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Summaries of Papers in this Issue

The Application of Non-flame Atom Cells in Atomic-absorption and Atomic-fluorescence Spectroscopy

A Review

SUMMARY OF CONTENTS

Introduction
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Filaments
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Conclusion

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G. F. KIRKBRIGHT

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

Analyst, 1971, **96**, 609-623.

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C. R. BOSWELL

Analytical Research and Development Unit, Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Analyst, 1971, **96**, 624–630.

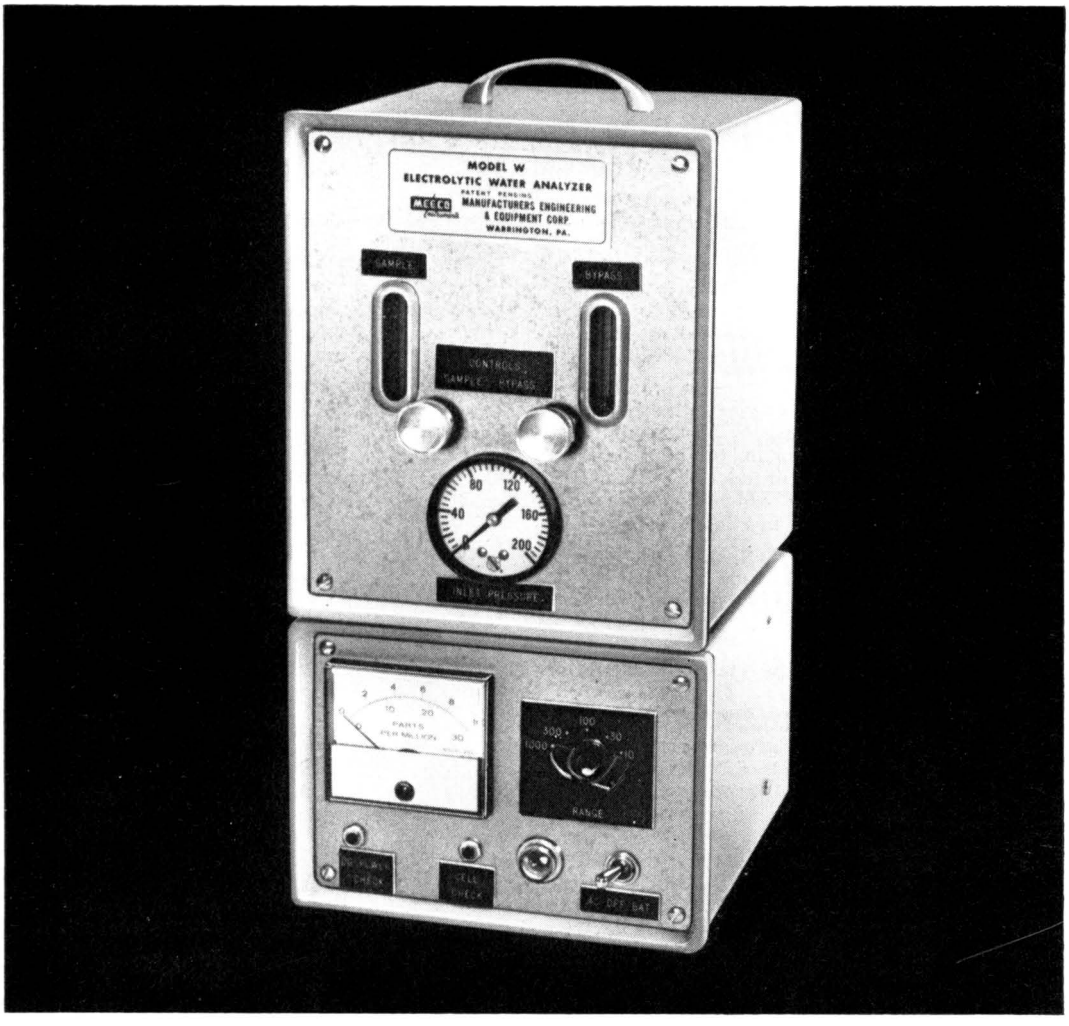
The Atomic-emission Spectroscopy of Rhenium in the Nitrous Oxide - Acetylene Flame

Rhenium can be determined by atomic-emission spectroscopy by use of a pre-mixed nitrous oxide - acetylene flame supported on a 6-cm slot burner. The limits of detection were 0·7 μg ml^{-1} (346·1 nm) and 1·5 μg ml^{-1} (488·9 nm); analytical working curves were linear for rhenium concentrations below 200 μg ml^{-1} at both wavelengths. Spectral interference from palladium, nickel, rhodium, cobalt and large amounts of lanthanum or phosphate occurred at 346·1 nm and from large amounts of aluminium at 488·9 nm. A number of elements gave rise to chemical interference, but this was eliminated by the addition of sulphuric or phosphoric acid. A monochromator giving a spectral band pass of the order of 0·1 nm must be used for the determination, and background corrections must be made either by wavelength scanning or by measurement at the peak and at an adjacent wavelength.

R. SMITH and A. E. LAWSON

Imperial Chemical Industries Ltd., Petrochemicals Division, Billingham, Teesside.

Analyst, 1971, **96**, 631–639.



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BOC

A Method for the Chemical Analysis of Magnesites and Dolomites

This paper includes a detailed description of a method for the analysis of magnesites and dolomites; the method has been accepted (in principle) by the British Standards Institution as a standard method. Determinations include SiO_2 (gravimetric), TiO_2, Fe_2O_3, Cr_2O_3, MnO (colorimetric) and Al_2O_3, CaO and MgO (complexometric). Notes on the development of the method and tables of co-operative results obtained by the Refractories Working Group of the Analysis Committee are included.

H. BENNETT and R. A. REED
The British Ceramic Research Association, Queens Road, Penkhull, Stoke-on-Trent, ST4 7LQ.

Analyst, 1971, **96**, 640–655.

4-[Bis(carboxymethyl)aminomethyl]-3-hydroxy-2-naphthoic Acid as a Fluorescent Indicator for the Complexometric Titration of Calcium *plus* Magnesium

4-[Bis(carboxymethyl)aminomethyl]-3-hydroxy-2-naphthoic acid, known also as 1-dicarboxymethylaminomethyl-2-hydroxy-3-naphthoic acid, a spectrofluorimetric reagent for beryllium, has been found to be an effective fluorimetric indicator for the complexometric titration of calcium *plus* magnesium when used in conjunction with a suitable fluorimetric titrimeter. A procedure is described in which the indicator is used in the titrimetric determination of magnesium in silicate rocks.

R. L. CLEMENTS, J. I. READ and G. A. SERGEANT
Department of Trade and Industry, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1971, **96**, 656–658.

Use of the Halphen Reaction for the Determination of the Cyclopropenoid Content of Lipids

An application to cottonseed oils of a quantitative version of the Halphen test for the determination of cyclopropenoid material has been published by other workers, but for other oils containing higher levels of cyclopropenoids, although the absorption at the 495 nm peak is linearly related to the concentration of each oil examined, the relationship differs among the oils. However, transmethylation of oil before applying the Halphen reaction has been found to give results that are in better agreement with titration with hydrogen bromide for oils with widely differing cyclopropenoid content. The use of pressurised capsules for carrying out the reaction with reduced loss of solvent has proved advantageous, as flatter peaks are obtained when optical absorption is plotted against time. The application of the modified technique to oils containing a wide range of concentrations of total cyclopropenoid material in the component fatty acids is described and discussed.

T. W. HAMMONDS, J. A. CORNELIUS and L. TAN
Foreign and Commonwealth Office (Overseas Development Administration), Tropical Products Institute, 56/62 Gray's Inn Road, London, W.C.1.

Analyst, 1971, **96**, 659–664.

Determination of Clamidoxic Acid in Serum by Gas - Liquid Chromatography

A method has been developed for the determination of clamidoxic acid [2-(3,4-dichlorobenzamido)phenoxyacetic acid] in serum by using gas chromatography with electron-capture detection. Clamidoxic acid is extracted from acidified serum into toluene and returned to an aqueous sodium hydroxide phase. The amide is hydrolysed to 3,4-dichlorobenzoic acid which, after acidification, is extracted into toluene containing an internal standard. The acid is converted into its methyl ester by the addition of a solution of diazomethane in diethyl ether, excess of diazomethane is destroyed with acetic acid, and an aliquot analysed.

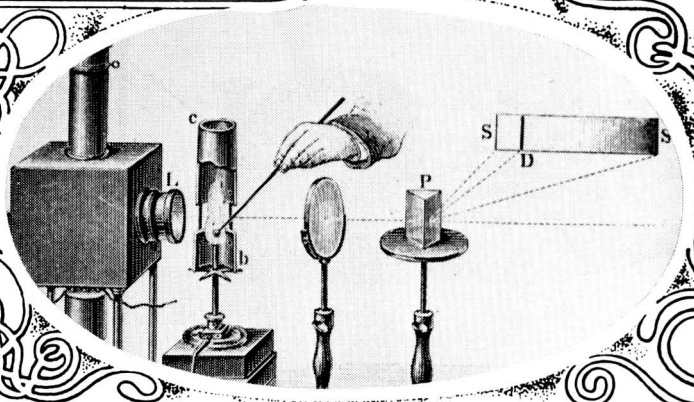
L. SHERMAN and (the late) G. A. TAYLOR
Smith & Nephew Research Limited, Gilston Park, Harlow, Essex.

Analyst, 1971, **96**, 665–670.

Circa **1870**

Early Spectroscopy

The incandescent light source (left) gives continuous spectrum, via condenser lens & prism P, and sodium on rod held in gas flame; this gives sodium absorption line D. (Ronan Picture Library)



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The Application of Non-flame Atom Cells in Atomic-absorption and Atomic-fluorescence Spectroscopy

A Review*

By G. F. KIRKBRIGHT

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

Summary of contents

Introduction
General considerations
Furnaces
Filaments
Cathode sputtering cells
Other non-flame cells
Conclusion

In the past decade, atomic-absorption spectroscopy (AAS) has been widely demonstrated to provide a sensitive and selective technique for inorganic trace analysis. Atomic-absorption spectrophotometers are now available from more than twenty instrument manufacturers throughout the world. Atomic-fluorescence spectroscopy (AFS) has been shown by several groups of workers to be a complementary technique that may permit higher analytical sensitivity than AAS for the determination of some elements. In both techniques the attainable sensitivity and precision are limited by the characteristics of the primary radiation source, and by the technique with which atoms of the analyte element are formed from the sample to be examined. Although considerable effort has been devoted to the development of improved hollow-cathode lamps and electrodeless discharge-tube sources, and the selectively modulated and pulsed operation of sources, the most long-standing and widely used method of atomisation has been that with the flame. All commercial instrumentation available is equipped with flame atomiser facilities, and this situation will undoubtedly continue for some time. The fact that flames were inherited as AAS atom cells from the older technique of flame-emission spectroscopy may account in part for their popularity, although they also have the following advantages for use in the analytical techniques of AAS and AFS.

(*i*) They are convenient to use, reliable and relatively free from a tendency to memory effects. Most flames in common use can be made noiseless and safe to operate.

(*ii*) Most burner systems are small, durable and inexpensive. Sample solutions are easily and rapidly handled by the use of relatively simple nebuliser assemblies.

(*iii*) A wide variety of flames is available to allow the selection of optimum conditions for many different analytical purposes.

(*iv*) The signal-to-background and signal-to-noise ratios obtainable are sufficiently high to allow adequate sensitivity and precision to be obtained in a wide range of analyses at different wavelengths between 200 and 800 nm.

Flame-atomisation systems exhibit some disadvantages, however, which limit the attainable sensitivity and convenience in their use for analysis. These disadvantages have led many workers to devise techniques for the atomisation of samples for analysis that are not based on chemical flames. This paper reviews some of the non-flame cell devices that have been described for use in AAS and AFS.

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

General considerations

Some of the possible disadvantages of flames for analytical work are given below.

(*a*) The volume of the sample solutions available may frequently be less than that required for use with an indirect nebuliser system. For low analyte concentrations it may not be possible to dilute the solution to overcome this limitation. With indirect nebulisers used with pre-mixed flames only a small fraction of the sample solution enters the flame.

(*b*) Flame cells are only rarely able to atomise solid samples directly.

(*c*) Flame background absorption and emission at the wavelength of the resonance line of the analyte element, or thermal emission from the analyte or concomitant elements at this wavelength, may give rise to unacceptable signal noise with consequent loss of precision.

(*d*) In some locations it may be inconvenient to use high-pressure cylinders of support and fuel gas, and in closed automated systems where no operator is in attendance it may not be desirable to use a flame as the atom cell.

In addition to these practical disadvantages, other more fundamental factors act in flames to limit the sensitivity and selectivity that may be achieved. These are as follows.

(1) The attainable atom concentration in flames is limited by the dilution effect of the relatively high flow-rate of unburnt gas used to support the flame and to transport small volumes of sample solution to the flame. The atom concentration is also limited by the flame gas expansion that occurs on combustion.

(2) Precise control over the chemical environment of the analyte and concomitant atoms in flame cells is not possible. The degree of control of chemical composition that can be obtained by variation of the fuel-to-oxidant concentration ratio is accompanied by simultaneous changes in the flame temperature and its spectral absorption and emission characteristics. For many elements, particularly those that form thermally stable oxides, the efficiency of free atom production from the sample introduced into the flame is low.

(3) In the technique of AFS, the flame that produces the greatest freedom from inter-element effects may also produce low fluorescence efficiency through quenching of radiationally excited analyte atoms by flame gas molecules.

For the analysis of small liquid or solid samples, and for the determination of trace amounts of many elements in larger samples, it would be advantageous to achieve a higher concentration of atoms in a small cell volume than is possible with flames with which solution-nebulisation techniques are used; this can be accomplished in non-flame cells. Winefordner,[1] for example, in a study of a typical graphite cell technique, has demonstrated that a substantially higher peak concentration of atoms may be expected in such a cell than in a flame. This gain results directly from avoidance of the limiting sample dilution effects that occur in flame cells. To assist the formation and maintenance of a high free-atom fraction for the analyte element for AAS and AFS, it is also an advantage in non-flame cells that the chemical environment of the cell can be controlled by the use of an inert gas atmosphere; also in AFS the selection of a suitable inert supporting gas may result in greater fluorescence efficiency by the reduced quenching of radiationally excited atoms. With suitably designed non-flame cells a considerable advantage over flames in the recorded noise caused by background absorption or emission or sample emission, which originates from the cell, would result.

It is apparent, therefore, that non-flame devices may find widespread application in AAS and AFS, provided their simplicity and reliability are comparable with those of flame cells.

Furnaces—

The use of high-temperature furnaces offers the possibility of a high concentration of atoms within a well defined volume with very low background emission and noise for AAS and AFS. Several furnace devices that permit a long path length for AAS have been described. However, for those in which the operating temperature is below about 1500 °C,

the range of elements that can be atomised is restricted, and chemical interferences may be encountered with complex sample matrices. These disadvantages may be outweighed by the potentially high sensitivity obtained for particular elements in this type of cell.

Mislan[2] has described the construction and performance of an atomic-absorption spectrophotometer that involves the use of a 36-cm silica tube of 2·5 cm i.d. heated to a maximum temperature of 1250 °C by a wire-wound resistance furnace. Sample solutions were transferred to the absorption tube through a conventional indirect nebuliser - spray chamber assembly. The device was used for the determination of cadmium and excellent detection limits were obtained. Hudson[3] reported AAS measurements on sodium vapour produced in a stainless-steel absorption cell heated by a resistance wire. Atomic-absorption studies by using furnaces have also been made by Vidale,[4] Choong and Loong-Seng[5] and by Tomkins and Ercoli.[6]

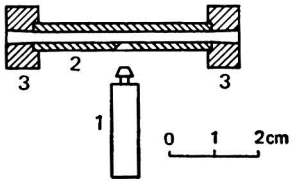

Fig. 1. Graphite tube assembly of L'vov furnace (from L'vov[16]): 1, electrode with sample; 2, crucible; and 3, graphite contacts placed inside coolers

Several satisfactory devices involving graphite furnaces of the type used by King[7] have been constructed for analytical use in both AAS and AFS, the earliest and best known of which is the furnace device first described by L'vov.[8] During the past 10 years, L'vov and his co-workers have undertaken extensive AAS studies with various models of the original graphite furnace.[9 to 17] This work has been reviewed by L'vov in his textbook[15] and elsewhere.[16] A diagram of the basic graphite tube assembly used in later models of the device is shown in Fig. 1. Graphite cylinders 30 to 50 mm in length and of 2·5 to 3 mm i.d., depending on the analytical requirements, can be used. The furnace can be heated electrically by a.c. current from a 4-kW transformer at 10 V, and the temperature to which the tube is heated is regulated by changing the voltage supply to the primary circuit of the transformer. In early forms of the furnace the inside wall of the tube was lined with tantalum or tungsten foil to eliminate diffusion of vapour through the porous walls. More recently, preference has been given to tubes lined both inside and outside with a layer of pyrographite, which has low gas permeability, high heat conductivity and resistance to oxidation, so that it precludes diffusion of vapour through the walls and ensures uniform heating of the tube and a longer lifetime. The sample (solid or liquid) is introduced into the tube on an auxiliary carbon-rod electrode 6 mm in diameter, the tip of this rod being shaped to fit an orifice in the tube wall. In operation, the sample to be analysed can be placed on this electrode as a solution or powder. The electrode is positioned below the graphite tube, the chamber enclosing the tube assembly is closed and purged with argon, and the tube is heated (for 20 to 30 s) to the required temperature. The auxiliary electrode is moved into place to fit the orifice in the tube wall and is heated electrically by an a.c. current from the secondary winding of a 1-kW step-down transformer (220/15 V), from the electrode to the tube. The sample is vaporised and the atomic-absorption signal is recorded. In the original form of the L'vov furnace, the pulse vaporisation of the sample was achieved by using a d.c. arc between an electrode in the crucible and the auxiliary electrode mounted under the crucible. The graphite crucible pulse-vaporisation method has been used by L'vov with a two-channel atomic-absorption spectrophotometer that permits simultaneous recording of absorption for two elements, one of which can be an internal standard. A continuum source can be used to correct for any interference caused by non-selective molecular absorption and scattering of source radiation. The high-intensity atomic-line sources used may be either high-frequency electrodeless discharge tubes or hollow-cathode lamps operated from a pulsed power supply.

The radiation emitted by the two sources is combined by means of a semi-reflecting mirror. This beam is then modulated, merged with the continuum source radiation by using a rotating mirror chopper and passed through the graphite crucible atom cell.

Table I shows some results for sensitivity obtained by L'vov;[16] the absolute amounts of different elements actually measured are given, together with the corresponding experimental conditions used and the extrapolation of the sensitivity results to the absolute amount of each element that would produce 1 per cent. absorption for a 2·5-mm graphite tube. The attainable precision claimed for the graphite tube technique operated with small liquid samples (2 to 5 μl) corresponds to a relative r.m.s. error in a single measurement of 5 to 8 per cent.

