

The ANALYST

The Journal of the
Society for Analytical Chemistry

A monthly International Publication
dealing with all branches of
Analytical Chemistry

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE

Volume 92

No. 1101, Pages 723 - 788

December 1967

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

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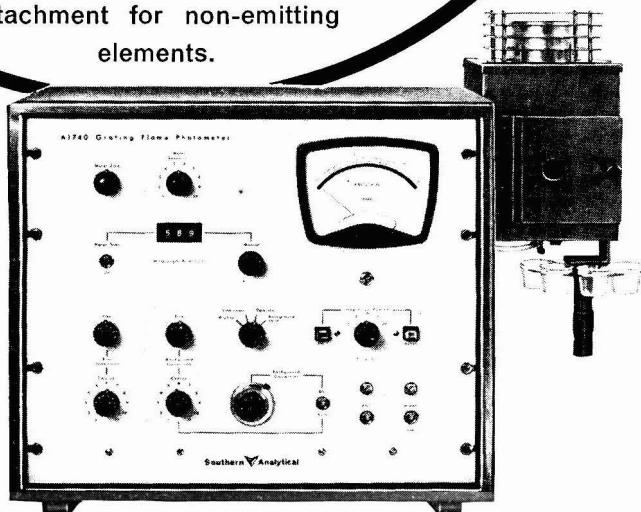
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THE ANALYST

Industrial Gas Analysis

A Literature Review*

BY (THE LATE) H. N. WILSON AND G. M. S. DUFF

(Imperial Chemical Industries Ltd., Agricultural Division, P.O. Box No. 6, Billingham, Co. Durham)

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IN this review we have covered the years from 1958 to about mid-1966, because a chapter on gas analysis by A. E. Heron and H. N. Wilson in Volume 1A of "Comprehensive Analytical Chemistry" (Elsevier Publishing Co. Ltd., Amsterdam and London, 1959, pp. 236 to 327) gives a survey of developments up to 1958. We have not attempted to list every paper, but have tried to present a reasonably comprehensive review of the present methods of gas analysis. We have omitted many papers that roused our scepticism rather than approval and have commented on some of the papers to which we have referred.

In no branch of analysis is the swing towards physical methods more marked than in gas analysis. There have been no important developments of the conventional methods during the last 10 years; the chief advances have been the application of galvanic methods to "traces" of certain gases, and gas chromatography. Indeed, although such apparatus as Orsat's, Haldane's and Bone and Wheeler's still have their place, in some industries they are obsolete and in others obsolescent. Dr. E. A. C. Chamberlain, Divisional Chief Scientist, National Coal Board, Scottish Division, informs us that in the analysis of mine air the gas chromatograph is now the apparatus usually used, and that in a survey of the atmosphere in one pit, as many as 17,000 samples have been analysed over a period of 12 weeks by this method. The rapid spread of the electrogalvanic methods for the "on-stream" determination of traces is also most significant. The other most noticeable feature is the vast and increasing attention being paid to atmospheric pollutants of all kinds, particularly sulphur dioxide, sulphuric acid and hydrocarbons.

PERMANENT AND INORGANIC GASES

GENERAL—

There have been few papers dealing with the older methods of gas analysis; these methods had all been developed to such an extent that major improvements were becoming rare; usually if quicker or more precise analyses are required, it is necessary to have recourse to a physical or instrumental method.

There are a few papers to record that deal with Orsat's apparatus.

Charpenat¹ measures all gas volumes over mercury at constant pressure and, as a further departure from the usual method of working, dries the gas before and after each absorption. The minimum volume of de-gassed reagent solution is sprayed on to the walls of the absorption tubes; explosion with oxygen is retained, but the eudiometer is made of stainless steel. The apparatus is recommended for checking the purity of such gases as carbon dioxide from cylinders, and high accuracy is claimed, but there seems to be no reason why this apparatus should be more accurate than a well designed constant-volume apparatus.

* Reprints of this paper will be available shortly. For details see Summaries in advertisement pages.

Blakemore² combines the Orsat with a gas-chromatographic apparatus on Janák's system³; this apparatus is intended for analysing town gas made from, or enriched with, petroleum hydrocarbons. Three components, carbon dioxide, oxygen and, if desired, unsaturated hydrocarbons are successively removed by absorption and the residual gases passed on to the gas-chromatographic part of the apparatus. An activated-carbon column separates the permanent gases, and either alumina or diethyldigol is used to separate the hydrocarbons. Blakemore prefers the Janák system to the more usual detectors as he considers it more suitable for operation by junior staff, but this opinion is no longer held in many laboratories.

Barnard and Hughes⁴ describe modifications of absorption methods for determining carbon monoxide, oxygen and methane. Bracht⁵ compares the precision of modified Orsat apparatus between operators and between laboratories, and makes a comparison with gas-chromatographic apparatus. Schoedler⁶ compares the Orsat analysis of furnace gases with a 2-column chromatographic technique, and Ebersbach⁷ reviews Orsat reagents. Lloyd⁸ describes a modification of Haldane's apparatus, perhaps the most important modification being a multi-channel tap,⁹ and Gooderham¹⁰ describes modifications to the constant-volume apparatus, for which Chapman and Murche¹¹ have designed an absorption pipette with a magnetic shaker.

Schwab and Neuwirth¹² describe a continuous gas analyser in which the flow of gas (corrected for viscosity effects) through a series of absorbers, connected by capillary flowmeters, is recorded.

Kienitz¹³ reviews classical and modern methods, including chromatography and infrared analysis of organic and inorganic gases, giving 33 references; modern methods of gas analysis are reviewed by Kainz¹⁴ and physical methods by Guerin.¹⁵ Non-dispersive infrared gas analysers ("Luft" gas analysers) are described in a detailed review,¹⁶ and a versatile transistorised double-beam infrared gas analyser, suitable for use in a potentially explosive atmosphere, is described by Hill and Stone.¹⁷ An infrared analyser in which the radiation source is a heated cavity containing the component in question is described by Sall and Stanevich.¹⁸

Mass-spectrographic methods are dealt with by van Katwijk,¹⁹ and Carnides,²⁰ who deals with gases with identical mass numbers. McLafferty²¹ reviews applications of mass spectroscopy to production, *e.g.*, argon in ammonia plant gases, while another paper on the application of mass spectroscopy deals with the analysis of the rare gases in works control.²² Permanent gases, free from corrosive components, can be analysed with a coefficient of variation of 5 per cent. at the 1 per cent. level. This is particularly suitable for mixtures containing hydrogen, helium, oxygen, argon, carbon monoxide and carbon dioxide.²³ A U.S. Atomic Energy Report²⁴ describes modifications to a single-focusing mass spectrometer to enable it to be used for the analysis of mixtures of carbon monoxide and nitrogen. Lauder²⁵ measures the oxygen-18 abundance in determining oxygen in carbon monoxide-carbon dioxide mixtures. The omegatron is discussed by Wagener and March.²⁶

McGrath, Magee, Pickering and Wilson²⁷ give a theoretical and experimental discussion and a literature review of analysis by molecular-emission spectroscopy, especially of the methods of excitation of permanent gases; application to hydrocarbon gases is probably not feasible. Electronic molecular spectra, particularly of organic compounds, are also reviewed by McGrath, Pickering, Magee and Wilson.²⁸ Despite the lack of specificity for given wavelengths and rather difficult conditions, the high sensitivity of the method may lead to its being used for very small samples; the spectra of nitrogen, hydrogen and ammonia are, as yet, affected too much by impurities.²⁹ High frequency discharge is applied by Botschkowa, Frisch and Schreider³⁰ to the determination of impurities in the inert gases, and of krypton in oxygen, and Stolov³¹ used this method to analyse mixtures of nitrogen and carbon dioxide (1.5 to 33 per cent.). The whole field of spectroscopic analysis of gas mixtures is covered in a recently published text.³²

The use of gas chromatography in the analysis of permanent gases is rapidly increasing and the subject has been comprehensively dealt with by Jeffery and Kipping³³ in a book that covers the whole field of gas chromatography, as applied to the analysis of gas mixtures.

The replacement of the Orsat by gas chromatography has been comparatively slow, partly because no single chromatographic column has been discovered that is capable of separating all of the components determined by this apparatus. The development of molecular sieves solved the problem of the separation of hydrogen, nitrogen, carbon monoxide and

methane, but carbon dioxide requires separate treatment and the separation of argon and oxygen requires special conditions.^{34 to 45} The use of argon as carrier gas simplifies the determination of oxygen, and careful design of columns and flow-circuits enables the remainder of the above gases to be determined on a single apparatus.⁴⁶ The results obtained with such a system have been compared with those obtained by using a Bone and Wheeler apparatus,⁴⁷ with satisfactory agreement. The conditioning and preparation of molecular sieve columns have been described by Janák⁴⁸ and Farré-Ruis and Guichon,⁴⁹ among others, the latter authors contriving to separate hydrogen, oxygen, nitrogen, methane and carbon monoxide in the extremely short time of 15 seconds. It has been shown that the life of a molecular sieve column is vastly increased if both samples and carrier gas are rigorously dried.⁵⁰ The problems of precise quantitative measurement have been discussed by Vizard and Wynne,⁵¹ and by Kipping,⁵² who describe zero-suppression circuits that are necessary for the accurate direct determination of major components in a mixture. The use of a cross-section ionisation detector for permanent gases is claimed to have the advantages of sensitivity and wide linear range,^{53,54} but despite this it has not been applied widely, as yet, and some of the claims have been disputed.⁵⁵ The instrumentation of the Janák method of measurement to give a digital print-out has been described by Kateman and Rijks.⁵⁶ Lacy, Woolmington and Hill⁵⁷ and Lacy⁵⁸ describe the application of gas chromatography to the gases used in the industrial synthesis of ammonia, while Cerrone, Piatti and Rio describe a multi-column system for the products from the steam-cracking of hydrocarbons.⁵⁹

Adlard and Hill⁶⁰ describe the analysis of anaesthetic gases. They separate carbon dioxide, nitrous oxide and oxygen over 20 per cent. dimethyl sulphoxide at 20° C, and ether and fluothane on a column of 15 per cent. dimethyl phthalate at 70° C parallel with the first column, hydrogen being used as carrier gas; the time taken for an analysis is 4 to 5 minutes.

Some interest is being displayed in sonic gas analysers. Martin⁶¹ discusses the principles involved, and, with Mourfield, has issued several patents.⁶² The instrument is made by Howard Grubb Parson Ltd., and its practical advantages and disadvantages are discussed by Haswell.⁶³ Stott⁶⁴ discusses a continuous sonic analyser for carbon dioxide in expired air, covering the range 0 to 10 per cent.

TRACE ANALYSIS—

General—This section is restricted to the determination of trace constituents in gases other than air (liquefied gases have been excluded, the determination of trace constituents in these being referred to later).

The most important general technique is the ubiquitous gas chromatography. Extremely sensitive detectors have been developed for organic molecules, which have made the determination of amounts down to parts per million, or even per hundred million, no longer a problem. The various types of ionisation detector suitable for this application have been reviewed by Lovelock⁶⁵; unfortunately, these detectors do not respond readily to the inorganic and permanent gases, and no simple universal technique has been evolved. Probably the best detector so far is the radioactive ionisation detector, with helium as carrier gas, that has been developed by Berry.⁶⁶ The metastable helium ions formed on irradiation are used in this detector to ionise the components being determined; this calls for intensive purification of the carrier gas as well as exclusion of air. Rules for optimisation of the responses are given by Bothe and Leonhardt⁶⁷ and a system for purification of helium by Bourke, Grey and Denton.⁶⁸ Limits of detection are given by Parish and Parsons.⁶⁹ With a 5-ml sample they could detect 10 p.p.m. of hydrogen, 0.5 p.p.m. of oxygen, 2 p.p.m. of nitrogen, 5 p.p.m. of carbon monoxide and 0.5 p.p.m. of carbon dioxide. More recently a variant with very low internal volume has been discussed with limits of detection claimed to range from 1 to 20 p.p.m.,⁷⁰ and another design has been used in vacuum fusion.⁷¹ Several workers have used impure helium and observed the diminution in the standing current when other permanent gases are present,^{72,73,74} but these methods have not the sensitivity nor the stability of Berry's system. Previously, several workers had tried sensitising the original argon detector by adding an organic vapour, but this method appears to have fallen into disuse.⁷⁵ Probably the simplest method, when rapid analysis is not required, is to use standard gas-chromatographic techniques after a concentration stage in which a cold absorption column is used.^{76,77} This technique enables the average laboratory instrument to be extended into the p.p.m. range and further examples are given under the headings of specific gases. Several

workers have modified mass-spectrometer design to cover the p.p.m. range, in which it is extremely valuable for the determination of the permanent and noble gases in small amounts or when at high vacuum. Modifications to a commercial model to extend the range to detect 1 p.p.m. of helium in nitrogen or hydrogen in argon have been described by Parkinson and Toft,⁷⁸ while an instrument capable of working in the range 5×10^{-10} torr has also been described.⁷⁹ A procedure for the determination of helium at the p.p.m. level has been described.⁸⁰ The production of condensation nuclei by suitable reactions followed by electronic counting has been applied to ammonia, carbon dioxide, sulphur dioxide and mercury, and developed into a commercial apparatus.^{81,82}

Argon—The separation of argon from oxygen by gas chromatography is extremely difficult and no completely reliable method has yet been developed. The use of a column of firebrick impregnated with bull's blood has been reported⁸³; this must be the only recent use of this reagent, and it has obvious disadvantages. The separation on molecular sieve 5A generally requires operation at inconveniently low temperatures, e.g., -72°C ,³⁴ -78°C ,^{35,36} and -50°C ,³⁷ with long columns that result in broad, ill defined peaks. Better results have been achieved recently, giving separation at -9°C ,³⁸ and several authors have claimed separation at room temperature, with molecular sieve 5A that had been activated at 350°C *in vacuo*,³⁹ in helium,⁴⁰ at 400°C in purified helium⁴¹ and at 450°C in argon containing 100 p.p.m. of water.⁴² Other workers have resorted to removal of the oxygen by catalytic hydrogenation to water. In such a system⁴³ the argon and oxygen are first measured together and then the argon alone after removal of the oxygen, while in another method the oxygen is measured as a water peak after separation on a column of Triton X305,⁴⁴ or as acetylene after reaction of the water with calcium carbide.⁴⁵

If the determination of oxygen is not required, then it is possible to carry out a simple determination of argon by using oxygen as carrier gas.⁸⁴

Argon in ammonia synthesis gas can be determined by transferring the residual gas from an Orsat apparatus to an interferometer,⁸⁵ and Hoffman and Helle⁸⁶ determine argon in synthesis gas by absorption of soft X-rays. Chakrabati, Magee and Wilson⁸⁷ determine argon when mixed with carbon dioxide (9 to 10 per cent. of argon) by high frequency excitation at 230 Mc/s, measuring the emission with a quartz prism spectrophotometer (a determination takes about 1 minute).

Carbon dioxide—There is little new work to report on the determination of carbon dioxide. Earnshaw⁸⁸ reviews methods for its determination, and Kiff and Partridge⁸⁹ describe an indicator-tube method for the range 10 to 50 per cent., in which the reagent is sand-impregnated with rosaniline hydrochloride decolorised with hydrazine; Bunker, Bendixen and Murphy⁹⁰ measure the change in pressure of a 45-ml sample on removing carbon dioxide with soda lime (for the determination of carbon dioxide in anaesthetic gases a commercial apparatus is available in the U.S.A.).

The best method for routine laboratory determination of traces of carbon dioxide depends upon measurement of the change in conductivity when the gas is absorbed in a suitable reagent. In a typical apparatus a spiral absorber is used to obtain the necessary contact for efficient absorption of carbon dioxide.^{91,92} A particularly neat conductivity cell has been described by Piringier⁹³ and a recording instrument by Dijkstra.⁹⁴ Other designs have been described by Szekiela,⁹⁵ Ehrenburg⁹⁶ and Priscott,⁹⁷ and the last of these also measures carbon dioxide. Violante⁹⁸ claims increased linearity by saturating his barium hydroxide reagent with barium carbonate to ensure precipitation of all of the absorbed carbon dioxide as carbonate, while Bartscher⁹⁹ has published conductivity graphs and coefficients of absorption for a sodium hydroxide reagent containing 2-aminoethanol. There are several titration methods; one based on barium hydroxide involves the use of barium chloride and ethanol to suppress hydrolysis of carbonate,¹⁰⁰ another involves the use of a semi-automatic titration to overcome interference by atmospheric carbon dioxide.¹⁰¹ In a method in which sodium hydroxide is used as reagent, butanol and ethanol are added to suppress hydrolysis,¹⁰² and in another method, in which the same reagent is used, a spectrophotometric end-point detection is described.¹⁰³ Methods in which non-aqueous media are used have been described by Grant, Hunter and Massie¹⁰⁴ (dimethylformamide and thymolphthalein; titrated with potassium methoxide) and by Patchornik¹⁰⁵ (benzylamine and thymol blue; titrated with sodium methoxide). It is difficult to see the advantage of these methods, although possibly they give a more definite end-point. A colorimetric method involving

continuous measurement of the colour of a solution of phenolphthalein in sodium hydroxide has been described by Juranek.¹⁰⁶ In a most unusual method¹⁰⁷ the gas is absorbed in paper saturated with barium hydroxide and held between silver electrodes. After exposure to the gas, a current is passed and the number of coulombs required to decolorise phenolphthalein indicator is a measure of the carbon dioxide absorbed. A particularly sensitive d.c. discharge detector for gas chromatography is claimed to detect 5×10^{-13} mole of carbon dioxide,¹⁰⁸ while a method in which katharometers are used and the sample volume is increased to 94 ml has detected 13 p.p.m.¹⁰⁹ A method for the preparation of calibration gas mixtures by electrolysis of oxalic acid has been described by Přibyl.¹¹⁰

Carbon monoxide—Stewart and Evans¹¹¹ prefer a copper(I) sulphate - 2-naphthol reagent for the determination of carbon monoxide with Orsat's apparatus. Moureau, Chovin, Truffert and Lebbe¹¹² describe the preparation of standard mixtures for calibrating an infrared absorption analyser.

The oxidation of carbon monoxide to carbon dioxide by iodine pentoxide, followed by gravimetry, conductivity or iodimetry, is well known and is one of the best methods for determining traces of carbon monoxide, and the difficulty occasionally encountered in preparing or obtaining a satisfactory reagent is also well known. An alternative reagent, not much used outside the field of microchemistry, is decomposed silver permanganate,¹¹³ which might have some advantages. An extremely sensitive colorimetric method that is not affected by 100 per cent. of either oxygen or hydrogen involves the reaction of carbon monoxide with the silver salt of *p*-sulphamylbenzoic acid.^{114,115} A sensitive method for routine work is by reduction to methane by hydrogen over reduced nickel and determination of the methane by gas chromatography with flame-ionisation detection.^{116,117} There is no doubt that this method is capable of giving rapid, reproducible measurements on small samples (about 10 ml) and could be extended below the p.p.m. level.

Carbon suboxide—The gas-chromatographic determination of carbon suboxide, C_3O_2 , and its preparation have been described by Hirt.¹¹⁸

Helium—The determination of the rare gases has been described by Gnauk¹¹⁹ and gas-chromatographic methods for helium, neon and krypton are described. Several authors have described the determination of helium in natural gas.^{120,121,122,123} The separation of hydrogen and helium is probably best achieved with molecular sieve 5A,^{124,125,126} while for extreme sensitivity a preliminary enrichment of the sample by frontal analysis has been suggested.¹²⁷

Melhuish and Chapman have described the mass-spectrometric determination of helium at the 10^{-12} level.¹²⁸

Hydrogen—There are two problems associated with the gas-chromatographic determination of hydrogen. First, with helium as the carrier gas, anomalous katharometer responses are obtained at certain concentrations,^{129,130} which necessitate the use of a mixed carrier (92 per cent. of helium and 8 per cent. of hydrogen). Secondly, the high sensitivity obtained with other carriers makes it necessary to apply a back-e.m.f., rather than to attenuate the signal if good precision is to be obtained at concentrations of 40 per cent. of hydrogen¹³¹ and above.

There is a revival of interest in diffusion through palladium, especially for very small samples at low pressures. Young and Whitten¹³² detect hydrogen down to a partial pressure of 10^{-7} torr by passing the sample over an evacuated palladium thimble at 500° C, the pressure of hydrogen accumulating inside the thimble being measured by a thermocouple gauge or a manometer. A continuous analyser with a palladium - silver alloy has been described.¹³³ Deuterium in hydrogen is measured continuously by thermal conductivity.¹³⁴

An electrolytic method for hydrogen in the range 1 to 1000 p.p.m. has been described by Frey.¹³⁵ In this method the gas, stripped of carbon dioxide and oxygen, is passed over a platinised platinum electrode partially immersed in a solution of mercury(I) chloride and sodium chloride in hydrochloric acid. The other electrode is a calomel half-cell and the current is proportional to the hydrogen concentration. A method, in which the "Hersch" galvanic oxygen sensor is used to determine the reduction of oxygen consequent upon reaction with hydrogen in the gas stream, is described by Marsh,¹³⁶ while with another technique the electrolytic hygrometer is utilised to measure the water formed.¹³⁷ A detector tube for hydrogen in oxygen involves the reduction of ammonium molybdate in the presence of palladium sulphate at 100° C.¹³⁸ As carbon monoxide, hydrogen sulphide, arsine, phosphine, acetylene and olefins all interfere in some way, it is difficult to see a real use for this tube.

Oxygen—Naumann¹³⁹ reviews commercial equipment for concentrations of 5 to 50 per cent. of oxygen. The chief, and spectacular, advance in the determination of oxygen from very low concentrations upwards is the application of the galvanic cell. This has been known in one form or another since about 1913, but recently it has come into extensive use as a recording instrument. Hersch¹⁴⁰ gives an extensive account of principles and applications, with 192 references; the ground covered has not been included in this review. He also gives a brief and clear account of the system and an example of its application to traces of hydrogen in a carrier gas, *e.g.*, as evolved from metals on heating,¹⁴¹ besides many contributions to the literature that are mostly concerned with details of instrumentation. Heinmann¹⁴² determines up to 99 per cent. of oxygen on a small sample. Oxygen is usually separated from nitrogen by gas chromatography on a molecular sieve 5A, but Rein, Miviele and Fainberg¹⁴³ claim to separate nitrogen and oxygen at 30° C by a 50-foot column of 33 per cent. Silicone Oil 200 on Chromosorb P; retention times for oxygen and nitrogen are 7.3 and 7.6 minutes, respectively, which may be barely adequate in many instances. Reports on chemical methods include the preparation of a modified sodium dithionate absorption reagent.¹⁴⁴ A method for measuring very small differences in oxygen concentration, for example, in air, by determining the differences in pressure on absorption of the oxygen in pyrogallol, the small amount of carbon monoxide evolved being allowed for, has been described by Lindstrom-Lang.¹⁴⁵ A chemical detector tube for oxygen, in which manganese(II) oxide is dispersed on silica gel in an evacuated tube, has been described; on breaking the end of the tube the manganese oxide changes colour and the length of the stain is a measure of the oxygen present.¹⁴⁶ Schulek and Purgot¹⁴⁷ describe the preparation of manganese(II) oxide from manganese(II) carbonate and its use for absorbing oxygen, nitrous oxide and "oxides of nitrogen." A novel method is that by Cole.¹⁴⁸ At 900° C the electrical conductivity of copper(I) oxide varies with the partial pressure of oxygen in the circumambient gas, and this is used to measure the concentration of oxygen. Sulphur or halogen can be measured in a similar way by using copper(I) sulphide or halide.

The major recent advance in the determination of traces of oxygen is the development of galvanic analysis by Hersch, referred to above. The general principle is to cause the gas being determined to become a reactant at one of a pair of electrodes and measure the current produced; besides its original application to oxygen, it has also been applied to the determination of hydrogen, halogen, ozone, oxides of nitrogen, carbon monoxide, carbon dioxide, water vapour, "reductants" and methane. Most commercial instruments have been developed for "on-line" operation. A simple cell suitable for laboratory use (and laboratory construction if suitable skills are available) has lead and silver electrodes and potassium hydroxide electrolyte,¹⁴⁹ while a modification suitable for use in the presence of carbon dioxide has saturated potassium hydrogen carbonate solution as electrolyte.¹⁵⁰ A recent development is to use this type of cell as a detector at the exit of a chromatographic column.¹⁵¹ A related technique is the use of the wide-bore dropping-mercury electrode after dissolution of the oxygen in water or other suitable reagent,¹⁵² although this does not seem to have any advantage for gaseous oxygen.

Several colorimetric methods have also been described, some involving the use of anthraquinone-2-sulphonic acid,¹⁵³ its sodium salt¹⁵⁴ or 9,10-anthra-diol-2-sulphonic acid.¹⁵⁵ An old technique, in which the colour of copper(II) chloride in a solution of copper(I) salt is used,^{156,157} has been extended by measurement of the copper(II) ion by electrolytic reduction.¹⁵⁸ Similarly, a continuous coulometric instrument has been developed, in which chromium(II) chloride is oxidised and subsequently reduced at a mercury cathode; the current is adjusted to maintain a constant chromium(II) level.¹⁵⁹ Another paper describes the polarographic determination of the chromium(II).¹⁶⁰ A technique, in which an ionisation detector is used to measure negative ions may offer potential development, but does not yet seem to have received much application.¹⁶¹ The quenching of the phosphorescence of tryptoflavine by oxygen has been proposed at the p.p.m. level.¹⁶²

Ozone—The determination of ozone in oxygen by thermal conductivity is described by Burlant and Cannon.¹⁶³

INORGANIC GASES—

Gas chromatography is applicable to the separation of mixtures of reactive gases. Runge¹⁶⁴ separates carbon monoxide, carbon dioxide, hydrogen chloride, hydrogen cyanide, cyanogen, chlorine, cyanogen chloride, phosgene, nitrosyl chloride and sulphur dioxide on

a column of chlorinated biphenyl or chlorofluorohydrocarbons on PTFE; similar systems are used by Araki, Kato and Atobe¹⁶⁵ and Huillet.¹⁶⁶ Philips and Gimms¹⁶⁷ discuss applications of chromatography to the identification and determination of silanes, germanes, silico-germanes and substituted borazoles. The log of the retention time can be used to estimate the number of atoms present in a molecule and the type of chain branching. Substances not previously known have been identified and determined. The separation of the methylsilanes has been described by Williams and Murray.¹⁶⁸

Ammonia—This is determined in gas mixtures by equilibrating with ammonium chloride solution and measuring the pH.¹⁶⁹ At high temperature and pressure, ammonia, carbon dioxide and water can be determined by direct infrared spectroscopy.¹⁷⁰ Gas-chromatographic methods, in which catalytic decomposition to nitrogen over a hot wire,¹⁷¹ or hypobromite¹⁷² is used, overcome some of the problems of absorption inherent in the direct method.

Boranes—Fristrom, Bennett and Berl¹⁷³ determine boron hydride vapours by burning to boric acid, and colorimetric determination with carmine. If hydrogen is present, Putnam and Myers¹⁷⁴ separate the boranes in a cold trap at -78°C and remove the hydrogen in a stream of argon; the boranes are then allowed to vaporise. They determine boranes and chloroboranes by passing them in a stream of argon through a column of molecular sieve moistened with water, the resultant hydrogen being measured. They also separate chloroboranes, diboranes and hydrogen chloride¹⁷⁵ on columns of Teflon, Silicone Oil 703, Fluorolube and liquid paraffin. Relative retention volumes are given for hydrogen, diborane, chlorodiborane, dichloroborane, boron trichloride and hydrogen chloride. Hill, Kuhns, Merrill, Palm, Seals and Urquiza¹⁷⁶ utilise the red colour produced when triphenyltetrazolium chloride, dissolved in pyridine, is reduced, to monitor atmospheres for boranes and other reducing agents.

