganic Chemistry and they should help the advanced student to a fuller understanding of his subject. Among analysts, only those who have some knowledge of modern ideas on inorganic chemistry are likely to be interested.

L. S. THEOBALD

Publications Received

STANDARD METHODS OF CHEMICAL ANALYSIS. Sixth Edition. Volume II. INDUSTRIAL AND NATURAL PRODUCTS AND NONINSTRUMENTAL METHODS. PARTS A AND B. Edited by FRANK J. WELCHER, Ph.D. (Part A), pp. xiv + 1282; (Part B), pp. x + 1283–2613. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Company Inc. 1963. Price (both parts) £9 9s.

MASS SPECTRAL CORRELATIONS. By FRED W. MCLAFFERTY. Pp. vi + 117. Washington, D.C.: American Chemical Society. 1963. Price $4.75.
Advances in Chemistry Series No. 40.

ION EXCHANGE SEPARATIONS IN ANALYTICAL CHEMISTRY. By OLOF SAMUELSON. Pp. 474. Stockholm, Goteborg and Uppsala: Almqvist & Wiksell; New York and London: John Wiley & Sons. 1963. Price 72s.

PRINCIPLES OF CATALYSIS. By G. C. BOND, B.Sc., Ph.D., F.R.I.C. Pp. vi + 51. London: The Royal Institute of Chemistry. 1963. Price 6s.
Monographs for Teachers No. 7.

IDENTIFICATION OF ORGANIC COMPOUNDS: A STUDENT'S TEXT USING SEMIMICRO TECHNIQUES. By NICHOLAS D. CHERONIS and JOHN B. ENTRIKIN. Pp. xii + 477. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1963. Price 65s.

PARTICLE SIZE: MEASUREMENT, INTERPRETATION AND APPLICATION. By RIYAD R. IRANI and CLAYTON F. CALLIS. Pp. x + 165. New York and London: John Wiley & Sons. 1963. Price 60s.

ADVANCES IN X-RAY ANALYSIS. Volume 6. Edited by WILLIAM M. MUELLER and MARIE FAY. Pp. xii + 480. New York: Plenum Press Inc. 1963. Price $17.50.
Proceedings of the Eleventh Annual Conference on Application of X-Ray Analysis, held August 8th—*10th*, 1962.

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WEST-EUROPEAN SYMPOSIA ON CLINICAL CHEMISTRY. Volume 2. THE CLINICAL CHEMISTRY OF MONOAMINES. Edited by HAROLD VARLEY, M.Sc., F.R.I.C., and A. H. GOWENLOCK, M.Sc., M.B., Ch.B., Ph.D. Pp. xvi + 242. Amsterdam, London and New York: Elsevier Publishing Company. 1963. Price 60s.
Proceedings of the Symposium held in Manchester, 1962.

CHROMATOGRAPHIC REVIEWS: PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS. Volume 5. Edited by MICHAEL LEDERER. Pp. x + 244. Amsterdam, London and New York: Elsevier Publishing Company. 1963. Price 60s.

MASS AND ABUNDANCE TABLES FOR USE IN MASS SPECTROMETRY. By J. H. BEYNON and A. E. WILLIAMS. Pp. xxii + 570. Amsterdam, London and New York: Elsevier Publishing Company. 1963. Price 80s.

TOPICS IN MODERN CHEMISTRY. By C. J. MANDLEBERG, M.A., B.Sc., F.R.I.C. Pp. xii + 228. London: Cleaver-Hume Press Ltd. 1963. Price 37s. 6d.

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ADVANCES IN ORGANIC CHEMISTRY: METHODS AND RESULTS. Volume 3. Edited by RALPH A. RAPHAEL, EDWARD C. TAYLOR and HANS WYNBERG. Pp. viii + 333. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1963. Price 105s.

HANDBUCH DER ANALYTISCHEN CHEMIE. Edited by W. FRESENIUS and G. JANDER. Part 2. QUALITATIVE NACHWEISVERFAHREN. Volume IVaα. ELEMENTE DER VIERTEN HAUPTGRUPPE. I. KOHLENSTOFF; SILICIUM. By DR. H. GRASSMANN. Pp. xvi + 220. Berlin, Gottingen, Heidelberg: Springer-Verlag. 1963. Price (paper) DM 57; (cloth) DM 61.

REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY. Volume XLVII: 1962. Editor: H. S. ROOKE, M.Sc., F.R.I.C. Pp. vi + 859. London: Society of Chemical Industry. 1963. Price 140s.

ANALYSIS INSTRUMENTATION: 1963. Edited by DR. L. FOWLER, R. D. EANES and T. J. KEHOE. Pp. x + 261. New York: Plenum Press. 1963. Price $12.50.

Proceedings of the Ninth National Analysis Instrumentation Symposium held April 29th—May 1st, 1963, at Houston, Texas.

REPORT OF THE PROCEEDINGS OF THE THIRTEENTH SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS. Hamburg, Germany, 1962. Pp. viii + 125. Paris: I.C.U.M.S.A. 1962. Price 28s.; NF 19.00.

Obtainable from Monsieur R. Saunier, Secretaire, ICUMSA, Syndicat National des *Fabricants de Sucre de France, 23 Avenue d'Iena, Paris XVI^e^, France.*

ATOMIC STRUCTURE AND CHEMICAL BONDING: A NON-MATHEMATICAL INTRODUCTION. By FRITZ SEEL. Translated from the fourth German edition and revised by N. N. GREENWOOD and H. P. STADLER. Pp. viii + 112. London: Methuen & Co. Ltd.; New York: John Wiley & Sons. 1963. Price 15s.

MODERN POLAROGRAPHIC METHODS. By HELMUT SCHMIDT and MARK VON STACKELBERG. Translated by R. E. W. MADDISON. Pp. viii + 99. New York and London: Academic Press. 1963. Price 44s.

RESIDUE REVIEWS: RESIDUES OF PESTICIDES AND OTHER FOREIGN CHEMICALS IN FOODS AND FEEDS. Volume 3. Edited by FRANCIS A. GUNTHER. Pp. iv + 170. Berlin, Gottingen and Heidelberg: Springer-Verlag. 1963. Price DM 22.

COLORIMETRIC ANALYSIS. VOLUME II. By NOEL L. ALLPORT, F.R.I.C., and JOHN E. BROCKSOPP. Second Edition. Pp. x + 368. London: Chapman & Hall Ltd. 1963. Price 60s.

Reprints of Review Papers

"Beer's Law and its Use in Analysis"

REPRINTS of the Review Paper, "Beer's Law and its Use in Analysis," by G. F. Lothian, published in the September, 1963, issue of *The Analyst* (pp. 678–687), are available from the Secretary, Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, at 5s. per copy, post free.

"A Review of the Methods Available for the Detection and Determination of Small Amounts of Cyanide"

REPRINTS of the Review Paper, "A Review of the Methods Available for the Detection and Determination of Small Amounts of Cyanide," by L. S. Bark and H. G. Higson, published in this issue of *The Analyst,* will soon be available from the Secretary, Society for Analytical Chemistry, at the above address, price 5s. per copy, post free.

A remittance for the correct amount, payable to The Society for Analytical Chemistry, MUST accompany the order; these reprints are not available through Trade Agents.

Erratum

JULY (1963) ISSUE p. 540 line 3. For "0·1-mm cells" read "1·0-mm cells".

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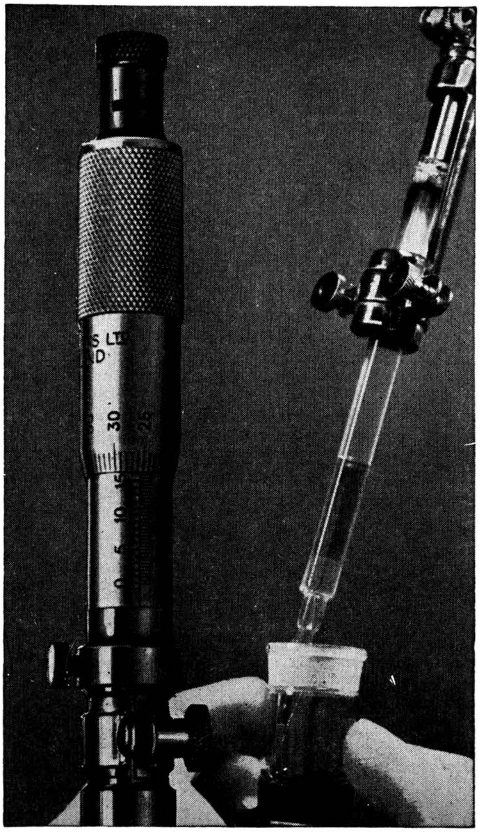