TABLE I

SENSITIVITY DATA WITH L'VOV FURNACE (FROM L'VOV[16])

Element line/nm	Tube diameter/ mm	Argon pressure/ atm.	Temperature/ °C	Measured amount/g	Sensitivity/ g per 1 per cent. absorption
Ag 328·1	2·5	2	1800	5×10^{-13}	1×10^{-13}
Al 309·3	4·5	1	2100	$2·5 \times 10^{-11}$	1×10^{-12}
Au 242·8	2·5	2	1700	7×10^{-11}	1×10^{-12}
B 249·8	2·5	2	2400	5×10^{-9}	2×10^{-10}
Ba 553·5	3·0	1	2200	1×10^{-10}	6×10^{-12}
Be 234·9	4·5	6	2400	$2·6 \times 10^{-12}$	3×10^{-14}
Bi 306·8	2·5	2	1800	$2·5 \times 10^{-11}$	4×10^{-12}
Ca 422.7	2·5	2	2300	$2·5 \times 10^{-11}$	4×10^{-13}
Cd 228·8	1·2	1	1500	6×10^{-14}	8×10^{-14}
Co 240·7	2·5	2	2200	$7·5 \times 10^{-12}$	2×10^{-12}
Cr 357·9	2·5	2	2200	5×10^{-11}	2×10^{-12}
Cs 852·1	2·5	2	1900	$6·6 \times 10^{-12}$	4×10^{-13}
Cu 324·7	2·5	2	2100	$6·3 \times 10^{-12}$	6×10^{-13}
Fe 248·3	2·5	2	2100	$2·5 \times 10^{-11}$	1×10^{-12}
Ga 287·4	2·5	2	2100	$2·5 \times 10^{-11}$	1×10^{-12}
Hg 253·7	2·5	2	700	$4·5 \times 10^{-10}$	8×10^{-11}
In 303·9	2·5	2	1900	8×10^{-12}	4×10^{-13}
K 404·4	2·5	2	1800	$6·3 \times 10^{-10}$	4×10^{-11}
Li 670·8	3·0	1	1900	5×10^{-11}	3×10^{-12}
Mg 285·2	4·5	2	1800	3×10^{-12}	4×10^{-14}
Mn 279·5	2·5	2	2000	$2·5 \times 10^{-12}$	2×10^{-13}
Mo 313·3	2·5	2	2500	5×10^{-11}	3×10^{-12}
Ni 232·0	2·5	2	2200	$2·5 \times 10^{-11}$	9×10^{-12}
Pb 283·3	2·5	2	1900	3×10^{-11}	2×10^{-12}
Pd 247·6	2·5	2	2100	5×10^{-11}	4×10^{-12}
Pt 265·9	2·5	2	2300	$2·5 \times 10^{-10}$	1×10^{-11}
Rb 780·0	2·5	2	1900	$7·5 \times 10^{-12}$	1×10^{-12}
Rh 343·5	2·5	2	2300	$6·3 \times 10^{-11}$	8×10^{-12}
Sb 231·1	2·5	2	2000	5×10^{-11}	5×10^{-12}
Se 196·1	2·5	2	1600	2×10^{-10}	9×10^{-12}
Si 251·6	2·5	2	2250	$2·7 \times 10^{-12}$	5×10^{-14}
Sn 286·3	2·5	2	2000	1×10^{-11}	2×10^{-12}
Sr 460·7	3·0	1	2200	2×10^{-11}	1×10^{-12}
Te 214·3	2·5	2	2000	$7·6 \times 10^{-12}$	1×10^{-12}
Ti 365·3	2·5	2	2500	5×10^{-10}	4×10^{-11}
Tl 276·8	2·5	2	1800	$2·5 \times 10^{-12}$	1×10^{-12}
Zn 213·8	4·5	4	1500	1×10^{-12}	3×10^{-14}

In addition to the extensive use of the graphite tube furnace for the determination of trace amounts of elements whose resonance lines lie above 200 nm, L'vov,[16] in work by himself and Khartsyzov, has examined the possibility of its application to the determination of sulphur, phosphorus and iodine in the ultraviolet region between 170 and 190 nm. By using electrodeless discharge-lamp sources, the conventional argon-purged graphite furnace, lithium fluoride windows and lenses and a vacuum monochromator, sensitivities (for 1 per cent. absorption) of 3×10^{-12} g of phosphorus at 177·5 nm, 3×10^{-11} g of iodine at 183·0 nm and 1×10^{-10} g of sulphur at 180·7 nm were attained with AAS. L'vov and co-workers[13,15,17] have also made use of the favourable properties of the graphite furnace to study the Lorentz widths of resonance lines, the determination of absolute values of oscillator strengths and the estimation of atomic-diffusion coefficients.[18]

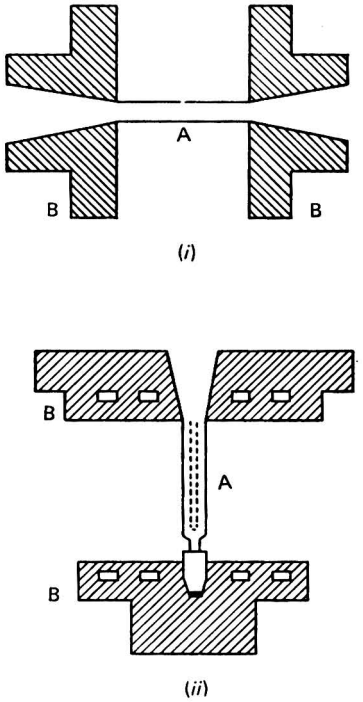

Fig. 2. (*i*), Graphite cuvette assembly for AAS (from Massman[19]); and (*ii*), for AFS (from Massman[19]). A, graphite tube or cuvette; and B, steel holders

Massman[19] has described graphite cuvette devices for use in both AAS and AFS. The furnace arrangements used are shown in Fig. 2. The graphite tube used for AAS is 55 mm long, of 6·5 mm i.d. and 1·5-mm wall thickness. An orifice 2 mm in diameter is cut into the centre of the tube length so that the sample can be introduced with a micropipette. For AFS, a cup-shaped graphite cuvette, 40 mm long and of 6·5 mm i.d. and 1·5-mm wall thickness, is used. The source radiation enters at the open top of the cuvette, and the fluorescence radiation is viewed through a slit cut into its wall. The sample is inserted into the fluorescence cuvette at its open top. Both the tube and cuvette can be heated to 2600 °C within a few seconds by using a power supply capable of supplying up to 400 A. The absorption tube is purged with argon, but the optical path through the tube is open to the atmosphere. Emission from the fluorescence cuvette, which is similarly purged with argon, is viewed through a silica window in the side of the chamber. Modulated radiation from hollow-cathode lamp sources can be used for both techniques; so as to obtain high fluorescence intensities with these sources, however, they were operated for short periods of time at high current levels. Sample solution volumes of between 5 and 200 μl were used for AAS work and of 5 to 50 μl for AFS studies. Solid samples of up to 1 mg in weight were reported by Massman to be acceptable with his apparatus; for larger samples, unacceptable background absorption effects were encountered. The same worker[20] also corrected for non-selective background absorption in AAS by using a two-channel spectrometer and monitoring the absorption of a nearby elemental non-resonance or filler gas line from the source. Table II shows detection limits obtained by Massman for sixteen elements by atomic-absorption spectroscopy and nine elements by atomic-fluorescence spectroscopy. Only for zinc and cadmium were clearly superior detection limits obtained with the latter technique, and for other elements the available source intensities were insufficient to permit low detection limits with it. The analytical precision achieved in AAS and AFS was similar when the dissolved solid content of sample solutions

TABLE II

DETECTION LIMITS BY AAS AND AFS WITH GRAPHITE CUVETTES (FROM MASSMAN[19])

Element	Line/nm	Detection limit by AAS/g	Detection limit by AFS/g
Zn	213·86	8×10^{-13}	4×10^{-14}
Cd	228·80	2×10^{-12}	$2{\cdot}5 \times 10^{-13}$
Ag	328·07	8×10^{-13}	$1{\cdot}5 \times 10^{-12}$
As	189·04	6×10^{-10}	—
Se	196·09	2×10^{-9}	—
Sb	231·15	1×10^{-10}	2×10^{-10}
Fe	248·33	2×10^{-11}	3×10^{-9}
Hg	253·65	2×10^{-10}	—
Tl	276·79	4×10^{-11}	2×10^{-9}
Mn	279·48	8×10^{-12}	—
Pb	283·31	1×10^{-11}	$3{\cdot}5 \times 10^{-11}$
Mg	285·21	5×10^{-13}	$3{\cdot}5 \times 10^{-12}$
In	303·94	2×10^{-10}	—
Bi	306·77	2×10^{-10}	—
Cu	324·75	1×10^{-11}	$4{\cdot}5 \times 10^{-10}$
Na	588·99	7×10^{-12}	—

was 2 per cent. or less and not more than 100 and 30-μl sample volumes were taken, respectively. Standard deviations of between 4 and 12 per cent., depending on the matrix element and its concentration, were attained. Higher precision was achieved by use of an internal standard element whose absorption was measured simultaneously by using the two-channel spectrometer.

A graphite furnace similar to that described by Massman has recently been introduced as an accessory to a commercially available atomic-absorption spectrophotometer,[21] and its performance appears to be similar to that of the original device described by Massman. The determination of copper and strontium in milk, which is difficult by AAS with flames without sample pre-treatment, was chosen by Manning and Fernandez[21] for preliminary studies to illustrate the application of the technique. The signal recorded during the analysis sequence in this determination is shown in Fig. 3. The atomic-absorption signal is recorded

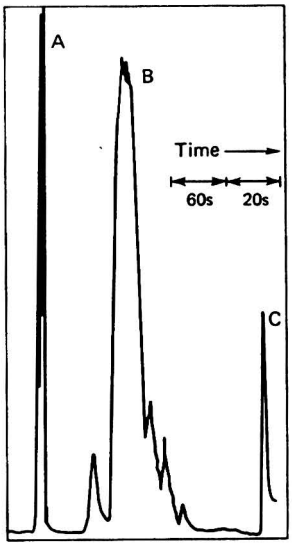

Fig. 3. Copper in milk with graphite furnace: A, drying; B, charring; and C, atomic-absorption signal shown; 25-μl sample.

TABLE III

SENSITIVITY DATA FOR ELEMENTS OBTAINED WITH FURNACE OF WOODRIFF, STONE AND HELD[22]

Element	Line/nm	Furnace temperature/°C	Sensitivity/g per 1 per cent. absorption	Detection limit/g*
Ag	328·1	1265	8×10^{-12}	$1{\cdot}2 \times 10^{-11}$
Cd	228·8	1200	9×10^{-12}	$1{\cdot}3 \times 10^{-11}$
Zn	213·9	1200	9×10^{-12}	$3{\cdot}9 \times 10^{-11}$
Pb	283·3	1200	1×10^{-11}	$5{\cdot}7 \times 10^{-11}$
Li	670·8	1200	1×10^{-11}	3×10^{-11}
Cu	324·7	1550	9×10^{-11}	$3{\cdot}2 \times 10^{-10}$
Mn	279·5	1200	8×10^{-11}	$2{\cdot}7 \times 10^{-10}$
Mg	285·2	1200	8×10^{-11}	$2{\cdot}5 \times 10^{-11}$
Fe	248·3	2200	1×10^{-10}	$2{\cdot}8 \times 10^{-10}$
Al	309·2	1550	2×10^{-10}	$5{\cdot}4 \times 10^{-10}$
Ni	232·0	2200	2×10^{-10}	$7{\cdot}3 \times 10^{-11}$
Dy	421·2	2200	1×10^{-10}	$2{\cdot}2 \times 10^{-10}$
Ho	410·4	2200	9×10^{-11}	$3{\cdot}3 \times 10^{-10}$
Er	400·8	2200	1×10^{-10}	$3{\cdot}7 \times 10^{-11}$
Ca	422·7	1200	1×10^{-10}	$5{\cdot}3 \times 10^{-10}$

* Amount producing absorbance value equal to twice experimental standard deviation of the blank.

for a 25-μl sample containing 0·05 p.p.m. of copper, which corresponds to the normal concentration in milk. This signal (C) is preceded by the non-specific absorption readings obtained at lower operating power during the evaporation of the water (A) and charring of the organic material (B) in the milk sample.

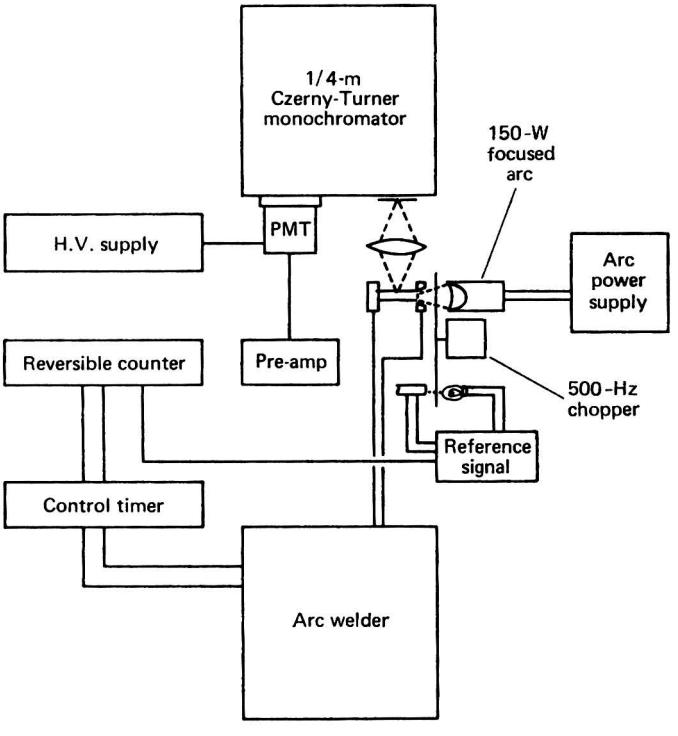

Fig. 4. Schematic drawing of graphite cell system for atomic-fluorescence spectroscopy. Photon counting detection system used (from Winefordner[1]) (PMT = photomultiplier)

Woodriff and co-workers[22,23,24] developed a graphite tube furnace device for AAS in which a tube 150 mm in length and of 7 mm i.d., heated by current from an electric-arc welder, is used. The sample is introduced into the tube on a carbon cup inserted through a side-arm of the tube, or it may be nebulised and carried into the tube with an inert gas; Table III illustrates the sensitivities obtained with this apparatus for fifteen elements. No significant matrix effects were observed from the presence of relatively large amounts of aluminium, chromium, copper, iron, nickel, manganese, zinc and magnesium on the atomic-absorption signal observed for 10^{-9} g of silver.

Winefordner[1] has described the construction of a graphite cell system for AFS studies. This is shown schematically in Fig. 4. The graphite tube is heated by an electric-arc welder of 300-A output, and sample solutions are introduced into the cell with a hypodermic syringe and needle inserted through a rubber septum in the front of the cell housing. A low flow-rate of argon is used to provide a continuously flushed cell. Radiation from a 150-W concentrated xenon arc lamp, modulated at 500 Hz by a mechanical chopper, is used as excitation source. A photon counting system is used to record the fluorescence emission after its detection through a $\frac{1}{4}$-m grating monochromator and photomultiplier. Analytical results obtained with this system have not yet been published, but it is expected that the apparatus will provide a versatile tool for AFS.

Headridge and Smith[25] have reported the construction of a simple induction furnace for determining volatile elements in solutions and volatile matrices by AAS. The arrangement of graphite tube and side electrode for sample introduction is similar to that of the L'vov furnace. The furnace is inductively heated to 1350 °C for routine use, although the maximum attainable furnace temperature is 1900 °C. The authors describe the use of the furnace for the determination of cadmium in 5-mg samples of zinc-base alloys within the concentration range 5 to 400 μg g^{-1} by using the cadmium 326·1 nm line, and in microlitre solution volumes, cadmium can be determined in the range 1 to 20 ng by using the cadmium 228·8 nm line.

FILAMENTS—

Atomisation techniques in which a wire loop or a sample boat carrying the sample is introduced into the hot flame gases above the primary reaction zone of pre-mixed flames can be traced back to the original work of Bunsen[26] in flame-emission photometry; several devices of this type have been re-introduced in the past 5 years for use in AAS. Several non-flame devices of the same type, but in which an electrically heated filament or boat is used, have also been reported recently. In these open devices, in which the atomic vapour released from the filament passes into an unconfined volume in the absorption or fluorescence light path, transient analytical signals are obtained, and it may be difficult to achieve freedom from interference effects when a large temperature gradient exists between the hot filament and the cooler volume above it in which atomic-absorption or atomic-fluorescence measurements are made. Because of the unconfined nature of the analytical cell volume in these devices, however, any tendency towards memory effects with some analyte elements may be minimised.

Ulfvarson,[27] Brandenburger and Bader[28] and Brandenburger[29] were able to detect nanogram amounts of mercury by collecting it as an amalgam on a wire and then heating the wire to vaporise the mercury into the optical path of an atomic-absorption spectrophotometer. Brandenburger and Bader[30,31] have also used this technique with a closed system in which the mercury vapour is confined within an absorption tube after vaporisation from the filament. The filament technique has also been applied to the AAS determination of cadmium, zinc, lead, tellurium, copper, silver, gold and platinum after electrolytic deposition on a wire filament.[28]

Bratzel, Dagnall and Winefordner[32] have described the application in AFS of a filament technique similar to that used by Brandenburger and Bader. In the device used by the former workers the sample solutions are vaporised from a platinum loop, which is positioned in a flowing stream of inert shielding gas. The vaporised analyte element is swept into the fluorescence light path where atomic fluorescence is excited by the electrodeless discharge tube; a d.c. electrometer system is used to measure the atomic-fluorescence signal. Typical absolute detection limits reported are cadmium, 10^{-15} g; mercury, 10^{-8} g; and gallium, 10^{-7} g.

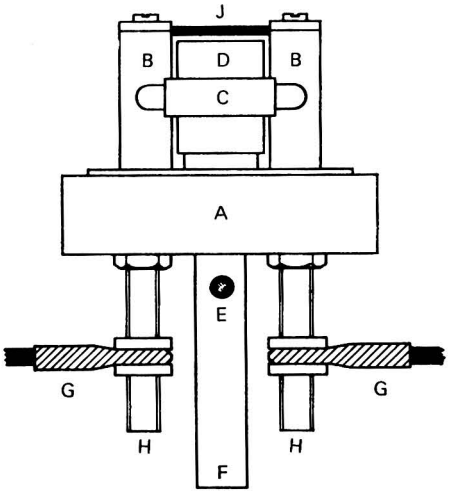

Fig. 5. Filament atom reservoir (from Alder and West[34]): A, base; B, water-cooled electrodes; C, water link between electrodes; D, laminar-flow box; E, inlet for shield gas; F, support stem for reservoir; G, transformer terminals; H, water inlet and outlet; and J, filament

West and Williams[33] have reported the construction and use in AAS and AFS of a device in which a graphite filament 2 mm in diameter and about 20 mm in length, supported by water-cooled stainless-steel electrodes, can be heated to between 2000 and 2500 °C within 5 s by passing a current of about 100 A at 5 V through it. The small liquid samples (5 μl) are placed on a depression in the filament and the assembly is housed within a chamber with quartz windows; this chamber can be purged with argon. The original device was used for the detection of silver and magnesium by AAS and AFS; 10^{-10}-g amounts of these elements were found to produce 1 per cent. absorption in AAS, while in AFS 10^{-16} g of magnesium and 3×10^{-11} g of silver could be detected. An improved design of the device, in which inert-gas shielding of the filament eliminates the need for a closed chamber assembly, is shown in Fig. 5.[34] Table IV shows the limits of detection and maximum amounts for a range of elements that can be determined by AFS with this type of assembly. Typical sensitivity values (for 1 per cent. absorption) and detection limits for AAS work with similar devices are given in Table V. As with other non-flame cells, *e.g.*, the L'vov and Massman furnaces, in

TABLE IV

DETECTION LIMITS AND UPPER DETERMINATION LIMIT DATA IN AFS WITH FILAMENT ATOM RESERVOIR OF WEST *et al.*

Element	Limit of detection/g*	Maximum determinable amount/g	Reference (West *et al.*)
Ag	1×10^{-12}	2×10^{-9}	35
Au	4×10^{-12}	—	36
Bi	1×10^{-11}	1×10^{-8}	35
Cd	$1{\cdot}5 \times 10^{-13}$	—	34
Co	2×10^{-11}	6×10^{-9}	37
Cu	1×10^{-12}	4×10^{-9}	37
Ga	5×10^{-11}	1×10^{-8}	35
Mg	1×10^{-12}	1×10^{-9}	35
Mn	5×10^{-12}	2×10^{-9}	37
Ni	5×10^{-12}	5×10^{-9}	37
Pb	1×10^{-11}	$1{\cdot}5 \times 10^{-7}$	35
Sb	1×10^{-9}	3×10^{-8}	37
Tl	5×10^{-11}	2×10^{-9}	35
Zn	2×10^{-14}	4×10^{-10}	35

* Signal: noise = 2.