Chlorine and chlorine compounds—A general test for halogen compounds is given by Dräger.¹⁷⁷ The gas, mixed if necessary with a combustible gas, is passed over heated copper and ignited; a green flame indicates the presence of a halogen compound. Spurny¹⁷⁸ determines chlorine by dissolution in carbon tetrachloride and measurement of the optical density at $335\text{ m}\mu$; the sensitivity is $1\text{ }\mu\text{g}$ per ml. Neely¹⁷⁹ analyses cell gas by chromatography on columns of Fluorolube grease on Chromosorb and molecular sieve 13X in series, while a simple chromatographic method for chlorine and hydrogen chloride has been described by Ruthven and Kenney.¹⁸⁰ Perugini¹⁸¹ describes apparatus for the analysis of hydrogen and chlorine mixtures and emphasises that light must be excluded. Spurny¹⁸² discusses the photometric determination of chlorine and its oxides, giving maxima for light absorption in carbon tetrachloride solution. Dichlorine monoxide and chlorine dioxide are photosensitive and decompose to chlorine and oxygen, while chlorine pentoxide and chlorine hexoxide are stable. Balashev, Kachalov and Bykova¹⁸³ give a chemical method for analysis of chlorine and chlorine dioxide mixtures based on reaction with solid sodium chlorate. Beregard and Gheshkova¹⁸⁴ describe the chemical analysis of a mixture of carbon monoxide, carbon dioxide, chlorine, phosgene, hydrogen chloride, oxygen and nitrogen; zinc and antimony sulphide are used to absorb hydrogen chloride and chlorine, and sodium iodide in acetone solution to absorb phosgene. A mixture of chlorine, nitrogen dioxide and nitrosyl chloride is analysed by passing the gases through sulphuric acid. Chlorine is unchanged, nitrosyl chloride converted into nitrosylsulphuric acid and nitrogen dioxide into nitric acid and nitrosylsulphuric acid. The sulphuric acid is analysed for nitrosylsulphuric acid by permanganate and for total nitrogen by nitrometer; the chlorine is trapped in iodide solution and titrated.¹⁸⁵ Analysis of mixtures of chlorosilanes by chromatography are described by Rotsche,¹⁸⁶ who uses a column of silicone oil, followed by a column of silica gel to resolve silane and nitrogen, and by Lengyel, Garzo and Székely,¹⁸⁷ who discuss various solid supports and stationary phases. They favour Celite impregnated with 23 per cent. of nitrobenzene.

Fluorine and its compounds—Horton¹⁸⁸ reviews trends in the determination of fluorine. Fluorine itself can be determined continuously by reaction with sulphur dioxide, the change in flow-rate being a measure of the fluorine content.¹⁸⁹ Harrison and Reid¹⁹⁰ determine hydrogen fluoride by infrared absorption, passing beams of two wavelengths through the sample, the second beam serving as a measure for correcting errors arising from window corrosion. Smith¹⁹¹ gives equations for band intensities against partial pressure of hydrogen fluoride when mixed with a foreign gas. Carbon tetrafluoride and hexafluoroethane mixtures can be analysed by reaction with water vapour; at 900°C only hexafluoroethane reacts; and at 1100° to 1200°C both compounds react.¹⁹² The most common method of analysing

mixtures of fluorinated materials is by gas chromatography. Lysij and Newton¹⁹³ discuss suitable apparatus and various stationary phases for the chromatographic separation of highly reactive gases such as chlorine trifluoride, hydrogen fluoride and fluorine; a preparation of halogenated polymers was the most satisfactory column packing. Mixtures that also contain uranium hexafluoride are discussed in two reports by Iveson.¹⁹⁴ Full details are given of apparatus, carrier gas and stationary phase [Kel-F40 polymer oils on Kel-F powder (polychlorotrifluoroethylene)] for these separations. Iveson and Hamlin¹⁹⁵ describe the analysis of a mixture of uranium hexafluoride, chlorine, chlorine monofluoride, chlorine trifluoride and hydrogen fluoride by packed column chromatography with katharometer detection; a 5 to 15-ml sample is analysed in about 40 minutes. Another U.K.A.E.A. report¹⁹⁶ describes apparatus and gives details of a chemical method for analysing a mixture of uranium hexafluoride, fluorine and nitrogen; standard deviations are given.

Nitrogen trifluoride and carbon tetrafluoride are separated by chromatography with a column of silica gel coated with halocarbon oil at 25° C.¹⁹⁷ Low molecular-weight fluorocarbons and compounds such as sulphur tetrafluoride, sulphur hexafluoride, thionyl fluoride and disulphur decafluoride are separated on a column of 33 per cent. Kel-F polymer oil on Chromosorb W at 25° C, with helium as carrier gas. The analysis requires recourse to be made to infrared spectrophotometry, as well as the usual chromatographic detector.¹⁹⁸ Robson and Askew¹⁹⁹ describe the chromatographic separation of silicon tetrafluoride and thionyl fluoride.

Nitrogen compounds—Jeffery and Kipping²⁰⁰ concentrate nitrous oxide, if necessary, (and also carbon dioxide) in mono-ethanolamine, and finally determine it by gas chromatography on a carbon column, while DeGrazio²⁰¹ prefers columns of silica gel and molecular sieve 13X.

Peters²⁰² describes solid absorbents for oxides of nitrogen, such as silver permanganate and sodium chlorite, and Ellis²⁰³ recommends a solid potassium permanganate absorbent. Faucett, McRight and Graham²⁰⁴ compared three methods for the determination of the oxidation state of the process gases from a nitric acid plant and concluded that the best method involved absorption in mixed acid, followed by permanganate titration.

Leffort²⁰⁵ separates nitrous oxide, nitric oxide and nitrogen on molecular sieve 5A at 80° C, with hydrogen as carrier gas; Sakaida, Rinker, Cuffet and Corcoran²⁰⁶ separate 0.1 to 1.0 per cent. of nitric oxide from nitrogen over a silica-gel column, after an elaborate pre-treatment of drying and conditioning. Morrison²⁰⁷ determines nitrogen dioxide in nitrogen and oxygen (5 to 150 p.p.m.) with an electron-capture detector; see also Soukup.²⁰⁸ Nitrogen dioxide is determined in a continuous recorder by Rostenbach.²⁰⁹ The nitrogen dioxide is absorbed in a bromide solution, releasing bromine, which depolarises the electrodes, and the current is measured. Sulphur dioxide interferes; the range is 0 to 5000 p.p.m. A colorimetric method covering the range 0.005 to 5 per cent. has been described by Norwitz.²¹⁰

The chromatographic separation of nitrogen dioxide is almost impossible because of its high reactivity, but one author has reported a technique in which a cold trap is used that is packed with glass beads coated with Carbowax.²¹¹ Gritzner²¹² describes the polarographic detection of nitrogen dioxide, nitric oxide, nitrous oxide and dinitrogen trioxide in anhydrous dimethyl sulphoxide.

The mass spectrometer is used by Tranchant and Moreau²¹³ for the analysis of mixtures largely consisting of oxides of nitrogen, *e.g.*, gases evolved on burning explosives in a bomb calorimeter. A gas-chromatographic method for similar mixtures has also been described.²¹⁴ Mixtures containing nitrosyl chloride, chlorine and hydrogen chloride can be analysed by a chemical method after absorption in sodium hydroxide solution.²¹⁵

Sulphur-containing gases—Fraade²¹⁶ monitors the conversion of hydrogen sulphide in a Claus reaction by gas chromatography. The gas-chromatographic determination of sulphur dioxide in the presence of carbon disulphide, carbon oxysulphide, carbon dioxide and the inert gases is described by Brinkmann.²¹⁷ Novak²¹⁸ measures sulphur compounds in technical gases by means of a carbon anode (2 to 3 cm²) and a zinc-amalgam cathode (for hydrogen sulphide) or a copper cathode (for sulphur dioxide), immersed in 0.05 to 1 M sulphuric acid solution. The gas is bubbled through the constantly flowing liquid and a continuous record is given for concentrations of 0.01 to 10 per cent. v/v; the sulphur dioxide recorder has run for 2 years without a change of electrodes. Experience with commercial colorimetric instruments for sulphur dioxide and hydrogen sulphide has been described by Clevett.²¹⁹

Adams, Koppe and Tuttle²²⁰ separated hydrogen sulphide, sulphur dioxide, methanethiol and permanent gases with Titron 45 and molecular sieve 5A columns in series. Beurman²²¹ uses a 20-foot column of dinonyl phthalate at 95° C to separate sulphur dioxide from oxygen and carbon dioxide. Robbins²²² separates carbon dioxide, hydrogen sulphide, hydrogen, oxygen, nitrogen, methane, carbon monoxide and sulphur dioxide on two columns consisting of 20 feet of 10 per cent. dibutyl sebacate and 7 feet of molecular sieve 13X, while Hodges and Matson²²³ separate carbon dioxide, carbon oxysulphide, hydrogen sulphide, carbon disulphide and sulphur dioxide on silica gel at 100° C.

An oxygen-lamp method for determining total sulphur compounds in gases is described by Mason and Hummel,²²⁴ and a method for determining elemental sulphur in liquefied petroleum gas is described by Gregory,²²⁵ in which the sulphur is dissolved in pyridine reagent and determined polarographically. Garbalinskii²²⁶ determines hydrogen sulphide in the presence of unsaturated hydrocarbons by absorption in copper sulphate solution, and he claims that this does not absorb hydrocarbons as much as cadmium or zinc acetate solutions. Another method for hydrogen sulphide involves titration with hydroxymercuribenzoic acid, which, it is claimed, is free from interferences by iodine, sulphite, chloride and thiocyanate.²²⁷ A complex system for determining hydrogen sulphide, carbon disulphide and carbon oxysulphide involves the use of acidic cadmium acetate to trap the hydrogen sulphide and ethanolic potassium hydroxide to collect the carbon disulphide and carbon oxysulphide as xanthates,²²⁸ while another system involves the use of aqueous potassium hydroxide to remove hydrogen sulphide and thiols and of ethanolic mono-ethanolamine to remove carbon oxysulphide²²⁹; the carbon oxysulphide is determined by titration with silver nitrate, with potentiometric end-point detection.

Methods for determining sulphuric acid mist in process-gas streams, with comparisons of impingers, sinters and electrostatic precipitators, have been given by Kerrigan²³⁰ and Patton.²³¹ A chemical procedure for determining carbon disulphide, carbon dioxide and hydrogen sulphide in waste gases from a carbon disulphide recovery plant has been described.²³²

Sulphur dioxide—This is determined by Barendrecht²³³ by continuous coulometry. The range covered is 0.1 to 100 per cent.

Carbon oxysulphide—Hobbs²³⁴ reviews the analytical chemistry of carbon oxysulphide. Schols^{235,236} describes a gas-chromatographic apparatus with thermistors, in which *NN'*-di-*N*-butylacetamide is the stationary phase, which covers the range 25 to 1000 p.p.m. Gamsjäger²³⁷ and Döring²³⁸ concentrate the gas by absorption in ethanolic potassium hydroxide solution or in acidic palladium chloride solution, when palladium sulphide is formed, and detect it by its catalytic effect in the reaction between azides and iodine; carbon disulphide, sulphides and hydrogen sulphide interfere. Bruss²³⁹ absorbs the gas in ethanolic mono-ethanolamine and titrates the solution with silver nitrate after removing hydrogen sulphide and thiols. An infrared method covering the range 0.3 to 1200 p.p.m. has recently been described.²⁴⁰

WATER—

The biggest advance in the determination of water has been the development of the coulometric cell based on absorption of the water by a film of phosphorus pentoxide, with continuous electrolysis by a pair of electrodes embedded in the film. The electrolysis current at a fixed flow-rate is a measure of the water content. The basic cell has been described by Keidel²⁴¹ and modified versions by Barendrecht,²⁴² Czuhá, Gardiner and Sawyer²⁴³ and Still and Cluley.²⁴⁴ Several patterns of this cell are commercially available and it is now finding wider use. Difficulties may be experienced in the measurement of water below the 10 p.p.m. level and in the presence of hydrogen or oxygen, but this is readily overcome by the simple technique of measuring the water content at two flow-rates.²⁴⁵ Surprisingly, this technique has been patented.²⁴⁶ The cell is also subject to interference by any gas that reacts with phosphorus pentoxide, but this has been overcome by Penther,²⁴⁷ who separated water and hydrocarbons by gas chromatography before passing the water to the cell. The determination of water at the p.p.m. level by gas chromatography has not been as successful. A simple technique in which the water from a 10-litre sample is collected in a column packed with a polyethylene glycol coated support at 10° C, then removed by heating to 80° C in a flow of helium, is described by Carlstrom.²⁴⁸ A similar method, in which a cold trap at -85° C is used, followed by vaporisation directly into a katharometer, has been described

by Séris.²⁴⁹ Techniques involving conversion of the water to hydrogen by reaction with calcium hydride,^{250,251} and to acetylene by reaction with calcium carbide²⁵² have also been described and patented²⁵³; neither of these techniques is satisfactory, and direct chromatography with a column packed with Fluon granules coated with polyethylene glycol^{252,253,254} or packed with microporous polymer beads^{255,256} is probably best. Two papers describe ionisation chambers in which the water is determined by formation of negative ions.^{257,258} Two papers describe reaction with magnesium nitride to form ammonia, which is then determined either by conductivity or with Nessler's reagent.^{259,260} It seems unlikely that this method would be satisfactory, as ammonia is probably absorbed by magnesium oxide, and it seems likely that the reaction of water with magnesium nitride is far from complete. A layer of magnesium hydroxide is formed and inhibits further reaction. Belcher, Otten-dorfer and West²⁶¹ studied the reaction of water vapour with acid chlorides to release hydrochloric acid, which could then be titrated. Of the nine compounds examined, $\beta\beta$ -dimethylglutonyl chloride and β -methyl- β -ethylglutonyl chloride were the most satisfactory. An indirect method involves the use of the reaction with 2,2-dimethoxypropane in the presence of a catalyst to form acetone, which is determined by measurement of the infrared absorption.²⁶² A paper by Kobayashi²⁶³ describes several detector tubes for water, and examines interferences.

The rather specialised instance of the determination of water in the presence of hydrogen fluoride has been studied by Pappas.²⁶⁴ This is obviously extremely difficult and it is not at all certain that any method will give the true result.

Coleman and Elkins²⁶⁵ determine water vapour in a version of Gooderham's apparatus,⁷¹¹ in which the first rotameter is heated to 105° C to measure the steam-to-gas ratio.

ANALYSIS OF LIQUEFIED OR PURE GASES

Anhydrous ammonia—Carbon dioxide is determined in anhydrous ammonia by evaporation of a known volume. At -70° C the carbon dioxide remains as carbonate. This is decomposed with dilute acid, and the carbon dioxide is collected in excess of baryta solution, which is back-titrated with oxalic acid; in the range 5 to 50 p.p.m. the standard deviation is 3 p.p.m.²⁶⁶ Water in "anhydrous" ammonia is determined coulometrically by Klingelhoefer.²⁶⁷ The liquid ammonia is passed through a tube packed with dry potassium chloride into an electrolytic cell with a diaphragm; some potassium chloride dissolves and the potassium formed at the cathode reacts with the water in the sample. At the end-point the conductivity changes and relays cut off the current; the range is 1 to 1000 p.p.m. of water.

Argon—Nitrogen can be determined by the intensity of emission at suitable wavelengths. At atmospheric pressure, excitation can be by means of a silent discharge,²⁶⁸ or by the use of a high frequency discharge.²⁶⁹ (Hydrogen and neon in helium, and neon and helium in nitrogen can also be determined by high frequency discharge methods.²⁷⁰) The determination of nitrogen in argon by gas chromatography requires concentration of the nitrogen from a large sample volume in a cooled column packed with molecular sieve 5A to obtain adequate sensitivity. The nitrogen is then desorbed by heating and separated from residual argon by a normal chromatographic system.^{271,272,273} Oxygen in argon is determined by Mitchell,²⁷⁴ who used a galvanic cell based on zirconia and calcium oxide at 950° C. The apparatus is calibrated by oxygen liberated from nickel - nickel oxide at temperatures between 1000° and 1300° C. For most purposes simpler methods are available, for example, the Hersch cell.

Liquid carbon dioxide—The use of liquid carbon dioxide by atomic power stations has caused considerable work to be carried out on the analysis of the very pure gas used. The sampling of the liquid at a pressure of about 350 lb per inch² and the subsequent evolution of the gaseous carbon dioxide have been described.²⁷⁵ The "residual gases," *i.e.*, gases not dissolved in potassium hydroxide, are measured in a capillary tube in a special apparatus (range up to 0.01 per cent. v/v)²⁷⁶; the residual gases are, if necessary, analysed by a mass spectrometer.²⁷⁷ The determination of hydrogen, argon, oxygen, nitrogen, methane and carbon monoxide (5 to 20 p.p.m.) by gas chromatography is described by Timms, Konrath and Chirnside,²⁷⁸ who trap the carbon dioxide in soda lime and the water in magnesium perchlorate, and separate the other gases on a molecular sieve 5A, with katharometers as detectors and helium, or argon, as carrier gas.

The U.K. Atomic Energy Authority²⁷⁹ trap boron in 2 M sodium hydroxide solution and finally determine it with curcumin. Traces of oil in liquid carbon dioxide are determined

by the evaporation of the sample through pure carbon tetrachloride. The residue in the sample cylinder is also extracted with carbon tetrachloride, and the oil is determined by measurement of the optical density at 2890 cm^{-1} (C-H stretching frequency). This is valid down to 0.0005 per cent. w/v of oil in the carbon tetrachloride.²⁸⁰ Carbon oxysulphide can be determined (0.5 to 2700 p.p.m.) by gas chromatography on a silica-gel column at 25°C , with argon as carrier gas and an ionisation detector.²⁸¹ Sulphur compounds can be determined by oxidation to sulphur dioxide, absorption in tetrachloromercurate solution and colorimetric determination.²⁸²

Carbonyls of iron and nickel are determined by passing the gas over a quartz-wool plug at 350°C . It is cooled under argon, then the metals are extracted with dilute acid and determined spectrophotometrically.²⁸³ Oxygen is determined by Koyama²⁸⁴ by using a galvanic cell, with potassium hydrogen carbonate as electrolyte.

Chlorine—The assay of liquid chlorine for chlorine, water, residue and nitrogen trichloride is described in a British Standard.²⁸⁵ The gas can be analysed for general impurities by gas chromatography.²⁸⁶ Jakšić and Bulimbašić²⁸⁷ determine water in gaseous chlorine by absorption in phosphorus pentoxide or magnesium perchlorate. de Vries and Savarier²⁸⁸ measure the residual gases after removing chlorine by its reaction with mercury, determining iron(III) chloride on the residue after evaporation, silicon tetrafluoride by the molybdenum-blue reaction and chloroform by the pyridine method, although this is not specific.

Helium—Bourke²⁸⁹ determines permanent gases in helium at the p.p.m. level by using a chromatograph with a β -ray "argon" detector, while Purer and Seitz²⁹⁰ achieve a high sensitivity with a large sample on a Beckmann GC-24, and Purer²⁹¹ determines neon, hydrogen, argon, oxygen, krypton, nitrogen, methane and xenon at the p.p.m. level after a concentration stage. Excitation by high frequency electrodeless discharge is used by Bochkova and Chernysheva²⁹² for determining small amounts of hydrogen and nitrogen, the hydrogen line used being 4816 \AA . At a pressure of 20 torr, 10 p.p.m. of hydrogen can be determined in a 15-mm diameter tube. Nitrogen interferes, but can be neglected if less than 0.02 per cent. is present. To determine nitrogen, the lines N^+ , 4278 \AA , and He, 5047 \AA , are used. Emmott²⁹³ determines nitrogen in helium by measurement of the intensity of Tesla discharge. Sagaidak²⁹⁴ uses external electrodes for determining hydrogen and states that for the range 500 to 2500 p.p.m. of hydrogen the error is ± 10 per cent. The conversion of a conventional mass spectrometer to determine impurities at the p.p.m. level has recently been described.²⁹⁵

Hydrogen—The analysis of electrolytic, compressed hydrogen for hydrogen, oxygen, carbon dioxide, carbon monoxide, nitrogen and mercury is described in a British Standard.²⁹⁶ To determine carbon monoxide in hydrogen, Ciuhandu²⁹⁷ passes the gas through an aqueous solution of the silver compound of *p*-sulphamidobenzoic acid at 0°C . The reagent is reduced by carbon monoxide, giving a yellow or brown colour; extinction at $420\text{ m}\mu$ is measured to determine the carbon monoxide (range 0.001 to 0.3 per cent. of carbon monoxide). Smolkova, Feltl and Grubner²⁹⁸ report on the determination of impurities in electrolytic hydrogen, and Brenner and Ettore²⁹⁹ isolate nitrogen and oxygen from other impurities with a condensing trap of silica gel at -80°C .

Anhydrous hydrofluoric acid—A U.K. Atomic Energy Authority Report³⁰⁰ gives full details for the analysis of hydrofluoric acid. The gas is dissolved in glacial acetic acid; water is determined by the conductivity of the solution and sulphur dioxide by reduction of iodine in acetic acid solution, the excess being back-titrated with thiosulphate; total sulphur is determined gravimetrically after oxidation with bromine water; silicon tetrafluoride is converted to silicate and determined colorimetrically with molybdate; and hydrogen sulphide is determined by precipitation of cadmium sulphide and iodimetry. Water is determined³⁰¹ by using potassium fluoride to fix the hydrofluoric acid as potassium hydrogen fluoride and then titrating with Fischer's reagent, and also³⁰² by determining the electrical conductivity of the liquid hydrogen fluoride in a poly(chlorotrifluoroethylene) cell and correcting if sulphuric acid or fluorosilicic acid are present.

Nitrous oxide—Nitrogen and oxygen are separated from nitrous oxide, and from each other, on a column of molecular sieve 5A, while a column of high viscosity liquid paraffin on brick dust gives a good nitrous oxide peak.³⁰³

Oxygen— C_1 to C_4 hydrocarbons in liquid oxygen are determined by gas chromatography, with a modified alumina column.³⁰⁴ Suzuki, Araki and Hirano³⁰⁵ concentrate the impurities in a cold trap and examine them with a mass spectrometer; they found nitrous oxide, carbon

dioxide, C₂ to C₅ hydrocarbons, xenon and krypton. Shinohara, Ohkusa and Okada³⁰⁶ evaporate 100 ml of liquid oxygen through a U-trap cooled in liquid oxygen; the contents of the trap are examined by gas chromatography. The column consists of 15 metres of benzyl ether and 2 metres of silicone grease at 30° C, and a typical sample contained 3 p.p.m. of nitrous oxide, 4 p.p.m. of propane and 2 p.p.m. of butane. Alternatively, the concentrate is vaporised and analysed by infrared absorption in a cell 1 m long. The procedure of trapping the acetylene in silica gel followed by determination with copper(I) chloride reagent is reliable,³⁰⁷ although with the sensitive detectors now available it is simple to determine this impurity directly by gas chromatography. Carbon dioxide in oxygen³⁰⁸ (up to 10 p.p.m. of carbon dioxide) is absorbed on a molecular sieve column, desorbed by heating with a movable heater at 350° C, and determined by katharometry.

FUEL GASES

Coal gas—There is little to report on developments in the older methods of analysis; they continue in use virtually unchanged, but are in course of being replaced by gas chromatography and other physical methods. A British Standard³⁰⁹ describes the sampling and analysis of fuel gases and flue gases. Densham and Gough³¹⁰ reviewed the application of physical methods in the gas industry up to 1957, while Boreham and Armstrong³¹¹ have extended this review up to 1964. Colson and Brown³¹² describe the analysis of town gas by chromatography. They analyse for permanent gases, and for carbon dioxide, on a silica-gel column followed by molecular sieve 5A at 50° C, with helium as carrier gas, on a 1-ml sample. Hydrocarbons up to C₅ are separated on an alumina column (0.1 to 0.01 ml sample) with a flame-ionisation detector, the carrier gas being nitrogen - hydrogen mixture (60 + 40). They also describe the determination of tetrahydrothionaphthene, cyclopentadiene and but-1,3-diene, and point out that a flame-ionisation detector can be used, *e.g.*, in laboratories, as a portable leak-detector without a column. An apparatus for the comprehensive analysis of fuel gas by gas chromatography with five columns and an ionisation detector is described by Blakemore and Hillman.³¹³ In the analysis of coke-oven gas for minor components,³¹⁴ all except the permanent gases are condensed at liquid-air temperature in contact with Apiezon oil. The mass spectrograph was used to identify and determine twenty-eight substances present to less than 0.01 per cent. Prior chromatographic separation over squalane, or, better, benzoquinoline, gave greater enrichment and less overlapping of peaks. The numerous unsaturated compounds were hydrogenated and then identified by fourteen well separated peaks. By combination of chromatography, mass spectrography and hydrogenation, fifty compounds present from 0.0001 to 2.8 per cent. were identified.

Schubert³¹⁵ determines light oil in coal gas by trapping on silica gel and separating by liquid chromatography with isopropyl alcohol, and Sudan red (C.I. Solvent red 1) as indicator instead of the fluorescent indicators used in the petroleum industry. After 45 minutes the length of the red zone is measured and the light oil determined from a calibration graph.

Knipschild and Pagnier report on the determination of benzene hydrocarbons in coal gas³¹⁶ by gas chromatography. A further paper by the same authors³¹⁷ deals with naphthalene and methylnaphthalenes. An entirely different approach to the determination of aromatics is by means of the Hanovia benzole meter, which is essentially a simple ultraviolet photometer.³¹⁸

There have been three papers on the determination of naphthalene in coal gas by the picrate method,^{319,320,321} the last of which being the British Coke Research Association's recommended procedure. It is unlikely that any laboratory equipped for gas chromatography will make much use of this old procedure, familiar to all gas works and coke-oven chemists since before 1918. A comparison of the picrate method with an ultraviolet method for naphthalene in coal gas has also been published.³²²

Total sulphur is determined by combustion, the products of combustion being collected in dilute hydrogen peroxide. Günther³²³ describes a new apparatus and determines the sulphuric acid by conductimetric titration. Michaelis³²⁴ describes four methods for determining hydrogen sulphide in coke-oven gas that were studied on behalf of the German Coal Mining Association, *viz.*, with lead acetate paper, by precipitation as cadmium sulphide or absorption in sodium hydroxide solution, by oxidation to sulphate and by passing it through an ion-exchange column, followed by acidimetric titration.

Barendrecht and Jannsen³²⁵ describe an apparatus in which the gas is scrubbed with

water and the change in conductivity measured. This is applied to the determination of carbon dioxide and ammonia, but small and variable amounts of electrolytes interfere.

Borok³²⁶ determines nitric oxide continuously by oxidation with ozone and the colorimetric reaction with *m*-phenylenediamine, and Pierrain³²⁷ passes the gas through a cell in which oxygen is being electrically generated; the nitrogen dioxide formed is determined with the Griess - Ilosvay reagent.

The determination of iron and nickel carbonyls in town gas has recently become of considerable importance. Densham, Beale and Palmer³²⁸ have published two methods, colorimetric and atomic absorption, which can be applied at the very low levels currently of interest.

Methane - steam reformed gas—This is analysed by chromatography. A recommended procedure is with a molecular sieve 5A column for traces of carbon monoxide, active carbon for the general analysis and activated alumina or di-octyl phthalate for hydrocarbons from C₁ to C₄.³²⁹

Sewage sludge gas—Grune and Chueh^{330,331} describe sampling apparatus and column preparation for chromatographic analysis, and, in another paper,³³² the determination of methane, carbon dioxide, hydrogen, oxygen, nitrogen, hydrogen sulphide and ammonia.