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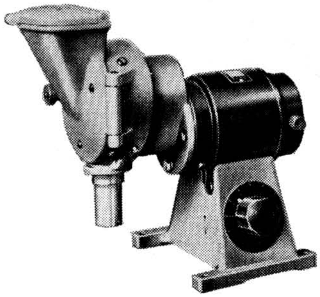

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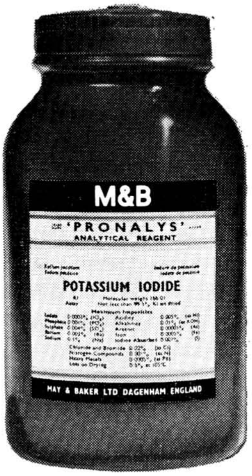

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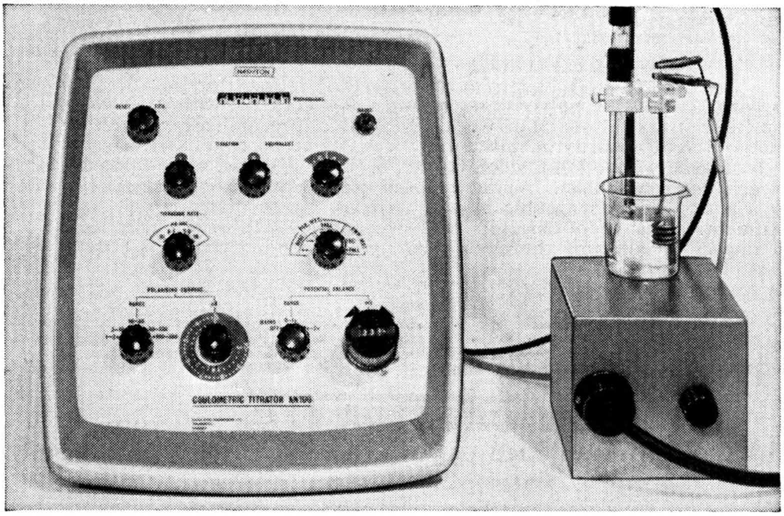

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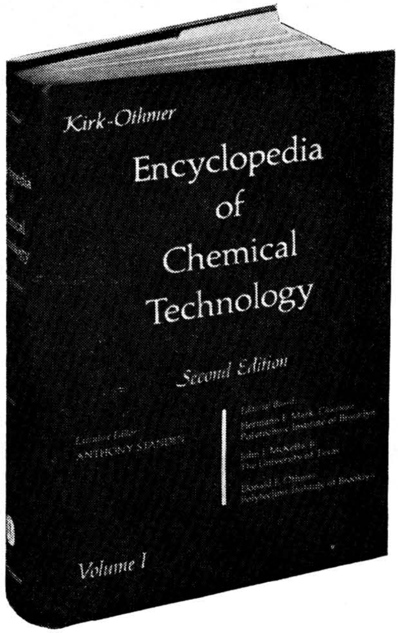

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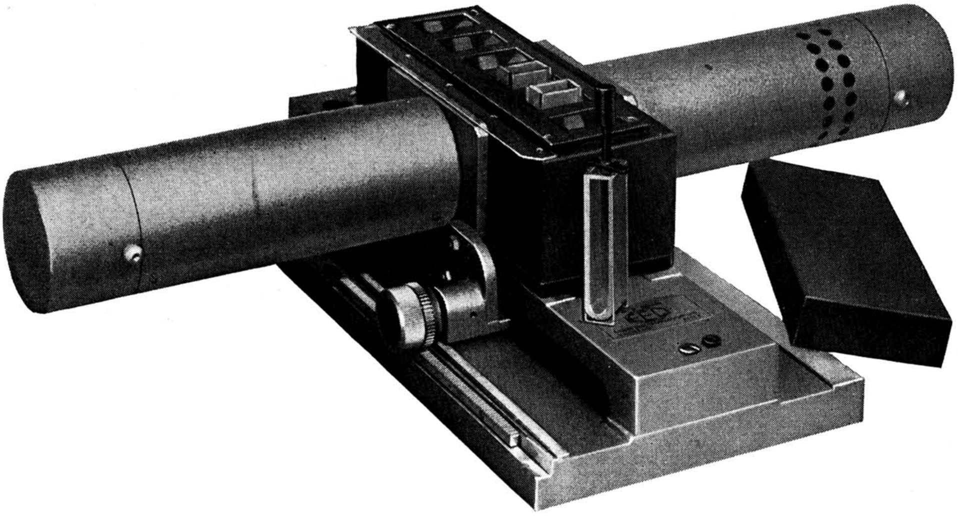