TABLE V

AAS SENSITIVITY DATA OBTAINED WITH CARBON FILAMENT ATOM CELL OF WEST *et al.*

Element	Sensitivity/g per 1 per cent. absorption	Detection limit/g	Reference (West *et al.*)
Al	6×10^{-10}	2×10^{-9}	39
Cu	$3{\cdot}3 \times 10^{-11}$	5×10^{-11}	39
Mn	5×10^{-11}	5×10^{-11}	40
Ni	$2{\cdot}4 \times 10^{-10}$	3×10^{-10}	39
Pb	7×10^{-12}	5×10^{-11}	39

which pulse atomisation is effected, it is important that the response time of the electronic circuitry used is fast enough to permit accurate recording of the AAS or AFS signal *versus* time relationship. Under these conditions either peak height or integration methods of measurement can be used. Additionally, with the filament device, and in contrast to the L'vov and Massman furnaces, no further energy is available in the space above the filament immediately after the vaporisation pulse to prevent condensation of the atomic vapour. The decay of the atomic population is therefore promoted by condensation of analyte atoms with their own species or with the atoms or molecules formed from concomitant elements present in the sample. The effective lifetime of the free atoms may therefore be considerably shorter than when a furnace system is used. Hence it is necessary to view the atomic vapour in AAS or AFS close to the filament if inter-element effects are to be minimised. Fig. 6 illustrates the manner in which the absorbance obtained for copper, nickel, lead and aluminium decreases as the height of observation above the filament is increased.[39] Interference effects from volatile matrix elements have been observed with the carbon-filament device to be generally more serious than those observed from these elements in flames; interference effects from refractory oxide-forming elements, however, appear to be significantly less troublesome with this device than the effects observed in flame cells. This most probably arises from the fact that inter-element effects occur in the vapour phase above the filament on condensation of those (more volatile) elements which readily vaporise from it, whereas it is difficult to vaporise the more refractory elements from the filament.

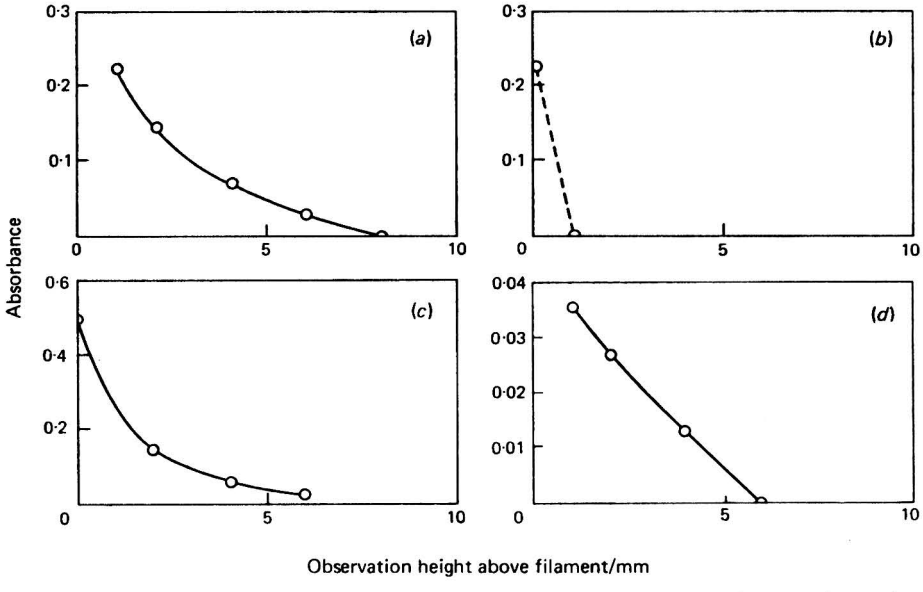

Fig. 6. Variation of absorbance with height of observation above filament for various elements (from Anderson, Johnson and West[39]): (*a*) copper; (*b*) aluminium; (*c*) lead; and (*d*) nickel

Amos[41] has described the use of a modified form of the carbon-filament device used by West *et al.*; a hole is drilled through the rod to form a sample cavity into which the small liquid sample can be introduced, and this cavity may permit the use of smaller sample volumes (0·5 to 1 μl) for AAS. Additionally, Amos describes the use of the filament device within a hydrogen-diffusion flame, which is produced by replacement of the argon or nitrogen shield gas by hydrogen. In operation, the glowing rod then ignites the hydrogen and a diffusion flame results. These modifications may give rise to improved atomisation, particularly for less volatile elements, and tend to minimise inter-element effects. In a study of the determination of lead in biological materials, for example, Amos *et al.*[42] observed considerably less serious spectral and chemical interferences from other ions when the rod was surrounded by the hydrogen-diffusion flame.

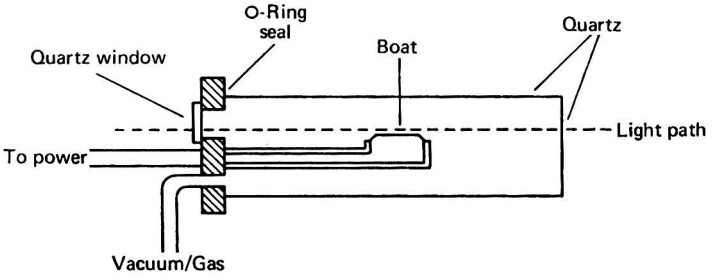

Fig. 7. Absorption chamber and filament assembly used by Donega and Burgess[43]

Donega and Burgess[43] have assembled a filament device similar to that used by West and co-workers, but in which sample boats are cut from graphite sheet or tantalum or tungsten foil to be 50 mm long and 6 mm in width. The assembly used is shown in Fig. 7. The sample boat is heated electrically with a current of 30 to 50 A at 12 V, which is sufficient to heat the boat to about 2200 °C in less than 0·1 s. The two copper rods that support the sample boat are insulated and pass through the brass base-plate, which contains an O-ring seal and to which a quartz window is also attached. The filament assembly is enclosed in a quartz tube 50 mm in diameter, which has an optical quartz window sealed on one end and an O-ring flange on the other. The chamber can be purged with inert gas and used at operating pressures between 1 and 760 torr. The device can be used with volumes of liquid samples as large as 50 to 100 μl. The mode of operation is similar to that used by West *et al.* for the carbon-filament atom cell. Table VI shows some sensitivities obtained. No results for the

TABLE VI

ABSOLUTE SENSITIVITIES REPORTED FOR FILAMENT TECHNIQUE OF DONEGA AND BURGESS[43]

Element	Wavelength	Sensitivity/g	Operating conditions*
Al	309·3	4×10^{-10}	1
Cr	359·4	6×10^{-12}	2
Cu	324·8	3×10^{-12}	2
Mn	279·5	3×10^{-12}	2
Mo	313·3	3×10^{-9}	3
Ni	341·5	3×10^{-9}	2
Pt	265·9	3×10^{-7}	2
Si	251·6	3×10^{-9}	2
Na	589·0	3×10^{-11}	4
V	318·4	6×10^{-10}	1

* 1. Tantalum boat, 300 torr hydrogen.
2. Tantalum boat, 300 torr argon.
3. Tungsten boat, 1 torr argon.
4. Graphite boat, 100 torr argon.

effect of matrix elements on the sensitivity have yet been reported. The method of operation at low pressure should result in low background absorption interference, in the same manner as that reported by Massman for the hot hollow-cathode technique, but this can be achieved only at the expense of short residence time in the effective absorption volume and the requirement of a fast-response detector system.

CATHODE-SPUTTERING CELLS—

The sputtering action, which is responsible for the production of atomic vapour within a hollow-cathode lamp, can be exploited for the atomisation of samples for AAS. Thus Walsh and co-workers[44,45] constructed a sputtering chamber in which metal samples, machined to the shape of an open-ended hollow cathode, were clamped. The chamber was then evacuated, filled with argon at the required pressure, and a discharge initiated as in a conventional hollow-cathode source. The sputtering chamber was fitted with silica windows and could be placed in the light path of an atomic-absorption spectrophotometer. The determination of silver and phosphorus in copper, and silicon in aluminium and steel, with this device has been reported.[46] A disadvantage of the technique is the need to prepare the cathode from the sample itself; this tends to restrict the technique to metal samples. In order to avoid this restriction, Goleb and Brody[47] evaporated sample solutions on to the inner wall of an aluminium hollow cathode, which was then used as part of a water-cooled de-mountable hollow-cathode lamp with a continuous flow low-pressure system. Only small sample volumes were required, and 1-μg amounts of sodium, calcium, magnesium, silicon and beryllium were detected; considerable inter-element effects were observed. Goleb[48] has also applied this device as an atom source for the isotopic analysis of uranium. Ivanov, Gusinsky and Jesikov[49] have used a graphite hollow cathode in a sputtering cell; in this way they achieved some of the advantages of the graphite cuvette technique in addition to those gained from the sputtering cell technique. Sample solutions were evaporated directly on to the walls or on to a fine molybdenum wire, which was then placed along the central axis of the cathode.

Massman[50] has described the use of a hot hollow-cathode assembly for AAS determinations with solid samples. In this apparatus a graphite tube (30 mm in length and of 7 mm i.d.) is supported on a small cylindrical graphite electrode that passes through the wall of the cathode tube. This carrier electrode also holds the solid sample in a depression 2 mm in diameter and 3 mm deep bored out of its end; the dimensions of this depression can be varied, depending on the sample size. The cathode assembly is mounted on a 2-mm diameter molybdenum rod whose insulated base passes through the water-cooled base-plate of the metal housing of the assembly. This housing acts as the anode and is at ground potential. The compartment is fitted with quartz windows and can be purged with argon. The discharge is then operated at an argon pressure in the range 1 to 10 torr at a power of up to 1 kW. When hollow-cathode cells of this type are used as the atom cell in AAS, the cathode continuum radiation and emission from the sample itself might be expected to interfere seriously with the measurement of the absorption of the radiation from the primary source. With cool cathodes this interference is difficult to avoid, as the atomic vapour persists only while the discharge current is being applied. Massman pointed out that this difficulty can be overcome with the hot-cathode device, as under suitable operating conditions atomic vapour may persist after the discharge current has been allowed to fall to zero. When the graphite hollow-cathode discharge is operated with a 50-Hz half-wave current, therefore, the discharge, which creates an atomic vapour, is present for only one half of the operating period. During the alternate discharge-free half-period the atomic vapour may still persist, so that its absorption of the primary source radiation can be measured without interference. In the instrumental assembly described by Massman, the radiation from the hot-cathode atom cell itself is prevented from being recorded at the monochromator - detector assembly by the use of a rotating sector, which is driven in phase with the discharge current cycle and is placed between the cell and the monochromator slit. This sector transmits the primary source radiation only during a prescribed period (just less than one half cycle) while the discharge current is at zero. The primary hollow-cathode lamp radiation is modulated at 450 Hz by a second rotating sector placed between the source and the graphite cathode cell. When the peak-absorption signal is measured, linear calibration is possible only over a narrow working range, *e.g.*, 1 to 10 p.p.m. of silver in a 30-mg sample of lead. When signal integration is used it is possible to achieve improved linear range. Thus, for example, 1 to 300 p.p.m. of

silver in lead then yields a linear working graph. In the analysis of lead, zinc or aluminium samples (30 mg) coefficients of variation of 8 to 15 per cent. were obtained. In the determination of silver in lead with integration of the absorption signal a standard deviation of 4 per cent. was achieved.

The hot graphite hollow cathode cannot be heated above about 2000 °C, so that only those samples whose evaporation proceeds rapidly below this temperature can be analysed. The method is more suitable for the determination of relatively low concentrations of volatile elements in milligram amounts of samples such as lead, zinc or aluminium than for the determination of small absolute amounts of analyte element. This situation results from the short residence time of the atomic vapour in the absorption volume at the low pressure used. The vaporisation rate of samples in which metals such as iron, nickel and copper are the major elements is too slow to allow their effective analysis by this technique. When these elements are present as impurities in more volatile matrices, however, the evaporation rate may be sufficiently high to permit their determination. Table VII shows the detection limits obtainable with this device for the determination of various elements in 30-mg samples of relatively volatile matrices. These values are compared with the detection limits obtained for the same samples by emission spectrography with a hot hollow cathode and a medium quartz spectrograph.[51] Even with large sample weights (100 mg) of lead, zinc, antimony or aluminium, less than 1 per cent. interference is encountered from background absorption at wavelengths greater than 220 nm. From this point of view the hot graphite hollow cathode operated at low pressure may be superior to graphite furnaces operated at atmospheric pressure for large samples.

TABLE VII

DETECTION LIMITS WITH HOT HOLLOW CATHODE FOR DETERMINATION OF VARIOUS ELEMENTS IN SOLID METAL SAMPLES (FROM MASSMAN[50,51])

		AAS method		Atomic-emission method	
Element	Sample 30 mg	Line/nm	Detection limit/p.p.m.	Line/nm	Detection limit/p.p.m.
Ag		328·0	0·3	328·0	0·1
Sb		231·1	50	252·85	1·0
Zn		213·9	0·05	213·9	0·5
Cu	Lead	324·7	2·8	324·7	0·3
Cd		228·8	0·01	228·8	0·2
Mg	Zinc	285·2	1·2	—	—
Mn		279·5	2·2	—	—
Cr	Aluminium	357·9	10	—	—

OTHER NON-FLAME CELLS—

The use of the d.c. arc for sample atomisation in AAS has been described by several workers.[52,53,54] Robinson[55,56] has reported that 20 per cent. absorption was obtained for aluminium by using a spark to atomise the sample; the solution was nebulised in the conventional fashion and the aerosol was passed between two electrodes between which the spark was struck. There have been several reports of the use of RF or microwave plasma sources to atomise samples for AAS. Wendt and Fassel[57,58] used an induction-coupled plasma together with a triple-glass optical system to obtain large absorbance signals for AAS. Friend and Diefenderfer[59] investigated the possibility of using a plasma jet for the determination of refractory elements. The RF plasma has recently been applied to AAS by three groups of workers.[29,60,61] These plasma systems, some of which have previously been used extensively for analytical emission spectroscopy, show great promise for AAS. The high energy available should permit considerable freedom from matrix interference effects, and the possibility of transferring samples to the plasma with low inert-gas flow-rates should result in high atomic concentration for the analyte element and high sensitivity. Greater control over the chemical environment can be achieved with plasma than with flames, and consequently the lifetime of free ground-state atoms may be greater in these atom cells.

The use of lasers offers the possibility of direct atomisation for the examination of solid surfaces by AAS. The heat produced at the solid when a focused laser beam strikes it may vaporise the solid material over a small area of the surface.[62,63,64] This technique has been

used in spark-emission spectroscopy; a spark is passed across electrodes placed just above the surface so that it passes through the plume of vapour produced by the laser. In AAS this direct sampling and atomisation method should provide for low-emission background and high sensitivity for small solid samples. In the laser microprobe - AAS assembly devised by Mossotti, Laqua and Hagenah[62] a pulsed laser system is used to produce rapid heating and vaporisation from the sample surface. The atomic absorption in the transient atomic vapour produced is then measured with a fast-response system.

Venghiattis[65] has proposed a technique for the direct conversion of solid samples into atomic vapour, in which the powdered sample is mixed with a solid-propellent powder; the mixture is then compressed and ignited. The atomic vapour of the analyte element in the gases of the "flame" that is produced then passes into the absorption light path of a conventional atomic-absorption spectrophotometer. Calibration can be performed by the similar technique of mixing standard samples with the propellent mixture. The technique has been applied to the determination of trace elements such as gold, silver, copper, lead and zinc in ores. Although it may be difficult to achieve better than 5 per cent. precision without very careful sample preparation, this technique may find considerable application in the field or "on-site" where the transportation or use of gas cylinders, solutions and chemicals is inconvenient.

Conclusion

The development of non-flame atom cells during the past few years has shown these devices to provide capabilities complementary to those of flame cells. High absolute sensitivity is attainable, which permits very small samples to be examined effectively by AAS. The analytical selectivity is high for these applications. Provided that suitable sources and detector systems are available, the use of non-flame cells should be of considerable benefit in AFS, with which the low emissive background obtainable in suitably designed non-flame cell systems should assist the attainment of high sensitivity. The results for precision obtained with many of the devices reviewed here are not as satisfactory as those obtainable with flame systems; when both the stability and response time of the detector as well as the cell design are optimised, however, it is the reproducibility of the sample transfer to the cell that may at present limit the precision attainable. Efforts to improve the sample transfer reproducibility are warranted only if the 5 to 10 per cent. coefficients of variation typically attained in normal working are unsatisfactory. For very small samples containing traces of analyte element, coefficients of variation of about 5 to 10 per cent. may often be acceptable.

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SLEPT: A Simple Computer Language for Examining Data Recorded on Punched Paper Tape

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A versatile language has been developed for the computer processing of paper tape output from multi-channel analysers. It is intended for use in laboratories in which the work load is too varied to justify writing a program, or suite of programs, dedicated to a specific set of operations. The language consists of a set of commands and associated information, which is read from cards and executed by a program written in FORTRAN IV. The program has a modular structure so that new commands can easily be incorporated into the language as required.

MANY nuclear experiments result in data, such as pulse height spectra, which are stored in multi-channel analysers and subsequently punched on to paper tape. In many instances the data required from the resultant tapes are few, *e.g.*, peak locations and areas, or the area under selected peaks. A large number of versatile and comprehensive programs have been written for digital computers for processing such information. For example, Wangen and Isenhour[1] have described the semi-quantitative analysis of mixed γ-ray spectra by computerised learning machines, while Hoffman and Wainerdi[2] have developed a computer program for least squares resolution of γ-ray spectra by using half-life information as well as γ-ray energies. Dams and Adams[3] have developed a program by using about 2000 precise γ-ray energies of 250 radioisotopes for the computer-assisted identification of individual γ-ray emitters in complex spectra. Black[4] and Connelly and Black[5] have investigated the use of cross-correlation techniques for the identification of structure in γ-ray, X-ray and neutron spectra, and for the calculation of peak areas. Several other programs are also available for the reduction of γ-ray spectra,[6,7,8] and Yule[9] has given an extensive discussion and review of the type of calculation carried out on pulse height spectra.

Many of the computer programs described in the literature have been developed for specific systems in which the tasks they are required to undertake are well defined. Also, they are used extensively, so that the effort expended in writing such programs can be readily justified. In many laboratories, however, particularly those conducting research and development, the number of tasks performed is varied, with little common activity between tasks. For example, one laboratory may be carrying out fast-neutron and thermal-neutron activation analysis, charged-particle activation analysis, prompt γ-ray studies, multi-scaling exercises, etc. Under such circumstances the data may consist of a relatively small number of spectra that have been obtained by using a set of unique instrumental settings. The intensity of effort on any one exercise may, therefore, not justify a large expenditure of programming time and expertise dedicated to each of the specific studies. In this type of situation, most of the information is often accumulated in multi-channel analysers operating in either the pulse height analyser or time-scaling mode, and recorded on punched cards, magnetic tape or punched paper tape before being further processed by an off-line digital computer.

SLEPT is a program written in FORTRAN IV and implemented on an IBM 360/75 computer. It has a simple language structure and has been developed for the off-line

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processing of information collected in multi-channel analysers and stored on punched paper tape. It consists of a series of commands that enables relatively simple operations to be carried out on the data to be manipulated.