Natural gas—The infrared analysis of natural gas from Lacq is described by Lafaix.³³³ The pressure is atmospheric, and a double-beam instrument with a calcium fluoride or lithium fluoride prism is used. The quantitative determination of methane, carbon dioxide, ethylene, propane, carbon oxysulphide and hydrogen sulphide is discussed. The gas-chromatographic determination of nitrogen, helium, argon and oxygen, after prior concentration on a column of molecular sieve or activated carbon at solid carbon dioxide or liquid-air temperature, is described by Zieliński.³³⁴ Klingman³³⁵ discusses sampling arrangements and gas-chromatographic determination of helium in natural gas. Sampling and analysis are also mentioned in a review by Verrien³³⁶ of the problems arising in the exploitation of natural gas. Thiols in natural gas can be separated by gas chromatography and determined by coulometric titration (1 p.p.m. and upwards).³³⁷ Carbon oxysulphide can similarly be determined by separation over a column of *NN'*-dibutylacetamide. Propane will interfere if more than 0.3 per cent. is present. Relative retention values for carbon oxysulphide and several other gases are given.²³⁶

Blast furnace gas—A U.S. Bureau of Mines Report³³⁸ describes a continuous, largely gravimetric, system for the determination of the main components in blast-furnace top gas, while a chromatographic method is described by Lueth.³³⁹

FLUE GASES

A series of British Standards deals with the sampling and analysis of flue gases.^{340,341} These cover the determination of moisture (gravimetric), dew-point, sulphur dioxide (by iodine solution), sulphur trioxide (by solution in isopropyl alcohol and titration with barium perchlorate solution), carbon dioxide (by conventional means, infrared absorption or thermal conductivity) and carbon monoxide (by infrared absorption, palladium sulphite tube, hopcalite or the iodine pentoxide method). Before the iodine pentoxide method is used, unsaturated compounds are removed by bromine on active charcoal. "Oxides of nitrogen" are oxidised to nitrate and determined by 2,4-xylenol.

Halpen and Ruegg³⁴² discuss the effect of sampling conditions on the apparent composition of hot-flame gases and recommend the use of water-cooled probes.

The use of isopropyl alcohol solution to trap sulphur trioxide (or sulphuric acid mist) and thus separate it from sulphur dioxide seems to have become standard practice in this country. Stone³⁴³ determines the sulphuric acid by turbidimetry. Crumley, Howe and Wilson³⁴⁴ describe an automatic method for precipitation of the barium sulphate and optical measurement of the suspension. Fielder and co-workers^{345,346} describe the determination of 0.50 p.p.m. of sulphur trioxide in the presence of up to 3000 p.p.m. of sulphur dioxide. The sulphur trioxide is trapped in isopropyl alcohol-water solution, and an aliquot is titrated with 0.0025 *M* barium perchlorate solution, with "thoron" as indicator; the sulphur dioxide is determined with iodine. Seidman³⁴⁷ uses a similar method for sulphur trioxide, but he traps the sulphur dioxide in the effluent gas from the sulphur trioxide absorber in dilute hydrogen peroxide, and finally titrates the resultant sulphuric acid in the same way. Jelgersma³⁴⁸ dislikes the isopropyl alcohol method, because the sulphur dioxide must be

separated from the alcohol before determination, and prefers to collect the sulphur trioxide in glycerol and measure the concentration by conductivity. Other methods involve the use of formaldehyde³⁴⁹ or acetaldehyde and furfural³⁵⁰ to inhibit the oxidation of sulphur dioxide. In an interesting method the gas is absorbed in a solution of iodine in barium chloride, and both sulphur dioxide and sulphur trioxide are determined from measurement of the total acidity and the iodine reduction.³⁵¹ An automatic apparatus based on measurement of the turbidity of barium sulphate in isopropyl alcohol has been described by Grandona.³⁵² Hissink³⁵³ describes a portable instrument for the simultaneous determination of sulphur trioxide and sulphur dioxide. The gas is cooled to below the "acid dew-point"; sulphuric acid mist is caught on a sintered-glass filter and sulphur dioxide is subsequently trapped in hydrogen peroxide. Both are titrated acidimetrically. It is claimed that all of the sulphur trioxide will be trapped if the temperature is maintained at between 60° and 90° C.^{354,355} A continuous-recording instrument based on the colour reaction with barium chloroanilate covers the range 0.2 to 10 p.p.m. and may well receive wide application.³⁵⁶ An unusual approach is that of Bond³⁵⁷; sulphur trioxide is reacted with oxalic acid to produce carbon monoxide, carbon dioxide and sulphur dioxide. The effluent gas is analysed by gas chromatography.

For the analysis of flue gases containing both organic and inorganic gases, Cvejanovitch³⁵⁸ describes a gas-chromatographic apparatus with multiple columns. Retention time and thermal-response factors are given for five permanent gases and twenty-three hydrocarbons; a complete analysis, including saturated and unsaturated hydrocarbons up to C₅, takes 3 hours. Formaldehyde in combustion products can also be determined by gas chromatography; Kyryacos³⁵⁹ used a column of 12 feet of octyl decyl phthalate at 105° C.

MOTOR EXHAUST GASES

Continued attention to atmospheric pollution has led to much work on the analysis of motor exhaust gases. King³⁶⁰ reviews methods of exhaust-gas analysis; Ellis, Kendall and Eccleston^{361,362} describe methods of sampling and determination of aldehydes, ketones, alcohols and oxides of nitrogen. Altshuller³⁶³ uses Mylar bags for sampling and the preparation of standard atmospheres, and determines aromatic hydrocarbons by gas chromatography. Feinland, Andreatch and Cotrupe³⁶⁴ determine hydrocarbons in motor-car exhausts with two chromatographic columns in parallel, and twin flame-ionisation detectors with a common recorder. With no prior concentration, the limit of detection for butane, with a 1-ml sample, is 0.01 p.p.m. An even more complex gas chromatograph that gives a more comprehensive separation has also been described.³⁶⁵ It is claimed that 85 components are separated in 13 minutes by a rapid gas-chromatographic procedure for C₁ to C₁₀ hydrocarbons, in which capillary columns and programmed temperature rise are used.³⁶⁶

Unsaturated hydrocarbons are determined by Mader, Schoenemann and Eye³⁶⁷ by absorption in carbon tetrachloride, followed by photometric titration with a special 0.01 N bromide-bromate solution. The range is 25 to 1000 p.p.m. v/v, but recovery of C₄ or lighter hydrocarbons is not good. Carbon dioxide can be determined in motor exhaust gases by an interference filter photometer at 4.29 μ ; the range is 1 to 18 per cent. v/v.³⁶⁸

Nicksic³⁶⁹ determines nitrogen dioxide in diesel exhaust gases by ultraviolet absorption. Nitric oxide is determined after oxidation to nitrogen dioxide by mixing with oxygen, and compression to accelerate the oxidation. A rapid method in which Saltzman's reagent is used is claimed to be as accurate as the phenoldisulphonic acid method.³⁷⁰

ANALYSIS OF MICRO SAMPLES

There have been comparatively few papers on the analysis of very small samples by modifications of absorption methods. Updegraff and Huckabay³⁷¹ have modified the apparatus of Berg.³⁷² Aqueous reagents are used and a sample of 50 to 100 μ l can be analysed for carbon dioxide, oxygen, hydrogen, hydrocarbons and inert gases in 15 minutes, with a precision of ± 0.5 to 10 per cent. for the various components. A semi-micro apparatus is described by Radley³⁷³ in which the gas burette is a tube 40 cm long, with a bore of about 2 mm diameter. The usual aqueous reagents are introduced by rolling one of two mercury globules, between which the sample is trapped, over a thin film of the absorbent in the tube, and the analysis is carried out by measuring the changes in length of the gas column.

Lefort³⁷⁴ describes a system of micro gas analysis, which is a combination of an ionisation

chamber with separation of components by a cold trap (carbon dioxide, water and nitrous oxide), diffusion through palladium (hydrogen) or chemical reaction (oxygen). Gas-chromatographic methods are usually applicable to samples in this size range.

The determination of gases in metals (by which the metallurgist does not necessarily mean gases absorbed or in solid solution in the metal, but any gases that are evolved on heating under specified conditions) is not really gas analysis as considered in this review, but is a subject of great and growing importance and, as it involves the analysis of small volumes of gas, it is appropriate to mention it here. The usual procedure is to heat the metal sample to a high temperature *in vacuo*, usually in a bath of a flux such as platinum or tin in which the sample dissolves, and often contained in an out-gassed graphite crucible. Dissolved or combined hydrogen, nitrogen or carbon monoxide is evolved, any oxygen present combines with the carbon and is also evolved as carbon monoxide, and also in most instances metal nitrides decompose and give up their nitrogen.

In a report³⁷⁵ full descriptions of the evolution of the gases and their subsequent analysis are given. In 1964, a review of later work appeared³⁷⁶ with 163 references.

The current tendency seems to be for the use of gas chromatography to increase.^{377, 378, 379, 380, 381}

Tyou³⁸² discusses the determination of hydrogen, nitrogen and oxygen in steel by gas chromatography, and Lysyj³⁸³ and Galwey³⁸⁴ discuss the application of gas chromatography to the determination of trace amounts of carbon in steel. Evans and Fassel³⁸⁵ determine as little as 0.003 up to 0.1 per cent. w/v of nitrogen or oxygen, or both, in steel by fusion under slightly reduced pressure by a d.c. arc; an aliquot of the resulting gas mixture is analysed on a 3-foot column of molecular sieve 5A. A routine analysis (coefficient of variation 2.5 to 10 per cent.) is complete in 10 minutes. Hillen³⁸⁶ determines helium and hydrogen in beryllium by vacuum fusion and gas chromatography. Suzuki³⁸⁷ analyses a 1-g sample by the vacuum fusion method, and on a molecular sieve 5A column, with argon as carrier gas, claims to determine hydrogen down to 0.00002 per cent., nitrogen to 0.0009 per cent. and oxygen to 0.0018 per cent.

Mickel³⁸⁸ describes the analysis of gases evolved during the arc melting of refractory metals.

After extracting hydrogen, nitrogen and carbon monoxide from steel, Koch, Eckhard and Stricker³⁸⁹ analyse the mixture by high frequency excitation and spectroscopy in the visible region.

Isotopic-dilution methods have also been applied to the determination of gases in metals.^{390, 391, 392, 393}

ATMOSPHERIC POLLUTANTS

GENERAL—

The field of atmospheric pollution proper has been extensively reviewed by Altshuler,^{394, 395} but he does not touch upon the wide field of industrial atmosphere analysis. The Air Pollution Control Association has recently issued a manual of standard methods for determining sulphur dioxide, hydrogen sulphide, oxidants, ozone, oxides of nitrogen, carbon monoxide, fluoride, hydrocarbons and aldehydes.³⁹⁶ A similar manual of methods for determining sulphur dioxide, nitric oxide, nitrogen dioxide, ozone, aldehydes, acrolein, formaldehyde, sulphate and nitrate has been issued by the U.S. Department of Health, Education and Welfare.³⁹⁷ The results of 5 years' operation of the U.S. National Gas Sampling Network, with details of apparatus and methods, have been described by Tabor and Golden.³⁹⁸ A compendium of methods for testing industrial atmospheres has recently been published.³⁹⁹

The collection and storage of large samples of air in plastic bags is assessed in two papers,^{400, 401} and the use of these bags, for the preparation of standard mixtures, in a third.⁴⁰² The collection of contaminants from the air by using absorbers is discussed and types of absorber reviewed in several papers.^{403, 404, 405} A special design, in which only 10 ml of reagent are used in a circulating system, is described by Kamphausen,⁴⁰⁶ and an unusual fritted design is described by Skare.⁴⁰⁷ This latter apparatus is similar to a design by Bergshoeff that has been in use for 5 years.⁴⁰⁸

An apparatus for the calibration of hand sampling pumps is described by Gage.⁴⁰⁹ A general-purpose apparatus is described by Kündig⁴¹⁰ in which the sample is aspirated through a quartz pyrolysis tube at 1000°C, then into water in a conductivity cell; it is suitable for

the determination of hydrogen sulphide, carbon disulphide and halogenated organic compounds, but is, of course, liable to considerable interference. Kinnear⁴¹¹ describes a paper tape sampler for the determination, by using suitably impregnated tapes, of hydrogen sulphide, hydrogen cyanide, phosgene, chlorine and sulphur dioxide, while Nichols⁴¹² lists modified reagents for use with a commercially available sulphur dioxide meter to convert it for the determination of hydrogen sulphide, chlorine, chloride, nitrogen dioxide, fluoride or organochlorine; the absorber used in this apparatus is described in a British Patent.⁴¹³ The use of detector tubes for the assessment of toxic hazards in factory atmospheres has increased greatly in recent years. Saltzman⁴¹⁴ reviews theory, evaluation and calibration of detector tubes, although his remarks on the performance of commercial tubes are now out of date. Kitagawa⁴¹⁵ also reviews detector tubes, principally his own, while Grosskopf⁴¹⁶ reviews several types of tube, including those by Dräger. Filyanskaya⁴¹⁷ describes the technique for the preparation of silica-gel based tubes, with suggestions for tubes sensitive to hydrogen sulphide, chlorine, ammonia, petroleum, benzene, toluene and nitrogen dioxide. A useful paper describing the preparation of standard atmospheres of 16 toxic gases suitable for the calibration of detector tubes or other instruments has been published by Saltzman.⁴¹⁸

ORGANIC VAPOURS—

The determination and identification of organic vapours in the atmosphere presents a difficult problem. Before the development of gas chromatography, mass spectroscopy was the only general method, and its application to the analysis of complex mixtures of organic compounds collected in urban atmospheres is described by Weaver, Hughes, Gunther, Schuhmann, Redfearn and Gorden.⁴¹⁹ The simpler problem of determining hydrocarbons alone is treated by Quiram and Biller.⁴²⁰

The application of gas chromatography is reviewed by Altshuller,⁴²¹ with particular reference to car-exhaust fumes, while a more general review is given by Lebbe.⁴²² Techniques of pre-concentration and drying are described by Farrington⁴²³ for the p.p.m. level, while Bellar⁴²⁴ and Feldstein and Balestrieri⁴²⁵ deal with the p.p.b. level. With such techniques, however, the analyst may have to choose between a system of low efficiency^{425, 426} or low capacity for certain constituents of the atmosphere he is testing,⁴²⁷ or risk using an adsorbent that may catalyse reaction of the collected pollutant. For example, silica gel may catalyse the conversion of alcohols to olefins, although, surprisingly, molecular sieve 5A appears to be free from this defect.⁴²⁸ Guerrant⁴²⁹ describes a portable gas chromatograph with silica gel or hexadecane columns and a flame-ionisation detector for field use, and Rasmussen and Went⁴³⁰ describe the rough quantitative measurement of organic compounds in forest air. In a paper by West, Buddhadev, Bharnt, Mallik and Sen Gupta,⁴³¹ retention results for numerous possible pollutants on columns of tritoyl phosphate and $\beta\beta$ -oxydipropionitrile are listed. The application of gas chromatography to the determination of a wide range of toxic substances in factory atmospheres is fully developed by Cropper and Kaminsky.⁴²⁷

Hydrocarbons—The modern technique for determining hydrocarbons in air involves the use of the flame-ionisation detector almost exclusively. Its use without chromatographic columns for total hydrocarbons is described by Andreach and Feinland,⁴³² and by Decristofaro,⁴³³ while separating columns for individual hydrocarbons are described by various authors.^{434, 435, 436, 437, 428} The older technique of combustion to carbon dioxide followed by infrared determination by its spectrophotometric absorption in the infrared region is described by Rosenbaum.⁴³⁹

Methane in mine air is traditionally determined by combustion over a platinum filament. A particularly sensitive design is described by Domanski, Jourdon and Eyraud⁴⁴⁰ and a catalyst for flameless combustion (platinum plus palladium on alumina) is described by Kravchenko.⁴⁴¹ The other popular instrument, the interferometer, has been reviewed by Baker, Hartwell and Windle, with special references to the effects of other gases.⁴⁴² The use of infrared spectroscopy at 7.6μ is covered by Colbasini and Watson.⁴⁴³

A simple chromatographic system for pollution studies is described by Ortman.⁴⁴⁴ A detector tube for ethylene makes use of the reducing action of this gas on a mixture of ammonium molybdate and palladium sulphate⁴⁴⁵; this is obviously subject to interference from other reducing gases. A simple field method for determining acetylene comprises absorption on silica gel at -78°C . The gel is allowed to return to atmospheric temperature and a solution of ammoniacal copper(I) chloride added; the colour produced is compared with a series of

permanent standards.⁴⁴⁶ A method for determining conjugated di-olefins involves the use of *p*-nitrophenyldiazonium fluoroborate in a 2-methoxyethanol-phosphoric acid solvent as absorption reagent; the extinction at 400 to 500 $m\mu$ is used, depending on the olefin measured.⁴⁴⁷

The determination of benzene, toluene and xylene in air is best achieved by gas chromatography, with, for example, a column of 5 per cent. di-octyl phthalate and a flame-ionisation detector,⁴⁴⁸ but there may be occasions when other techniques are preferred. One of these involves drawing air through methanol at solid carbon dioxide temperature for 30 minutes, followed by measurement of the extinction at 245.5, 268.5 and 272.0 $m\mu$, from which the concentration of each hydrocarbon can be calculated.⁴⁴⁹ Another ultraviolet method for determining benzene alone involves the use of a silica-gel trap, which is subsequently eluted by low boiling solvents, followed by a fractionation stage and spectrophotometry at 253 to 280 $m\mu$.⁴⁵⁰ Vlasak⁴⁵¹ describes two methods for determining benzene that depend upon nitration, while Blake and Rose⁴⁵² describe a method for determining toluene, which has been adopted as a standard method by H.M. Ministry of Labour.⁷¹² In this method the air is drawn through a solution of formaldehyde in a mixture of phosphoric and sulphuric acids until a colour of standard intensity is formed. By using 89.5 per cent. sulphuric acid alone, instead of the acid mixture, styrene can be determined without interference from either benzene or toluene. A method for determining α -methylstyrene involves the reaction with mercury(I) acetate and the colorimetric determination of the excess with diphenylcarbazide.⁴⁵³

Halogen compounds—A simple general method for determining organo-halides in air involves combustion in an ethanol flame that impinges on a copper wire; in the presence of organohalogen compounds the flame is usually coloured green.⁴⁵⁴ More specific results can be obtained by application of the many variations of the Fujiwara reaction, which are reviewed by Humold and Schuhlein,⁴⁵⁵ and the best conditions for seven chloro compounds are given. A more recent modification is described by Leibman,⁴⁵⁶ and a procedure suitable for chloride (but not specific) is described by Redford-Ellis and Kench.⁴⁵⁷ A colorimetric method for the determination of carbon tetrachloride in air is described by Belyakov.⁴⁵⁸ In this method the sample is collected in pyridine, made alkaline, allowed to react for 20 minutes at 85°C, acetic acid and aniline are added and the extinction is measured at 496 $m\mu$. A general method involving reduction with sodium biphenyl and titration of the chloride ions is described by Stier.⁴⁵⁹ The most specific methods involve the use of gas chromatography, either with a collection stage⁴⁶⁰ or else directly. The extremely sensitive electron-capture detector permits the direct determination of nanogram amounts.⁴⁶¹ Berton⁴⁶² described a general method for chlorinated ethylene in which the sample is irradiated with ultraviolet light to form cyanogen chloride, and is then passed through a paper containing *p*-dimethylaminobenzaldehyde and *NN*-dimethylaniline.

Two detector tubes for trichloroethylene with silica gel impregnated with potassium permanganate-orthophosphoric acid or *o*-tolidine hydrochloride are described by Gage.⁴⁶³ The latter is better, and, if correctly calibrated, is very effective. A detector tube for vinyl chloride in which the halide is oxidised by sulphuric and chromic acids is described by Kobayashi.⁴⁶⁴

Bencze⁴⁶⁵ describes a method for allyl chloride involving absorption in ethanolic phloroglucinol solution, colour development, and measurement of the extinction at 520 $m\mu$. Hughes⁴⁶⁶ gives a colorimetric method for 2,2-dichlorovinyl dimethyl phosphate, and Bencze⁴⁶⁷ gives one for pentachlorophenol by its reaction with phenazole to form a blue dye; most other chlorophenols form red dyes.

Berck and Solomon⁴⁶⁸ describe a polarographic method for chloropicrin. The use of a simple thermal-conductivity meter to determine methyl bromide in air is described by Heseltine, Pearson and Wainiman,⁴⁶⁹ although this is obviously not specific. Micro-sampling apparatus for the collection of brominated hydrocarbons is described by Call.⁴⁷⁰

Dibromomethane can be determined by absorption in methanolic potassium hydroxide, conversion to potassium bromide, and the bromide determined coulometrically.⁴⁷¹

ALDEHYDES AND KETONES—

A review of the determination of aldehydes in air is given by Altshuller.⁴⁷² The chromotropic acid method for formaldehyde is reviewed by Altshuller,⁴⁷³ and a modified version is

described in detail by the same author.⁴⁷⁴ A comparison of chromotropic acid with the more sensitive J-acid and phenyl-J-acid is given by Sawicki,⁴⁷⁵ while a fluorimetric determination, based on reaction with acetylacetone and claimed to detect 0.01 μg , is described by Belman.⁴⁷⁶ A method claimed to be specific and accurate to 5 to 10 per cent. in the μg range involves reaction with phenylhydrazine and oxygen in an alkaline medium to give a red product.⁴⁷⁷ Rayner and Jephcott⁴⁷⁸ describe a method in which Schiff's reagent is used with acetone added to increase the intensity and stability of the colour. With this they claim to detect 5 p.p.b. (10^9) in little more than 1500 ml of air; they also claim a 72 per cent. collection efficiency for an impinger containing 0.005 N hydrochloric acid, sampling at 1 foot³ per minute. Another method for the p.p.b. level involves the use of acid-bleached *p*-rosaniline and the dichlorosulphitomercurate complex⁴⁷⁹ and has been used successfully in a mobile laboratory for over 4 years. Silica gel impregnated with phenylhydrazine hydrochloride is used in the only detector tube for formaldehyde described during this period. After sampling, a red colour is developed by oxidation with potassium hexacyanoferrate(III).⁴⁸⁰

The determination of acrolein in the atmosphere can be accomplished by reaction with 4-hexylresorcinol and measurement of the spectrophotometric absorption at 605 $\text{m}\mu$.⁴⁸¹ A 10-litre sample is required to detect 0.1 p.p.m.

Acetone may be determined in air by adsorption on activated silica gel, followed by desorption in the presence of alkali and iodimetric determination.⁴⁸²

Cyanides—Methods for the determination of trace cyanides have been comprehensively reviewed by Bark and Higson,⁴⁸³ and alternative reagents to the carcinogenic benzidine have been investigated.⁴⁸⁴ These authors favour *p*-phenylenediamine but methods in which barbituric acid⁴⁸⁵ and *p*-toluidine⁴⁸⁶ are used as alternatives to benzidine have also been described. In a method for determining hydrogen cyanide and hydrogen sulphide, mercury(II) nitrate is used with diphenylcarbazone as indicator.⁴⁸⁷ A simple paper-stain method based on the formation of Prussian blue has been developed by Dixon, Hands and Bartlett,⁴⁸⁸ and a booklet describing this method and including a set of standard colour stains has been published by H.M. Stationery Office.⁴⁸⁹ In another paper method, impregnation with mercury - diphenylcarbazide and sodium hydrogen carbonate is used; by insertion of the paper in a suitable tube the concentration can be determined by measuring the length of the red stain produced.⁴⁹⁰ *o*-Tolidine and copper(II) sulphate on silica gel are used in a detector tube described by McConnaughey,⁴⁹¹ and one based on silver chloride or mercury(I) chloride plus bromothymol blue to detect the released hydrogen chloride is described by Hiedrich.⁴⁹² Hydrogen cyanide and cyanogen may be separated from air by gas chromatography by using a column of triacetin,⁴⁹³ or adiponitrile and the use of flame-ionisation detection is necessary to reach the p.p.m. range. An electrical method for determining hydrogen cyanide or hydrogen sulphide involves absorption in water and measurement of the e.m.f. developed between a rotating silver electrode and a calomel cell.⁴⁹⁴

Miscellaneous organic compounds—Acrylic and methyl methacrylate monomer vapours can be determined by collection in cooled isopropyl alcohol, conversion to hydroxamic acid and reaction with iron(III).⁴⁹⁵ Aliphatic amines may be identified in air by collection in acid, conversion to benzamides and separation by paper chromatography,⁴⁹⁶ or, alternatively, the original amines may be separated by gas chromatography.

The determination of aniline by absorption in hydrochloric acid, followed by diazotisation and coupling is described by Ponomarenko,⁴⁹⁷ while a paper-stain method in which *p*-dimethylaminobenzaldehyde is used is described by Gernet and Russkikh.⁴⁹⁸ The determination of benzidine in air is described by Kratochvíl, Langer and Vlasák.⁴⁹⁹ A method for determining carbon disulphide has been described that involves hydrolysis to hydrogen sulphide.⁵⁰⁰ Dibutyl phthalate can be collected in ethanol, allowed to react with alkali and hydroxylammonium chloride, and a colour developed by addition of iron(III) chloride.⁵⁰¹ Esters of other carboxylic acids interfere. Ethanediol can be determined by oxidation to formaldehyde followed by determination of the latter with chromotropic acid.⁵⁰² A detector tube for ethanol in breath, based on oxidation by chromic acid under controlled temperature conditions, is described by Kitagawa and Wright.⁵⁰³ The determination of ethylene oxide in the atmosphere by trapping in silica gel, hydrolysis and reaction with acetylacetone is described by Gage,⁵⁰⁴ while a detector tube involving the sulphuric acid - dichromate oxidation is described by Kitagawa and Kobayashi.⁵⁰⁵ Nitroglycerol can be determined by trapping in ethanolic potassium hydroxide, hydrolysis to nitrite and nitrate, and the nitrite determined by some

standard method,⁵⁰⁶ but in a better method gas chromatography is used with electron-capture detectors.⁵⁰⁷ A method for determining nitroethylene and 1-nitro-1-propene has been developed in which gas chromatography is used with electron-capture detection.⁵⁰⁸ Nitrobenzene may be collected in 2-ethoxyethanol, reduced by zinc amalgam, diazotised and coupled with R-salt.⁵⁰⁹ Fukuyama, Sato and Kimura⁵¹⁰ describe a method for phenol that involves absorption in alkali and coupling with diazotised *p*-nitroaniline. The reaction of pyridine with thiocyanogen bromide and aniline can be used for the determination of pyridine in air.⁵¹¹ A detector-tube field test for sulphur-containing stenching agents in liquefied petroleum gas is described by Peurifay.⁵¹² A paper by Feldstein, Balestrieri and Levaggi on the determination of thiols by gas chromatography gives retention times, small-detection limits, flame-ionisation detector response and a trapping technique in which mercury(II) cyanide is used.⁵¹³ Another paper describes a similar technique.⁵¹⁴ Methods for determining tolylene-2,4-di-isocyanate, involving hydrolysis, diazotisation and coupling with *N*-1-naphthylethylenediamine, are described by Reilly⁵¹⁵ and Marcali.⁵¹⁶ A detector tube for vinyl chloride in the presence of ammonia involves the use of silica gel to separate the gases, before the vinyl chloride is determined by reaction with chromic acid.⁵¹⁷

INORGANIC GASES—

Ammonia—The determination of ammonia in air is simple and obvious. The standard method of absorption in dilute acid, followed by determination with Nessler's reagent does not appear to have been credited with separate publication. This method cannot be adapted for continuous monitoring, however, and, for this purpose, recourse is made to measurement of the spectrophotometric absorption by the gas at 204.3 μ . Two papers by Kolbezen⁵¹⁸ and Gunther, Barkley, Kolbezen, Blinn and Staggs⁵¹⁹ describe this technique for the range 10 to 1000 p.p.m., differing mainly in the model of spectrophotometer used. A detector tube for ammonia, in which thymol blue and sulphuric acid are used on a methacrylate support, is described by Kobayashi, Matsumoto and Yamada,⁵²⁰ while a complex tube for ammonia and ethanolamine with ninhydrin on silica gel is described by Williams and Miller.⁵²¹ Of the colorimetric methods available, the indophenol reaction is probably the most robust^{522,523} and can be made more sensitive by extraction of the colour into isopentyl alcohol.⁵²⁴ The most sensitive method is probably the reaction with indanetrione hydrate⁵²⁵ or one of the several procedures in which chloramine is used, with the subsequent formation of a blue starch-iodine complex.⁵²⁶ These procedures require highly skilled analysts for their application. A galvanic cell for the determination of ammonia involves the use of a neutral electrolyte with aluminium and carbon electrodes⁵²⁷; this cell responds to many alkaline or acidic gases. In another continuous-recording instrument recently described titration with coulometrically generated hydrogen ions is utilised.⁵²⁸

Arsine—A detector tube for determining arsine in air in the range 1 to 50 p.p.m. involves the use of silica gel impregnated with mercury(II) chloride.⁵²⁹

Boranes—These can be determined down to 0.2 p.p.m. by scrubbing the air with sodium hydrogen carbonate - potassium iodide solution, followed by coulometric titration with iodine.⁵³⁰ This method is obviously not specific.