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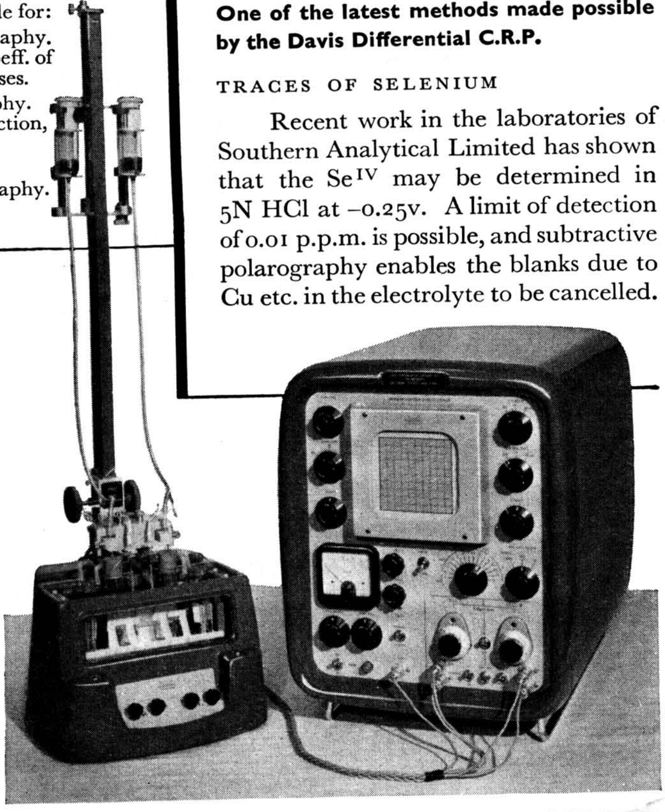

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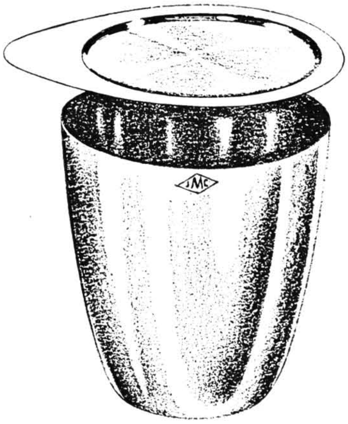

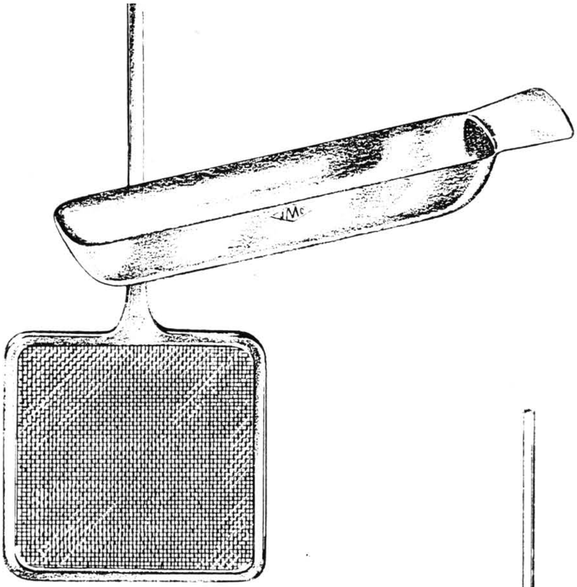

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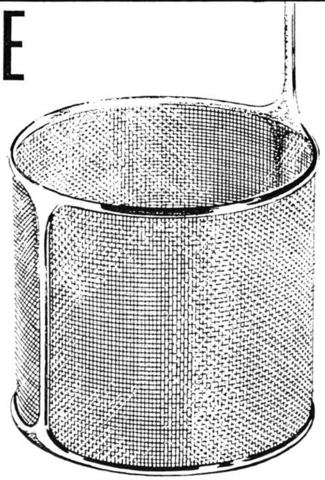

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