TABLE I

VOCABULARY OF SLEPT

Command	Information	Function
TITLE	Title associated with spectrum	Converts image of paper tape into integer values
EDIT	Number of channels between channel identifiers	Drops channel identifiers included in paper tape output
DROP	Number of channels at beginning of spectrum to be dropped	Drops the first "*n*" channels
CHANNEL ..	Number of channels in spectrum	Allows the first "*n*" only channels of a spectrum to be read in
DIGIT	Maximum number of digits in channel content	Controls number of digits per channel
FIND	Number of spectrum required	Permits jumping to any specified spectrum
SKIP	Number of spectra to be skipped	Omits the specified number of spectra before executing next TITLE
BGD	Title associated with background	Reads in a spectrum to be used as a background
DIFF	—	Calculates first forward differences
BEDIT	Number of channels between channel identifiers	As for EDIT but operates on spectrum read in by using BGD
BDROP	Number of channels at beginning of background spectrum to be dropped	As for DROP but operates on spectrum read in by using BGD
BDIFF	—	As for DIFF but operates on spectrum read in by using BGD
STANDARD ..	Two numbers the ratio of which gives the scaling factor	Adjusts the contents of all channels by a scaling factor
SMOOTH	Number giving number of channels to be used for smoothing	Smooths raw data
SUB	—	Subtracts background spectrum from spectrum under consideration
AREA	Two numbers identifying two channels	Sums the contents of all channels between and including those specified in information field
COVELL	Two numbers giving approximate peak position and number of channels either side of peak	Finds exact peak maximum and obtains Covell area
PEAKS	Number giving the number of channels used for smoothing	Smooths the raw data and locates peaks and valleys in spectrum
LIST	Number giving channels per line	Lists channel contents on line printer
PUNCH	—	Punches channel contents on to cards
PLOT	New title (if desired)	Plots data on plotter and line printer
SCALE	New title (if desired)	Plots data, with scale expansion, on plotter and line printer
LINE	—	Specifies line plotting on plotter
POINT	—	Specifies point plotting on plotter
END	—	Indicates end of data (optional)
Blank	Anything	If first four columns are blank treats remainder of the card as comment

GENERAL FEATURES—

Because of the diverse nature of the type of information stored on the paper tape and the variety of processing required, a simple language structure has been evolved for processing the data. The paper tapes are read into the computer, and the codes corresponding to each

character on the tape written sequentially on to magnetic discs. All that is required of the operator who needs to manipulate the stored data is that he should submit a series of punched control cards containing commands referring to the data manipulation required.

The control cards have been designed so as to have maximum clarity and as little format control as possible, and the control commands have been kept as close as possible to the actual words used to describe the operations performed. The card is split into two fields, the command being stored in the first eight columns and all other required information, in free format, in the remaining seventy-two columns of the card. When the command is executed by the program the data in the information field are processed as specified by the command. For example, when the command is that which requires a new spectrum to be read in, the data in the information field are taken as the title of the associated spectrum. If, on the other hand, the command is to find the area within a specified region of the spectrum, the data in the information field will give either the limits of integration or the approximate position of the peak, together with the number of channels either side of the peak over which integration is required, depending on the command given. Cards, each containing one command with the associated requisite information, are separately and sequentially processed until all have been treated. Because of the combination of commands resembling the operations specified, the restriction of one command to each card and the sequential processing of such cards, the input to the program thus has the appearance of a simple programming language. This has the advantage, among others, that it is very simple to learn, and involves the use of the minimum number of mnemonics and rules. Restriction of one command and its associated information to each card and the sequential processing of cards - commands enable a program of treatment given to any set of spectra to be easily and logically written and clearly followed. The program has been designed in a modular form so that, as new techniques for treating the data are required, suitable sub-routines can be added to the system and corresponding new commands added to the vocabulary of the language.

CURRENT STRUCTURE—

A list of the commands currently implemented in the language, together with the associated information and an outline of the corresponding action, is given in Table I. The commands can be categorised into three groups: (*a*) input of data and associated editing; (*b*) data processing; and (*c*) output of data; and will be discussed according to this classification.

Input and editing—Several analysers are available in this laboratory giving data output on to eight-hole paper tape in ASCII code under a number of different formats. These include either five or six digits per channel with, in some instances, the channel number at regular intervals for channel identification. In addition, output from one analyser is often produced in such a way that the sum of all previous channel contents is punched, rather than specific channel contents. To allow for the different number of digits per channel a command DIGIT is provided with the appropriate number in the information field to specify this value. Unless otherwise specified there is a value of six digits per channel automatically incorporated in the program. The command TITLE, on execution, reads the image of the paper tape stored on disc and converts it into a series of integer numbers corresponding to channel contents (and channel numbers if these are punched on to the tape). The data in the information field of a command card are assumed to be an alphanumerical identification of the spectrum, and are printed on the line printer as the command is executed. If channel identification is punched on to the tape, these values will be included in the data obtained with TITLE and can be eliminated with EDIT command. For the latter, the integer value in the information field specifies the number of channel contents punched between channel identifiers. Data punched on to tape in the integration mode can be restored to channel contents (after EDIT-ing, if necessary) by obtaining the forward differences with the command DIFF. Channels containing unwanted information at the beginning of the spectrum can be deleted with the DROP command. In this event, the integer in the information field gives the number of channels to be dropped. A background spectrum can be read in and stored separately by using BGD, which is effectively a TITLE command but with reserved storage for the resultant spectrum for subsequent background subtraction exercises on other spectra; BEDIT, BDROP and BDIFF are EDIT, DROP and DIFF commands, which operate only on the background spectrum. The command FIND is an instruction to prepare to start input on the n^{th} spectrum in the sequence of spectra stored on the paper tape, where n is an integer in the information

field. In normal use a new TITLE card causes the immediately subsequent spectrum on the tape to be read in. The use of the FIND command enables the spectra to be read in and treated in any desired order. In a similar manner, SKIP causes n spectra to be skipped before executing the next TITLE command, where n is an integer in the information field.

Data processing—Typical operations carried out on the resultant spectrum are peak location, the calculation of the number of counts between specified channels with background correction, determination of the area under a peak by using the method of Covell,[10] spectrum smoothing, the subtraction of a background spectrum and the multiplying of all the channel contents of a spectrum by a constant factor to allow standardisation to a normalised flux, live time, etc.

TABLE II

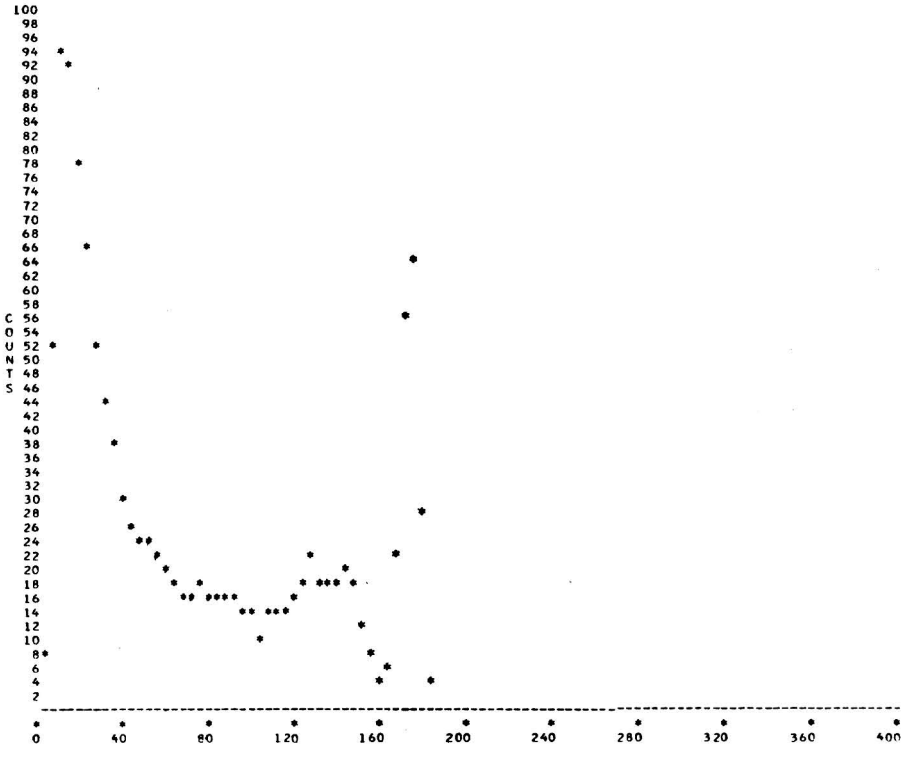
EXAMPLE OF A SLEPT PROGRAM
Tape 4CW6

Spectra of irradiated samples with decay curves taken 10 minutes after irradiation

```
TITLE    NO. 1, 5 MIN. IRR., 2 MIN. DELAY, 1 MIN. COUNT
EDIT     8
LINE
PLOT
LIST
COVELL   176 7
TITLE    NO. 1, MULTISCALING, 1 SEC. STEPS
EDIT     8
DROP     3
POINT
PLOT
PUNCH
LIST
CHANNEL 256
TITLE    NO. 2, 1 MIN. IRR., 1 MIN. DECAY, 5 MIN. COUNT
EDIT     8
LIST
LINE
PLOT
COVELL   176 7
CHANNEL 512
TITLE    NO. 2, MULTISCALING, 5 SEC. STEPS
EDIT     8
DROP     3
POINT
PLOT
LIST
PUNCH
END
```

A control card with the command SUB causes a 1 : 1 subtraction of a background spectrum, which is previously read in with a BGD command, from the spectrum currently being manipulated. An AREA control card instructs the program to calculate the total number of counts in the region bounded by the two channel numbers in the information field. The command SMOOTH permits smoothing of the spectrum, by quadratic convolution,[11,12] the number of points involved in the smoothing being given by the integer in the information field. The PEAKS command produces a listing of the channel numbers at which peaks and valleys occur in the spectrum. The criterion used is the change in sign of the first differential of the smoothed data and a statistical test for a peak. The number in the information field specifies the number of channels over which smoothing takes place. The area under a peak with a local maximum near channel "n" and "$2m + 1$" channels wide is obtained with the COVELL instruction, in which n and m are specified in the information field. The peak maximum does not need to be specified accurately as the program searches for the local maximum in the region. The command STANDARD permits normalisation to a given value of neutron flux, beam current, counting time, etc. Two values are provided in the information field, the first being the value of the parameter for the spectrum (actual flux, etc.) and the second the desired value. All channel contents are multiplied by the ratio of these numbers.

```
NO. 1 5 MIN ERR, 2 MIN. DELAY, 1 MIN. COUNT
              2CRB 946  BOSWELL POINT 2                3000
MAXIMUM COUNT IN ANY CHANNEL -    3903
NUMBER OF COUNTS PER LINE IN PAGE PLOT -   78
NUMBER OF CHANNELS IN SPECTRUM          -  512
NUMBER OF CHANNELS PER POINT IN PLOT    -    4
```



COUNTS IN CHANNEL

0	0	333	165	843	1293	1796	2144	3083	3526	3587
10	3903	3759	3743	3531	3526	3610	3389	3092	3007	2867
20	2745	2488	2619	2466	2257	2169	1893	1899	1893	1879
30	1636	1546	1577	1600	1532	1425	1370	1287	1169	1147
40	1083	1105	1051	978	1000	1010	977	912	969	965
50	1036	905	895	896	841	875	858	864	855	825
60	808	763	790	713	686	689	664	660	690	652
70	714	737	722	710	723	738	703	696	625	659
80	682	616	667	665	685	664	671	675	657	634
90	642	658	631	648	602	595	605	658	584	586
100	609	593	0	543	571	616	588	577	587	589
110	612	618	591	567	625	633	663	579	619	651
120	623	693	786	813	902	880	908	871	821	810
130	716	771	703	729	719	740	745	769	747	813
140	854	846	830	811	803	841	726	668	623	593
150	477	445	420	335	289	247	232	219	197	208
160	195	228	279	341	489	718	991	1351	1724	2079
170	2404	2644	2807	2687	2466	2130	1655	1230	931	671
180	399	238	148	96	60	42	27	24	19	18
190	14	17	13	19	14	19	17	13	18	22
200	18	19	7	13	10	17	18	16	11	15
210	9	13	14	14	5	14	6	10	10	6
220	7	6	7	7	4	7	10	5	11	13
230	8	5	7	10	10	10	5	3	6	8
240	4	6	7	12	13	17	8	17	18	16

```
COVELL METHOD

COUNTS IN REGION BETWEEN CHANNELS.  166 AND   180
                          TOTAL COUNTS =     26458
                          BACKGROUND   =      9723  BY TRAPEZOIDAL INTEGRATION
                          DIFFERENCE   =     16735
```

Fig. 1. Partial listing of results of first LIST command and that produced by the subsequent COVELL command

Output of data—The spectrum obtained after manipulation with any of the above commands can be printed on the line printer by using the command LIST with the number of channels printed per line given in the information field. Alternatively, it can be stored on punched cards for further processing with the control card PUNCH, while PLOT enables graphs of the data to be produced on both the line printer and an off-line plotter. Plotting with scale expansion of the ordinate is accomplished with SCALE. If the information field is blank in both PLOT and SCALE commands, then that from the TITLE card is reproduced on the graph for identification. Otherwise the content of the PLOT or SCALE control card information field is included as a title in the graph. Two plotting modes are available and are chosen by the appropriate command, *viz.*, POINT or LINE. Unless specified, line plotting is normally used and the selected mode is held until it is re-specified.

Two other control cards are used: END specifies the end of a batch of cards and is optional because if it is not included in the deck, the sub-routine, which reads in the control cards, creates a dummy end card. A card that has the first four columns blank is assumed to be a comment card, and any data stored in the other 76 columns are reproduced in the control card listing but are not processed.

A set of SLEPT cards is read and stored by the computer under the control of the main sub-routine of the program. Each card is then examined by a controlling sub-routine that checks the command against a dictionary of valid commands and calls the appropriate sub-routine. The content of the information field is transferred to this sub-routine as an array of literal data. If numerical values are required from this array they are extracted by the use of two further sub-routines, which effectively enable this array to be read, in free format, as a dummy data card. On completion of the processing specified by the command, control returns to the controlling sub-routine for processing of the next control card.

An example of the type of SLEPT program possible is shown in Table II. In this example, the paper tape input consisted of a series of γ-ray spectra, each separated by the

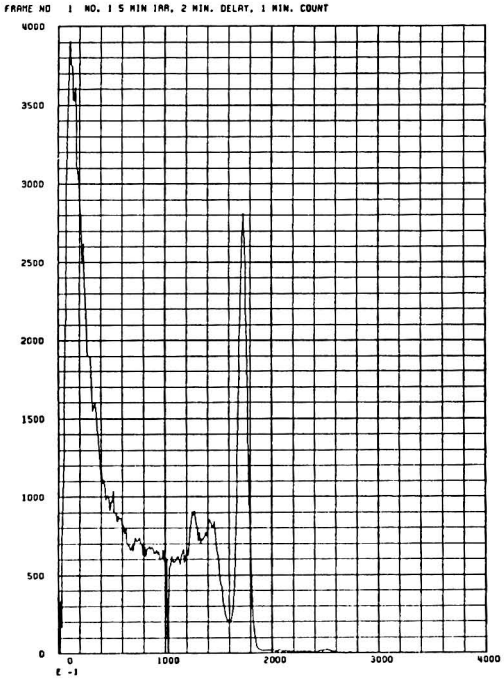


Fig. 2. Graph produced on the off-line plotter by PLOT command corresponding to results shown in Fig. 1

results obtained from a multi-scaling operation. Graphs of the former, obtained by using the line mode, were required as was the Covell area of a peak under channel 176. Point graphs of the multi-scaling operations were required after the contents of the first three channels had been dropped. The multi-scaled data were also required to be punched on to cards for further processing. All of the paper tape output had channel identifiers, after each 8-channel content, which had to be removed by editing. Only the first 256 channels of the last spectrum were required to be processed. As 512 channels were recorded in the multi-scale mode, it was necessary to re-set the number of channels read in after the CHANNEL command had set the number of channels to 256. Listings of all data were required.

Some of the output corresponding to the SLEPT program shown in Table II is given in Figs. 1 and 2. A partial listing of the results of the first LIST command and that produced by the subsequent COVELL command is given in Fig. 1. Fig. 2 is the graph produced on the off-line plotter by the corresponding PLOT command.

Discussion

One of the criteria in designing the program was to maintain its modular structure with as little interaction as possible between various commands. The program therefore consisted of a controlling sub-program and a modular set of sub-routines, all of which are virtually independent of each other. After constructing the spectrum with the TITLE, EDIT and DROP commands, the channel contents are stored in two separate arrays, one of which is used for data manipulation as in SMOOTH, etc., while the other is effectively a "read only" store that can be used for restoring the channel contents after such manipulation.

By design, all of the commands implemented in SLEPT perform relatively simple operations, but the structure of the program is such that any new features can be added to the language with considerable ease. It enables a wide variety of tasks to be performed on different types of information stored on paper tape in a number of formats. The program, together with library plotting sub-routines, currently occupies 220 K bytes and, apart from the plotting routines, requires no special facilities. In the version used here the image of the paper tape is stored on discs, but modification of the appropriate sub-routines will enable it to be adapted to any other system. The program with the corresponding SLEPT language can therefore be used on any system (provided the core storage is available) capable of handling IBM FORTRAN IV.

The use of SLEPT is particularly appropriate in laboratories that produce a wide variety of data which require simple non-routine processing. A SLEPT program is easy to write and is self-explanatory, and the language can be learnt and used in a very short time. A listing of the program is available from the author on request.

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The Atomic-emission Spectroscopy of Rhenium in the Nitrous Oxide - Acetylene Flame

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Rhenium can be determined by atomic-emission spectroscopy by use of a pre-mixed nitrous oxide - acetylene flame supported on a 6-cm slot burner. The limits of detection were 0·7 μg ml^{-1} (346·1 nm) and 1·5 μg ml^{-1} (488·9 nm); analytical working curves were linear for rhenium concentrations below 200 μg ml^{-1} at both wavelengths. Spectral interference from palladium, nickel, rhodium, cobalt and large amounts of lanthanum or phosphate occurred at 346·1 nm and from large amounts of aluminium at 488·9 nm. A number of elements gave rise to chemical interference, but this was eliminated by the addition of sulphuric or phosphoric acid. A monochromator giving a spectral band pass of the order of 0·1 nm must be used for the determination, and background corrections must be made either by wavelength scanning or by measurement at the peak and at an adjacent wavelength.

During the past decade, the use of atomic-emission spectroscopy in flames has been neglected compared with the rapid growth of atomic-absorption spectroscopy. However, in recent years there has been a renewal of interest in atomic-emission spectroscopy, mainly as a result of investigations with high-temperature pre-mixed flames and more sophisticated optical instrumentation than had been used previously. Pickett and Koirtyohann,[1] by using a nitrous oxide - acetylene flame supported on a conventional slot burner, have achieved detection limits for many elements that are comparable with those obtained by atomic-absorption spectroscopy. The advantages of pre-mixed, high-temperature flames and monochromators of moderately high dispersion (band passes of the order of 0·1 nm) have been emphasised by these authors,[1,2] and atomic-emission spectroscopy should shortly emerge as a complementary technique to atomic-absorption spectroscopy, particularly for the non-routine analysis of uncommon elements.

Atomic emission has been observed from rhenium in the oxygen - hydrogen turbulent flame,[3] the inner cone of the air - acetylene flame,[4] and in the pre-mixed oxygen - acetylene flame.[5,6,7] Schrenk, Lehman and Neufeld[8] have carried out an investigation into the atomic-absorption characteristics of this element in oxygen - acetylene flames, but almost no information is available concerning the formation of rhenium molecular species in flames. Pickett and Koirtyohann[1] have reported a detection limit of 0·2 μg ml^{-1} of rhenium by atomic-emission spectroscopy with a nitrous oxide - acetylene flame; this is substantially lower than could be obtained by atomic-absorption spectroscopy. However, no systematic examination of this element has yet been carried out.