Carbon dioxide—There are numerous chemical methods available. Toran and Heinrich⁵³¹ pass air through a suspension of an insoluble carbonate and measure the pH, while Lodge, Frank and Ferguson⁵³² improve on this by using fine marble chips. Deckert⁵³³ absorbs the carbon dioxide in 0.25 per cent. ammonia in ethanol at 80° C and titrates the solution with thymolphthalein indicator, or else uses 0.1 N ethanolic potassium hydroxide in three impinger bubblers and titrates between phenolphthalein and methyl-red end-points. It should be remembered that the absorption of carbon dioxide is relatively slow, even in alkaline solution. A colorimetric method with 0.001 N sodium hydrogen carbonate and added phenol red, with measurement at 590 μ , can be used in a continuous apparatus,⁵³⁴ while a similar method has been developed for field use, with the well known Lovibond disc method of colour comparison.⁵³⁵ Another simple field method involving titration, but in which the titrants are manipulated in hypodermic syringes to exclude contamination, has also been developed.⁵³⁶ In several simple instruments for the measurement of carbon dioxide at about the 1 per cent. level, diffusion between two porous pots is involved, one pot containing moist soda lime and the other cotton-wool coated with calcium chloride to produce a pressure difference proportional to the concentration.⁵³⁷ These instruments are cheap and robust and the results are

surprisingly reproducible. Two detector tubes have been described. In one,⁵³⁸ a sample of air is drawn through a tube packed with alumina impregnated with 0.4 N sodium hydroxide and thymolphthalein by means of a hand pump. In the other⁵³⁹ the tube is filled with acid-washed sand coated with rosaniline hydrochloride that has been decolorised by hydrazine hydrate, and the tube is evacuated before sealing. It thus draws its own sample when the seal is broken. A recording conductivity analyser is described by Holm-Jensen.⁵⁴⁰

Carbon monoxide—Detector tubes for the determination of carbon monoxide in air have been used for many years and a wide range is now commercially available. With some, the precision is not as high as could be desired and Murphy,⁵⁴¹ reporting a comparison of four such types of tube, showed differences among them indicating that some were as much as 100 per cent. high. The performance of one such type of tube has been examined in detail.⁵⁴² The interference from oxides of nitrogen may be overcome by passing the sample first through a tube packed with silica gel impregnated with a solution of chromic oxide in sulphuric acid.⁵⁴³ Rough qualitative indicators are gaining popularity as "substitute mice." The "detector" plate⁵⁴⁴ consists of a plastic plate with an inserted disc of silica gel impregnated with palladium chloride, which darkens in the presence of carbon monoxide, the time taken being an approximate measure of concentration. A similar technique can be used with paper soaked in a solution of gold(III) chloride and arsenic(III) oxide, which darkens on exposure to carbon monoxide⁵⁴⁵; with neither technique is a sample of defined size used, so that the indications are largely qualitative. A simple but precise instrumental method that has received much attention in this period makes use of the temperature rise in the air stream when carbon monoxide is oxidised over a catalyst such as hopcalite^{546, 547, 548, 549} and is useful when a continuous monitor is required, as in coal mining. A spectrophotometric method fully described by Ciuhandu^{550, 551} relies on the reduction of the silver salt of *p*-sulphamylbenzoic acid to give a silver sol. This method is very sensitive and is not affected by the presence of hydrogen. Finally, an electrochemical method involves the oxidation of carbon monoxide at a vibrating electrode immersed in a solution of borax or sodium dihydrogen orthophosphate.⁵⁵²

Carbonyl chloride (phosgene)—A qualitative indication of the presence of phosgene in the atmosphere can be obtained by the use of detector crayons. These consist of blackboard chalk impregnated with a solution of 4-benzylpyridine and barbituric acid. A line drawn by this chalk on paper will change colour in the presence of phosgene⁵⁵³; an alternative indicator can be prepared by soaking filter-paper in a solution of anabasin or a related alkaloid.⁵⁵⁴ A more precise paper-stain method involves drawing a measured volume of air through a paper impregnated with 4-*p*-nitrobenzylpyridine and *N*-benzylaniline.⁵⁵⁵ The colour produced is compared with a standard colour chart obtainable from H.M. Stationery Office, together with the booklet describing the method. Chemical methods are described by Terent'ev,⁵⁵⁶ who uses the reaction with hexamethyleneimine and by Crummett and McLean,⁵⁵⁷ who use the reaction with aniline to form 1,3-diphenylurea, which they measure by its absorption at 257 μ . An extremely sensitive method involves the use of a gas-chromatographic separation on a column of didecyl phthalate and an electron-capture detector⁵⁵⁸; it is claimed to cover the range 0.001 to 2 p.p.m. v/v.

Chlorine—The *o*-tolidine method, popular so long for determining chlorine in air, is likely to fall into disuse because of the suspected carcinogenic properties of *o*-tolidine. A suitable alternative is to be found in diethyl-*p*-phenylenediamine.⁵⁵⁹ Other, more complex, methods involving the oxidation of iodide to iodine are described by Hollata and Meissner⁵⁶⁰ and Kogan.⁵⁶¹ A simple but precise method used depends upon absorption of the chlorine in carbon tetrachloride and measurement of the ultraviolet extinction at 335 μ .⁵⁶²

Chlorine dioxide—This can be monitored by dissolution in water followed by cathodic reduction to chlorine; under controlled conditions the current can be made proportional to the chlorine dioxide concentration.⁵⁶³

Fluorine and fluorides—The determination of fluorine, hydrogen fluoride and particulate fluorides is largely a problem of collection and separation from interfering substances. Gwirtsman, Mavrodineau and Coe⁵⁶⁴ give a detailed description of a method that involves absorption in sodium hydroxide, steam-distillation and titration with thorium(IV) solution. Pack and Hill⁵⁶⁵ evaluated glass-fibre filters for the collection of fluorides and found 95 per cent. efficiency until 75 μ g of fluorine per sq. inch of filter area had been collected. Vrotek, Pozigun and Pokraka⁵⁶⁶ prescribe conditions for determination by iron(III) thiocyanate and

list interfering anions. Guntz and Arène⁵⁶⁷ studied the factors affecting the thorium alizarin sulphate method. Methods involving the bleaching action on methyl red are described by Peregud,⁵⁶⁸ and in a U.K.A.E.A. Report.⁵⁶⁹ In the same paper⁵⁶⁸ Peregud describes a technique in which the reaction with potassium bromide to release bromine, which converts fluorescein to eosin, is used, with measurement of the colour produced (this is not specific as chlorine acts in a similar way). In the following year Peregud and Boikina⁵⁷⁰ described a detector tube for fluorine dioxide that is based on the same principle. Some of the above methods, although described for fluorine in air, are likely to be equally sensitive to hydrogen fluoride and its inorganic salts, and the same is probably true of many methods described for hydrogen fluoride. For example, the method described by Huygen,⁵⁷¹ in which the hydrogen fluoride is collected by drawing the air through paper impregnated with potassium hydroxide and the fluoride determined by cerium(III) - alizarin complexan, will, of course, enable the total fluoride content of the air to be determined. This is probably also true of a method involving bleaching of a reagent prepared by dissolving titanium(IV) hydroxide in chromotropic acid⁵⁷² and perhaps to a lesser extent of a method in which the hydrogen fluoride is converted to fluorosilicic acid, which is then determined by a molybdenum-blue method.⁵⁷³ The separation of hydrogen fluoride from other atmospheric fluorine compounds is extremely difficult and there is no really satisfactory method.⁵⁷⁴ The trouble is caused by the ability of almost every surface to absorb hydrogen fluoride, and one author effects the separation by removal of the hydrogen fluoride from the air stream by passing it through a series of concentric aluminium tubes or glass tubes coated with sodium hydrogen carbonate. The particulate fluorides pass to an impinger, where they are determined separately.⁵⁷⁵ In one method responding to some organofluorine compounds, as well as to fluorine and fluorides, a form of flame-emission spectroscopy is used but a sensitivity of only 50 μg of fluorine per litre is claimed.⁵⁷⁶ A series of papers by Adams and co-workers describes a continuous automatic analyser, in which zirconium - Eriochrome cyanine R reagent is used, and the colour change is measured; this instrument detects down to 5 μg per cu. m.^{577,578,579} Ivie, Zielenski, Thomas and Thompson⁵⁸⁰ describe a continuous operating instrument in which sodium hydrogen carbonate coated tubes are used to give a differential measurement indicating the hydrogen fluoride concentration. Detection is by quenching of the fluorescence of a paper tape impregnated with the magnesium salt of 8-hydroxyquinoline; this apparatus is sufficiently robust to have survived 2 years of field use. A portable analyser for gaseous fluorides (hydrogen fluoride) depends upon absorption in acetic acid and detection with a fluoride-sensitive aluminium - platinum electrode pair.⁵⁸¹

Hydrogen peroxide—A detector tube for hydrogen peroxide has been described, based on silica gel impregnated with ethanolic titanium(IV) sulphate solution. Hydrogen peroxide in the air changes the colour to yellow.⁵⁸²

Lead—Lead is not a gas, but there are volatile organo-lead compounds and for this reason the inclusion may be justified. In the chemical determination of lead, dithizone is the preferred method and has been adopted for lead "fume" by the Ministry of Labour.⁵⁸³ This method, which involves collection on filter-paper, dissolution in nitric acid - hydrogen peroxide mixture and extraction into dithizone, followed by comparison of the colour with standards, was developed originally by Dixon and Metson.⁵⁸⁴ A convenient method of evaluating the lead content of the filter-paper (for those with access to the necessary equipment) is to use X-ray fluorescence.⁵⁸⁵ A similar method for organolead compounds in which the compounds are trapped on crystals of iodine, followed by dissolution in acidic potassium iodide, is described by Snyder and Henderson.⁵⁸⁶ An authoritative paper by Moss and Browett⁵⁸⁷ discusses the separation and determination of inorganic particulate lead and lead alkyls. Tetramethyl and tetraethyl-lead are oxidised by aqueous iodine monochloride solution to dialkyl-lead ions, which are determined by reaction with dithizone.

Mercury—A simple and effective method for determining mercury has been described.⁵⁸⁸ In this method the mercury is trapped in permanganate solution, followed by extraction into dithizone solution until the colour just changes; a similar amount of dithizone is then titrated with standard mercury solution to the same colour. In another simple method iodised activated carbon is used to trap the mercury, which is subsequently volatilised and passed through a selenium sulphide paper where a stain is formed.⁵⁸⁹ A detector tube is described by Dräger⁵⁹⁰ that is based on the reducing action of mercury on mercury(II)

bromide. The mercury(I) bromide thus formed in turn reduces gold(III) bromide to produce a gold sol.

Nickel carbonyl—Despite its extreme toxicity, there has not been much work carried out on the determination of nickel carbonyl in air. The best methods available are probably simple adaptations of those recently developed by the gas industry⁵²⁸ and the U.K.A.E.A.²⁸³ Apart from these there are several Russian methods in which either the nickel or the carbon monoxide after decomposition is determined. Belyakova⁵⁹¹ absorbs and decomposes it in a solution of chloramine B in hydrochloric acid and ethanol, while Fikhtengol'ts and Kozlova⁵⁹² collect it in a solution of iodine in carbon tetrachloride; in both a colorimetric finish based on dimethylglyoxime is used. On the other hand, Peregud and Boikina⁵⁹³ describe two detector tubes, one containing silver nitrate coated silica gel that gives a black stain sensitive to 5 μg per litre, and the other containing molybdovanadophosphoric acid coated silica gel giving a blue stain sensitive to 1 μg per litre.

Nitrogen oxides—The general method for nitrogen dioxide involves absorption in alkali followed by colorimetric determination of the nitrite ion produced. Over the past 10 years Saltzman reagent (naphthylethylenediamine) has gained precedence over the Griess - Ilosvay reagent (α -naphthylamine) in the air-pollution field, and detector tubes are becoming accepted for industrial hygiene. Murphy⁵⁴¹ compared the A.P.H.A. and Griess - Ilosvay methods, and two detector tubes, with the phenoldisulphonic acid method, in which the nitrite is converted into nitrate before determination. He found the detector tubes gave wide variations in response, and even the Griess - Ilosvay method could vary by ± 50 per cent. Similarly, Gill⁵⁹⁴ considers the phenoldisulphonic acid method best, at least down to 16 p.p.m. A method based on absorption in alkali followed by measurement of the ultraviolet absorption by the nitrite ion at 355 $m\mu$ is described by Altshuller and Wartburg,⁵⁹⁵ while a direct measurement at 400 $m\mu$ in a gas cell can be used at higher concentrations.⁵⁹⁶ Very low concentrations can be determined by infrared absorption at 4.5 μ , by using a long path cell,⁵⁹⁷ but another worker has suggested that interference by water vapour makes this method unsatisfactory.⁵⁹⁸ Before applying an ultraviolet method, Nicksic and Harkins⁵⁹⁹ dry the sample over calcium sulphate, presumably losing much of the nitrogen dioxide at the same time. As they were interested in car-exhaust gases in which the main oxide present is nitric oxide, this may not have been important, and they offer an interesting pressure-oxidation technique to speed up the conversion of nitric oxide in the dry gas. Many detector tubes have been described, all based on silica gel impregnated with an organic reagent, such as *o*-tolidine hydrochloride,⁶⁰⁰ tetraphenylbenzidine,⁶⁰¹ diphenylamine,⁶⁰² benzidine hydrochloride and 2-naphthol⁶⁰³ or *p*-aminobenzoic acid.⁶⁰⁴ Many of these do not appear to have been exploited commercially. A continuous automatic recording apparatus based on the use of Greiss - Ilosvay reagent is described by Thomas,⁶⁰⁵ while Jacobs and Hochheiser⁶⁰⁶ describe one in which naphthylethylenediamine is used. Saltzman⁶⁰⁷ describes a modified reagent for use in continuous recorders, and Pierce, Tokiwa and Nishikawa⁶⁰⁸ report the absorption efficiency obtained by using this formulation, among others. For rapid response the addition of R-salt is suggested.⁶⁰⁹ Saltzman and Wartburg⁶¹⁰ described a flow-dilution system for the preparation of standard atmospheres, and in tests of the Griess - Saltzman reagent found 1 mole of nitrogen dioxide is equivalent to 0.72 mole of sodium nitrite. This is confirmed by Rossano and Cooper,⁶¹¹ who use a similar apparatus, but Stratmann and Buck claim a 1 to 1 relationship,⁶¹² while Faucett⁶¹³ shows the factor to depend on the ratio of nitric oxide to nitrogen dioxide. An electrolytic generator for both nitric oxide and nitrogen dioxide that looks extremely elegant has been described by Hersch and Deuringer.⁶¹⁴ It is well known that the absorption and oxidation of nitric oxide is extremely difficult to effect. Kontorovich⁶¹⁵ tested the oxidation by permanganate solution on mixtures containing 1 per cent. of oxygen and 100 to 1000 p.p.m. of nitric oxide, with satisfactory results, while Anderson⁶¹⁶ described a method in which alkaline permanganate is used to oxidise nitric oxide to nitrogen dioxide, followed by determination as nitrite. On the other hand, Ripley⁶¹⁷ oxidises nitric oxide to nitrogen dioxide by passing it through a glass filter impregnated with sodium dichromate and sulphuric acid. The direct determination of nitric oxide can be achieved by gas chromatography, and a method in which a molecular sieve column and argon ionisation detector are used has been described by Kipping.⁶¹⁸

Ozone—A review and investigation of seven methods for the determination of ozone also describes a simple ozone generator.⁶¹⁹ The commonest method for determining ozone

depends upon the oxidation of potassium iodide and titration of the iodine released. Wadelin⁶²⁰ describes a method sensitive to 2 parts in 10^8 of ozone or other oxidants. The light sensitivity of acidic potassium iodide can be overcome by using a phosphate buffer, with acidification just before titration.^{621,622} A simple method based on the detection of the pH change in a 2 per cent. potassium iodide solution by an indicator, and measurement of the volume of gas required to produce this change, is described by Britaev,⁶²³ and another based on the reddening of iron(III) oxide - potassium thiocyanate paper, by Deckert.⁶²⁴ Two colorimetric methods have been described, one in which *N*-phenyl-*p*-naphthylamine in dichlorobenzene solution is used,⁶²⁵ and in the other sodium diphenylaminesulphonate in perchloric acid.⁶²⁶ Both are claimed to be relatively free from interference by nitrogen dioxide and other oxidants. An ingenious method is used with gallic acid as an ozone acceptor and rhodamine B as a chemiluminescent indicator.⁶²⁷ A continuous automatic determination in the range 0 to 100 parts per hundred million has been described,⁶²⁸ with direct ultraviolet absorption in a 300-foot path gas cell, but simpler monitoring instruments have been described based on electrochemical methods. For example, if a platinum electrode is covered with a thin film of neutral potassium iodide solution the iodine liberated by ozone produces a measurable flow of current,⁶²⁹ but in a more efficient reaction the halogen is reduced at the electrode.⁶³⁰ A combined ozone and sulphur dioxide analyser is based on the liberation of iodine by ozone and the consumption of iodine by sulphur dioxide; the iodine is measured amperometrically. The ozone is removed from the sulphur dioxide side by absorption by iron(II) sulphate, and the sulphur dioxide from the ozone side by a chromium(III) oxide - phosphorus pentoxide mixture.⁶³¹

Phosphine—A detector tube for phosphine has been described by Nelson and Milun⁶³² in which silica gel impregnated with silver nitrate is used and is subject to interference by arsine, stibine and hydrogen sulphide. In a sensitive conductimetric method the reaction with mercury(II) chloride is used to release hydrogen chloride, which raises the conductivity of the solution.⁶³³

Radon—Radon is conveniently measured by means of its radioactivity, and two methods in which concentration on active charcoal to achieve a high sensitivity is used have been described.^{634,635}

Stibine—A method for stibine has been described involving absorption in iodine solution followed by colorimetric determination.⁶³⁶

Hydrogen sulphide—The classical determination of hydrogen sulphide by lead acetate has been adopted as a paper-stain technique by the Ministry of Labour, and a chart of standard stains is provided.⁶³⁷ A series of field methods covering the range 0.0001 to 0.06 p.p.m. is reviewed by Smith, Jenkins and Cummingworth,⁶³⁸ who record a preference for silver nitrate impregnated paper. Probably the best method at the p.p.b. level is that based on the methylene-blue reaction, which is described in detail.^{639,640,641} The efficiency of absorption of hydrogen sulphide by sodium hydroxide in a Dreschel bottle and fritted bubbler has been shown to be greater than 90 per cent., at rates up to 3 litres per minute.⁶⁴² One paper describes the quantitative collection of hydrogen sulphide from the atmosphere with a filter-paper impregnated with potassium hydroxide, potassium zincate and glycerol followed by a methylene-blue finish.⁶⁴³ A combined method for determining hydrogen sulphide and carbon disulphide involves absorption in methanolic potassium hydroxide.⁶⁴⁴ In this method, carbon disulphide forms potassium methyl xanthate, which absorbs at 392 $m\mu$, and hydrogen sulphide forms potassium sulphide, which absorbs at 229 $m\mu$. Another method depends on the colour formed on reaction with decolorised thiofluorescein solution.⁶⁴⁵ In a turbidimetric procedure claimed to be an alternative to the methylene-blue method, the sol produced from reaction with bismuth acetate is used.⁶⁴⁶ A detector tube, involving the discoloration of copper sulphate deposited on an inert support is described.⁶⁴⁷ An instrumental method suitable for continuous monitoring, with a paper tape impregnated with lead acetate and sodium acetate and coated with gelatin, covers the range 0 to 500 p.p.m.⁶⁴⁸ but field experience has shown that large errors may result from fading of the stain if the sampling period is prolonged.⁶⁴⁹ This may be ameliorated by the incorporation of *ortho*-phenylphenol in the reagent, or by replacement of the lead acetate by mercury(II) chloride.⁶⁵⁰ A much more sensitive instrument is based upon absorption in a stream of liquid flowing in a spiral fashion down a rod, the hydrogen sulphide being determined by its quenching action on the fluorescence of tetra-acetoxymercurifluorescein.⁶⁵¹ A crude method of monitoring the hydrogen sulphide

content of the atmosphere is described by Gilardi,⁶⁵² who uses a tile coated with lead acetate in the way in which the "lead candle" is used for sulphur dioxide.

Sulphur dioxide—A handbook of recommended methods, both manual and instrumental, which also incorporates reviews of all the rejected methods, has been published by the U.S. Department of Health, Education and Welfare⁶⁵³; this is a most comprehensive publication. Reviews of methods have also been published by Welch,⁶⁵⁴ Thoenes,⁶⁵⁵ Herrmann⁶⁵⁶ and Thomas.⁶⁵⁷ Herrmann also reviews methods of preparing standard concentrations, and Thomas includes consideration of the results in his paper. Hochheiser⁶⁵⁸ examines the results obtained by using three techniques in several American cities and considers the effect of filtering the samples. The sampling procedure has been examined by Stratmann and Buck,⁶⁵⁹ who compared the efficiency of silica gel and tetrachloromercurate, and the errors in the associated method, and by Urone, Evans and Noyes,⁶⁶⁰ who used sulphur-35 tracer to compare a conductivity analyser with the tetrachloromercurate method. They found the conductimetric sampler to be unreliable below 0.1 p.p.m. Huygen⁶⁶¹ describes its collection by using a filter-paper impregnated with potassium hydroxide and glycerol, on which it is claimed the sulphur dioxide may remain unoxidised for several weeks, while Pate⁶⁶² describes a similar technique for the range 0.1 to 10 p.p.m. in which "Millipore" filters impregnated with 5 per cent. potassium hydrogen carbonate are used. Easily the best colorimetric method is that of West and Gaeke,⁶⁶³ in which the sulphur dioxide is trapped in sodium tetrachloromercurate, reacted with *p*-rosaniline hydrochloride and formaldehyde, and the colour developed measured at 560 m μ . The interference by nitrogen dioxide in this method may be overcome by the addition of sulphamic acid to the absorbent.^{664,665} The influence of various forms of *p*-rosaniline has been studied by Pate⁶⁶⁶ and a continuous analyser has been described in which the gas is absorbed directly by the *p*-rosaniline reagent.⁶⁶⁷ A modified method suitable for portable meters with a short sampling period has also been described,⁶⁶⁸ while others in which rosaniline chloride⁶⁶⁹ and *p*-aminoazobenzene⁶⁷⁰ are used are claimed to give more stable and reproducible colours. In Britain, a simple method involving absorption in "neutral" hydrogen peroxide and titration of the acid formed has been standardised for use in a national survey.⁶⁷¹ Although crude and subject to interference, this method is simple enough to be operated by non-scientifically trained personnel. The possibility of loss of sulphur dioxide by adsorption on the components of this apparatus has been examined.⁶⁷² The absorption efficiency of the Drechsel bottle used in this method has been found to be 99 per cent.,⁶⁷³ and in another study of similar bubblers the efficiency was found to be 97 per cent.⁶⁷⁴ Another method in which oxidation was used, but this time with potassium chlorate, the sulphate being determined by titration with barium chloride, has also been described.⁶⁷⁵ At the higher concentrations that are of interest in industrial hygiene, *i.e.*, p.p.m. instead of parts per hundred million, the standard method in this country is to use the stain produced on a paper impregnated with ammoniacal zinc nitroprusside.^{676,677} In this method interference by hydrogen sulphide is slight. A detector tube containing silica gel impregnated with iodine and 4,4'-tetramethyldiaminodiphenylmethane has been described by Kobayashi,⁶⁷⁸ and patented by McConnaughey.⁶⁷⁹ The sulphur dioxide concentration is measured by the length of the decolorised layer when a sample is drawn through the tube. In a similar type of tube the bleaching effect on starch-iodine deposited on "Sterchamol" inert support is used,⁶⁸⁰ while an alternative form with silica gel impregnated with ammonium metavanadate depends upon matching stain colours.⁶⁸¹ The need to monitor the atmosphere around power stations has led to the development of several instruments, some simple and others expensive; sensitive and precise German instruments have been described by Engelhardt⁶⁸² and Fuhrmann.⁶⁸³ Cummings and Redfearn⁶⁸⁴ describe an extremely good semi-portable colorimetric instrument based on the bleaching of a starch-iodine reagent along with a more precise, but much more cumbersome, conductivity analyser. The starch-iodine reagent is subject to interference by nitrogen dioxide and ozone, but both of these may be removed by catalytic reduction over platinum without affecting the sulphur dioxide concentration.⁶⁸⁵ This instrument can be modified to operate a recorder.⁶⁸⁶ Recently a semi-portable continuous recording instrument based on the conductivity principle, after absorption in hydrogen peroxide, has been described.⁶⁸⁷ In this instrument the contaminant is absorbed by the reagent when the stream of air impinges on the surface, a technique that has led to the development of a completely portable instrument⁶⁸⁸ and a pocket-sized transistorised model.⁶⁸⁹ Electrochemical methods have been described by Berton,⁶⁹⁰ who used micro piles of lead and oxidised copper, and Novak,⁶⁹¹ who

used a polarisable electrode such as carbon as an indicating electrode. A continuous polarographic recorder has been developed in Czechoslovakia.⁶⁹² In a coulometric apparatus, oxidation of the sulphur dioxide by electrically generated bromine, with potentiometric end-point detection, is used.⁶⁹³ Bersin⁶⁹⁴ has described a complex method in which the sulphur dioxide is allowed to react with sodium chlorite to release chlorine dioxide, which in turn reacts with a $C_6H_4(OH)_2Kr$ clathrate to liberate krypton-85, which is trapped and counted by normal radiochemical methods. Another radiochemical method involves the release of radioactive iodine and is claimed to cover the range 8×10^{-4} to 0.2 p.p.m.⁶⁹⁵ Methods of calibrating these instruments have been developed by Duckworth⁶⁹⁶ and by Kuczynski.⁶⁹⁷ A technique for the calibration of field monitors with standardised gas mixtures despatched by post in polythene-lined cardboard boxes from a central laboratory has also been described.⁶⁹⁸ The old, simple instrument, the lead candle, will become less frequently used now that more sophisticated apparatus is readily available, but its replacement will unfortunately be slow as a large body of more or less qualitative data based on this method is available. The method is described in detail in British Standards⁶⁹⁹ and by Thomas,⁷⁰⁰ and recently an improved simplified method has been described by Bowden.⁷⁰¹ A study of the critical parameters, such as particle size and binder concentration, has also been reported.⁷⁰² A very sensitive method based on the ring-oven technique and capable of detecting 0.1 μg has been developed by Huygen.⁷⁰³ An indirect ultraviolet method involves the absorption by lead(II) ions, which are reduced when lead sulphite is precipitated.⁷⁰⁴

Sulphur trioxide—There is no completely satisfactory method of measuring sulphur trioxide in air.⁷⁰⁵ It is likely that it is present as sulphuric acid droplets and, on this basis, a method involving collection on filter-paper, extraction with borax and back-titration with 0.01 N sulphuric acid has been evolved.⁷⁰⁶ A continuous analyser can be developed from the Thomas Autometer.⁷⁰⁷ A detector tube for acid mist in air contains silica gel impregnated with potassium bromide, potassium bromate, potassium hydroxide and fluorescein; acid liberates bromine, which converts the fluorescein to eosin, and the stain length is a measure of concentration.⁷⁰⁸ Acids other than sulphuric acid have the same effect. In colorimetric methods for determining sulphur trioxide, the reaction with barium chloroanilate in which purple chloroanilic acid is released⁷⁰⁹ or the bleaching of thorium - Eriochrome cyanine R is used.⁷¹⁰

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Received January 2nd, 1967

Some Observations on the Determination of Mercury by Atomic-absorption Spectroscopy in an Air-Acetylene Flame

BY D. N. HINGLE, G. F. KIRKBRIGHT AND T. S. WEST

(Chemistry Department, Imperial College, London, S.W.7)

The sensitivity obtained for mercury at 2537 Å in atomic-absorption spectroscopy in air-acetylene is greatly influenced by the valency state of mercury in the sample solution. Greater sensitivity is obtained for mercury(I) than for mercury(II), and further increase in sensitivity results when reducing and complexing agents are added to mercury(I) solutions. An explanation of this effect based on the disproportionation of mercury(I) into mercury(II) and elemental mercury is given.