Experimental

Apparatus—

Results were obtained by using a Techtron AA-5 atomic-absorption spectrophotometer with a mechanical chopper accessory for atomic-emission measurements. The 0·5-m Ebert monochromator with an f 10 aperture and a 50 × 50-mm^2 grating with 638 lines mm^{-1} gave a reciprocal linear dispersion at the exit slit of 3·3 nm mm^{-1} in the first order. An HTV R213 (Hamamatsu TV Co) photomultiplier was used as a detector, operating at 325 to 800 V. The signal was fed to a 285-Hz phase-sensitive amplifier, then to a potentiometric chart recorder (Servoscribe RE511, Smiths Industries Ltd.). A geared motor drive was made for the monochromator, which enabled wavelength scanning to be carried out at 0·6 nm min^{-1}.

A conventional 6-cm slot, grooved Techtron burner was used throughout. Gas flow meters on the spectrophotometer were calibrated at 20 °C for the gases used against a wet

gas flow meter that had recently been standardised. Instrument operating parameters are given in Table I.

REAGENTS—

Rhenium solutions were made by dissolving ammonium perrhenate (Johnson Matthey Chemicals Ltd.) in de-ionised distilled water. All other solutions were prepared from analytical-reagent grade materials when commercially available, otherwise general-reagent grade chemicals were used.

TABLE I

INSTRUMENT OPERATING PARAMETERS FOR OPTIMUM SIGNAL-TO-NOISE RATIO

Wavelength/nm	346·1 or 488·9
Slit width/μm	50
Spectral band pass/nm	0·17
Burner	6-cm slot
Observation height/mm	10
Acetylene flow-rate/l min^{-1}*	3·9
Nitrous oxide flow-rate/l min^{-1}*	7·0
Solution uptake rate/ml min^{-1}	7·2

* Fuel flow-rates refer to volumes at 20 °C and atmospheric pressure. The height of the red reaction zone in the flame was about 12 to 13 mm.

RESULTS AND DISCUSSION

EXPERIMENTAL CONDITIONS—

No emission was detected at wavelengths of 346·1 or 488·9 nm from 500 μg ml^{-1} rhenium solutions when using air - acetylene or nitrous oxide - hydrogen flames supported on the 6-cm slot burner and covering a wide range of fuel-to-oxidant ratios. A nitrogen-separated nitrous oxide - acetylene flame, supported on a circular slot burner,[9] gave a limit of detection of 8 μg ml^{-1} of rhenium at 346·1 nm with a solution uptake rate of 7·2 ml min^{-1}. As the detection limit was 14 μg ml^{-1} without separation, it appeared that this poor performance was a result of the relative incompatibility of this burner configuration with the optics used, and that the separated nitrous oxide - acetylene flame, supported on a slot burner, might be worth investigating. Atomic emission was observed at the wavelengths listed in Table II when using a pre-mixed nitrous oxide - acetylene flame supported on a conventional atomic-absorption slot burner. All further work was carried out with this system.

TABLE II

LIMITS OF DETECTION AND INTENSITIES OF RHENIUM EMISSION LINES

Wavelength/ nm	Detection limit for rhenium/ μg ml^{-1}	Uncorrected intensity		Corrected intensity	
		Peak*	Background	Peak*	Background
345·2	4	34	18	35	18
346·1	0·7	124	19	124	19
346·5	2·5	78	19	77	19
488·9	1·5	128	28	75	17
527·6	4	43	32	28	21

* The peak signal is measured from the level of the flame background. The background signal is measured from zero.

The principal rhenium emission wavelengths are 346·1 and 488·9 nm, the former of which gives the lowest detection limits while the latter gives greater freedom from spectral interference. Rhenium gives maximum emission intensity in a fuel-rich flame that lacks luminosity caused by incandescent carbon particles. The nitrous oxide flow-rate was fixed at 7·0 l min^{-1}, giving a solution uptake rate of 7·2 ml min^{-1}. The acetylene flow-rate for maximum intensity was 4·0 l min^{-1}, giving a red reaction zone in the flame approximately 15 mm high. The optimum signal-to-noise ratio, however, was obtained by using a slightly lower acetylene flow-rate (3·9 l min^{-1}), giving a red zone 12 to 13 mm high when measurements were carried

out at 346·1 nm. For measurements carried out at 488·9 nm either 3·9 l min^{-1} or 4·0 l min^{-1} gave equal signal-to-noise ratios. The emission signal and the background noise level were particularly dependent on the acetylene flow-rate. The flame background at the lower rhenium wavelengths was a continuum interposed between the strong NH band system at 336 nm and the strong CN violet system at 359 nm (Fig. 1). The background at 488·9 nm arises from a number of weak C_2 bands and the Q branch band head of the CH system at 489·0 nm. A difference of 0·1 l min^{-1} in the acetylene flow-rate can affect the signal-to-noise ratio by about 10 per cent. at both 346·1 nm and 488·9 nm.

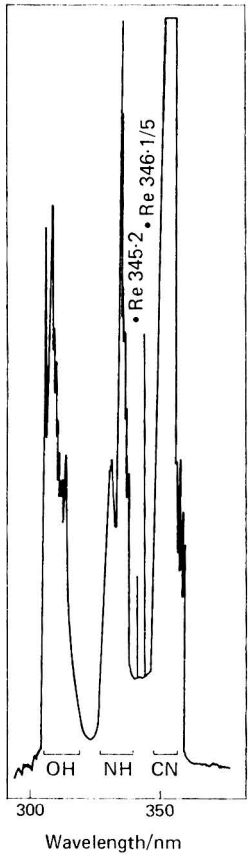

Fig. 1. Emission spectrum of rhenium at 345·2, 346·1 and 346·5 nm

Maximum emission intensity was obtained if measurements were carried out within the red reaction zone of the nitrous oxide - acetylene flame (approximately 8 mm above the upper surface of the burner). However, the flame background was high and the noise level prohibitive in these circumstances. The maximum signal-to-noise ratio for 346·1 nm and 488·9 nm was found when measurements were carried out at a height 9 to 11 mm above the burner. The optical axis of the instrument is then just below the upper tip of the red reaction zone of the flame.

A slit width of 50 μm (spectral band pass 0·17 nm) was found to give the maximum signal-to-noise ratio at 346·1 nm and 488·9 nm and represented a reasonable compromise between signal intensity and spectral resolution. A band pass of 0·8 nm resulted in a reduction of the signal-to-noise ratio by approximately 50 per cent. at the 20 μg ml^{-1} concentration level.

SENSITIVITY—

Limits of detection, obtained under the conditions listed in Table I, are given in Table II. The detection limit is defined as the concentration of rhenium in aqueous solution that gives a signal-to-noise ratio of unity, the noise being the peak-to-peak noise of the flame background when de-ionised water is aspirated. Four pairs of measurements of background and test solution intensity were taken for each detection limit given by using the maximum damping available on the instrument and carrying out the measurements with a rhenium concentration no greater than five times the limit of detection. Intensity measurements of the rhenium emission lines (in arbitrary units) were also made (Table II) and were corrected for the spectral response factors of the monochromator and photomultiplier, obtained from the instrument manufacturer's data.

Limits of detection for rhenium by atomic absorption have been reported by Slavin[10] as being 1·5 μg ml^{-1} and by Shrenk *et al.*[8] as 1 to 2 μg ml^{-1}. A similar detection limit should be obtainable on the instrument used for this investigation. In contrast, the detection limit by atomic emission is unquestionably lower: 0·7 μg ml^{-1} reported in this paper and 0·2 μg ml^{-1} by Pickett and Koirtyohann.[1,2]

Detection limits by atomic emission can, in principle, be reduced by the use of more sophisticated instrumentation. In particular, the use of a high-dispersion monochromator, narrower band width amplifier and more sensitive detector would be expected to give substantial improvements in signal-to-noise ratios. Corresponding reductions in atomic-absorption detection limits could not easily be obtained.[2] Analytical working curves were found to be linear up to 200 μg ml^{-1} of rhenium and only slightly curved up to 1 mg ml^{-1} at both 346·1 nm and 488·9 nm.

SPECTRAL INTERFERENCES—

If the practice of carrying out measurements at the emission line wavelength only is followed, it is not possible to correct for increases in signal caused by molecular band emission,

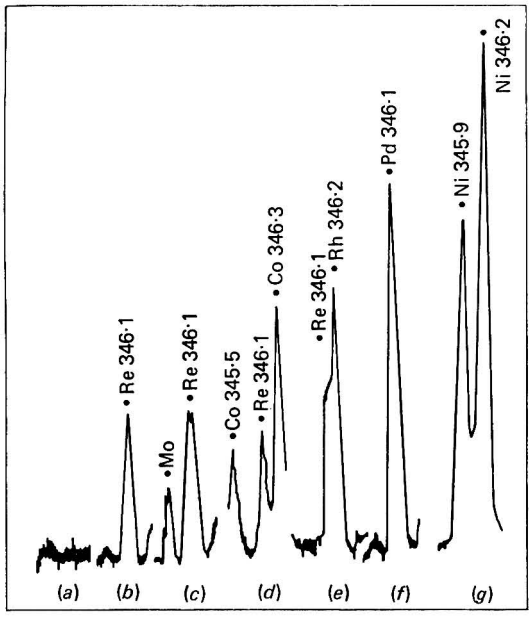

Fig. 2. Spectral line interferences at the Re 346·1 nm wavelength: (*a*), de-ionised water only; (*b*), 20 μg ml^{-1} rhenium; (*c*), 20μg ml^{-1} rhenium, 200μg ml^{-1} molybdenum; (*d*), 20 μg ml^{-1} rhenium, 200 μg ml^{-1} cobalt; (*e*) 20 μg ml^{-1} rhenium, 200 μg ml^{-1} rhodium; (*f*), 20 μg ml^{-1} rhenium, 200 μg ml^{-1} palladium; and (*g*), 20 μg ml^{-1} rhenium, 200 μg ml^{-1} nickel

light scatter within the monochromator, or partially resolved atomic-line emission from concomitant elements. If the analyst scans the characteristic emission line, or makes measurements at an adjacent "background" wavelength, continuum interference from broad molecular bands or scattered light can be eliminated entirely.[2] Further, the presence of partially resolved atomic-line interference is immediately indicated and it is frequently possible to make useful measurements if the lines are moderately resolved. Alternatively, measurements can be made at another wavelength.

Solutions of the following metals (rhenium free) were aspirated into the flame and scans made over the wavelength ranges 345·6 nm to 346·6 nm and 488·4 nm to 489·6 nm; concentrations (μg ml^{-1}) are given in brackets:Ag (5000), Al (10 000), As (5000), B (1000), Ba (1000), Ca (1000), Cd (1000), Co (1000), Cr (1000), Cs (10 000), Fe (1000), In (1000), Ir (1000), K (10 000), La (10 000), Li (10 000), Mg (10 000), Mn (1000), Mo (500), Na (10 000), Ni (1000), Os (1000), Pb (10 000), Pd (1000), Pt (2000), Rh (1250), Ru (100), Sb (1000), Si (2000), Sn (5000), V (1000), W (500) and Zn (5000). Also, the following acids were examined after one 100-fold dilution of the concentrated acid: acetic, hydrochloric, hydrofluoric, nitric, perchloric, phosphoric and sulphuric. The amplification was adjusted so that 30 μg ml^{-1} of rhenium gave a full-scale recorder deflection.

The flame background spectrum obtained on aspirating de-ionised water is a featureless horizontal line between 345·6 nm and 346·6 nm. Important spectral lines in this range occur at the cobalt 346·28 nm, cobalt 345·52 nm, palladium 346·08 nm, nickel 346·17 nm, nickel 345·85 nm and rhodium 346·20 nm wavelengths; in addition, a line at about 345·5 $\pm$ 0·2 nm caused by molybdenum was encountered. This line was approximately one twentieth of the intensity of the rhenium 346·1 nm line (for equal concentrations by weight) and could not be readily identified as a genuine molybdenum atomic line, MoO molecular band or even as a probable impurity. However, the line was well resolved from the rhenium emission at 346·1 nm and caused no interference. Fig. 2 shows the interference from atomic lines on the rhenium 346·1 nm atomic emission.

Palladium 346·08 nm line is the most serious spectral interference as it is indistinguishable from the 346·05 nm rhenium line even on scanning. However, it is almost exactly one tenth of the intensity of the rhenium line.

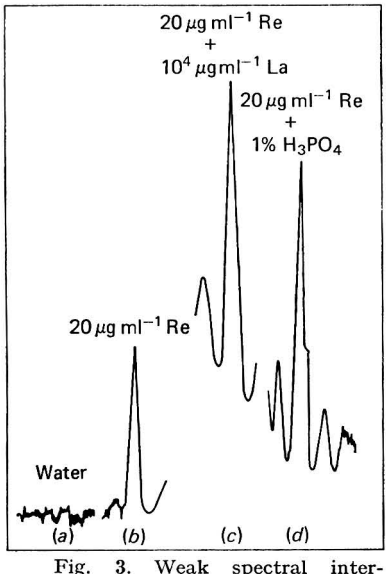

Fig. 3. Weak spectral interferences at the Re 346·1 nm wavelength: (*a*), de-ionised water only; (*b*), 20 μg ml^{-1} rhenium; (*c*), 20 μg ml^{-1} rhenium, 10^4 μg ml^{-1} lanthanum; and (*d*), 20 μg ml^{-1} rhenium, 1 per cent. phosphoric acid

The two nickel lines at 346·17 nm and 345·85 nm were completely resolved from one another but were of comparable intensity to the rhenium emission and could not be resolved from this line. It is essential to use the rhenium 488·9 nm line if nickel is present in any sample.

Partial resolution of the rhenium 346·1 nm and rhodium 346·2 nm lines was possible and was sufficient to indicate the presence of rhodium in a sample and the need to use an alternative rhenium line. The rhodium line is approximately one tenth as intense as the rhenium emission. Resolution of the cobalt 346·3 nm and rhenium 346·1 nm lines was almost complete and the 345·5 nm line was completely resolved (Fig. 2). Useful analyses can therefore be obtained even in the presence of a considerable excess of cobalt, especially if narrow slits are used.

Lanthanum exhibits a pair of weak lines (Fig. 3), or perhaps part of a band system, which is about two hundred times less intense than the emission from an equal concentration of rhenium. Phosphoric acid gives rise to a series of weak PO molecular bands in this region also (Fig. 3). The latter are so weak as to cause concern only when large amounts of phosphoric acid are present in the analyte and in these circumstances this would usually be known and an approximately equal amount of the acid could be added to the standards. Several elements gave rise to slight increases in the general background level of the spectrum (*e.g.*, 10 mg ml^{-1} amounts of alkali metals) but these could easily be overcome by scanning and would not present difficulties, even in the determination of less than 5 μg ml^{-1} of rhenium.

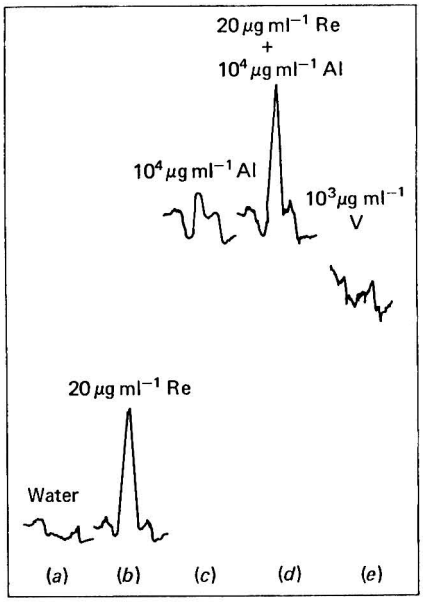

Fig. 4. Emission characteristics of concomitant elements at the Re 488·9 nm wavelength: (*a*), de-ionised water only; (*b*), 20 μg ml^{-1} rhenium; (*c*), 10^4 μg ml^{-1} aluminium; (*d*), 20 μg ml^{-1} rhenium, 10^4 μg ml^{-1} aluminium; and (*e*), 10^3 μg ml^{-1} vanadium

Between 488·4 nm and 489·6 nm, the flame background spectrum consists of two small peaks on either side of the rhenium 488·9 nm wavelength. Spectral interferences are practically insignificant at this wavelength; only large amounts of concomitant elements cause any difficulty. Aluminium (10 mg ml^{-1}) gives a substantially increased background (Fig. 4) and a peak height (equivalent to that of about 8 μg ml^{-1} of rhenium) that is probably part of the AlO band system, with band head at 488·84 nm. Line interference from second-order

spectral interferences is unlikely as no strong lines are present in the 244 nm region. Of the elements listed, vanadium (1 mg ml^{-1}), lanthanum (10 mg ml^{-1}) and molybdenum (10 mg ml^{-1}) gave unusually high continuum backgrounds, which do not present problems at the 20 μg ml^{-1} rhenium level. Other elements give smaller over-all increases in the level of the background emission. Wavelength tables indicate that gadolinium may give rise to spectral interference at 489·2 nm from the GdO molecular band head, but as this band system is degraded to the red end of the spectrum, the band may be completely resolved from the rhenium emission. A detailed study of rare earth spectral interferences was, however, considered to be outside the scope of this work.

CHEMICAL INTERFERENCES—

The determination of rhenium by atomic absorption in oxygen - acetylene flames[8] was shown to be prone to chemical interference (*i.e.*, inter-element effects caused by the formation of involatile species in the flame), and the study carried out here indicates similar behaviour in the pre-mixed nitrous oxide - acetylene flame.

The effects of common acids (addition of 1 per cent. of the concentrated acid) on the emission of 20 μg ml^{-1} of rhenium were first investigated. Phosphoric and hydrochloric acids gave decreased signals of 76 and 88 per cent., respectively, relative to aqueous ammonium perrhenate solution. Acetic, hydrofluoric, nitric and sulphuric acids gave no interference. During further studies on the interference effects of cations, measurements were carried out in 1 per cent. nitric acid solution in an attempt to overcome the effects of concomitant anions. This was successful when tests were made with sodium chloride and sodium nitrate, neither of which caused interference in the presence of 1 per cent. nitric acid.

TABLE III

CHEMICAL INTERFERENCES IN THE DETERMINATION OF RHENIUM

Added element*	1 per cent. of nitric acid†	1 per cent. of hydrofluoric acid†	1 per cent. of sulphuric acid†	1 per cent. of phosphoric acid†
Re only	100	100	100	63
Ag	100	—	—	—
Al	70	75	100	101
As	102	—	—	—
B	84	100	100	100
Ba	0	18	98	99
Ca	13	94	100	99
Co	89	89	100	100
Cr	85	79	103	98
Cs	100	—	—	—
Cu	101	—	—	—
Fe	99	—	—	—
In	101	—	—	—
Ir	101	—	—	—
K	100	—	—	—
Li	55	51	102	101
Mg	45	75	100	101
Mn	83	70	99	99
Mo	99	95	100	99
Na	103	—	—	—
Ni	93	98	100	98
Os	101	—	—	—
Pb	96	86	100	100
Pd	99	—	—	—
Pt	100	—	—	—
Rh	100	—	—	—
Ru	100	—	—	—
Sb	46	50	99	98
Si	101	—	—	—
Sn	100	—	—	—
Sr	2	11	97	101
V	100	—	—	—
W	56	58	101	100
Zn	101	—	—	—

* Effects of 200 μg ml^{-1} of added element were investigated on 20 μg ml^{-1} of rhenium.
† 1 per cent. of concentrated acid.

Cationic interferences were investigated by using 200 μg ml^{-1} of the foreign element, 20 μg ml^{-1} of rhenium and 1 per cent. nitric acid. Blanks containing no rhenium were also measured and the blank value was subtracted from the total signal. In practice, blanks of this kind would not be available, but the blank value could be obtained at an adjacent background wavelength or by scanning. The results of this study are summarised in Table III; comparable effects were obtained at 346·1 nm and 488·9 nm. Where spectral interferences were known to occur, measurements were carried out at an alternative wavelength. A definite interference was assumed to be present when the intensity of the rhenium emission was changed by an amount greater than $\pm$4 per cent. relative to the pure solution. The presence of lead represented the only borderline case (96 per cent. signal intensity) and was assumed to give rise to a genuine interference effect.

It must be stressed that this type of interference will occur in both atomic-absorption and atomic-emission spectroscopy, and that the magnitude of the effect will be similar for measurements carried out by the two techniques on any particular instrument. The results given in Table III are similar to those obtained by Schrenk *et al.*[8] by using atomic absorption in turbulent oxygen - acetylene flames. Calcium was found[8] to reduce the rhenium absorption seriously, but the effect was not quite so marked as indicated in Table IV; the interference from manganese, however, was much more serious in the oxygen - acetylene flame. In addition, Schrenk *et al.*[8] reported interference from iron, potassium and molybdenum, none of which was encountered in this work.

TABLE IV

EFFECTS OF TYPICAL RELEASING AGENTS ON THE INTERFERENCE OF CALCIUM (200 μg ml^{-1}) ON RHENIUM (20 μg ml^{-1})

Releasing agent	Rhenium emission intensity*	Background intensity†
None	11	0
0·1 per cent. Al (as Al_2SO_4) ..	45	43
10 per cent. EDTA (at pH 11) ..	12	11
0·1 per cent. Si (as Na_2SiO_3) ..	102	38
10 per cent. La (as $LaCl_3$)	50	120
5 per cent. H_3PO_4	116	17
5 per cent. HF	109	0
5 per cent. H_2SO_4	100	0

* After correction for background from releasing agent and calcium.
† The emission intensity of the releasing agent at 346·1 nm.

As the alkaline earth elements represent the most significant chemical interferences efforts were concentrated on the elimination of effects arising from the presence of these metals. Various releasing agents were examined; in particular, those which were known to form involatile alkali-metal species were chosen (*e.g.*, aluminium, silicate, sulphuric acid and phosphoric acid) as well as some well known releasing agents for the alkali metals (*e.g.*, ammoniacal solution of EDTA, lanthanum). The effects of the releasing agents are summarised in Table IV. Apart from the alkaline EDTA solution, almost all of the compounds examined considerably suppressed the calcium interference. However, many of the releasing agents (*e.g.*, aluminium, lanthanum, silicate) gave rise to an inconveniently high background emission. This could be compensated for fairly easily but such a compensation was unnecessary as dilute hydrofluoric, sulphuric and phosphoric acids were equally effective as releasing agents for calcium and did not give rise to increased flame background.

The dilute solutions of mineral acids containing 1 per cent. of concentrated acid were then investigated for use as general releasing agents for all of the elements that interfere in the rhenium determination. These results are also included in Table III. Hydrofluoric acid, although acting as a releasing agent for the effect of calcium on rhenium, allowed many other elements to interfere, including strontium and barium. The interference of boron (as borate) was removed and the effects of aluminium and magnesium were reduced. Sulphuric and phosphoric acids (added as 1 per cent. of concentrated acid), however, acted as releasing agents for all of the interfering metals examined and are the most convenient releasing agents for general use. With phosphoric acid the rhenium emission is considerably depressed (Table III) but this effect is overcome when small amounts of a third element are present.

At the 20 μg ml^{-1} of rhenium level, the excess of the third element should be about three times (expressed on a molar concentration basis) that of rhenium. However, this appears to be a fairly complex ternary system and for analytical purposes it is sufficient to be aware of its existence and to take the necessary precautions. The small spectral interference of phosphoric acid (Fig. 3) at 346·1 nm is also a disadvantage. Sulphuric acid is the recommended releasing agent, but the choice may well be made on the basis of the most suitable acid for the dissolution of the sample.

Conclusions

The determination of rhenium can be conveniently carried out by atomic-emission spectroscopy in the pre-mixed nitrous oxide - acetylene flame if a monochromator of moderate dispersion is available. Measurements carried out at the recommended wavelength of 346·1 nm are subject to spectral interference from cobalt, nickel, palladium and rhodium, as well as from very large amounts of lanthanum or phosphate. The alternative wavelength of 488·9 nm is subject to spectral interference only from large concentrations of aluminium but the emission detection limits are higher. The use of scanning or measurement at the wavelength peak and an adjacent wavelength was found to be necessary to compensate for variations in the background level of the sample relative to standards. Chemical interferences are many, but can easily be prevented by addition of sulphuric or phosphoric acid. The same chemical interferences will be present in the corresponding determination by atomic-absorption spectroscopy, although the emission method gives lower detection limits.

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A Method for the Chemical Analysis of Magnesites and Dolomites*

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This paper includes a detailed description of a method for the analysis of magnesites and dolomites; the method has been accepted (in principle) by the British Standards Institution as a standard method. Determinations include SiO_2 (gravimetric), TiO_2, Fe_2O_3, Cr_2O_3, MnO (colorimetric) and Al_2O_3, CaO and MgO (complexometric). Notes on the development of the method and tables of co-operative results obtained by the Refractories Working Group of the Analysis Committee are included.

This method, a schematic diagram of which is shown in Fig. 1, has been developed by the Refractories Working Group of the British Ceramic Research Association Analysis Committee, and will, after approval by the Analysis Committee, be submitted to B.S.I. for acceptance as a standard method.

Co-operative results obtained by the Working Group on two magnesites and two dolomites are given so that the capabilities of the method can be assessed. The method has been under development for several years and in this time the Working Group have attempted a considerable number of procedures, meeting with little success in many instances. This work has not been reported in detail, but some indication of the Group's activities has been given in the form of notes on the development of the method.

METHOD

The method covers the determination of loss on ignition and of SiO_2, Fe_2O_3, TiO_2, MnO, Cr_2O_3, Al_2O_3, CaO and MgO in magnesites and dolomites suitable for industrial refractories. In general, the method is not sufficiently sensitive for the analysis of samples of special high purity MgO.

Principle of the method

Loss on ignition—

The loss on ignition is determined at 1025 ± 25 °C.

Determination of oxides of silicon, iron(III), titanium(IV), manganese(II), chromium(III), aluminium(III), calcium and magnesium—

The sample is decomposed with hydrochloric acid and the silica separated by coagulation and filtration. The crucible containing the silica is ignited and weighed before and after treatment with hydrofluoric and sulphuric acids. The silica remaining in the filtrate is subsequently determined by a spectrophotometric method based on the formation of molybdenum blue in a portion of the solution used for the determination of Fe_2O_3, TiO_2, MnO, Cr_2O_3, Al_2O_3, CaO and MgO.

The residue from the silica is fused with sodium carbonate and boric acid and the cold melt dissolved in the filtrate from the silica. After dilution to a standard volume aliquots are used for the determination of iron(III) oxide spectrophotometrically with 1,10-phenanthroline, titanium(IV) oxide with hydrogen peroxide, manganese(II) oxide with potassium periodate and chromium(III) oxide with diphenylcarbazide for very low chromium contents and as the chromium(III) - EDTA complex for materials containing more than about 0·1 per cent. of chromium(III) oxide. For the aluminium(III) oxide determination, oxides of elements in the ammonia group of the scheme for systematic analysis in a measured volume of the solution are precipitated with ammonia solution to remove most of the magnesium

* A Report prepared by the Refractories Working Group of the Analysis Committee of the British Ceramic Research Association.

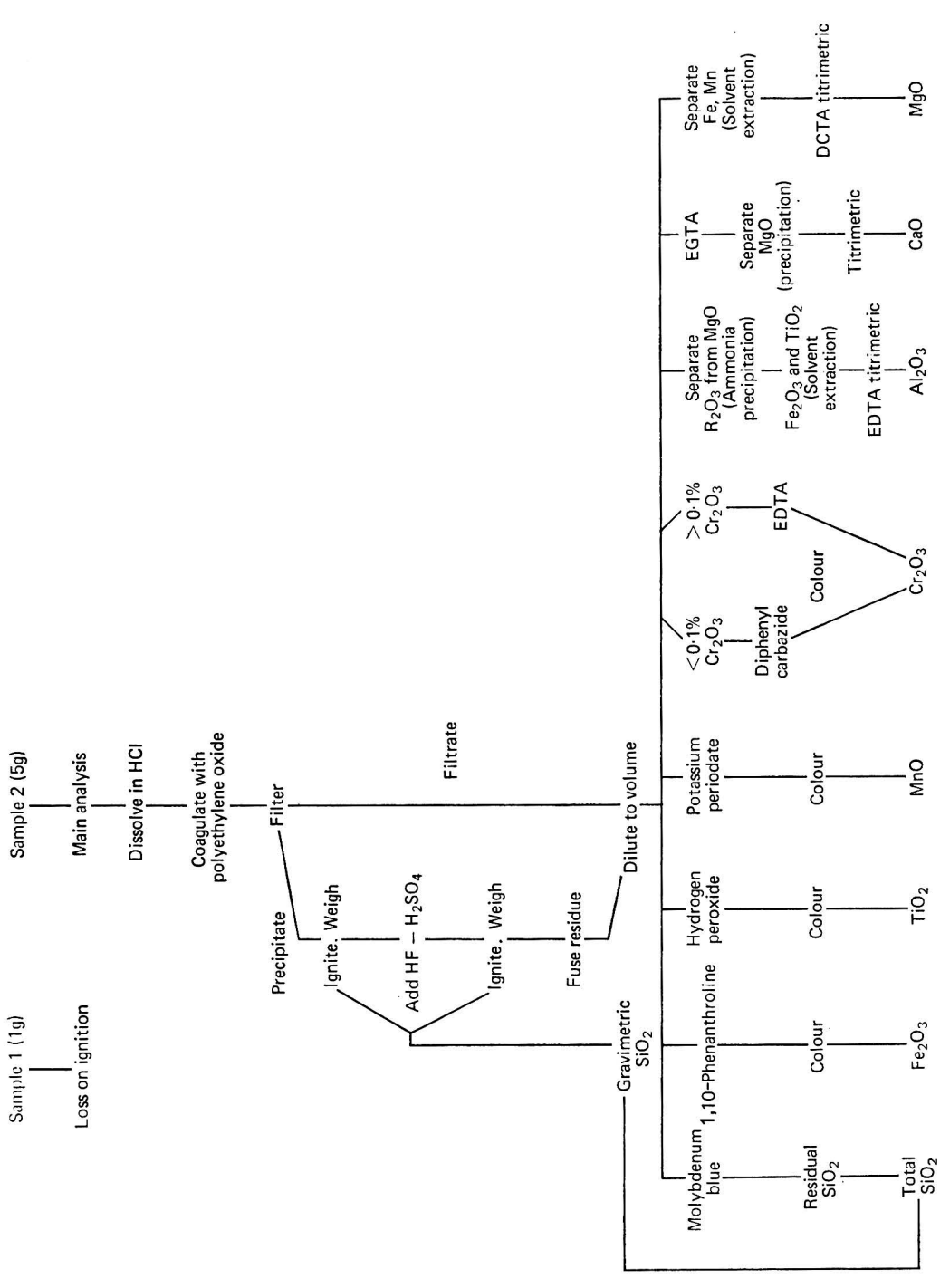

Fig. 1. Schematic diagram of the analysis of magnesites and dolomites

oxide. The precipitate is dissolved in hydrochloric acid and the iron(III) and titanium(IV) ions are removed by a cupferron - chloroform solvent extraction. The determination is completed titrimetrically with ethylenediaminetetraacetic acid (EDTA) and zinc, with dithizone as indicator. This titration includes the amount of EDTA consumed by the Cr_2O_3, which must be allowed for. The use of diaminocyclohexanetetraacetic acid (DCTA) in place of EDTA enables Al_2O_3 to be determined directly.[1] Lime is determined on a measured volume of the solution to which triethanolamine is added to complex interfering elements. A known volume of standard 1,2-bis-(2-aminoethoxy)ethanetetraacetic acid (EGTA), sufficient to complex all the calcium, is added, and the magnesium is then precipitated with potassium hydroxide. The excess of EGTA is titrated with a calcium solution, Calcein being used as indicator. Magnesium oxide is determined titrimetrically on a measured volume of the solution after removal of iron(III), manganese(II) and most of the titanium(IV) ions by a sodium diethyldithiocarbamate - chloroform solvent extraction. Aluminium(III) and any remaining titanium ions are complexed with triethanolamine and the magnesium is titrated with DCTA in a strongly ammoniacal solution containing ammonium chloride. If more than 1 per cent. of Al_2O_3 is present, both it and TiO_2 are removed by a buffered cupferron - chloroform solvent extraction. The titration also includes the titration for lime, which must be allowed for.

DETERMINATION OF ALKALI-METAL OXIDES—

If a simple filter flame photometer is used the alkali-metal oxides can be determined by the method described by Eardley and Reed[2] under the heading "High lime materials."

REAGENTS—

Unless otherwise stated, all reagents must be of analytical-reagent grade when available, and distilled water must be used throughout the analysis. The following reagents are required.

Ammonium chloride.

Boric acid.

Calcein indicator—Mix, by grinding together, 0·2 g of Calcein, 0·12 g of thymolphthalein and 20 g of potassium chloride.

Potassium periodate.

Silica—A quartz or sand of known purity, not less than 99 per cent.

Sodium carbonate, anhydrous.

Solochrome black 6B (also known as Eriochrome blue-black B)—Mix, by grinding together, 0·5 g of Solochrome black 6B and 20 g of sodium chloride.

Thymolphthalein.

Acetic acid, glacial.

Acetone.

Ammonia solution, sp.gr. 0·88.

Ammonium acetate solution, approximately 10 *per cent.*—Dilute 140 ml of glacial acetic acid to 1700 ml with water and add 140 ml of the ammonia solution. Mix, cool and adjust to pH 6·0 to 6·5.

Ammonium acetate buffer (for aluminium(III) oxide determinations)—Add 120 ml of glacial acetic acid to 500 ml of water, followed by 74 ml of the ammonia solution. Cool the mixture, dilute it to 1 litre and mix.

Ammonium acetate buffer (for magnesium oxide determinations)—Dilute 5 ml of the ammonia solution to 100 ml with distilled water and add 30 ml of glacial acetic acid. Adjust the solution to pH 3·8 by using a pH meter and then dilute to 200 ml with distilled water.

Ammonium cerium(IV) nitrate solution, 1 per cent. w/v—Dissolve 2·5 g of ammonium cerium(IV) nitrate in about 200 ml of water, cautiously add 7 ml of sulphuric acid (sp.gr. 1·84), cool, dilute to 250 ml and mix.

Ammonium molybdate solution, 8 per cent. w/v—Discard after 4 weeks, or earlier if any appreciable deposit is observed.

Ammonium nitrate solution, approximately 1 per cent.—Dilute 10 ml of nitric acid (sp.gr. 1·42) to about 200 ml. Add ammonia solution (1 + 1) until the solution is slightly alkaline to bromophenol blue, then cool and dilute it to 1 litre.

Bromophenol blue solution—Grind and dissolve 0·1 g of bromophenol blue in 1·5 ml of sodium hydroxide solution (0·4 per cent. w/v), dilute the solution to 100 ml with water and mix.

Chloroform, B.P. grade.

Cupferron, 6 per cent. w/v—This solution must be freshly prepared.

Saturated 2,4-dinitrophenol solution—Dissolve 0·1 g of 2,4-dinitrophenol in 100 ml of hot water, allow to cool and filter.

Diphenylcarbazide, 1 per cent. w/v solution—Dissolve 0·1 g of diphenylcarbazide in 10 ml of acetone. This solution must be freshly prepared.

Dithizone solution—Dissolve 0·025 g of dithizone in 100 ml of 95 per cent. ethanol.

Ethanol, 95 per cent.—Industrial methylated spirit, 95 per cent.

Ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA)—A 5 per cent. w/v solution.

Hydrochloric acid, sp.gr. 1·18.

Hydrofluoric acid, 40 per cent. w/w.

Hydrogen peroxide, 20 volume.

Hydroxylammonium chloride, 10 per cent. w/v.

Magflok, approximately 2 per cent. w/v—The resin is a thick viscous liquid and it is therefore most convenient to transfer a drop to a beaker and weigh the amount taken. Sufficient water is then added to make up a solution approximately 2 per cent. w/v. The resin is available from Ridsdale & Co. Ltd., Newham Hall, Newby, Middlesbrough.

Magnesium sulphate solution—Dissolve 6·11 g of magnesium sulphate heptahydrate in water, filter and dilute to 500 ml (50 ml ≡ about 0·1 g of MgO).

Naphthol green B, 0·1 per cent. w/v.

Nitric acid, sp.gr. 1·42.

1,10-Phenanthroline hydrate, 1 per cent. w/v—Prepare enough solution for immediate use at a concentration of 0·1 g per 10 ml of acetic acid (1 + 1).

Phosphoric acid, sp.gr. 1·75.

Polyethylene oxide, 0·25 per cent. w/v—Add 0·5 g of polyethylene oxide slowly to 200 ml of water with stirring, preferably on a mechanical stirrer, until dissolved. Discard this solution after 2 weeks. Union Carbide Polyox resins WSR-35, WSR-N-80, WSR-205, WSR-N-750 and WSR-N-3000 are suitable as sources of polyethylene oxide.

Potassium hydroxide solution, 25 per cent. w/v.

Sodium azide solution, 2 per cent. w/v.

Sodium diethyldithiocarbamate, 10 per cent. w/v—This solution must be freshly prepared.

Sodium sulphite, 5 per cent. w/v—This solution must be freshly prepared.

Tin(II) chloride, 1 per cent. w/v solution—Dissolve, by warming, 1 g of tin(II) chloride in 1·5 ml of the hydrochloric acid. Cool the solution and dilute it to 100 ml. This solution should not be kept for more than 24 hours.

Sulphuric acid, sp.gr. 1·84.

Sulphurous acid—Saturate 250 ml of water with sulphur dioxide.

Triethanolamine.

STANDARD SOLUTIONS—

Calcium solution, 0·05 M—Dissolve 5·0045 g of calcium carbonate (dried at 150 °C) in a slight excess of hydrochloric acid (1 + 4). Boil the solution to expel carbon dioxide, cool it and dilute to 1 litre.

Chromium solution A (0·5 mg ml^{-1} of Cr_2O_3)—Dissolve 0·9677 g of potassium dichromate (dried at 150 °C) in water and dilute to 1 litre.

Chromium solution B (0·025 mg ml^{-1} of Cr_2O_3)—Dilute 25 ml of the chromium solution A to 500 ml.

Solution of 1,2-diaminocyclohexanetetraacetic acid (DCTA), about 0·05 M—Dissolve 18·2175 g of DCTA in 500 ml of water by the progressive addition of the minimum amount of potassium hydroxide solution (25 per cent. w/v). Dilute to 1 litre. Standardise this solution against standard magnesium solution.

Ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA), 0·05 M—Dissolve 18·6125 g of the salt in warm water, filter if necessary, cool and dilute to 1 litre. Standardise the resulting solution against the standard zinc solution, dithizone being used as indicator.

1,2-bis(aminoethoxy)ethanetetraacetic acid (EGTA), about 0·05 M—Dissolve 19·0174 g in 500 ml of water by the progressive addition of the minimum amount of potassium hydroxide solution (25 per cent. w/v). Dilute to 1 litre. Standardise the solution against standard calcium solution.