THE determination of mercury by atomic-absorption spectroscopy in conventional flames has a rather limited sensitivity. During a study of the determination of mercury and several other elements in a long-path separated air-acetylene flame,¹ we observed that the sensitivity was greatly influenced by the valency state of the mercury introduced into the flame. These observations, with a relatively unusual (*i.e.*, separated) flame, led us to pursue the investigation of this phenomenon in a conventional 10-cm air-acetylene flame of the type available on most commercial atomic-absorption spectrophotometers. We have found, as reported elsewhere,² that an enhancement of the sensitivity is obtainable when mercury is presented to the flame as mercury(I) rather than mercury(II), and also that the addition of reducing or complexing agents to the mercury sample solutions can result in an even greater increase in the absorbance for mercury at 2537 Å. The results of these experiments are described in this paper.

EXPERIMENTAL

APPARATUS—

Techtron AA4 flame spectrophotometer and 10-cm air-acetylene burner. The source of resonance radiation used was a microwave-excited mercury-discharge tube as described elsewhere.¹ The instrument settings used throughout were: slit width, 50 μ; wavelength, 2537 Å; air pressure, 15 p.s.i.; acetylene flow-rate, 2.5 litres per minute. The microwave power output from 2450 Mc/s generator to discharge tube was 7 watts.

REAGENTS—

All materials should be of analytical-reagent grade.

Mercury(I) stock solution—Dissolve 0.140 g of mercury(I) nitrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, in 0.5 M nitric acid and dilute to 100 ml with 0.5 M nitric acid. Store over a small amount of metallic mercury. Dilute this 1000 p.p.m. stock solution as required.

Mercury(II) stock solution—Dissolve 0.1708 g of mercury(II) nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, in 0.5 M nitric acid and dilute to 100 ml with 0.5 M nitric acid. Dilute this 1000 p.p.m. stock solution as required.

Ascorbic acid.

Tin(II) chloride.

EDTA (disodium salt).

Citric acid.

Tartaric acid.

Potassium cyanide.

Gelatin.

RESULTS

The optimum conditions of slit width, fuel flow-rate and microwave discharge-tube power were established for the determination of mercury at 2537 Å. The absorbance produced under these conditions for 40 p.p.m. of mercury(I) and mercury(II) nitrate solutions was recorded in the presence, and absence, of excess of ascorbic acid, tin(II) chloride, EDTA, citric acid, tartaric acid, potassium cyanide and gelatin. Care was taken to establish blank absorbance values for each solution nebulised. The results obtained are shown in Table I.

TABLE I
EFFECT OF REDUCING AND COMPLEXING AGENTS ON ABSORPTION BY MERCURY AT 2537 Å
Sample solution containing 40 p.p.m. of mercury

Hg(II)		Net mercury absorbance at 2537 Å*	Hg(I)		Net mercury absorbance at 2537 Å*
+ Nitric acid, 0.5 M	0.010	+ Nitric acid, 0.5 M	0.040
+ EDTA (disodium salt), 5 mg per ml	..	0.011	+ EDTA (disodium salt), 5 mg per ml	..	0.108
+ Ascorbic acid, 5 mg per ml	0.163	+ Ascorbic acid, 5 mg per ml	0.160
+ Tin(II) chloride, 5 mg per ml	0.160	+ Tin(II) chloride, 5 mg per ml	0.160
+ Citric acid, 5 mg per ml	0.012	+ Citric acid, 5 mg per ml	0.062
+ Tartaric acid, 5 mg per ml	0.012	+ Tartaric acid, 5 mg per ml	0.047
+ Potassium cyanide, 5 mg per ml	..	0.012	+ Potassium cyanide, 5 mg per ml	..	0.010

* These values were obtained at a constant burner height above the primary zone in the flame.

In order to assist the interpretation of these results, the variation in absorbance for mercury at 2537 Å with height in the flame was investigated during aspiration of solutions of mercury(I) and mercury(II) nitrates, and of mercury(II) nitrate immediately after the addition of excess of ascorbic acid solution. The corresponding absorption profiles are shown in Fig. 1. The absorbance growth curves in the flame for mercury(I), mercury(II) and mercury(II) - ascorbic acid solutions were also obtained at the height in the flame of maximum absorbance for these solutions. These calibration curves are shown in Fig. 2.

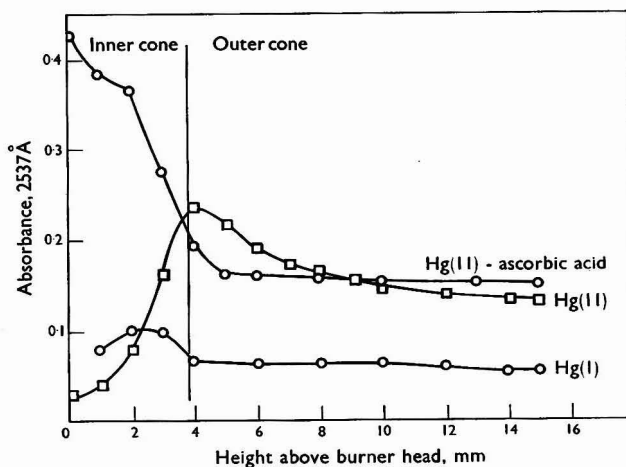


Fig. 1. Variation of absorbance at 2537 Å with position of light-path above burner head for mercury(I) (10 p.p.m.), mercury(II) (250 p.p.m.) and a mercury(II) solution (20 p.p.m.) containing 5 mg per ml of ascorbic acid

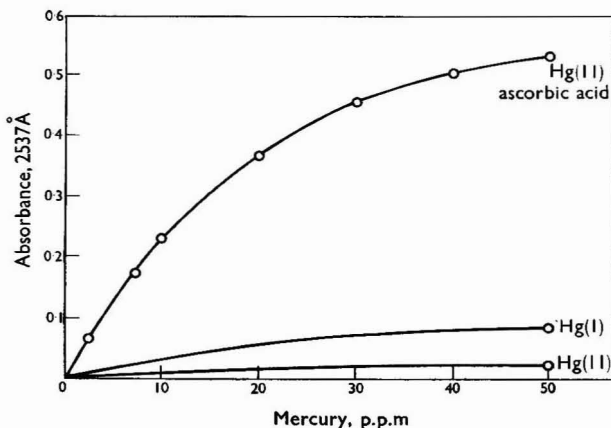


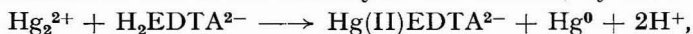
Fig. 2. Absorbance growth curves for mercury(I), and mercury(II) solutions and mercury(II) solutions containing 5 mg per ml of ascorbic acid. These graphs were obtained at the optimum burner height for each solution

The results shown in Table I can be explained by consideration of the unique property of the mercury(I) ion, Hg_2^{2+} , whereby it disproportionates readily to form the mercury(II) ion and free elemental mercury



When mercury(I) solutions are nebulised this reaction proceeds to some extent as the sample mist passes into the pre-heating zone of the burner. Consequently a partial pressure of elemental mercury vapour is available very low in the flame. This effect is much less marked with mercury(II) solutions. The addition of excess of ascorbic acid or tin(II) chloride solution to either mercury(I) or mercury(II) nitrate solutions results in complete reduction of the mercury to the elemental form in the dilute solution so that an enhancement from this effect is observed. The sample solution then contains the mercury in colloidal elemental form.

The addition of EDTA to mercury(I) solutions promotes the disproportionation by formation of a strong complex with the mercury(II) ion. Thus the effect of EDTA is to enhance the absorbance by promotion of the liberation of elemental mercury. As shown in Table I, the addition of EDTA to mercury(II) nitrate solution has no significant effect on the absorbance. As even the complete disproportionation of the mercury(I) ion by EDTA only results in liberation of half of the mercury as the element, by the reaction



it would be expected that, at most, EDTA could only produce half of the enhancement in absorbance provided by complete reduction with ascorbic acid or tin(II) chloride. This is true to a first approximation, as shown in Table I. The failure of citric and tartaric acids to enhance the absorbance significantly may result from the fact that mercury(II) does not form stable citrate and tartrate complexes at the acidity used. Potassium cyanide also causes no enhancement of the absorbance. Indeed, addition of potassium cyanide to mercury(I) solutions results in an absorbance characteristic of the same concentration of mercury(II). It is probable that the elemental mercury formed by the disproportionation is re-dissolved in the nitric acid - potassium cyanide medium to form the stable mercury(II) cyanide complex Hg(CN)_4^{2-} .

The manner in which the absorbance at 2537 Å varies with height in the flame for the introduction of mercury(I), mercury(II) and colloidal elemental mercury also supports the explanation suggested. It may be seen from Fig. 1 that once the mercury passes the primary zone of the air - acetylene flame, little decrease in absorbance with height is observed, regardless of the form in which the mercury is introduced into the flame. Thus little depletion of the ground-state atomic population appears to occur as the temperature decreases and the flame plasma becomes more oxidising in nature. This would be expected, as the reaction

$\text{HgO} \longrightarrow \text{Hg} + \text{O}$ favours elemental mercury above about 500°C . Thus the increased sensitivity that results from the introduction of the sample as mercury(I), or elemental mercury, is preserved well above the primary zone. The absorption - height profiles low in the flame (including those within the primary zone) are also of interest. Thus when a mercury(II) solution is nebulised, maximum absorbance is not obtained until slightly above the primary zone in the hottest part of the flame. This can be explained by the need for a relatively high temperature (above 500°C) to decompose mercury(II) nitrate and mercury(II) oxide clotlets efficiently. When elemental mercury is introduced, however, maximum absorbance is observed immediately above the burner-plate within the primary zone (in the pre-heating zone, in fact). The decrease in absorbance with height in the pre-heating zone behind the flame front may possibly be explained by the expansion of the sample - gas mixture as the temperature rises with height throughout this zone. This causes a dilution of the sample as the gas mixture expands.

Fig. 2 shows the absorbance growth curves obtained for mercury(I), mercury(II) and elemental mercury. These calibrations are repeatable but non-linear. The cause of the non-linearity is difficult to explain unequivocally, and may be caused by either pressure broadening of the mercury-line profile in the flame, or by some reversal in the mercury microwave discharge source. The possibility of curvature of absorbance growth curves because of fluorescence emission when high intensity sources are used has already been noted elsewhere.³ Because of the non-linearity, even at low absorbances, we suspected that the intense emission of the 2537 \AA line from the microwave-excited source was producing significant resonance fluorescence of the 2537 \AA line in the flame, thus diminishing the expected absorbance signal. Experiments in which the spectrometer is placed at 90° to the optical axis of the 10-cm flame and excitation source reveal that although significant fluorescence is emitted, because of the focusing arrangement used, this contributed little to the 2537 \AA radiation reaching the narrow monochromator entrance slit.

It must be noted that, while pre-treatment of mercury sample solutions with excess of reducing agents leads to considerably increased sensitivity, the absorbance thus produced is rather dependent on ageing of the solution following addition of the reductant. This results from the rapid aggregation of the finely dispersed nuclei that are initially formed. The use of gelatin in an attempt to stabilise the mercury sol is ineffective in the presence of ascorbic acid and tin(II) chloride. The stability of the mercury(I) - EDTA solution is improved, however, possibly because EDTA has less tendency to flocculate the colloidal element.

The sensitivity of the determination of traces of mercury by atomic-absorption spectroscopy may thus be increased four-fold by introduction of the sample as mercury(I) rather than mercury(II). Treatment of mercury(II) solutions with excess of reductant results in about a sixteen-fold enhancement in sensitivity, but, in order to obtain good repeatability, the absorbance at 2537 \AA must be measured immediately after addition of the ascorbic acid or tin(II) chloride solution. Similarly the treatment of a mercury(I) solution with excess of reductant provides a four-fold enhancement for this ion.

As stated previously, the unusual dependence of absorbance signal on valency state is not observed with most other multivalent elements and arises for mercury because of the unusual nature of the mercury(I) ion.

We are grateful to Murex Ltd. for provision of study leave to one of us (D.N.H.), and for the loan of the flame spectrophotometer used in this work.

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Received July 12th, 1967

The Determination of Vanadium in Silicate Rocks and Minerals with *N*-Benzoyl-*o*-tolylhydroxylamine

BY P. G. JEFFERY AND G. O. KERR

(Warren Spring Laboratory, Ministry of Technology, Stevenage, Hertfordshire)

In 4 to 8 *N* hydrochloric acid, *N*-benzoyl-*o*-tolylhydroxylamine is an almost specific reagent for vanadium, and can be used in the analysis of rocks and minerals. After removal of silica by evaporation with hydrofluoric acid, the insoluble residue is fused with potassium pyrosulphate and dissolved in dilute sulphuric acid. The violet-coloured complex with the reagent is formed in 6 *N* hydrochloric acid solution, extracted into carbon tetrachloride and measured at 510 m μ . Fluoride addition prevents interference from titanium, while the use of PTFE and silica apparatus avoids contamination and interference from platinum.

IN the course of a recent investigation of supposed vanadium poisoning, it was necessary to devise a reliable, sensitive and specific procedure for the determination of vanadium in urine. Rockhold and Talvitie¹ have devised a test for vanadium based on the catalytic oxidation of *p*-aminodiethylaniline. This test is used for screening purposes and is not specific for vanadium. Sandell² describes a method with 8-hydroxyquinoline, based upon other work by Talvitie,³ but this procedure is long, tedious and subject to interference from several elements. A literature search showed that, although a wide variety of reagents had been advocated for the determination of vanadium in pure solutions, few of the methods based upon them were easily or directly applicable to urine.

N-Cinnamoyl-*N*-phenylhydroxylamine has been recommended⁴ as a sensitive reagent, but is not specific for vanadium. *N*-Benzoyl-*N*-phenylhydroxylamine is more selective,⁵ but also reacts with molybdenum, titanium and zirconium to give yellow-to-orange coloured complexes⁶ that interfere with the determination of small amounts of vanadium.

Benzoyl-*o*-tolylhydroxylamine seemed to us to combine the necessary sensitivity and specificity to vanadium, but we were unable to obtain reliable results by the procedure described by Majumdar and Das.⁷ After suitable modification, the procedure has been found to be acceptable for the determination of vanadium in urine. These modifications have also enabled the reagent to be applied to the determination of vanadium in silicate rocks and minerals. The procedure devised for this is applicable to silicate materials containing from a few parts per million of vanadium to parts per thousand, or more. It is considerably more rapid than the procedure formerly used in this laboratory, which is based on a chloroform extraction of the complex with 8-hydroxyquinoline, followed by photometric measurement as phosphovanadotungstate.

EXPERIMENTAL

PREPARATION OF THE REAGENT—

The reagent *N*-benzoyl-*o*-tolylhydroxylamine was obtained by following the directions given by Majumdar and Das.⁷ The yield (half quantities) was 7.5 g, or about 15 per cent. This poor yield was attributed to the excessive formation of reduction products other than tolylhydroxylamine, particularly *o*-toluidine. No improvement was obtained by using the method of reduction described in detail by Cohen⁸ for the preparation of phenylhydroxylamine, but a significantly lower yield was obtained by the procedure described by Vogel.⁹

REACTION WITH VANADIUM—

Although Majumdar and Das prepared their vanadium extracts from a vanadate solution, it is not clear from either their original⁷ or a later¹⁰ paper that the reaction with vanadium

does not take place unless it is in the quinquivalent state. It was noted that somewhat lower calibration graphs were obtained when aliquots of standard vanadate solution were not re-oxidised prior to reaction with *N*-benzoyl-*o*-tolylhydroxylamine.

For this oxidation an aqueous solution of potassium permanganate was used. This was added drop by drop until the pink reagent colour persisted for 5 minutes. The slight excess was decomposed by adding hydrochloric acid, and any chlorine liberated was removed by adding sulphamic acid.

The molar extinction coefficient for the *o*-tolyl reagent was found to be 5250. It is therefore slightly more sensitive than *N*-benzoyl-*N*-phenylhydroxylamine ($\epsilon = 4650$) and less sensitive than *N*-cinnamoyl-*N*-phenylhydroxylamine ($\epsilon = 6300$).⁴

INTERFERENCES—

The most serious interference noted by us in the determination of vanadium in silicate materials is from the intense yellow-coloured complex formed by the reagent with titanium. In all the samples examined by us, this colour was completely suppressed by the addition of a small amount of saturated sodium fluoride solution.

The reagent also gives yellow colours, not previously recorded, with gold and platinum. The small amounts of gold and platinum that occur in silicate rocks are insufficient to interfere with the determination of vanadium, although platinum introduced following a pyrosulphate fusion in platinum apparatus will completely obscure the violet colour from rocks containing only a few p.p.m. of vanadium. For this reason prolonged fusion in platinum apparatus should be avoided, and the alternative decomposition in PTFE and silica used, particularly for samples low in vanadium.

EXTRACTION OF THE VANADIUM COMPLEX—

The complex formed between vanadium and *N*-benzoyl-*o*-tolylhydroxylamine is soluble in several organic solvents. Solutions in carbon tetrachloride, chloroform, isobutyl methyl ketone and toluene all gave similar calibration graphs. Chloroform was rejected because of possible interference from the presence of ethanol, which gives rise to a yellow coloured complex of vanadium with the reagent. Carbon tetrachloride was finally selected, being more convenient to use than the lighter solvents.

METHOD

REAGENTS—

N-Benzoyl-*o*-tolylhydroxylamine solution—Dissolve 0.02 g of the recrystallised reagent in 100 ml of carbon tetrachloride.

Potassium permanganate solution—Approximately 0.02 M.

Sulphamic acid solution—Approximately 0.05 M.

Sodium fluoride solution—Saturated solution in water. Store in a polythene bottle.

PROCEDURE—

Decompose a 100-mg portion of the finely powdered silicate material by evaporating it in platinum (or PTFE apparatus for samples low in vanadium) with sulphuric, nitric and hydrofluoric acids in the usual way, removing excess sulphuric acid by heating on a hot-plate. Fuse the dry residue in platinum, or preferably silica, with potassium pyrosulphate and extract the fused melt with 10 ml of water containing 2 drops of 20 N sulphuric acid. Transfer the solution to a separating funnel and add potassium permanganate solution drop by drop until an excess giving a pink colour that persists for 5 minutes is present.

The volume of the solution at this stage should be about 20 ml. Add 2 ml of sulphamic acid solution, 2 ml of sodium fluoride solution and 20 ml of concentrated hydrochloric acid. Now add by pipette 10 ml of the *N*-benzoyl-*o*-tolylhydroxylamine solution, stopper and shake the funnel for 30 seconds. Allow the layers to separate and filter the lower layer through a small wad of cotton-wool into a 2-cm spectrophotometer cell. Measure the optical density of this solution, relative to a reagent blank, at a wavelength of 510 m μ .

For the calibration graph, transfer aliquots of a standard vanadate solution containing 10 to 50 μ g of vanadium to a series of separating funnels and dilute each to 20 ml. Add potassium permanganate solution drop by drop to each until an excess is present, and continue as described for the sample solution above.

RESULTS

This procedure has been used to determine vanadium in a wide variety of silicate materials. The results obtained for a series of standard rocks are given in Table I. One sample (GSP-1) was analysed ten times, giving an average value of 43 p.p.m. of vanadium, a standard deviation of 1.7 p.p.m. and a coefficient of variation of 4 per cent.

TABLE I
A COMPARISON OF RESULTS FOR SOME SILICATE ROCKS

Sample No.	Description and locality	Vanadium, p.p.m.	
		N-Benzoyl-o-tolyhydroxylamine	Other reported results
G-1	Granite, Rhode Island, U.S.A.	13, 15, 15, 16	16*
G-2	Granite, Rhode Island, U.S.A.	28, 30, 34, 34	37† (18)
W-1	Diabase, Virginia, U.S.A.	240, 222, 266, 234	240*
T-1	Tonalite, Msusule, Tanzania	81, 77, 83, 81	96‡
R117	Granite, Shetland, U.K.	2, 2, 2	6§
R204	Nepheline-syenite, Khibina, U.S.S.R.	42, 46, 48, 49	—
AGV-1	Andesite, Oregon, U.S.A.	100, 104, 109	134† (18)
PCC-1	Peridotite, California, U.S.A.	30, 24, 24	29† (18)
DTS-1	Dunite, Washington, U.S.A.	10, 10, 12	11† (15)
BCR-1	Basalt, Washington-Oregon, U.S.A.	315, 398, 396	339† (18)
GSP-1	Granodiorite, Colorado, U.S.A.	45, 41, 41, 46, 42 45, 42, 43, 43, 42	53† (18)

* Ahrens and Fleischer,¹¹ "recommended values."

† Flanagan,¹² "average of spectrochemical determinations" (with number of determinations).

‡ Average of reported results.¹³

§ Result obtained previously by method of Bennett and Pickup.¹⁴

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Received July 6th, 1967

Isotopic-dilution Analysis with a Modified Substoichiometric Residue Method for Carbonate and Sulphate

By J. K. JOHANNESSON

(Auckland Technical Institute, Wellesley Street, Auckland, New Zealand)

A new modification of the substoichiometric isotopic-dilution method is presented. After the addition of a standard amount of labelled compound, the isotopically diluted compound is then isolated, as a residue of constant weight, and the beta activity measured. The method applied to the determination of sulphate and carbonate is applicable in the range 10 to 100 μg for these anions.

ISOTOPIC-DILUTION methods based on the use of substoichiometry have been reviewed by Lambie,¹ who outlined the three methods that had been published at that time. Firstly, the use of a deficiency of the complexing agent for solvent extraction of the isotopically diluted substance into water-immiscible solvents, as developed by Ružička and Štary.² Secondly, the decomposition of equal weights of metal by the passage of equal amounts of electrical current, also by Ružička.³ Thirdly, the method used by the present author,⁴ where equal amounts of an isotopically diluted element are precipitated by using a constant amount of a precipitant, which amount is, however, less than that required to precipitate all of the element being determined. The particular method described was the determination of chloride with a substoichiometric amount of silver as the precipitant.

This paper presents a fourth method whereby a constant weight of a compound, of the substance to be determined, is left as a residue of constant weight following volatilisation of the excess of substance over the substoichiometric amount. Two variations of this method are described, one for the determination of sulphate and the other for the determination of the carbonate.

DETERMINATION OF SULPHATE

The principle of this method is that the test solution is first passed through a column of an ion-exchange resin, in the hydrogen form, to convert any salts to free acids, and to this solution is added a known amount of dilute sulphuric acid labelled with sulphur-35, followed by a known amount of standard barium nitrate solution, insufficient to combine with all of the added labelled sulphuric acid. The mixture is evaporated in a suitable container, which also acts as the mount for counting. Volatile acids and excess of sulphuric acid are volatilised, leaving a constant weight of barium sulphate, the beta activity of which is then determined under a thin end-window Geiger - Müller counter. The method has the advantage of constant weight for counting, and thus no allowance has to be made for self-absorption. Non-volatile acids such as silicic and orthophosphoric acids interfere, whereas acids such as hydrochloric, nitric, acetic and other organic acids are readily volatilised under the experimental conditions.

The calculation is as follows—

$$W_1 = W_2 \left(\frac{A_2}{A_1} - 1.0 \right)$$

where W_1 is the weight of the unknown sulphate ion,

W_2 is the weight of the added sulphur-35 labelled sulphuric acid,

A_2 is the activity in counts per minute when only the labelled sulphuric acid was present and

A_1 is the activity in counts per minute found when an unknown amount of sulphate was being determined.

APPARATUS—

Porcelain crucibles—These should be of uniform size, *i.e.*, 2 cm high with a 2.5 cm diameter at the top and 1 cm diameter at the base.

PROCEDURE—

To the solution containing 10 to 15 μg of sulphuric acid add 1.00 ml of 0.001 M sulphuric acid labelled with sulphur-35, and, after careful and complete mixing in the crucible with a jet of air playing on to the surface of the liquid, add 1.00 ml of 0.0004 M barium nitrate solution, again with careful mixing. Evaporate the contents of the crucible to dryness under an infrared drying lamp, then ignite at a dull red heat for exactly half a minute. The crucible is supported in a frame and the Geiger - Müller counter inserted to within a fixed distance from the bottom of the crucible and the beta radiation measured. The time taken for a count of ten thousand is accurately determined and it is found that the repeatability is within the statistical limits of *plus* or *minus* twice the standard deviation for the counting, even when the crucible is removed and returned to the frame between successive counts. Thus, the times for a repeat count to ten thousand, with removal and replacement of the crucible in the frame are 17.85 and 17.60 minutes, respectively.

A typical series of results for a set of known sulphuric acid samples is as shown in Table I.

TABLE I
APPLICATION OF THE METHOD TO THE DETERMINATION OF SULPHATE

Sulphuric acid added, μg	Counts per minute (corrected for background)	Sulphuric acid found, μg	Error, per cent.
0	760	—	—
25	616	24	-4
50	496	53	+6
75	439	73	-3
150	313	142	-6

The standard deviation for the accuracy of counting for this set of results was 2 per cent.

THE EFFECT OF IGNITION TIME—

The time for ignition must be kept short or a loss of activity occurs. There is need for ignition because of the apparent formation of some barium hydrogen sulphate that is not decomposed by use of the heating lamp alone. If ignition times are prolonged, then loss of activity occurs as shown.

Time of heating at red heat, minutes	0.5	5	15	45	85
Counts per minute	803	645	590	500	435

For the amounts of sulphate taken the accuracy attained is comparable with other analytical methods, especially in the presence of other acids. Improvement of this method will require investigation of the techniques of heating to decompose the barium hydrogen sulphate, without any decomposition of the barium sulphate.

DETERMINATION OF CARBONATE

The method for the determination of carbonate involves the addition of a constant amount of carbonate, labelled with carbon-14, to the sample which has been made sufficiently alkaline to prevent loss of carbon dioxide to the air, but not so alkaline as to absorb it rapidly from the air (pH = 8 is about the optimum). To the well mixed solution is added hydrochloric acid (1 + 4), the liberated gas is absorbed in a small volume of a solution of barium hydroxide, such that the weight of this latter substance, and hence of the barium carbonate formed, is constant. Further, the stoichiometric amount of barium hydroxide added is equal to about half of the added labelled carbonate. In this way a constant amount of carbon dioxide is absorbed in each determination. The activity of the dried barium carbonate is counted by using a thin end-window Geiger - Müller tube and, as discussed under the sulphate method, the constant weight of the source eliminates the errors and corrections needed when self-absorption has to be considered. The method of calculation is the same as for the sulphate method.

The initial experiments were made with an apparatus in which the unknown and labelled carbonate solutions were mixed in a reaction vessel, acidified, and the evolved carbon dioxide aspirated through a solution of barium hydroxide contained in an absorption tube. The suspension of barium carbonate was transferred to a planchet, evaporated, and the activity measured. This method was found unsatisfactory in that losses of barium carbonate occurred from adhesion to the sides of the absorption tube. The necessary use of wash water to effect transfer of the suspension required that the planchet be re-filled several times, thus giving an unsatisfactory distribution of the powder.