Iron solution A (0·1 *mg ml*$^{-1}$ *of* Fe_2O_3)—Dissolve 0·0699 g of the oxide-free metal wire in a slight excess of hydrochloric acid (1 + 9); add 5 ml of hydrogen peroxide and boil for 15 minutes. Cool the solution and dilute it to 1 litre.

Iron solution B (0·01 *mg ml*$^{-1}$ *of* Fe_2O_3)—Dilute 50 ml of the iron solution A to 500 ml.

Magnesium solution (5 *mg ml*$^{-1}$ *of MgO*)—Dissolve 3·016 g of the oxide-free metal in a slight excess of hydrochloric acid (1 + 9), cool and dilute to 1 litre.

Manganese solution A (0·1 *mg ml*$^{-1}$ *of MnO*)—Dilute the calculated volume of previously standardised (about 0·1 N) potassium permanganate to 1 litre. (With exactly 0·1 N potassium permanganate, 70·5 ml are required.)

Manganese solution B (0·01 *mg ml*$^{-1}$ *of MnO*)—Dilute 50 ml of the manganese solution A to 500 ml.

Potassium permanganate solution, about 0·1 N—Dissolve about 3·2 g of potassium permanganate in 1 litre of water to obtain an approximately 0·1 N solution; boil for 5 minutes, filter through a sintered-glass crucible of porosity grade No. 4 and cool. Standardise the solution against sodium oxalate and store it in an amber-glass bottle.

Silica solution A (*approximately* 0·5 *mg ml*$^{-1}$ *of* SiO_2)—Fuse 0·5000 g of pure silica (>99 per cent. purity) with 5 g of anhydrous sodium carbonate in a platinum crucible. Cool the mixture and dissolve it in water in a polythene beaker. Cool again and dilute the solution to 1 litre. This solution will remain stable for at least 6 months.

Silica solution B (*approximately* 0·020 *mg ml*$^{-1}$ *of* SiO_2)—Dilute 20 ml of the silica solution A to 500 ml.

Titanium solution A (1·0 *mg ml*$^{-1}$ *of* TiO_2)—Ignite some pure TiO_2 and then fuse 1·000 g with 10 g of potassium pyrosulphate. Allow to cool and dissolve the melt, at a low temperature to prevent hydrolysis, in 200 ml of water to which 20 ml of the sulphuric acid have been cautiously added. Cool again and dilute the solution to 1 litre.

Titanium solution B (0·04 *mg ml*$^{-1}$ *of* TiO_2)—Dilute 20 ml of the titanium solution A to 500 ml.

Zinc solution, 0·05 M—Dissolve 3·2685 g of the oxide-free metal in 50 ml of hydrochloric acid (1 + 4), cover the beaker with a watch-glass and allow to stand overnight on a steam-bath. Cool and dilute to 1 litre (1 ml ≡ 2·55 mg of Al_2O_3).

STANDARDISATIONS—

EGTA against calcium—Transfer 50 ml of the magnesium sulphate solution to a 250-ml calibrated flask and add 50·0 ml of the EGTA solution. Dilute to 150 ml, add potassium hydroxide solution (25 per cent. w/v) until no further precipitation occurs and then add 10 ml in excess, followed by 10 ml of Magflok solution. Dilute the mixture to 250 ml, shake and allow it to stand for about 10 minutes to settle. Filter it through a dry 125-mm Whatman No. 541 filter-paper into a dry beaker. Pipette 200 ml of the filtrate into a 500-ml conical flask and add 15 ml of potassium hydroxide solution. Titrate with standard calcium solution (0·05 M), with screened Calcein as indicator, to the first appearance of green fluorescence (1 ml of 0·05 M EGTA ≡ 2·804 mg of CaO).

DCTA against magnesium—Transfer 50·0 ml of the standard magnesium solution to a 500-ml conical flask. Add 100 ml of the DCTA solution followed by 2 g of ammonium chloride and 25 ml of ammonia solution. Titrate with the DCTA solution, with Solochrome black 6B as indicator, from red, through purple, until the last change in colour to a clear ice blue (1 ml of 0·05 M DCTA ≡ 2·016 mg of MgO).

EDTA against zinc—Transfer 50·0 ml of the EDTA solution to a 500-ml conical flask and add 5 to 6 drops of hydrochloric acid. Add a few drops of bromophenol blue solution and then add ammonium acetate buffer solution (for aluminium(III) oxide determination) until the indicator turns blue, followed by an excess of 10 ml. Add a volume of the ethanol equal to the total volume of existing solution, followed by 1 to 2 ml of dithizone solution, and titrate with the standard zinc solution from green to the first appearance of a permanent pink colour (1 ml of 0·05 M EDTA ≡ 2·55 mg of Al_2O_3).

BLANK DETERMINATIONS—

Blank determinations should be carried out on all reagents in accordance with the general scheme of analysis. When carrying out the blank determination for lime, it is necessary to add 50 ml of the magnesium sulphate solution before the addition of the standard EGTA solution.

PREPARATION OF SAMPLE—

The sample prepared for analysis should be ground to pass a 125-μm B.S. test sieve. A non-metallic (*e.g.*, 120-mesh nylon bolting cloth) sieve is preferable.

Many of these materials are comparatively soft and may be ground in an agate mortar without appreciable contamination. In a few instances the material may be sufficiently hard to be contaminated and it is then necessary to prepare two samples, one ground in an iron mortar (most of the iron in the sample being removed with a magnet), and the other sample ground in an agate mortar. The first sample is used for the main analysis and the second for the determination of iron(III) oxide, the results obtained on the first sample being corrected for iron contamination.

EXPERIMENTAL DETAILS OF THE METHOD

DETERMINATION OF LOSS ON IGNITION—

Weigh 1·000 g of the finely ground sample, previously dried at 110 °C, into a platinum crucible. Cover the crucible almost completely with a lid and start the ignition over a low mushroom flame, slowly increasing the temperature to full heat over a period of about 20 minutes, after which the crucible is transferred to a furnace at 1000 °C for 30 minutes. Remove the crucible from the furnace, cover it completely with a lid and weigh as soon as possible.

DETERMINATION OF OXIDES OF SILICON, IRON(III), TITANIUM(IV), MANGANESE(II), CHROMIUM(III), ALUMINIUM(III), CALCIUM AND MAGNESIUM—

Decomposition of the sample—Weigh 5·000 g of the finely ground sample, previously dried at 110 °C, and transfer to a 250-ml beaker. Add 25 ml of water and 40 ml of hydrochloric acid and cover the beaker with a clock-glass. Then transfer it to a sand-bath and boil the mixture for 30 minutes.

Determination of the main silica—Allow the beaker and contents to cool and rinse the clock-glass with water into the solution. Add a Whatman accelerator tablet and stir to break up the pulp, then add, with stirring, 2 to 3 ml of polyethylene oxide solution and allow to stand for 5 minutes. Filter the solution through a 110-mm Whatman No. 42 filter-paper and transfer the silica to the filter with hot dilute hydrochloric acid (1 + 19), scrubbing the beaker with a rubber-tipped glass rod. Wash the precipitate six times with hot dilute hydrochloric acid (1 + 19) and then with hot water until it is free from chlorides. Reserve the filtrate and washings.

Transfer the paper and precipitate to an ignited and weighed platinum crucible. Ignite them at a low temperature until the precipitate is free from carbonaceous matter and then heat in a muffle furnace at 1200 °C to constant weight, 30 minutes being normally sufficient.

Moisten the contents of the cold crucible with water, add 5 drops of sulphuric acid (1 + 1) and about 10 ml of hydrofluoric acid. Evaporate the mixture to dryness on a sand-bath in a fume cupboard. For the evaporation, the crucible and contents should be heated from below as the use of top heating alone, as with a radiant heater, may result in incomplete elimination of silica by the hydrofluoric acid. Heat the crucible and residue, cautiously at first, over a gas flame and finally for 5 minutes in a furnace at 1200 °C, cool and weigh. If the residue weighs more than 30 mg repeat the treatment with sulphuric and hydrofluoric acids to ensure that all of the silica is removed. The difference between the two weights represents the "gravimetric" silica.

PREPARATION OF A SOLUTION FOR THE DETERMINATION OF THE RESIDUAL OXIDES—

Fuse the residue from the hydrofluoric acid treatment of the "gravimetric" silica with 2 g of sodium carbonate and 0·4 g of boric acid. Place the crucible containing the cooled melt, *plus* the lid, into the filtrate and washings from the main silica. When the melt has dissolved remove the crucible and lid, scrubbing them with a rubber-tipped glass rod. Cool, dilute the solution to 500 ml in a calibrated flask and mix. This solution is referred to as the stock solution.

Determination of residual silica—Transfer 5·0 ml of the stock solution to a 100-ml calibrated flask (A) and add 15 ml of water. Add 2 drops of 2,4-dinitrophenol indicator and dilute ammonia solution (1 + 1) dropwise until the indicator turns yellow (note the amount of ammonia solution used), then add 5 ml of dilute hydrochloric acid (1 + 4).

To another 100-ml calibrated flask (B), add 20 ml of water and the same amount of ammonia solution (1 + 1) as was used to neutralise the aliquot in flask A. Add 2 drops of 2,4-dinitrophenol indicator followed by dilute hydrochloric acid (1 + 4) until the solution is neutral and then 5 ml in excess.

To both flasks add 6 ml of ammonium molybdate (8 per cent. w/v) and stand them for 5 to 10 minutes at a temperature of not less than 20 °C and not more than 30 °C. Then add, with swirling, 45 ml of dilute hydrochloric acid (1 + 1) and leave to stand for 10 minutes. Add 10 ml of tin(II) chloride solution (1 per cent. w/v), dilute to 100 ml and mix. The deep yellow - brown colour that appears on addition of the tin(II) chloride is quite normal and does not interfere at the wavelength used. Measure the optical density of the solution in flask A against the solution in flask B in 10-mm cells at 800 nm, or by using a colour filter (Ilford 609) in a suitable instrument. The colour is stable for between 5 and 30 minutes after the addition of the tin(II) chloride solution. Determine the silica content of the solution by reference to a calibration graph, then add the figure for residual silica content to that obtained for the "gravimetric" silica to obtain the total silica content.

Determination of iron(III) oxide—This determination is for total iron expressed as iron(III) oxide. Any iron normally present in the sample should have been oxidised to the iron(III) state during the determination of loss on ignition. The recording of total iron as iron(III) oxide takes account of this and results in correct analysis totals.

Dilute 50·0 ml of the stock solution to 250 ml in a calibrated flask and mix. This solution is referred to as the dilute stock solution and is also used for the determination of magnesium oxide. Transfer 5·00 ml of the dilute stock solution to a 100-ml calibrated flask. Add 2 ml of hydroxylammonium chloride solution (10 per cent. w/v), 5 ml of 1,10-phenanthroline solution (1 per cent. w/v) and 2 ml of ammonium acetate solution (about 10 per cent.). Allow the solution to stand for 15 minutes, dilute to 100 ml and mix.

Measure the optical density of the solution against water in 10-mm cells at 510 nm, or by using a colour filter (Ilford 603) in a suitable instrument. The colour is stable for 15 to 75 minutes after addition of the ammonium acetate solution. Determine the iron(III) oxide content of the solution by reference to a calibration graph.

Determination of titanium(IV) oxide—If the sample has a high chromium(III) oxide content giving a very yellow solution, the chromium in the control solution must be reduced by the addition of 2 ml of hydroxylammonium chloride solution (10 per cent. w/v).

Transfer 40·0 ml of the stock solution to each of two 100-ml calibrated flasks, A and B. To each flask add 10 ml of phosphoric acid (2 + 3) and, to flask A only, add 10 ml of hydrogen peroxide solution. Dilute the solution in each flask to 100 ml and mix. Measure the optical density of the solution in flask A against the solution in flask B in 40-mm cells at 398 nm, or by using a colour filter (Ilford 601) in a suitable instrument. The colour is stable from 5 minutes to 24 hours after addition of the hydrogen peroxide solution. Determine the titanium(IV) content of the solution by reference to a calibration graph.

Determination of manganese(II) oxide—Transfer 10·0 ml of the stock solution to a 250-ml beaker. Add 10 ml of dilute sulphuric acid (1 + 1), 10 ml of dilute nitric acid (1 + 1) and evaporate to strong fumes to remove chlorides. Add 20 ml of nitric acid, 10 ml of dilute phosphoric acid (1 + 9) and about 50 ml of water. Boil the solution to remove any nitrous fumes, filter it through a Whatman No. 40 filter-paper, then add about 0·2 g of potassium periodate. Boil until the pink colour develops and then for a further 2 minutes. Transfer the beaker to a steam-bath and keep it hot for 10 minutes. Allow the solution to cool and transfer it to a 100-ml calibrated flask. Dilute the solution in the flask to 100 ml and mix.

Measure the optical density of the solution against water in 40-mm cells at 524 nm, or by using a colour filter (Ilford 604) in a suitable instrument. Determine the manganese(II) oxide content of the solution by reference to a calibration graph.

Determination of chromium(III) oxide (a) *by diphenylcarbazide method (for Cr_2O_3 contents of up to approximately 0·1 per cent.)*—Transfer 10·0 ml of the stock solution to a 100-ml beaker, add 5 ml of dilute sulphuric acid (1 + 9) and 5 ml of nitric acid and evaporate the mixture to dryness. To the dry residue add 2 ml of dilute sulphuric acid (1 + 9) and about 15 ml of water. Warm to dissolve as much of the residue as possible, then filter, if necessary, through a Whatman No. 42 filter-paper and wash the residue with warm water. Evaporate the solution and washings to about 20 ml, add 2 ml of ammonium cerium(IV) nitrate solution

(1 per cent. w/v) and allow to stand on a steam-bath for 25 minutes. Cool to 10 °C and add sodium azide solution (2 per cent. w/v), dropwise, to destroy the colour of the excess of cerium(IV) ions.

Transfer the solution to a 100-ml calibrated flask containing 3 ml of dilute sulphuric acid (1 + 9) and dilute to about 90 ml. Add 2 ml of diphenylcarbazide solution (1 per cent. w/v), dilute to 100 ml and mix. Allow to stand for 5 minutes. Measure the optical density of the solution against water in 10-mm cells at 540 nm, or by using a colour filter (Ilford 605) in a suitable instrument. Determine the chromium(III) oxide content of the solution by reference to a calibration graph.

Determination of chromium(III) oxide (b) *by EDTA method* (*for Cr_2O_3 contents above approximately* 0·1 *per cent.*)—Transfer 50·0 ml of the stock solution to a 500-ml separating funnel (a Squibb type is recommended). Add 20 ml of chloroform and 10 ml of sodium diethyldithiocarbamate solution (10 per cent. w/v), stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Then wash the aqueous solution with 10-ml portions of chloroform until the chloroform layer is colourless (at least three washes are required) and discard the chloroform extracts.

Transfer the aqueous phase to a 400-ml beaker, boil off any traces of chloroform and cool to room temperature. Add 20 drops of hydrochloric acid, followed by 10 ml of sodium sulphite solution, with stirring, and boil for 5 minutes. Cool to room temperature, then add 10 ml of EDTA solution followed by ammonia solution, dropwise, until the first appearance of a slight permanent precipitate. Dissolve this precipitate by adding 20 drops of dilute acetic acid (1 + 1) and dilute to about 200 ml. Heat the solution to boiling and boil for 10 to 15 minutes, cool, dilute to 250 ml in a calibrated flask and mix.

Measure the optical density of the solution against water in 40-mm cells at 550 nm, or by using a colour filter (Ilford 605) in a suitable instrument. Determine the chromium(III) oxide content of the solution by reference to a calibration graph.

Determination of aluminium(III) oxide—Transfer 100·0 ml of the stock solution to a 400-ml beaker. Add 10 ml of sulphurous acid and boil off the excess sulphur dioxide. Cool slightly, add 5 ml of nitric acid and boil for 15 minutes. Cool to about 80 °C, add 5 g of ammonium chloride and stir to dissolve, then add dilute ammonia solution (1 + 1), with stirring, until the solution is just alkaline to bromophenol blue. Boil off the slight excess of ammonia.

Allow the solution to stand for 5 minutes for the precipitate to settle, then filter it through a Whatman No. 541 filter-paper. Rinse the beaker with hot, slightly ammoniacal, ammonium nitrate solution and pour the washings through the filter. Wash the precipitate well with more hot, slightly ammoniacal, ammonium nitrate solution, and discard the filtrate and washings. Place the precipitation beaker under the funnel and dissolve the precipitate through the filter with 40 ml of hot, dilute hydrochloric acid (1 + 1). Wash the paper thoroughly with hot water and discard it.

Cool the solution and transfer it to a separating funnel. The volume at this stage should be about 100 ml. Add 20 ml of chloroform and 10 ml of cupferron solution (6 per cent. w/v). Stopper the funnel and shake it vigorously, releasing the pressure in the funnel by carefully removing the stopper. Rinse the stopper and neck of the funnel with water, allow the layers to separate and withdraw the chloroform layer. Confirm that extraction is complete by checking that the addition of a few drops of cupferron solution does not produce a permanent coloured precipitate. Add 10-ml portions of chloroform and repeat the extraction until the chloroform layer is colourless. At this point wash the stem of the funnel inside and out with chloroform.

Discard the chloroform extracts and transfer the aqueous solution to a 500-ml conical flask. Add a few drops of bromophenol blue solution and then add ammonia solution dropwise until the solution is just alkaline. Re-acidify it quickly with hydrochloric acid and add 5 to 6 drops in excess. Add 10·0 ml of standard EDTA solution (0·05 M); this is sufficient for 2·5 per cent. of alumina. Then add ammonium acetate buffer solution (for alumina determination) until the indicator turns blue, followed by 10 ml in excess. Boil the solution for 10 minutes and cool. Add a volume of 95 per cent. ethanol equal to the total volume of the solution, followed by 1 to 2 ml of dithizone solution and titrate with the standard zinc solution (0·05 M), which is run in from a semi-micro or similar burette, from green to the

first appearance of a permanent pink colour. (The pinkish tinge that sometimes appears in the solution after the addition of the dithizone and the purple colour due to the chromium - EDTA complex can both be screened out by the dropwise addition of naphthol green B solution.) If the EDTA solution is not exactly 0·05 M, calculate the equivalent volume of exactly 0·05 M solution. Correct for the blank determination.

If V ml is the volume of 0·05 M EDTA solution and v ml is the volume of zinc solution used in the back-titration, then the percentage of aluminium(III) oxide is $0{\cdot}255\ (V - v)$. This figure must be corrected for any chromium(III) oxide in the sample. Multiply the percentage of chromium(III) oxide content by 0·667 and deduct this figure from the percentage of aluminium(III) oxide.

Determination of lime—Transfer a 50-ml aliquot of the stock solution to a 250-ml calibrated flask. Add 5 ml of dilute triethanolamine solution (1 + 1), a slight excess (10 ml for magnesites, or as appropriate for dolomites) of EGTA solution (approximately 0·05 M) and dilute to 150 ml. Add potassium hydroxide solution (25 per cent. w/v) until no further precipitation takes place and then add 10 ml in excess, followed by 10 ml of Magflok solution. Dilute to 250 ml, shake and allow the mixture to stand for about 10 minutes to settle. Filter it through a 150-mm dry Whatman No. 541 filter-paper into a dry beaker. Then pipette 200 ml of the filtrate into a 500-ml conical flask and add 15 ml of potassium hydroxide solution followed by about 0·03 g of screened Calcein indicator and titrate with standard calcium solution (0·05 M) until the first appearance of a green fluorescence. The titration is best carried out in good daylight, but direct sunlight should be avoided.

If the EGTA solution is not exactly 0·05 M, calculate the equivalent volume of exactly 0·05 M EGTA solution. If V ml of 0·05 M EGTA are taken and v ml of calcium solution (0·05 M) are used for back-titration, then the percentage of lime $= 0{\cdot}701 \times (4/5\ V - v)$. Correct for the blank determination.