The method finally decided on involved the use of the Conway diffusion apparatus, with a stainless-steel planchet in the central compartment containing a small amount of aqueous barium hydroxide in the form of a drop of constant volume in the centre of the planchet. In this way, the carbon dioxide liberated from the outer reaction compartment was absorbed directly into the barium hydroxide solution in the planchet. This was then dried and counted, thus eliminating the need to transfer the barium carbonate that had been formed. By adding, accurately, 0.100 ml of standard barium hydroxide to the centre of the planchet, the final barium carbonate of constant weight was obtained as a thin film over a small central area of the planchet, thus giving good geometry for counting.

PROCEDURE—

Place 1 ml of the sample to be analysed, containing between 10 and 400 μg of carbonate, in the outer compartment of the Conway cell. Add 1.00 ml of the labelled 0.01 N sodium carbonate and mix the solutions carefully by gentle swirling. Prepare the labelled sodium carbonate solution by adding 1.0 ml of 0.003 N sodium carbonate, with an activity of 10 microcuries, to a 100-ml graduated flask, followed by 10.0 ml of 0.10 N sodium carbonate and then make up to the mark with water. Transfer, by micropipette, a 0.10-ml aliquot of 0.04 N barium hydroxide solution on to the centre of a stainless-steel planchet, then quickly transfer it to the central compartment of the Conway unit and place the cover on without delay. Slide the cover slightly to one side to allow the addition of 1 ml of hydrochloric acid (1 + 4) and replace the lid, then swirl the unit gently and allow to stand for several hours. At the end of this time open the unit, dry under a drying lamp, and count the activity.

A typical set of results is given in Table II.

TABLE II
APPLICATION OF THE METHOD TO THE DETERMINATION OF CARBONATE

Carbonate, as μg of CO_2 taken	Counts per minute (corrected for background)	Carbonate, as μg of CO_2 found	Error, per cent.
0	1518	0	—
55	1205	51	-8
110	1006	106	-4
220	715	240	+9

The standard deviation for the activity counting was 2 per cent.

This paper demonstrates the use of the residue modification of the substoichiometric method for isotopic-dilution analysis. The examples given above show accuracies comparable with other analytical methods for the range of concentrations and absolute amounts present.

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Received July 27th, 1967

A Radiochemical Separation Technique for Palladium

BY G. G. J. BOSWELL AND T. MCGEE

(*University of Salford, Salford 5, Lancashire*)

The solvent extraction of palladium acetylacetonate with benzene was studied and shown to be a rapid, efficient and selective method for the radiochemical separation of palladium from fission and spallation products.

The yield of the palladium was 90 per cent. in the absence of chloride ions, and the radiochemical purity was shown to be good.

THE majority of radiochemical separation techniques reported for palladium¹ depend on the formation of the dimethylgloxime complex. These methods involve lengthy procedures to remove silver contamination. The work in our laboratory required a rapid and simple method that would separate palladium, radiochemically pure, especially from silver. It was decided to investigate a solvent-extraction procedure based on the pH dependence of metals extracted as the acetylacetonate. The use of acetylacetone as a chelating agent and its application to solvent extraction have been reviewed.² Stary and Hladký³ have determined the extraction constants for the extraction of thirty metals by acetylacetone, from which the optimum separation conditions for palladium can be predicted.

EXPERIMENTAL

The method was developed with radioactive palladium-103 as a tracer. The effectiveness of decontamination from neighbouring elements was tested with molybdenum-99, technetium-99, ruthenium-106, rhodium-106, silver-110, cadmium-109 and indium-114.

All of the isotopes except technetium-99 emitted gamma radiations or high energy beta radiations and were detected on an Ekco 1.75-inch diameter by 2-inch sodium iodide-thallium well scintillation counter (well volume 5 ml), and on a 3 by 3-inch sodium iodide-thallium crystal coupled to a Laben 512 multichannel analyser. The decay of the palladium isotopes was followed on a Nuclear Enterprises Gamma-Matic scintillation spectrometer; the scintillator was a well-type 3 by 3-inch sodium iodide-thallium crystal with a well volume of 12 ml. Technetium-99, which decays with low energy beta radiations, was counted on a Panax thin end-window Geiger-Müller counter. The samples for the Gamma-Matic were counted in 5-ml screw-topped glass vials. Samples counted on the Ekco well crystal were placed in 2-ml polythene vials. Technetium-99 solutions were evaporated to dryness on 1-inch dimpled planchets before being counted on the Panax end-window Geiger-Müller counter.

The phases were equilibrated by stirring with an Electrothermal mini-stirrer, and pH adjustments were made with a Pye Dynacap pH meter.

REAGENTS—

All reagents used were of analytical-reagent grade. The radioisotopic tracers were obtained from the Radiochemical Centre, Amersham. The fission product mixture was obtained by irradiating U_3O_8 in the Manchester and Liverpool Universities' Research Reactor.

The palladium carrier was prepared by evaporating to dryness a solution containing a known amount of palladium(II) chloride with concentrated nitric acid, until all of the chloride was removed. The residue was taken into solution with concentrated sulphuric acid, and the pH was adjusted to zero (with sulphuric acid-sodium hydroxide). The solution was diluted with sulphuric acid (pH = 0) so that it contained 0.5 mg of palladium per ml of solution.

"Holdback" carriers were not used in our experiments as we were developing the method for general use, but if required they should be added before the evaporation stage in the procedure.

PROCEDURE—

Add 0.5 mg of inactive palladium carrier to the sample solution (add holdback carriers if required). If chloride ions are likely to be present, evaporate the solution to dryness with nitric acid until a test for chloride is negative. Dissolve the residue in sulphuric acid and adjust the pH to 0 with sulphuric acid and sodium hydroxide. Mask any interference caused by the presence of molybdenum by adding 0.5 ml of 30 per cent. v/v hydrogen peroxide⁴ to the solution. Equilibrate 5 ml of this solution with an equal volume of 0.1 M acetylacetonate in benzene by mechanically stirring the phases for 5 minutes in a 50-ml centrifuge tube. Separate the phases by centrifugation and wash the organic phase with 5 ml of sulphuric acid (pH = 0) for 30 seconds. Separate the phases and withdraw 2 ml of the acetylacetonate layer for counting.

RESULTS AND DISCUSSION

The time required to reach extraction equilibrium was investigated by determining the count-rate of 2 ml of the acetylacetonate phase, obtained by intimately mixing 5 ml of 0.1 M acetylacetonate in benzene, for different times with 5 ml of a sulphuric acid solution (pH = 0) containing 0.5 mg of palladium carrier and equal amounts of palladium tracer. Fig. 1 shows

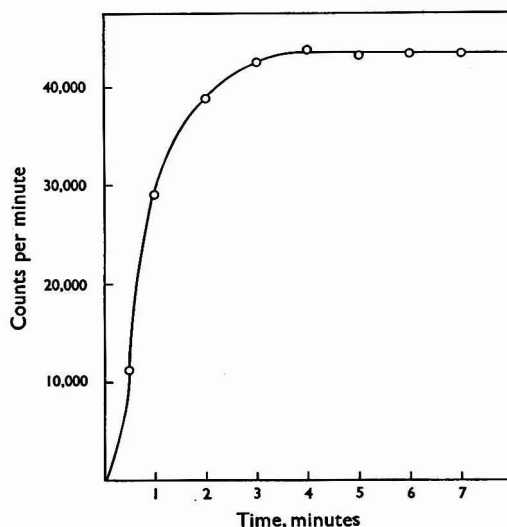


Fig. 1. Time required to reach extraction equilibrium in the extraction of palladium with acetylacetonate in benzene

the activity of the extracts plotted against the time of stirring. Equilibrium conditions are reached after 3 minutes. For all subsequent experiments an extraction time of 5 minutes was used.

TABLE I

EFFECT ON THE EXTRACTION OF PALLADIUM AS THE ACETYLACETONATE FROM SULPHURIC ACID SOLUTION (pH = 0) INTO BENZENE WHEN OTHER SUBSTANCES ARE PRESENT

Species in 5 ml	Activity of extract	
	Counts per minute	Extraction, per cent.
None	24,565	94.5
0.5 ml of 30 per cent. hydrogen peroxide	24,513	94.3
1 ml of 30 per cent. hydrogen peroxide	24,440	94.0
0.5 ml of concentrated nitric acid	24,001	92.3
0.5 ml of 70 per cent. perchloric acid	23,473	90.3
0.001 M Cl ⁻ (sodium chloride)	15,074	58.0
0.01 M Cl ⁻ (sodium chloride)	5,160	19.9
0.1 M Cl ⁻ (sodium chloride)	678	2.6

The effect of hydrogen peroxide, nitric acid, perchloric acid and chloride ions on the extraction of palladium as acetylacetonate was investigated, as these substances may be specified in certain analytical procedures. Solutions were prepared containing palladium-103, 0.5 mg of inactive palladium carrier and the substances to be investigated. The solutions were made up to a volume of 5 ml in sulphuric acid so that the final pH was 0. Each solution was then mixed with 5 ml of 0.1 M acetylacetonate in benzene for 5 minutes. Table I shows the effect of the various substances added on the percentage extraction of palladium.

The extraction of the palladium was accompanied by a colour change of the organic phase to yellow; the rate of this colour change indicated that most of the palladium was extracted in the first few minutes. Chloride ions were found to interfere with the extraction. The yield when chloride ions were absent was 94 ± 1 per cent., compared with a yield of only 58 per cent. when the chloride ion concentration was 0.001 M. Higher concentrations of chloride ions reduce the yield of the palladium even further.

TABLE II
CONTAMINATION OF PALLADIUM BY NEIGHBOURING ISOTOPES⁵

Isotope*	Counter	Activity added to aqueous phase, counts per minute	Activity found in organic phase, counts per minute	Contamination, per cent.
^{114m} In Ec, γ Well	216,582	125	0.06
¹⁰⁹ Cd Ec, γ Well	189,528	461	0.24
^{110m} Ag β , γ Well	220,602	61	0.03
¹⁰⁶ Ru/Rh β , γ Well	208,922	37	0.02
⁹⁸ Tc β G.M.	325,181	3	0.001
⁹⁹ Mo β , γ Well	18,680	281	1.5

* Symbols used were: Ec electron capture.
 β electrons.
 γ gamma radiation.

The contamination of the palladium, extracted as the acetylacetonate, by isotopes likely to interfere when palladium is produced by fission or spallation reactions, was examined. The contaminating activity was added to the aqueous phase containing 0.5 mg of palladium carrier. The activity of this solution was determined by counting a 2-ml aliquot. The palladium was extracted with the acetylacetonate into the benzene layer, which was then washed with sulphuric acid (pH = 0). The phases were separated, and 2 ml of the organic layer were counted. The results are summarised in Table II.

The greatest contaminant of palladium is, as shown in Table II, molybdenum. The extraction of molybdenum can be reduced from 1.5 to 0.13 per cent. by the addition of hydrogen peroxide to the aqueous phase. The peroxide competes with the acetylacetonate for molybdenum ions. The yield of palladium was not affected.

The effectiveness of the method for the separation of palladium from a spallation reaction mixture was shown by extracting the palladium from a molybdenum target that had been bombarded with 120-MeV carbon ions in the Manchester University Linac for 30 minutes. The reactions of heavy ions are complex,^{6,7} as well as "compound nucleus" formation and its subsequent de-excitation by nucleon and electromagnetic radiation emission, there occur "tunnelling" and "transfer" reactions, so that several different nuclides are formed. The palladium isotopes are formed by the reactions Mo (C,2p,xn) Pd, and by the decay of the silver isotopes produced. The target was dissolved in 8 M nitric acid and left to cool for 2 hours to allow palladium-98 and palladium-99 to decay out. The reaction mixture was evaporated to dryness, the residue dissolved in concentrated sulphuric acid and the pH adjusted to zero (sodium hydroxide - sulphuric acid); 0.5 ml of 30 per cent. hydrogen peroxide was added and 5 ml of this solution was treated as previously stated in Procedure. A 4-ml sample of the organic phase was withdrawn for counting and the decay of the palladium fraction followed on an automatic gamma counter. The decay of the component when the longer lived contributions, from palladium-100 and palladium-103, are stripped off is shown

in Fig. 2. A half-life of 8.4 hours was obtained, which agrees with the published value of the half-life of palladium-101,⁸ thus indicating that the palladium fraction was radiochemically pure.

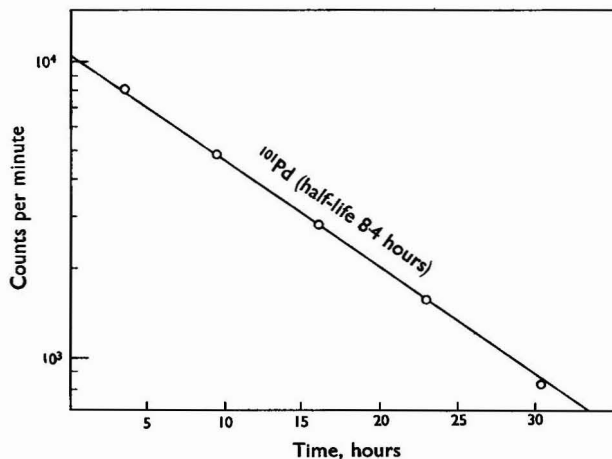


Fig. 2. The decay of palladium (formed by Mo (C, 2pxn) Pd reactions) extracted as the acetylacetonate into benzene, 2 hours after the end of the irradiation

To examine the contamination of a palladium fraction extracted by the above method from a fission product mixture, the active palladium was removed from a 0.25 N nitric acid solution of the fission products by adding 10 mg of inactive palladium carrier and 5 ml of 1 per cent. v/v dimethylglyoxime solution⁹ and the palladium dimethylglyoximate precipitated by centrifugation. This was repeated twice more to ensure the complete removal of the palladium. The solution was evaporated to dryness and heated to destroy any excess of dimethylglyoxime complex. The residue was dissolved in concentrated sulphuric acid, the pH of the solution adjusted to zero, then 0.5 mg of inactive palladium carrier was added and the above extraction procedure carried out. Comparison of the activity of the fission product mixture and the activity of the extracted palladium gave a decontamination factor of 10^3 for the separation.

This simple, elegant method can be adapted to the many situations when isolation of palladium in a radiochemically pure state is required.

We wish to express our appreciation to the staff of the Manchester University Heavy Ion Linac, and of the Manchester and Liverpool Universities Research Reactor, Risley, for the provision of irradiation facilities.

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Received April 4th, 1967

Determination of Small Amounts of Formaldehyde in Acetaldehyde

By S. HARRISON

(Research Department, Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, Organic House, Billingham, Co. Durham)

Two methods are described for the determination of formaldehyde in acetaldehyde based on gas-chromatographic separation of mixtures before, or after, the reduction of formaldehyde to methanol with borohydride. The latter technique is capable of determining 400 p.p.m. of formaldehyde in acetaldehyde but the presence of methanol and methyl formate will interfere. The former technique, in which a borohydride reactor reduces formaldehyde after separation, will determine down to 10 p.p.m. of formaldehyde in acetaldehyde in the presence of methanol and methyl formate.

THERE are numerous methods for the determination of formaldehyde involving the use of titrimetry, colorimetry, polarography and gas chromatography.

The most sensitive methods are colorimetric, those based on the reactions with chromotropic acid and acetylacetone being particularly suitable in the range of 1 to 100 p.p.m.

The method, based on the reaction of formaldehyde with chromotropic acid, has been used to determine micro amounts of formaldehyde, e.g., 0.01 to 0.05 mg,¹ in the presence of large concentrations of various organic compounds, which are removed, in the analytical procedure, by evaporation. In this method formaldehyde can be determined in the presence of a 20,000-fold excess of chloroform, carbon tetrachloride, ethanol, methanol, butyl alcohols, acetone and ethyl methyl ketone, 1000 to 2000-fold excess of acetic acid, propionic acid and benzyl alcohol and 100-fold excess of acetaldehyde and benzaldehyde. Similarly, micro amounts of formaldehyde in gases have been determined² by the chromotropic acid method, but again acetaldehyde interferes if present in substantial proportion.

Attempts have been made in this laboratory to extend the chromotropic acid method to tolerate higher proportions of acetaldehyde, but in spite of testing numerous variations of the analytical procedure it was not found possible to improve the method to tolerate appreciably higher proportions than 100-fold excess of acetaldehyde.

An extremely sensitive method developed by Tanenbaum and Bricker³ involved the time-sensitive reaction of formaldehyde with phenylhydrazine and potassium ferricyanide. This procedure is capable of determining less than 15 mg of formaldehyde in 0.6 ml of sample. However, its application is limited by the fact that methanol, ethanol, butyl alcohols and acetaldehyde interfere.

Sawicki⁴ made a comparative study of colorimetric methods with chromotropic acid, 6-amino-1-naphthol-3-sulphonic acid (J-acid) and 6-anilino-1-naphthol-3-sulphonic acid (phenyl-J-acid) for the determination of formaldehyde and formaldehyde-releasing compounds.

A further sensitive colorimetric method, applicable to less than 10-p.p.m. formaldehyde concentrations, is that based on the reaction of formaldehyde and acetylacetone in the presence of ammonia to give yellow-coloured diacetyldihydrolutidine. Investigations of the method in this laboratory have shown it to be sensitive down to 1 p.p.m. of formaldehyde, but it will not tolerate more than a 100-fold excess of acetaldehyde.

Polarographic methods can be used to determine small amounts of formaldehyde, and have been shown to be sensitive down to about 5 p.p.m.⁵ Work carried out by Woodroffe (personal communications), who used a cathode-ray differential polarograph, has enabled formaldehyde down to the 0.4 p.p.m. level to be determined by this technique but, again, will not tolerate more than a 100-fold excess of acetaldehyde.

Methods based on gas chromatography have demonstrated that formaldehyde can be effectively separated from a variety of compounds including acetaldehyde,^{6,7,8,9,10} but, so far, the technique has not been found suitable for determining formaldehyde in the p.p.m. range because of problems in detection at these concentrations. Bambaugh and Bull⁹ report the gas-liquid chromatographic determination of formaldehyde in water-alcohol mixtures and in high purity (formaldehyde) gas. Kelker also describes¹⁰ the separation and quantitative determination of formaldehyde in mixtures containing alcohols (methyl and ethyl), water and ethyl methyl ketone. However, all of the reported separations have been applied to the 1 to 40 per cent. formaldehyde range.

The purpose of the present work was to develop methods capable of extending the range of formaldehyde determination down to a few p.p.m. in acetaldehyde, or in the presence of a large excess of acetaldehyde in organic mixtures.

At the p.p.m. level there are two main problems, first, that of obtaining a sufficiently good separation system and, secondly, the fact that the detectors normally used in gas chromatography do not have sufficient sensitivity for p.p.m. concentrations of formaldehyde.

To overcome the latter problem, methods were considered for converting the formaldehyde into a more easily determined component.

Borohydrides have been used to reduce carbonyl compounds to their alcohols, and this reaction has been used to remove carbonyl compounds quantitatively from, and to determine total aldehydes and ketones in, alcohols.^{11,12,13,14}

In the first method developed, the sample is dissolved in water and allowed to react with an aqueous solution of sodium borohydride-sodium hydroxide. The formaldehyde is quantitatively converted to methanol, which can then be determined by gas-liquid chromatography.

In the second method the borohydride (KBH_4) is contained in a small reactor tube attached to the end of a gas-liquid chromatographic column and the sample is injected directly on the column. In this case separation of the components takes place before the reduction of the formaldehyde.

METHOD I—EXPERIMENTAL

REAGENTS—

Sodium borohydride solution—Use a solution of 5 N sodium borohydride (NaBH_4) in N sodium hydroxide.

APPARATUS—

A Perkin-Elmer F11 chromatograph was used with the following conditions—

Column—10-feet \times $\frac{1}{8}$ -inch i.d. copper tube.

Packing—Ten per cent. polyethylene glycol "1500" on Chromosorb W.

Detector—Flame-ionisation detector.

Pressure—Ten p.s.i.g.

Carrier gas—Nitrogen.

Column temperature—60° C.

Pre-heater setting—2½ (about 150° C).

Injection—One microlitre.

PROCEDURE—

Weigh accurately about 1 g of sample into 5 ml of ice-cold water. Cool in ice and slowly add 2.5 ml of borohydride solution that has been previously cooled. Mix gently by swirling the solution and then allow it to warm up slowly to room temperature. Finally make up to 10 ml with water.

Inject 1 μl of this solution on the gas-liquid chromatographic column. Measure the height of the methanol peak, and calculate the formaldehyde content from the calibration graph.

CALIBRATION—

Synthetic samples of acetaldehyde containing formaldehyde over the concentration range 400 to 2000 p.p.m. were run as above. The heights of the methanol peaks were measured and plotted as concentration of formaldehyde against methanol peak heights.

DISCUSSION

By this procedure the formaldehyde is quantitatively converted to methanol. This was shown by running standard solutions of aqueous formaldehyde and standard formaldehyde free methanol solutions and comparing peak heights.

It has been found possible to analyse acetaldehyde - formaldehyde mixtures in ratios as high as 2500:1. In 1 μ l of sample, 0.1 to 0.2 μ g of methanol can be detected, thus providing a viable method for the determination of formaldehyde at the 400 p.p.m. level, and above.

Although this method is an advance on the colorimetric technique, in that it extends the permissible concentration of acetaldehyde and has the advantage of being a simple procedure, it is subject to serious limitations with regard to interfering substances. As the method is based on the reduction of formaldehyde to methanol in aqueous solution, the presence of methanol or any substance, *e.g.*, methyl esters, which will form methanol by hydrolysis or reduction, will interfere. By keeping the reaction solution cool, hydrolysis of methyl acetate and higher esters may be prevented, but it was found that methyl formate hydrolyses under these experimental conditions.

METHOD II—EXPERIMENTAL

APPARATUS—

For the gas - liquid chromatographic work a Perkin-Elmer F11 chromatograph operating under the following conditions was used—

Column—10-feet \times $\frac{1}{4}$ -inch i.d. Staybrite tubing.

Packing—Five per cent. of Citroflex A8 (*o*-acetyl triethylhexyl citrate), which may be purchased from Pfizer Ltd., and 0.5 per cent. of orthophosphoric acid on Chromosorb G.

Detector—Flame-ionisation detector.

Pressure—Thirty p.s.i.g.

Linear gas flow-rate—3 cm per second.

Carrier gas—Nitrogen.

Column temperature—60° C.

Pre-heater setting—4 (about 200° C).

Column conditioning—The column should be "aged" at 120° C for 12 hours.

Injection—One microlitre.

Attached to the end of the gas - liquid chromatographic column is a reactor of the following specifications: 3 \times $\frac{1}{4}$ -inch i.d. Staybrite tube packed with evenly ground potassium borohydride.

CALIBRATION—

Prepare a 1 per cent. w/w solution of formaldehyde in acetaldehyde. Dilute the solution further with acetaldehyde to give a series of standards containing from 10 to 250 p.p.m. w/w of formaldehyde.

Inject 1.0 μ l of each standard on the chromatograph and measure the height of peak due to formaldehyde.

Plot the peak heights against concentrations.

PROCEDURE—

Inject 1.0 μ l of sample on the column and measure the height of peak due to formaldehyde, then calculate the formaldehyde concentration from the calibration graph. If several samples are being analysed it is necessary to allow about 30 minutes between each injection.

DISCUSSION

Initially, an attempt was made to combine a reactor packed with borohydride and a gas - liquid chromatographic column, with the reactor at the front of the column. In such a system the gas - liquid chromatographic column would be required to separate methanol from ethanol, residual acetaldehyde and other components that might be present. Satisfactory separations were obtained, but it was difficult to obtain reproducible quantitative results at the 50 to 200 p.p.m. of formaldehyde level, and the life of the reactor was short.

However, these preliminary experiments did indicate that such a technique could form the basis of a viable analytical method.

The alternative arrangement was to have the reactor after the column, but this would require a separation system that would separate formaldehyde from other components, particularly acetaldehyde, and preferably one in which formaldehyde would have a shorter retention time than acetaldehyde. The latter condition is not obtained in most of the gas-liquid chromatographic separations reported in the literature, but Kelker¹⁰ describes a gas-liquid chromatographic system, with Citroflex A8 as a stationary phase, which achieved this type of separation with formaldehyde in the several per cent. range.

A column was therefore prepared as follows: 10-foot \times $\frac{1}{4}$ -inch i.d. stainless-steel tubing, packed with 5 per cent. Citroflex A8 on Chromosorb G, and incorporated in a Perkin-Elmer F11 chromatograph. Various mixtures of formaldehyde and acetaldehyde were examined and it was shown that separations were taking place at relatively high concentrations of formaldehyde. However, at the levels required, *i.e.*, 50 to 1000 p.p.m. of formaldehyde, there were no detectable peaks for formaldehyde, as can be seen in the gas-liquid chromatographic traces in Fig. 1 with reactor, and Fig. 2 without reactor.

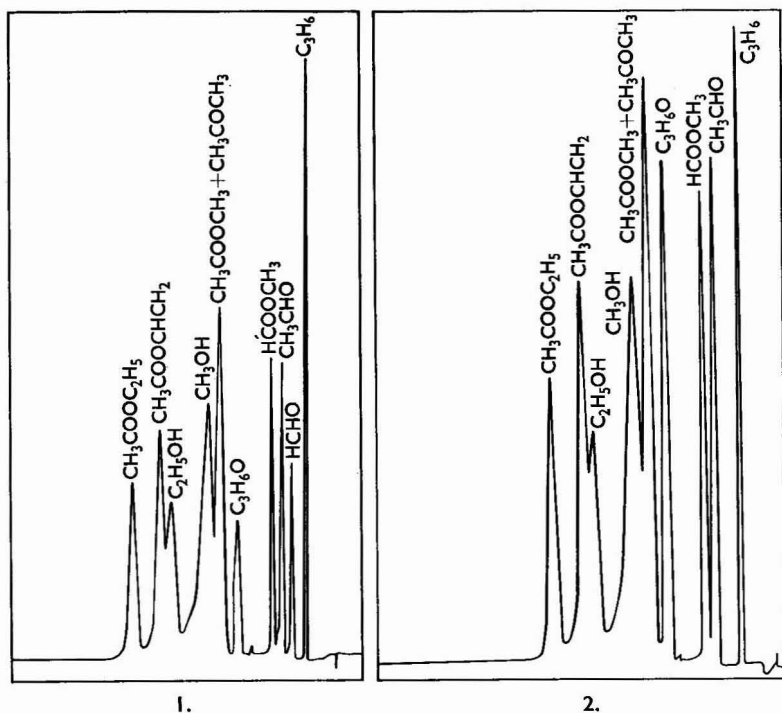


Fig. 1. Chromatogram for the determination of formaldehyde with potassium borohydride reactor

Fig. 2. Chromatogram with mixture as for Fig. 1 without potassium borohydride reactor

At this stage a borohydride reactor (3-inches \times $\frac{1}{4}$ -inch i.d. tube, packed with potassium borohydride) was attached to the end of the gas-liquid chromatographic column and a further series of formaldehyde-acetaldehyde mixtures was examined. The formaldehyde was converted to methanol in the reactor, and thus made it possible to detect the equivalent of 50 p.p.m. of formaldehyde. At this level considerable tailing of peaks was experienced, but this was substantially reduced by incorporating 0.5 per cent. of orthophosphoric acid in the column packing. It then became possible to detect down to 5 p.p.m. of formaldehyde in acetaldehyde (see Fig. 3).

A series of formaldehyde standard solutions in acetaldehyde covering the range 10 to 200 p.p.m. was examined, and a linear peak height against concentration of formaldehyde relationship was obtained (see Figs. 3, 4 and 5).

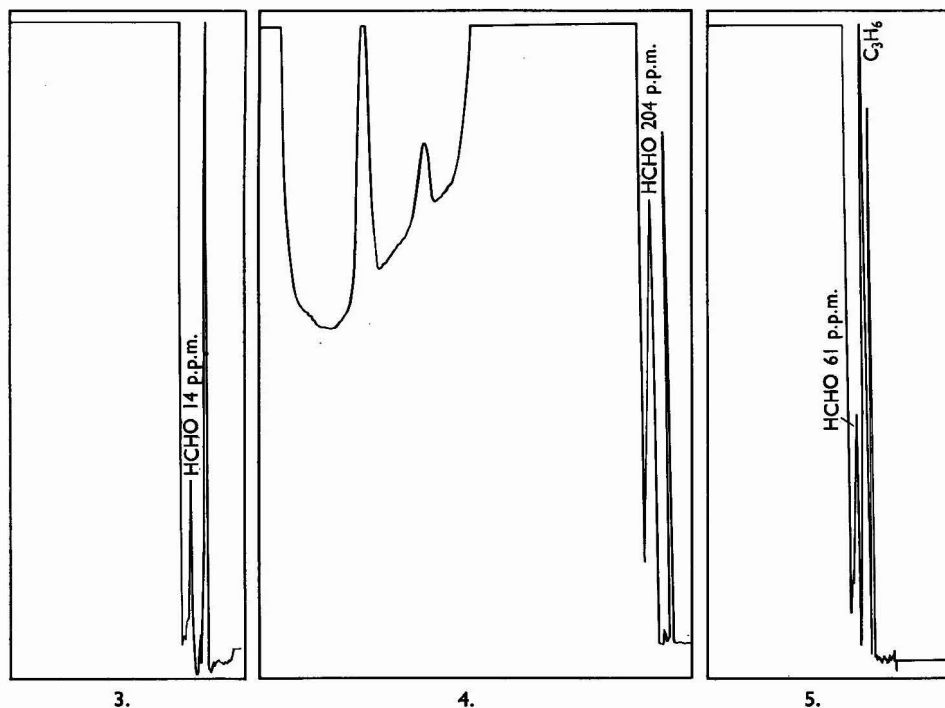


Fig. 3. Chromatogram of 14 p.p.m. of formaldehyde in acetaldehyde

Fig. 4. Chromatogram of 204 p.p.m. of formaldehyde in acetaldehyde

Fig. 5. Chromatogram of 61 p.p.m. of formaldehyde in acetaldehyde containing propylene

As a check on possible interfering substances, a random mixture was prepared containing formaldehyde, acetaldehyde, methyl formate, ethyl acetate, methyl acetate, vinyl acetate, methanol, ethanol, acetone, propylene oxide and propylene. With adjustment of temperature and pressure conditions good separations were obtained (as can be seen in Fig. 1).

CONCLUSIONS

Colorimetry and polarography both provide techniques for determining small amounts of formaldehyde but are limited by interference from the presence of acetaldehyde.

More versatile in application are the two methods described, which are based on gas-chromatographic separations and reduction of formaldehyde with borohydride. In method II, this versatility is combined with a sensitivity that enables 10 p.p.m. of formaldehyde in acetaldehyde to be determined easily (see Table I).

TABLE I
DETERMINATION OF FORMALDEHYDE IN ACETALDEHYDE (METHOD II)

Added, p.p.m.	Found, p.p.m.	
14	16	13
33	32	34
61	58	68
109	109	107
156	152	—
204	205	204

The separation of a random mixture of liquid organic components indicates the general usefulness of the method, thus considerably extending the field of application for the determination of small amounts of formaldehyde in the industrial field.

The author thanks Mr. D. L. Stanton for his assistance in this work.

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Received September 13th, 1966

A Modification of Miles' Method for Determining Azinphos-methyl Residues in Crops

By N. A. SMART

(Plant Pathology Laboratory, Ministry of Agriculture, Fisheries and Food, Harpenden, Hertfordshire)

Meagher's, Bluman's and Miles' methods for determining azinphos-methyl residues were assessed on a range of crops. Some shortcomings were encountered with the three methods and, to overcome them, a modification of Miles' method, involving the use of acetone extraction, is proposed and evaluated. The cleaned-up extract can also be used in an established chromatographic identification procedure.

GIANG and Schechter,¹ Kawashiro and Takeuchi,² Meagher, Adams, Anderson and MacDougall,³ Bates,⁴ Miles⁵ and Adams and Anderson⁶ have published specific methods for the quantitative determination of residues of azinphos-methyl, *S*-(3,4-dihydro-4-oxobenzo-[*d*]-1,2,3-triazin-3-ylmethyl) dimethyl phosphorothiothionate, in crops. Meagher's method has been adopted as A.O.A.C. first action,⁷ following collaborative study.^{7,8,9} An unpublished method of Bluman has also been investigated collaboratively by A.O.A.C.¹⁰ Several general screening techniques for organophosphorus pesticide residues, such as those of Bates¹¹ and Kovacs,¹² may also be used to determine azinphos-methyl residues.

We required a method for determining azinphos-methyl residues in a range of fruits and vegetables to serve as a basis for collaborative work with other laboratories in the United Kingdom and Europe. The method should attain, in the hands of reasonably experienced workers, an accuracy of within a few tenths of a part per million of insecticide, and should preferably be suitable for use in an analytical laboratory that is not equipped with highly specialised apparatus. The methods of Meagher, Bluman and Miles were studied on six crops by one worker, so that the relative merits and defects of the methods could be assessed without variation caused by the different techniques of workers making comparison difficult or invalid.

The crops chosen for investigation were apples, pears, cucumbers, tomatoes, Brussels sprouts and peas. Meagher's method gave a mean recovery over all determinations of 79 per cent., with a standard deviation of ± 0.03 p.p.m. at 1 p.p.m. level over 21 determinations. The recoveries with peas were only 63 per cent. The method was lengthy because of emulsion difficulties. Bluman's method gave a mean recovery over all determinations of 78 per cent., with a standard deviation of ± 0.07 p.p.m. at 1 p.p.m. level over 21 determinations. Recoveries with cucumbers were only 55 per cent. The method is rapid: two determinations can easily be made in 1 day and six in 2 days. Miles' method gave a mean recovery over all determinations of 78 per cent., with a standard deviation of ± 0.04 p.p.m. at 1 p.p.m. level over 21 determinations. The original method described the maceration of the crop sample with chloroform but, in this laboratory, it led to a variable recovery of about 50 per cent. from apples because of the difficulty in separating the chloroform phase. Shaking the diced fruit with chloroform was used to obtain the above results.

As Meagher's method was time consuming, Bluman's method involved the extensive use of toxic benzene and gave low recoveries with cucumber and Miles' method gave incomplete extraction, a modification of Miles' method, involving an efficient acetone extraction, was developed. A further advantage gained by using acetone extraction was that the initial extract could be used for other established residue analysis procedures (*e.g.*, that of Bates), which might not work following a straightforward chloroform extraction. The chromatographic systems of Bates were used to identify the insecticide.

EXPERIMENTAL

A 200-g sample of fruit or vegetable was macerated with 200 ml of acetone for 5 minutes in a Waring blender and filtered on a Whatman No. 541 filter-paper on a slit-sieve Buchner funnel. The solid on the filter-paper was again macerated with 200 ml of acetone for 5 minutes and filtered. The combined filtrates were filtered again through two thicknesses of Whatman No. 541 filter-paper. The clear filtrate was diluted with 300 ml of water and one quarter taken for analysis. The aliquot of the aqueous acetone extract was shaken with successive 50, 25, 25 and 25-ml portions of chloroform in a 500-ml separating funnel, shaking it only gently for the first two extractions. Any emulsions were readily broken by warming the funnel and its contents under the hot water tap, swirling, and adding a few milligrams of sodium chloride. The combined chloroform extracts were washed with 50 ml of water, and the washing back-extracted with 25-ml of chloroform. The combined chloroform extracts were evaporated just to dryness in a 250-ml flask on a steam-bath in a current of air. The residue was then taken up in 10 ml of acetone, cleaned up, and determined by Miles' procedure.

CHROMATOGRAPHIC IDENTIFICATION

A volume of the cleaned-up extract from the method, corresponding to a 25-g sample, was evaporated to small volume in a flask on the water-bath and then just to dryness in a tapered test-tube. The residue was taken up in about 20 to 25 μ l of chloroform and spotted 1 inch from the corner of a 10 \times 10-inch Whatman No. 20 chromatographic paper. Marker azinphos-methyl spots were applied in two adjacent corners.

The paper was then dipped in 30 per cent. v/v dimethylformamide in acetone and, after drying, it was run in hexane. After drying, the paper was dipped in 5 per cent. v/v liquid paraffin in diethyl ether, dried, and run at right angles in diethylformamide - water (1 + 1). The position of insecticide on the chromatogram was detected with 2,6-dibromo-*p*-benzoquinone-4-chloroimine.

RESULTS

Reagent blanks were 0.02 and 0.06 p.p.m. of apparent azinphos-methyl. Table I gives the blank values and recovery results obtained by using the modified Miles' method on locally purchased crops.

TABLE I
MODIFIED MILES' METHOD FOR ANALYSIS OF AZINPHOS-METHYL IN
FRUITS AND VEGETABLES

Crop	Crop blank,† p.p.m.	Recovery of 1 p.p.m. of insecticides*		
		Mean, p.p.m.	Standard deviation p.p.m.	Number of determinations
Apples	0.04	0.80	± 0.04	5
Pears	0.13	0.79	—	2
Cucumbers	0.09	0.73	—	2
Tomatoes	0.08	0.80	± 0.03	5
Brussels sprouts	0.14	0.70	± 0.03	5
Peas	0.06	0.65	—	2

* Corrected for crop blank and reagent blank.

† Mean of two determinations and corrected for reagent blank.

A 25- μ g extract of insecticide from 25 g of apples, pears, cucumbers, tomatoes, Brussels sprouts or peas was clearly visible as a red - brown compact spot having R_F 0.06 to 0.15 in hexane and R_F 0.80 to 0.85 in 1 + 1 dimethylformamide - water. No other spots developed, except with Brussels sprouts when a yellow - brown spot also appeared, R_F nil in hexane, R_F 0.8 in 1 + 1 dimethylformamide - water. This spot, although near the azinphos-methyl, was quite distinct from the insecticide. The R_F values of other organophosphorus insecticides that might be present in practice are given in Bates' paper.

This modification of Miles' method overcomes the difficulties of Meagher's method, Bluman's method and Miles' original method, and merits collaborative study. The method is as accurate and sensitive as Meagher's method. One quantitative determination takes 3 hours and four may be made in 1 day.

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Received January 27th, 1967

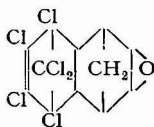
The Separation of Dieldrin from Pentachlorophenol

By J. N. WILSON, M. C. FRANKS AND D. R. SHERLOCK

(The British Petroleum Company Limited, B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex)

BEFORE a pesticide can be marketed, the governments of many countries require that the specifications available include acceptable methods of analysis for the active constituents. Recently such a specification, for a wood preservative, was required to include a method for the determination of 0.5 per cent. of dieldrin in the presence of 5 per cent. of pentachlorophenol. The base solvent was an aromatic petroleum fraction.

The active principal of dieldrin is HEOD, I.



I

Being heavily chlorinated it may readily be determined by chlorine assay, for example, by the oxygen-flask technique,¹ but as this determination is not possible in the presence of a second chloro-compound, a preliminary separation must be made. Removal of the pentachlorophenol by extraction with aqueous alkali is difficult to achieve and leads to inaccurate results because of the occurrence of entrainment and sometimes emulsion formation. These difficulties have been overcome by the use, under non-aqueous conditions, of a macro-reticular strong anion-exchange resin, such as De-Acidite K (Permutit Company Limited) or Amberlyst 29 (Rohm and Haas). A column of the resin is first generated in the hydroxide form by passing four bed volumes of 2 N aqueous sodium hydroxide. After copious washing with de-ionised water to remove excess of alkali and all traces of chloride (the resins are supplied in the stable chloride form), water is removed by passing dry methanol. The sample is diluted with dry methanol and percolated through the resin column. The pentachlorophenol is retained on the resin, while the dieldrin is found in the effluent. The column is washed with four bed volumes of methanol, the washings being added to the effluent. After removal of methanol on a water-bath, the residue is assayed for chlorine by the oxygen-flask technique.¹ Hydrochloric acid is determined by the method proposed by White,² which involves titration with a solution of mercury(II) nitrate in aqueous ethanol, and the percentage of dieldrin calculated. Some typical results are given in Table I.

TABLE I
DETERMINATION OF DIELDRIN BY THE OXYGEN-FLASK TECHNIQUE

Solution in aromatic solvent	Dieldrin, per cent., calculated from chlorine in effluent
Pentachlorophenol, 5 per cent.	0.03
Dieldrin, 0.9 per cent.	0.91
Pentachlorophenol, 5 per cent., with dieldrin, 0.5 per cent.	(i) 0.50; 0.49; 0.51 (ii) 0.51; 0.51

The separation procedure may readily be adapted to accommodate samples varying widely in size and concentration of chlorinated compounds. In the present experiments, 1 g of resin, as supplied, per g of sample (5 per cent. pentachlorophenol) was used. Fifty-milligram samples of the residue were adequate for the oxygen-flask combustion.

Although the method has been used only for this specific separation, it would, with minor modifications, serve equally well to separate other chlorinated pesticides commonly used in combination with pentachlorophenol, for example, BHC and DDT.

REFERENCES

1. Analytical Methods Committee, *Analyst*, 1963, **88**, 415.
2. White, D. C., *Mikrochim. Acta*, 1961, 449.

Received June 6th, 1967

Book Reviews

CHROMATOGRAPHIC REVIEWS, PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS. VOLUME 8. Edited by MICHAEL LEDERER. Pp. viii + 298. Amsterdam, London and New York: Elsevier Publishing Company. 1966. Price 110s.

This series of annual volumes, most ably edited by M. Lederer, has, since its inception in 1959, undergone several changes in the choice and presentation of the subject matter. What started as a vehicle for review articles worth reprinting has gradually developed into a collection of original contributions by specialists chosen from fields of particular interest. As such, each volume performs a valuable function in providing information in a co-ordinated, comprehensive and time-saving form. The appearance quite recently of a similar American series does by no means make the publication of Chromatographic Reviews redundant.

The present volume opens with a most interesting chapter by G. Guiochon, on the flow of gases in porous media, raising fundamental issues connected with the successful operation of gas-chromatographic columns. The review may, in parts, be too mathematical for the average chemist, but it also contains a great deal of practical advice for the correct measurement of flow-rate, gas volume and porosity of column, including descriptions of flow-rate regulating and programming systems.

Of equal interest is the chapter, by R. L. Levy, on the rapidly expanding technique of pyrolysis gas chromatography. The analysis of products of pyrolysis, or thermal breakdown, by gas chromatography for identification and characterisation purposes is akin, in principle, to several other techniques in use, *i.e.*, those based on a combination of pyrolysis with mass spectrometry, infrared or ultraviolet spectrophotometry. Pyrolysis gas chromatography is particularly useful in the analysis of complex non-volatile, insoluble organic materials, *e.g.*, some synthetic or natural polymers.

The use of gas chromatography for trace analysis is authoritatively surveyed by J. Janák and collaborators. Methods may depend on the sensitivity of detectors, on preliminary concentration of the trace component, or both. Consequently, the authors describe, extensively, the design and physical principles of various highly sensitive detectors, and advise on their characteristics and suitability.

The importance of trace analysis at concentration levels of p.p.b., in problems of air pollution, industrial hygiene, pesticides and herbicides in agriculture, and additives in the food industry, is well known. A technique that promises higher sensitivity and selectivity can only be welcome.

The chapter by A. Kuksis on quantitative lipid analysis by combined thin-layer and gas-liquid chromatographic methods should be of great use to clinical and physiological chemists concerned with the preparation and analysis of lipoproteins, phospholipids and lipid patterns in human and animal tissues.

A closely related subject, the chromatography of triglycerides, is reviewed by F. B. Padley. The difficulty of analysis of a large number of similar triglycerides occurring in natural fats has been reflected in the great variety of techniques developed for the purpose of producing reliable results.

Surveying the various techniques of column, paper, thin-layer and gas-liquid chromatography, the author concludes that, although there is still no single technique for the analysis of natural fats, the application of a combination of several techniques, including thin-layer and gas-liquid chromatography, appears to be yielding the most satisfactory answer to the problem.

In a brief chapter on fibrous proteins, Z. Deyl and J. Rosmus deal with separation techniques for collagen, myosin, keratin and their degradation products. The information includes separation by gel filtration, electrophoresis and carboxymethylcellulose columns.

Interesting applications of techniques, based on various types of ion-exchange papers, to the resolution of complex mixtures of inorganic ions, *e.g.*, radionuclides and lanthanide elements, are described by G. Alberti, an active worker in this field. Although work utilising paper impregnated with organic ion-exchange resins is mentioned, the review deals predominantly with results obtained by use of paper impregnated with inorganic ion exchangers, such as zirconium phosphate and ammonium molybdophosphate. From the same laboratory, a review by V. Carunchio and G. Grassini Strazza makes up the volume by reporting on the use of chromatography in the study of structure, reactivity and synthesis of inorganic co-ordination compounds. Separations are

effected either on the basis of charge differences or configurational differences. This lucidly written chapter should prove particularly helpful to research workers in the more theoretical fields of inorganic chemistry.

The volume can be unhesitatingly recommended to anyone interested in chromatographic methods. It is neatly produced, well illustrated and reasonably priced. The only feature open to criticism is the several pages of commercial advertisements carried at the back of the book.

D. GROSS

TRACE CHARACTERIZATION—CHEMICAL AND PHYSICAL. By W. WAYNE MEINKE and BOURDON F. SCRIBNER. Pp. xviii + 580. Washington, D.C.: National Bureau of Standards Monograph 100. 1967. Price \$4.50.

It is obvious that our knowledge of the significance of trace constituents is increasing daily, with studies in this direction stimulated by the known or suspected rôle of trace elements in all phases of our everyday life. From the smallest individual organism to man himself, their presence in prescribed amounts is essential for a healthy existence, while their absence may have the opposite effect.

In this modern age, *e.g.*, in engineering, especially nuclear engineering, limitations are imposed on the presence of some elements for entirely new reasons, and the analyst is faced with additional problems involving determinations at the parts, or even fractions of a part, per million level.

In October 1966, the U.S. National Bureau of Standards held its first Materials Research Symposium, in Gaithersburg, Maryland, and this publication contains the invited papers and summaries of other papers presented at that Symposium, together with subsequent Symposium discussions.

This occasion must have been unique in bringing together so many internationally recognised experts from a wide field of scientific interests. Symposia so often tend to provide a common platform for exhaustive discussion within narrow areas of competence, but the title of this Symposium was ideally suited to remove the demarcations that still exist, for example, between the physicist, on the one hand, and the chemist on the other.

The main chapter headings are Trace Characterization and the Properties of Materials; Electrical Measurements for Trace Characterization; Trace Characterization by Electrochemical Methods; Optical and X-ray Spectroscopy; Effects of Trace Impurities on X-ray Diffraction; Physical Optical Methods; Chemical Spectrophotometry in Trace Characterization; Radioactivity Techniques in Trace Characterization; Nuclear Methods; Spark Source Mass Spectrometric Analysis of Solids; Preconcentration in Trace Analysis; and The Study of Crystal Imperfections by Means of Optical Methods and by Means of Electron Microscopy and Electron Diffraction.

The busy analyst, who tends to work within the narrow confines dictated by his particular circumstances, should benefit from this authoritative appraisal of how the same problems are approached elsewhere, and a publication such as this (the reviewer has queried its low price) that gives a clear, concise and up-to-date account of the state of the art, should have a strong appeal to anyone involved in "Trace Characterization."

W. T. ELWELL

CONTAMINATION ANALYSIS AND CONTROL. By JAMES DWYER. Pp. vi + 343. New York: Reinhold Publishing Corporation. 1966. Price 120s.

With the advancement of technology, there has been an increasingly important need to control particulate contaminants and to apply stringent requirements to them. For those interested in particulate contamination, this book provides a comprehensive review of the practical aspects of the subject. The titles of the 11 chapters give a general indication of the scope of the book as the following show: Particles and droplets in gases—sources: Properties of aerosols: Aerosol sampling: Sample analysis: Contaminants on surfaces—sampling and analysis: Contamination control of airborne particulates: Control of contaminants in liquids: Cleaning of surfaces.

Contamination of plant and components by dirt is a common but serious problem today, and those working in a wide variety of industries will find this book useful, in fields as diverse as electronic devices, aerospace or the chemical, photographic and food industries. Dust or other airborne particles need to be excluded from industrial processes, and the author describes the methods for controlling this contamination and its analysis, including sampling for particles of micron size, although specific details of analytical procedure are omitted. However, the bibliography gives copious references to the literature on the subject.

The chapters on control of contaminants in liquids and the cleaning of surfaces succeed in condensing considerable information on two vast subjects into a small space. The various methods of filtration of liquids are referred to, as also are the use of coagulants and coagulants aids in settling particles in suspension in water. Similarly, the chapter on cleaning surfaces briefly refers to acid, alkali, emulsion and vapour-phase cleaners, and the methods used for their application. It would have been helpful, however, if the bibliography had contained more references to the literature on these subjects to supplement the understandably brief descriptive material.

E. L. STREATFIELD

PROGRESS IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. Volume 2. Edited by J. W. EMSLEY, J. FEENEY and L. H. SUTCLIFFE. Pp. viii + 271. Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris and Braunschweig: Pergamon Press. 1967. Price 90s.

This book is the second volume in a series edited by Emsley, Feeney and Sutcliffe. This series is of considerable importance in the rapidly expanding field of high resolution nuclear magnetic resonance spectroscopy. The object of this series is to make available a continuous supply of up-to-date authoritative reviews dealing with topics of current interest; the second volume certainly satisfies this condition.

The contents of volume 2 include work on high resolution nuclear magnetic resonance, and also on magnetic resonance of paramagnetic systems. I congratulate the editors of this series for continuing to make the series readable to both nuclear magnetic resonance spectroscopists, and electron spin resonance spectroscopists. The book continues with the high standard set by the first volume of the series and will be extremely useful, particularly to nuclear magnetic resonance specialists.

Chapter 1 by O'Reilly is concerned with chemical shift calculations. The chemical shift of nuclei in molecules and solids is determined by the interaction of the nuclear magnetic moment with orbital currents of electrons induced by the applied magnetic field. In these determinations perturbational methods are employed, which yield results that are examined in detail, and justification for its use is given. Calculations are made for atoms, molecules and solids. All results are summarised.

The next section by Buckingham and McLaughlin deals with high resolution nuclear magnetic resonance in partially oriented molecules. Both molecules and liquids are discussed in some detail, and all results on anisotropies in the shielding constants, molecular structural parameters, the absolute signs of isotropic spin-coupling constants, anisotropies in spin-coupling constants, nuclear quadrupole coupling constants and the mean orientation of the molecule in an isotropic environment are discussed and tabulated.

De Boer and van Willigen then discuss nuclear magnetic resonance of paramagnetic systems and survey the theoretical background of the direct and indirect methods of studying paramagnetic systems by using nuclear magnetic resonance techniques.

The fourth chapter, on the calculations of line shapes by density matrix methods, by Lynden-Bell contains description of the density matrix and those of its properties which are used in nuclear magnetic resonance problems, descriptions of the nuclear magnetic resonance spectrum of a single spin nucleus by means of the density matrix and discussion of the line shapes in systems with chemical exchange. Relaxation effects and double resonance are also discussed in some detail.

The concluding chapter by Zurcher, on the cause and calculation of proton chemical shifts in non-conjugated organic compounds, discusses general theory as applied to methyl groups and rigid systems.

The binding, the typography and the index are good, and the price is reasonable at 90s.

H. M. ASSENHEIM

A SYSTEMATIC APPROACH TO THE INTERPRETATION OF INFRARED SPECTRA. By HERMAN A. SZYMANSKI. Pp. vi + 154. New York: Hertillon Press. 1967. Price \$2.00.

Any publisher who is sufficiently enterprising to issue a well printed and lavishly illustrated advanced text for the price of two dollars deserves to succeed, and it is therefore all the more disappointing to have to say that this text cannot be unreservedly recommended. In this field, perhaps more than any other, it is vital that the student should grasp the limitations of the technique as clearly as he understands its potential, and this is not brought out as clearly as it should be. Indeed, the foreword contains the statement "If the spectrum is a complete unknown he (the student) should be able to make fairly reasonable assignments of all bands." I do not believe the

author intended this to be taken literally, but it illustrates the loose wording that could well generate a dangerous degree of over-confidence. There are other deficiencies also; the illustrations, for example, are not always well chosen for teaching purposes. The student will be confused by a spectrum illustrating a primary amide in which the separate Amide I and II bands cannot be distinguished (p. 119), and probably also by the inclusion of the spectra of gases in which rotational structure is present. The formulae on p. 104 include three identical structures that are assigned different carbonyl frequencies, and the interpretation of the doubling of the CO band of benzoyl chloride (p. 107) is not that which is generally accepted.

It is, of course, always easy for a reviewer to pick on defects of this kind and to ignore the fact that the main bulk of the text is factually sound and informative. For the man with some knowledge and experience this is a useful text that is good value for money, but for the reasons given I would be rather more hesitant in putting it in the hands of a complete beginner in this field.

L. J. BELLAMY

SIMPLIFIED ANALYSIS OF HYDROPONIC SOLUTIONS. By M. SCHWARZ and E. SZEKELY. Pp. iv + 34. The National Council for Research and Development, The Negeve Institute for Arid Zone Research, Hydroponic Department. Beer-Sheba, Israel. 1967.

This booklet, in typescript form, is intended for use by farmers and scientifically unskilled persons concerned with growing vegetables, flowers and fruits under conditions calculated to give optimum growth by using the techniques of soilless culture, where accurate control of nutrient concentration and pH is essential and the accumulation of undesired elements must be prevented. The use of sophisticated equipment and lengthy processes is avoided. Relatively straightforward tests for the estimation or determination of nitrate, ammonium, phosphate, iron, boron, chloride, zinc and copper, and manganese, often involving comparison with standard nutrient solutions for which the preparations are given, are clearly described. Minor printing errors not indicated by the errata slip are unimportant.

The booklet is well worth looking at for the new methods and modifications of accepted methods developed at the Negeve Institute. Of general interest are tables of optimum concentrations of nutrients and the pH recommended in each case for growing various plants in gravel culture. The bibliography lists eleven books published from 1944 onwards. B. J. MOODY

ANALITICHESKAYA REAKSIONNAYA GAZOVAYA KHROMATOGRAFIYA (ANALYTICAL REACTION GAS CHROMATOGRAPHY). By V. G. BEREZKIN. Pp. 184. Moscow: Iz. Nauka. 1966. Price 56 Kop.

The term "reaction gas chromatography" was used by F. Drawert in 1962 at the Fourth Symposium on Gas Chromatography at Hamburg to describe the miscellany of procedures in which chemical reactions are used in gas-chromatographic schemes. The present monograph is devoted to analytical uses of reaction gas chromatography (*cf.* V. G. Berezkin and O. L. Gorshunov, *Usp. Khim.*, 1965, **34**, 1108) as distinct from kinetic and catalytic studies. The reactions take place in reactors, which can be situated either before or after the column, but analytical methods in which chemical conversions of a sample are carried out as separate operations in vessels not linked with the gas-chromatographic column are excluded from "analytical reaction gas chromatography."

Among the reasons for combining chemical transformations with gas chromatography are the possibility of the formation of new compounds that are more easily separated on the usual columns or more easily detected, or both, the possibility of determining unstable and highly reactive compounds, and the possibility of extending the range of the flame-ionisation detector to the determination of nitrogen, oxides of carbon, water, etc.

The first methods published in the de-limited field were those of N. H. Ray (*Analyst*, 1955, **80**, 853), who used a column of bromine-impregnated charcoal to absorb ethylene before determining the impurities originally present in the ethylene on a column of activated charcoal, and A. E. Martin and J. Smart (*Nature*, 1955, **175**, 422), who oxidised organic vapours eluted from a column to carbon dioxide (and water), and then used an infrared analyser.

In this book the author summarises the work already published in the field, both in theory and practice, giving short accounts of methods and details of ranges of application. He attempts some systematisation of results and makes suggestions on the possible directions of future development. References are given at the end of each of the 8 chapters and the total number, without allowing for some repetitions, is over 350, some of which are as recent as 1966.

In Chapter I, the main paths of development of analytical-reaction gas chromatography are outlined, further details being given in subsequent chapters. Chapter II is mainly theoretical, and Chapter III describes possible types of apparatus trains. Chapter IV is concerned with the analysis of complex mixtures by the use of hydrogenation, dehydrogenation, esterification, hydrolysis, pyrolysis (of volatile compounds), dehydration, decarboxylation and oxidation. Chapter V deals with the determination of impurities by reactions leading to the absorption of the main component before the column separation (*e.g.*, N. H. Ray, *Analyst*, 1955, **80**, 853), processes that are effective only for impurities of a different type; the formation of more volatile compounds from the impurities, *e.g.*, in the determination of sulphur in organic compounds by hydrogenation, followed by condensation of hydrogen sulphide and methane and their gas-chromatographic separation (I. Okuno, J. C. Morris, and W. E. Haines, *Analyt. Chem.*, 1962, **34**, 1427); the formation of compounds of low volatility from the impurities, *e.g.*, in the determination of carbon dioxide and hydrogen sulphide as impurities by absorbing them in ethanolamine at room temperature, followed by their release at a higher temperature for separation on a column of hexadecane; the conversion of gases that are not registered by a flame-ionisation detector to others that can be detected, *e.g.*, in the determination of oxygen in a two-stage operation by converting it to carbon monoxide, followed by the reduction of the latter to methane (V. G. Berezkin, A. E. Mýsak and L. S. Polak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 1871); and by many reactions of other types.

Analytical-reaction gas chromatography is of great value in the analysis of polymers and other non-volatile compounds (Chapter VI), as decomposition into simpler and more volatile compounds by pyrolysis, or sometimes by oxidation processes and radiolysis, is essential for the application of the usual methods of gas chromatography, although the author refers to a non-destructive method for detecting functional groups, determining molecular weights and studying phase transitions. In this method the stationary liquid phase (the polymer) is the unknown factor and the mixture of gases for chromatographic separation is the known factor. From the gas-chromatographic spectra of the standard mixtures much information on the composition of the polymer can be obtained.

In Chapter VII, various methods of elemental organic analysis and the determination of carbon-to-hydrogen ratios are described, and the author draws the conclusion that reaction gas-chromatographic methods are generally simpler than those normally used in elemental analysis, although the results are comparable in accuracy, those for nitrogen showing smaller errors. Chapter VIII deals with reactions that can be used to change the sensitivity and selectivity of detectors, and to provide information on functional groups.

This comparatively short volume is likely to be valuable for reference as it is the first to appear in this heterogeneous field. At present the subject is not categorised in the Index to "Analytical Abstracts." The book can be recommended to those in search of fresh ideas for the solution of a variety of analytical problems.

G. S. SMITH

CHEMISTRY. A CONCEPTUAL APPROACH. By CHARLES E. MORTIMER. Pp. xii + 692. New York, Amsterdam and London: Reinhold Publishing Corporation. 1967. Price 71s. 6d.

The acquisition of a good appreciation of the fundamentals of chemistry is achieved in many ways, and no two students are likely to have had precisely the same basic training.

We live in an age when scientific innovations rapidly become part of our everyday life, when new approaches are made to elucidate, or extend, the theories of yesterday, and modern scientific tools are available for solving current problems.

Whilst the basis of our modern scientific thinking remains largely unchanged, those responsible for teaching advanced chemistry and its inseparable associations with other branches of related sciences, have an increasingly difficult task to perform.

Professor Mortimer has a reputation for presenting general chemistry in such a way as to make the subject interesting and understandable, and the impression gained from reading this publication is that the claim is justified.

The author displays a commendably clear style of presentation, and the reader is helped, not only by the clarity and relative simplicity of the reading matter, but by the typography of the book, and the excellent diagrams and tables that are attractively presented in a blue colour scheme.

Throughout the book, problems are posed, and solved with stepwise explanations, and answers to selected numerical questions are given in the final pages. Each chapter concludes with a list of selected references, under the heading, Some Suggested Readings.

The chapters are largely devoted to inorganic chemistry (in the broad sense), under such headings as Atomic Structure, Chemical Bonding, Chemical Equations and Quantitative Relationships, Electrochemistry, Elements of Chemical Thermodynamics, Chemical Kinetics and Chemical Equilibrium, Ionic Equilibria, Metals and Complex Compounds.

Subjects covered in the 42-page chapter on Organic Chemistry range from Alkanes to Polymers, and the final chapter, Chapter 18, Nuclear Chemistry, takes up 23 pages.

For the advanced student, or anyone needing a refresher, this book should provide an excellent companion to textbooks that cover the individual fields in much more detail. W. T. ELWELL

DIE ORGANISCHE CHEMIE DES ZINNS. By PROF. DR. WILHELM P. NEUMANN. Pp. xii + 232. Stuttgart: Ferdinand Enke Verlag. 1967. Price (paper) DM 65.50; (linen) DM 69.

Between 1852, the year of the first publication describing an organotin compound, and 1935, fewer than 200 papers appeared on this subject, and all of the then known information could be contained in 60 pages of the book on organometallic compounds published by Krause and Grosse in 1937. In the last 30 years, however, well over 3000 publications have appeared, and this increase in the interest in organotin chemistry may be said to have started, in the early 1950's, with the researches of Van der Kerk and his co-workers in Holland. At first the main emphasis was on methods of preparation, but, later, with the developments in the chemistry of the tin-hydrogen bond, interest shifted to the study of reaction mechanisms, and it is this aspect of organotin chemistry that has mainly interested Professor Neumann.

Since 1959, he has been leading an active team of investigators at the University of Giessen, and has published numerous papers in this time. He has now written an excellent concise account of the whole field of organotin chemistry, although naturally the main emphasis, more than a third of the book, is concerned with the organotin hydrides and their reactions. In particular, he gives a detailed account of the two important subjects of hydrostannation, *viz.*, the addition of organotin hydrides to double and triple bonds, with the formation of tin-carbon bonds; and hydrostannolysis, their reductive cleavage of alkyl halides and of tin-element bonds, and their reaction with acids, bases and inorganic halides, both fields in which he himself has made important contributions. This latter class of reactions can cover such a large variety of compounds that it is possible that the most important use of organotin compounds in the future may be as intermediates in organic synthesis rather than as stabilisers or biocides.

A short, 4-page summary is given of analytical methods including the chromatographic and chemical procedures available for the separation and determination of the different types of organotin compounds, and this is followed by a useful table of infrared and Raman absorption bands, and their assignments.

In a chapter on the technology of organotin compounds, the available methods of manufacture are mentioned; the industrial use of the dialkyltin compounds as stabilisers and the biocidal applications of the tri-alkyl and tri-aryl compounds are briefly discussed. There is also an account of the published work on the toxicology of these compounds. The book concludes with a selected bibliography of over 900 items, most of them references to work published within the last 7 years.

J. W. PRICE

MÉTHODES D'ANALYSE CETAMA—1966. MÉTHODES 151 À 200. COMMISSARIAT A L'ÉNERGIE ATOMIQUE ET COMMISSION D'ÉTABLISSEMENT DES MÉTHODES D'ANALYSE. Parte 3. Pp.vi + 285. Paris: Presses Universitaires de France. 1966. Price 75F.

This volume brings up to date the methods of analysis accepted by the French Atomic Energy Commission. A further 50 methods are now described, which are principally concerned with the application of known procedures to the technical problems associated with the analysis of nuclear materials. As such, it contains little of particular interest to the analyst who is not concerned with such materials, and little by way of novelty to those who are.

W. I. STEPHEN

Erratum

NOVEMBER (1967) ISSUE, p. 688, 3rd line above Table I. For "1.003 for iron(III)" read "0.997 for iron(III)".

Summaries of Papers in this Issue

Industrial Gas Analysis

A Literature Review

SUMMARY OF CONTENTS

Introduction
Permanent and inorganic gases
Analysis of liquefied or pure gases
Fuel gases
Flue gases
Motor exhaust gases
Analysis of micro samples
Atmospheric pollutants

(The late) H. N. WILSON and G. M. S. DUFF

Imperial Chemical Industries Ltd., Agricultural Division, P.O. Box No. 6, Billingham, Co. Durham.

Analyst, 1967, **92**, 723-758.

REPRINTS of this Review paper will soon be available from The Society for Analytical Chemistry, Book Department, 9/10 Savile Row, London, W.1, at 7s. 6d. per copy, post free.

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

Some Observations on the Determination of Mercury by Atomic-absorption Spectroscopy in an Air - Acetylene Flame

The sensitivity obtained for mercury at 2537 Å in atomic-absorption spectroscopy in air - acetylene is greatly influenced by the valency state of mercury in the sample solution. Greater sensitivity is obtained for mercury(I) than for mercury(II), and further increase in sensitivity results when reducing and complexing agents are added to mercury(I) solutions. An explanation of this effect based on the disproportionation of mercury(I) into mercury(II) and elemental mercury is given.

D. N. HINGLE, G. F. KIRKBRIGHT and T. S. WEST

Chemistry Department, Imperial College, London, S.W.7.

Analyst, 1967, **92**, 759-762.

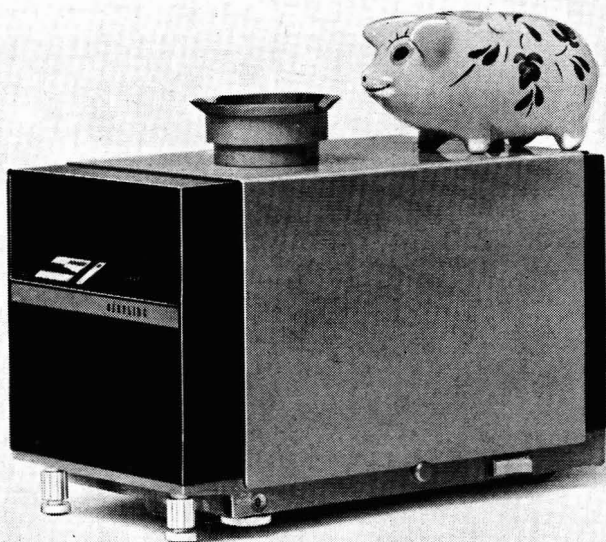
The Determination of Vanadium in Silicate Rocks and Minerals with *N*-Benzoyl-*o*-tolylhydroxylamine

In 4 to 8 N hydrochloric acid, *N*-benzoyl-*o*-tolylhydroxylamine is an almost specific reagent for vanadium, and can be used in the analysis of rocks and minerals. After removal of silica by evaporation with hydrofluoric acid, the insoluble residue is fused with potassium pyrosulphate and dissolved in dilute sulphuric acid. The violet-coloured complex with the reagent is formed in 6 N hydrochloric acid solution, extracted into carbon tetrachloride and measured at 510 m μ . Fluoride addition prevents interference from titanium, while the use of PTFE and silica apparatus avoids contamination and interference from platinum.

P. G. JEFFERY and G. O. KERR

Warren Spring Laboratory, Ministry of Technology, Stevenage, Hertfordshire.

Analyst, 1967, **92**, 763-765.



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Isotopic-dilution Analysis with a Modified Substoichiometric Residue Method for Carbonate and Sulphate

A new modification of the substoichiometric isotopic-dilution method is presented. After the addition of a standard amount of labelled compound, the isotopically diluted compound is then isolated, as a residue of constant weight, and the beta activity measured. The method applied to the determination of sulphate and carbonate is applicable in the range 10 to 100 μg for these anions.

J. K. JOHANNESSON

Auckland Technical Institute, Wellesley Street, Auckland, New Zealand.

Analyst, 1967, **92**, 766-768.

A Radiochemical Separation Technique for Palladium

The solvent extraction of palladium acetylacetonate with benzene was studied and shown to be a rapid, efficient and selective method for the radiochemical separation of palladium from fission and spallation products.

The yield of the palladium was 90 per cent. in the absence of chloride ions, and the radiochemical purity was shown to be good.

G. G. J. BOSWELL and T. McGEE

University of Salford, Salford 5, Lancashire.

Analyst, 1967, **92**, 769-772.

Determination of Small Amounts of Formaldehyde in Acetaldehyde

Two methods are described for the determination of formaldehyde in acetaldehyde based on gas-chromatographic separation of mixtures before, or after, the reduction of formaldehyde to methanol with borohydride. The latter technique is capable of determining 400 p.p.m. of formaldehyde in acetaldehyde but the presence of methanol and methyl formate will interfere. The former technique, in which a borohydride reactor reduces formaldehyde after separation, will determine down to 10 p.p.m. of formaldehyde in acetaldehyde in the presence of methanol and methyl formate.

S. HARRISON

Research Department, Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, Organic House, Billingham, Co. Durham.

Analyst, 1967, **92**, 773-778.

A Modification of Miles' Method for Determining Azinphos-methyl Residues in Crops

Meagher's, Bluman's and Miles' methods for determining azinphos-methyl residues were assessed on a range of crops. Some shortcomings were encountered with the three methods and, to overcome them, a modification of Miles' method, involving the use of acetone extraction, is proposed and evaluated. The cleaned-up extract can also be used in an established chromatographic identification procedure.

N. A. SMART

Plant Pathology Laboratory, Ministry of Agriculture, Fisheries and Food, Harpenden, Hertfordshire.

Analyst, 1967, **92**, 779-781.

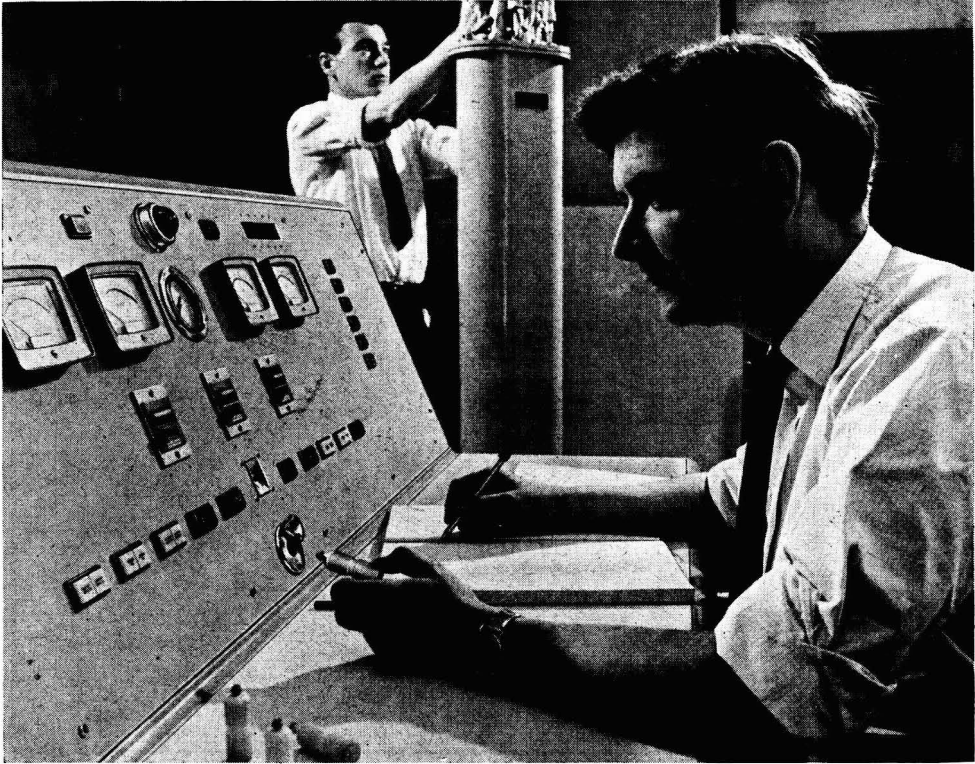
The Separation of Dieldrin from Pentachlorophenol

A method for separating dieldrin from pentachlorophenol, involving the use of a macro-reticular strong anion-exchange resin, is described.

J. N. WILSON, M. C. FRANKS and D. R. SHERLOCK

The British Petroleum Company Limited, B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex.

Analyst, 1967, **92**, 782.



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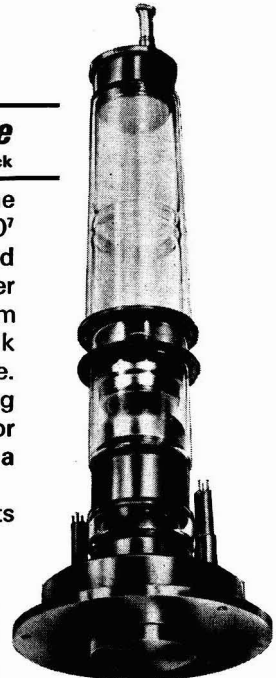


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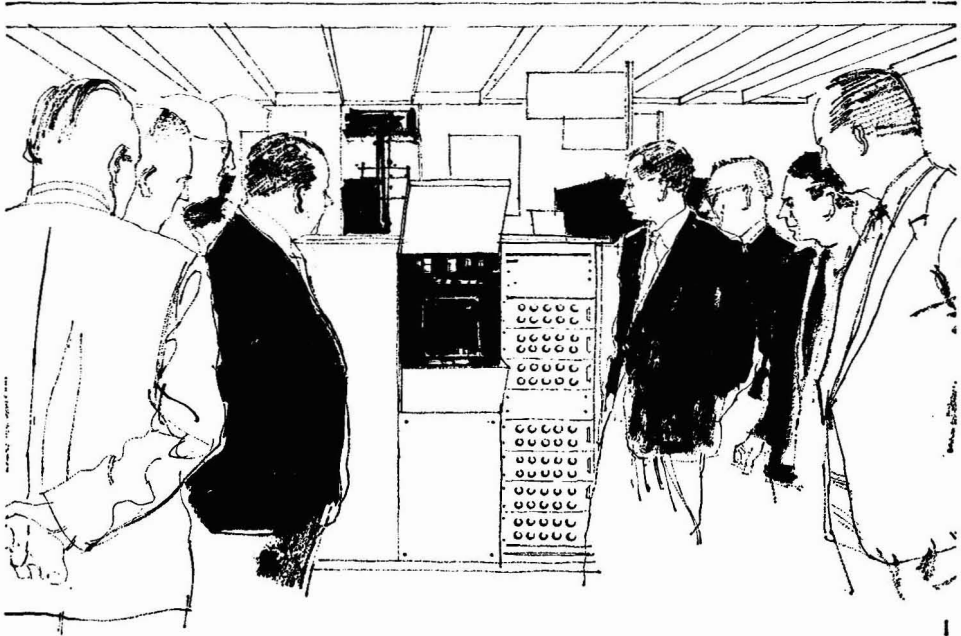
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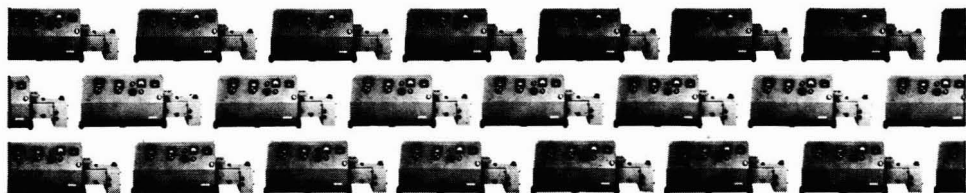


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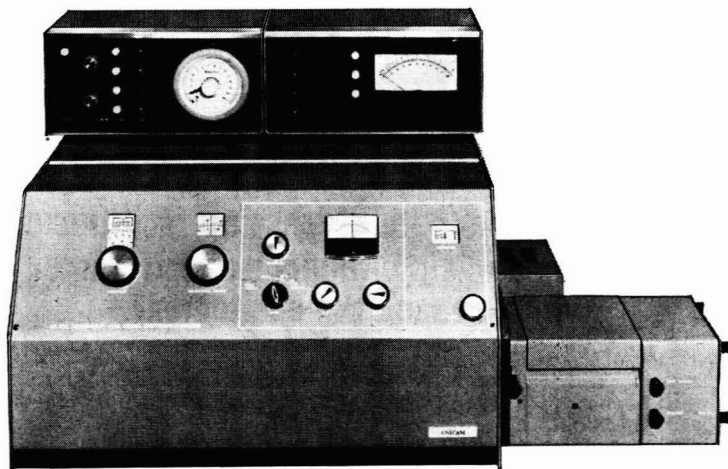
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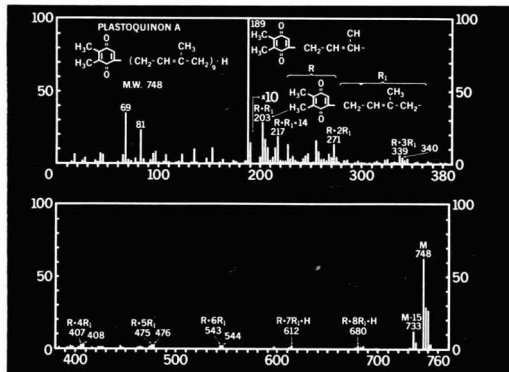
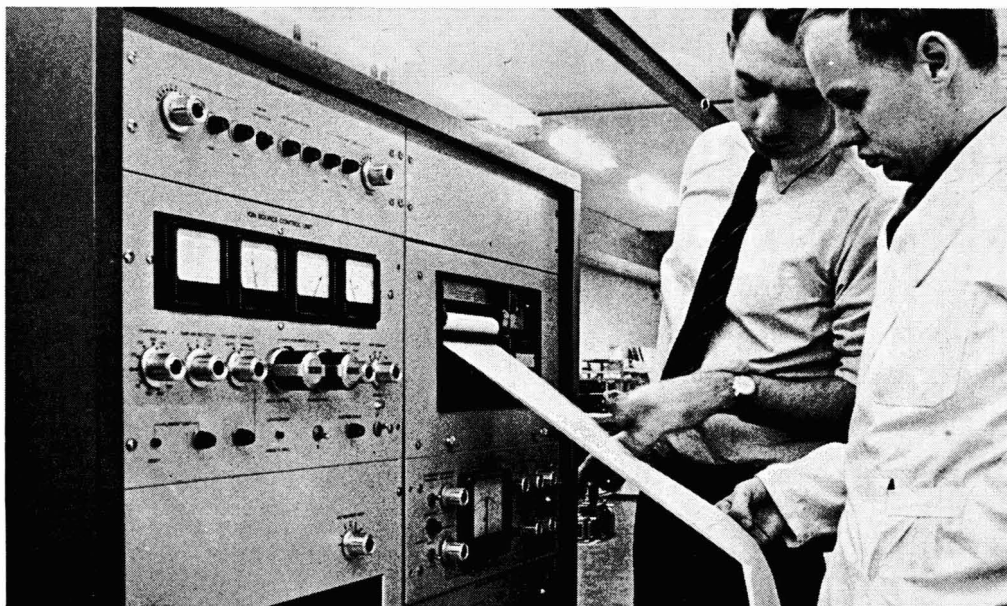
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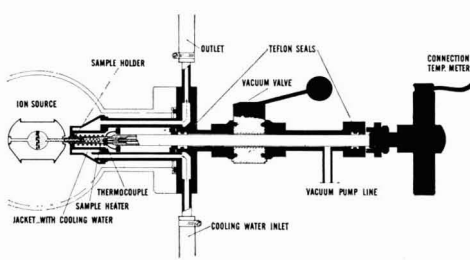
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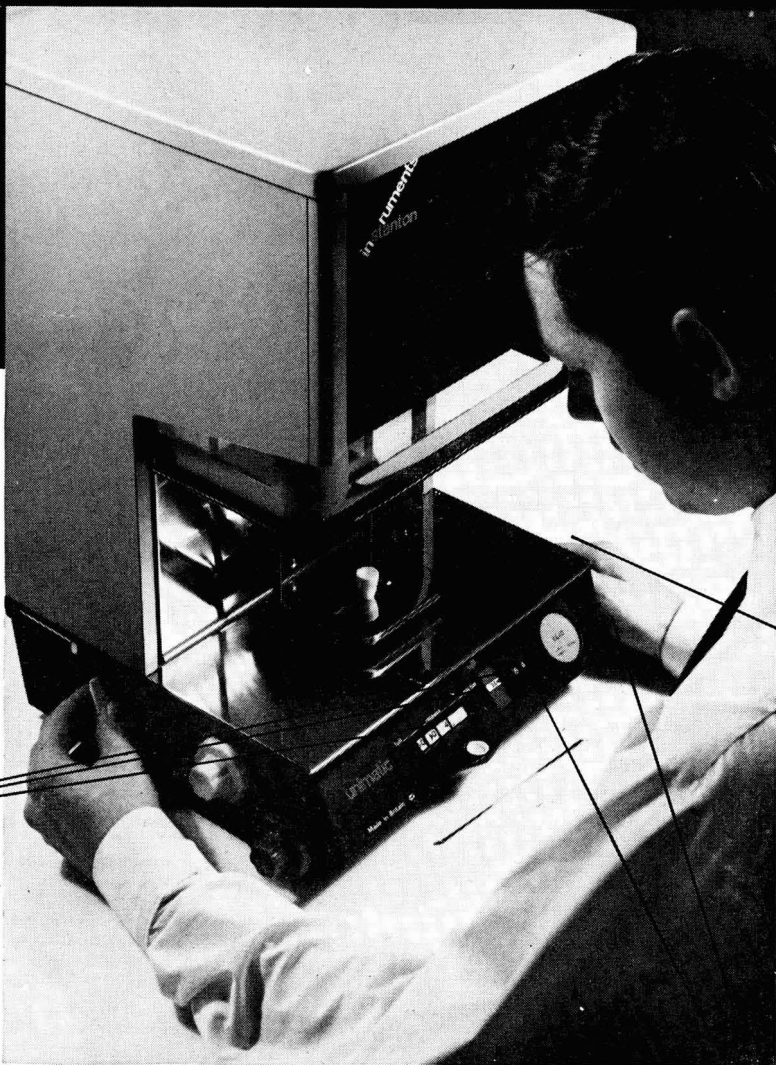
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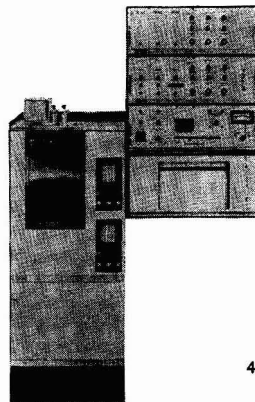
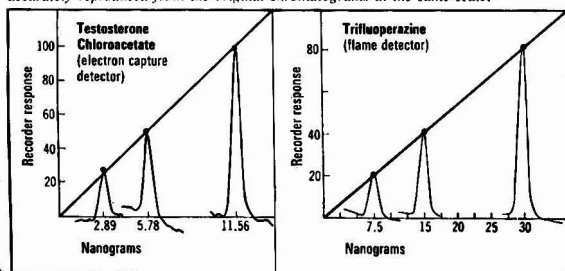
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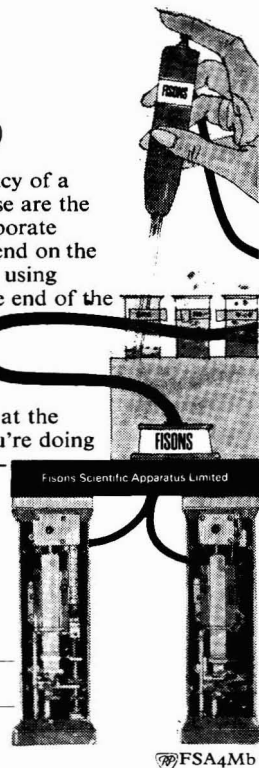
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