Determination of magnesium oxide—Transfer 100·0 ml of the dilute stock solution [see Determination of iron(III) oxide] to a 500-ml separating funnel. Add dilute ammonia solution (1 + 1) dropwise, until the solution is slightly alkaline to bromophenol blue. Just re-acidify with dilute hydrochloric acid (1 + 3) and then add 4 ml in excess. Add 20 ml of chloroform and 10 ml of sodium diethyldithiocarbamate solution (10 per cent. w/v), then stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. (If an emulsion has formed, it will be necessary to add a few drops of hydrochloric acid and re-shake the mixture.) Add 10-ml portions of chloroform and 5-ml portions of diethyldithiocarbamate solution, repeating the extraction after each pair of additions until the additions no longer cause a coloured precipitate to form. Finally, wash the aqueous phase three times with 10-ml portions of chloroform. This separation will remove iron and manganese.

If the sample contains more than approximately 1 per cent. of aluminium(III) oxide it will be necessary to carry out a buffered cupferron - chloroform solvent extraction as follows. Add dilute ammonia solution (1 + 1) dropwise until the solution is just alkaline to bromophenol blue. Just re-acidify with dilute hydrochloric acid (1 + 9) and add 20 ml of the ammonium acetate buffer solution. Add 20 ml of chloroform and 10 ml of cupferron solution (6 per cent. w/v), stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Repeat the extraction with a further 10 ml of cupferron solution and finally wash the aqueous phase three times with 10-ml portions of chloroform. This separation will remove aluminium and titanium.

Transfer the aqueous phase from either the diethyldithiocarbamate separation or, if aluminium(III) oxide has been removed, from the buffered cupferron separation to a 500-ml conical flask and boil off any traces of chloroform. Cool, add 2 g of ammonium chloride and 2 ml of dilute triethanolamine solution (1 + 1) with swirling, followed by an appropriate, known amount of about 0·05 M DCTA solution (*e.g.*, 80 ml for magnesites or 40 ml for dolomites). This addition is made to complex most of the magnesium before the solution is made alkaline, so that the tendency for magnesium hydroxide to precipitate is greatly reduced. Then, add 30 ml of ammonia solution followed by 5 ml of hydroxylammonium chloride solution.

Add approximately 0·015 g of Solochrome black 6B indicator and titrate the solution with the standard DCTA solution from red, through purple, until the last change in colour to a clear ice blue. This titration also includes the titration for lime in the sample, and this must be determined by the method given.

If the DCTA solution is not exactly 0·05 M, calculate the equivalent volume of exactly 0·05 M DCTA solution. Then, if V is the total amount of 0·05 M DCTA added and v is the calculated amount of 0·05 M EGTA required to react with the lime in a 0·2-g sample, $(V - v) \times 1{\cdot}008$ = percentage of magnesium oxide in the sample.

REPORTING OF RESULTS—

Results should be reported with respect to either the dried material (dried to constant weight at 110 °C), or the ignited (at 1000 °C) material (calculated to zero loss on ignition).

CALIBRATIONS FOR COLORIMETRIC METHODS—

Residual silica—Transfer 0, 2·0, 4·0, 6·0, 8·0 and 10·0-ml portions of the standard silica solution B to 100-ml calibrated flasks and add 20, 18, 16, 14, 12 and 10 ml of water, respectively. This will give a calibration for 0 to 0·4 per cent. of SiO_2. Add to each flask, with swirling, 5 ml of dilute hydrochloric acid (1 + 4) followed by 6 ml of ammonium molybdate solution and leave them to stand for 5 to 10 minutes at a temperature of not less than 20 °C and not greater than 30 °C. Then add, with swirling, 45 ml of dilute hydrochloric acid (1 + 1) and leave to stand for 10 minutes. Add 10 ml of tin(II) chloride solution (1 per cent. w/v), dilute the solution in each flask to 100 ml and mix.

Measure the optical densities of the solutions against the zero solution in 10-mm cells at 800 nm, or by using a colour filter (Ilford 609) in a suitable instrument. The colour is stable for 5 to 30 minutes after the addition of the tin(II) chloride solution. Prepare a calibration graph from the optical densities.

Iron(III) oxide—Transfer 0, 10·0, 20·0, 25·0, 40·0 and 50·0-ml portions of the standard iron solution B to 100-ml calibrated flasks. This will give a calibration graph for 0 to 5 per cent. of Fe_2O_3. Add to each flask 2 ml of hydroxylammonium chloride solution, 5 ml of 1,10-phenanthroline solution and 2 ml of ammonium acetate solution (approximately 10 per cent.). Allow to stand for 15 minutes, dilute the solution in each flask to 100 ml and mix.

Measure the optical densities of the solutions against water in 10-mm cells at 510 nm, or by using a colour filter (Ilford 603) in a suitable instrument. The colour is stable for 15 to 75 minutes after the addition of the ammonium acetate solution. From the optical densities prepare a calibration graph.

Titanium(IV) oxide—Transfer in duplicate 0, 10·0, 20·0, 25·0, 40·0 and 50·0-ml portions of the standard titanium solution B to 100-ml calibrated flasks. This will give a calibration graph for 0 to 0·5 per cent. of TiO_2. Add to each flask 10 ml of dilute phosphoric acid (2 + 3) and to one of each pair only add 10 ml of hydrogen peroxide solution. Dilute the solution in each flask to 100 ml and mix.

Measure the optical densities of the pertitanic acid solutions against the appropriate control solution in 40-mm cells at 398 nm, or by using a colour filter (Ilford 601) in a suitable instrument. The colour is stable for 5 minutes to 24 hours after the addition of the hydrogen peroxide solution. From the optical densities prepare a calibration graph.

Manganese(II) oxide—Transfer 0, 10·0, 20·0, 25·0, 40·0 and 50·0-ml portions of the standard manganese solution B to 100-ml calibrated flasks. This will give a calibration graph for 0 to 0·5 per cent. of MnO. Dilute the solution in each flask to 100 ml and mix.

Measure the optical densities of the solutions against water in 40-mm cells at 524 nm, or by using a colour filter (Ilford 604) in a suitable instrument. From the optical densities prepare a calibration graph.

Chromium(III) oxide—For method (*a*), the diphenylcarbazide method, transfer 0, 1·0, 2·0, 3·0, 4·0 and 5·0-ml portions of the standard chromium solution B to 100-ml calibrated flasks. This will give a calibration graph for 0 to 0·125 per cent. of Cr_2O_3. Add to each flask 5 ml of dilute sulphuric acid (1 + 9) and dilute to about 90 ml. Add to each 2 ml of diphenylcarbazide solution (1 per cent. w/v), dilute to 100 ml and mix. Allow to stand for 5 minutes.

Measure the optical densities of the solutions against water in 10-mm cells at 540 nm, or by using a colour filter (Ilford 605) in a suitable instrument. From the optical densities prepare a calibration graph.

TABLE I

RESULTS ON MAGNESITE SAMPLE AN 31 (IGNITED AT 1000 °C)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Fe_2O_3, per cent.	Al_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Total,* per cent.
A	2·50	0·03	1·75	0·84	0·07	0·09	2·31	92·11	99·70
	2·48	0·03	1·76	0·85	0·07	0·09	2·30	91·97	99·55
	2·50	0·03	1·75	0·86	0·07	0·09	2·32	91·97	99·59
B	2·43	0·05	1·83	0·88	0·07	0·08	2·30	92·04	99·68
	2·46	0·05	1·77	0·89	0·07	0·075	2·31	92·04	99·67
	2·49	0·04	1·83	0·88	0·07	0·08	2·30	92·27	99·96
C	2·48	0·04	1·74	0·87	0·07	0·11	2·33	92·62	100·26
	2·49	0·04	1·73	0·86	0·08	0·12	2·32	92·48	100·12
	2·48	0·04	1·73	0·86	0·07	0·11	2·34	92·78	100·41
D	2·46	0·039	1·76	0·85	0·066	0·087	2·31	92·30	99·88
	2·46	0·037	1·75	0·87	0·067	0·087	2·35	92·46	100·09
	2·45	0·039	1·76	0·85	0·067	0·087	2·31	92·52	100·09
E	2·49	0·03	1·79	0·84	0·08	0·10	2·32	92·17	99·82
	2·50	0·04	1·81	0·85	0·07	0·12	2·31	92·03	99·59
	2·51	0·03	1·76	0·84	0·08	0·10	2·34	92·17	99·83
F	2·51	0·03	1·76	0·84	0·08	0·09	2·34	92·04	99·70
	2·51	0·03	1·76	0·84	0·08	0·09	2·31	92·17	99·79
	2·52	0·03	1·75	0·84	0·08	0·09	2·31	92·17	99·79
G	2·48	0·03	1·80	0·84	0·07	0·12	2·28	92·14	99·76
	2·52	0·03	1·78	0·84	0·06	0·12	2·33	91·80	99·48
	2·48	0·02	1·77	0·82	0·07	0·11	2·30	92·03	99·60
Mean	2·49	0·04	1·77	0·85	0·07	0·10	2·32	92·20	
Standard deviation	0·02	0·01	0·03	0·02	0·01	0·01	0·02	0·24	

* The alkali-metal oxides in this sample total about 0·05 per cent. and have not been included in the total.

TABLE II

RESULTS ON MAGNESITE SAMPLE AN 32 (IGNITED AT 1000 °C)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Fe_2O_3, per cent.	Al_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Total,* per cent.
A	0·95	0·01	5·49	0·99	0·76	0·11	1·79	89·60	99·70
	0·93	0·02	5·49	0·99	0·76	0·11	1·78	89·68	99·76
	0·94	0·02	5·49	0·99	0·76	0·11	1·77	89·55	99·63
B	0·97	0·026	5·41	0·91	0·76	0·08	1·78	89·91	99·85
	0·97	0·026	5·49	0·93	0·74	0·09	1·79	89·80	99·84
	0·96	0·026	5·49	0·93	0·76	0·075	1·78	89·76	99·79
C	0·95	0·02	5·31	1·05	0·74	0·16	1·78	89·59	99·60
	0·94	0·03	5·43	1·09	0·77	0·16	1·76	89·41	99·59
	0·95	0·02	5·33	1·02	0·77	0·15	1·74	89·36	99·34
D	0·98	0·029	5·40	0·98	0·80	0·109	1·81	89·50	99·61
	0·98	0·027	5·40	0·99	0·77	0·109	1·79	89·45	99·52
	0·98	0·027	5·45	0·99	0·77	0·109	1·80	89·37	99·50
E	0·99	0·03	5·46	1·01	0·72	0·13	1·70	89·47	99·51
	0·97	0·02	5·42	0·99	0·72	0·12	1·76	89·47	99·47
	1·00	0·02	5·45	1·00	0·68	0·12	1·70	89·60	99·55
F	1·01	0·02	5·42	1·01	0·74	0·13	1·78	89·76	99·87
	0·99	0·02	5·38	1·01	0·74	0·13	1·75	89·75	99·77
	1·01	0·02	5·42	1·00	0·75	0·14	1·75	89·81	99·90
G	1·00	0·03	5·45	0·96	0·72	0·13	1·73	89·36	99·38
	0·97	0·02	5·50	0·98	0·74	0·12	1·70	89·47	99·50
	0·98	0·02	5·50	0·98	0·74	0·12	1·70	89·23	99·27
Mean	0·97	0·02	5·44	0·99	0·75	0·12	1·76	89·57	
Standard deviation	0·02	0·01	0·05	0·04	0·03	0·02	0·04	0·18	

* The alkali-metal oxides in this sample total about 0·04 per cent. and have not been included in the total.

For method (*b*), the EDTA method, transfer 0, 5·0, 10·0, 15·0 and 20·0-ml portions of the standard chromium solution A to 400-ml beakers and add 50, 45, 40, 35 and 30 ml of water, respectively. This will give a calibration graph for 0 to 2 per cent. of Cr_2O_3. Add to each 20 drops of hydrochloric acid, followed by 10 ml of sodium sulphite solution (5 per cent. w/v) with stirring, and boil for 5 minutes. Cool to room temperature, add 10 ml of EDTA solution (5 per cent. w/v) followed by ammonia solution dropwise, until the first appearance of a permanent precipitate. Dissolve this precipitate by adding 20 drops of dilute acetic acid (1 + 1) and dilute to about 200 ml. Heat the solutions to boiling and boil for 10 to 15 minutes, cool, dilute to 250 ml in calibrated flasks and mix.

Measure the optical densities of the solutions against water in 40-mm cells at 550 nm, or by using a colour filter (Ilford 605) in a suitable instrument. From the optical densities prepare a calibration graph.

Results

The results obtained by the Refractories Working Group are shown in Tables I to IV. The samples are two magnesites (Tables I and II) and two dolomites (Tables III and IV); the dolomite in Table III, B.C.S. 368, is a standard sample.

Table III

Results on dolomite sample B.C.S. 368 (dried at 110 °C)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Fe_2O_3, per cent.	Al_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Loss, per cent.	Total, per cent.
A	0·90	<0·01	0·22	0·17	<0·01	0·04	30·66	20·97	46·78	99·74
	0·92	<0·01	0·22	0·17	<0·01	0·04	30·68	20·97	46·81	99·81
	0·93	<0·01	0·22	0·18	<0·01	0·04	30·68	20·92	46·82	99·79
B	0·92	0·005	0·21	0·17	0·009	0·058	30·75	20·93	46·80	99·86
	0·91	0·005	0·22	0·17	0·010	0·055	30·77	20·86	46·80	99·81
	0·93	0·005	0·21	0·17	0·009	0·060	30·75	20·97	46·70	99·81
C	0·93	<0·01	0·22	0·15	<0·01	0·06	30·81	20·67	46·77	99·61
	0·95	<0·01	0·22	0·15	<0·01	0·06	30·85	20·69	46·77	99·69
	0·94	<0·01	0·21	0·15	<0·01	0·05	30·83	20·77	46·77	99·72
D	0·89	0·006	0·22	0·16	0·006	0·06	30·70	20·84	46·68	99·57
	0·90	0·006	0·22	0·17	0·006	0·06	30·69	20·90	46·67	99·63
	0·91	0·006	0·22	0·18	0·006	0·06	30·69	20·80	46·67	99·55
E	0·90	<0·01	0·24	0·14	0·010	0·06	30·70	21·27	46·59	99·91
	0·93	<0·01	0·24	0·14	0·008	0·06	30·84	21·27	46·60	100·09
	0·90	<0·01	0·24	0·13	0·009	0·06	30·84	21·08	46·50	99·76
F	0·92	0·005	0·24	0·16	0·013	0·06	30·88	20·76	46·67	99·67
	0·94	0·005	0·24	0·16	0·012	0·06	30·84	20·84	46·67	99·72
	0·93	0·005	0·25	0·16	0·013	0·06	30·84	20·85	46·67	99·73
G	0·92	0·01	0·23	0·18	0·01	0·03	30·91	20·30	46·86	99·45
	0·93	0·01	0·22	0·17	0·01	0·04	30·84	20·40	46·82	99·44
	0·92	0·01	0·23	0·18	0·01	0·04	30·80	20·40	46·86	99·45
H	0·89	0·004	0·23	0·17	0·006	0·06	30·91	20·88	46·50	99·65
	0·92	0·004	0·23	0·17	0·006	0·06	30·81	20·88	46·38	99·46
	0·90	0·004	0·21	0·17	0·006	0·06	30·81	20·88	46·46	99·50
I	0·90	0·003	0·24	0·19	0·01	0·07	30·52	21·04	46·54	99·51
	0·89	0·002	0·21	0·16	0·005	0·06	30·66	21·14	46·59	99·72
	0·91	0·002	0·25	0·20	0·01	0·06	30·66	21·04	46·52	99·65
Mean	0·92	0·004	0·23	0·17	0·007	0·055	30·77	20·86	46·68	
Standard deviation	$0·01_7$	0·003	$0·01_2$	$0·01_6$	0·004	0·010	$0·09_4$	0·23	0·13	

Development of the method and discussion of results

Loss on ignition—

No difficulty was experienced with this determination as it was appreciated that when large volumes of carbon dioxide were to be evolved, care would be needed during the warming-up stage. It was also realised that the crucibles used would need to have well fitting lids so as to minimise re-carbonation during cooling.

The results of analyses shown in Tables I to IV are calculated with respect to ignited material, with the exception of the dolomite (B.C.S. 368), which was a raw sample. As the

TABLE IV

RESULTS ON DOLOMITE SAMPLE AN 34 (IGNITED AT 1000 °C)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Fe_2O_3, per cent.	Al_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Total, per cent.
A	1·04	0·01	1·04	0·38	0·01	0·13	57·06	39·92	99·59
	1·04	0·01	1·06	0·36	0·01	0·15	57·13	39·99	99·75
	1·06	0·01	1·04	0·38	0·01	0·15	57·06	39·99	99·70
B	0·97	0·005	1·14	0·38	<0·01	0·10	57·14	39·80	99·54
	1·02	0·005	1·14	0·38	<0·01	0·10	57·12	39·72	99·49
	0·99	0·005	1·13	0·39	<0·01	0·10	57·26	39·76	99·64
C	1·05	0·02	1·06	0·37	0·01	0·16	57·09	40·19	99·95
	1·05	0·03	1·06	0·39	0·01	0·16	57·17	40·08	99·95
	1·05	0·03	1·05	0·39	0·01	0·16	57·15	40·26	100·10
D	1·04	0·026	0·98	0·36	0·009	0·15	57·29	40·03	99·90
	1·01	0·026	0·98	0·38	0·009	0·14	57·31	39·80	99·66
	1·04	0·026	0·99	0·36	0·009	0·14	57·49	39·71	99·77
F	1·03	0·01	1·04	0·38	0·01	0·14	56·95	39·90	99·46
	1·03	0·01	1·04	0·37	0·01	0·14	56·99	39·87	99·46
	1·04	0·01	1·03	0·37	0·01	0·14	56·97	39·94	99·51
G	1·02	0·01	1·08	0·38	0·01	0·14	57·25	39·90	99·79
	1·03	0·02	1·07	0·37	0·01	0·14	57·40	39·76	99·80
	1·03	0·01	1·08	0·37	0·01	0·13	57·25	39·90	99·78
H	0·95	0·015	1·04	0·40	0·006	0·16	57·17	40·11	99·86
	0·95	0·015	1·04	0·40	0·006	0·16	57·04	39·92	99·54
	0·96	0·015	1·00	0·39	0·008	0·16	57·17	39·74	99·45
I	1·02	0·025	1·06	0·39	<0·01	0·15	57·21	40·35	100·21
	1·04	0·020	1·06	0·40	<0·01	0·16	57·27	40·22	100·17
	1·02	0·025	1·06	0·39	<0·01	0·16	57·14	40·22	100·02
Mean	1·02	0·016	1·05	0·38	0·007	0·14	57·17	39·96	
Standard deviation	$0·03_2$	0·008	$0·04_3$	$0·01_3$	0·004	0·02	0·13	0·19	

samples (particularly dolomite) are unstable when exposed to the atmosphere after grinding the calculation of results on an ignited basis is the only reasonable method of comparing analytical results. Only when the materials are in their natural (unfired) state can comparisons be made on a dried (at 110 °C) basis.

DETERMINATION OF SILICA—

In the method originally proposed[3] the sample was decomposed with hydrochloric acid and the insoluble residue fused with sodium carbonate. After this treatment, silica was determined gravimetrically by means of a single dehydration. This process was very time consuming and attempts were made, for routine use, to eliminate the fusion stage. It was found that solutions of samples decomposed with hydrochloric acid, even if evaporated to dryness and re-dissolved in dilute hydrochloric acid, were very slow to filter; substitution of perchloric acid for the hydrochloric acid, and evaporation, first to fumes and then for a further 30 minutes, instead of dehydration, improved the speed of filtration considerably.

Co-operative results with perchloric acid, together with a 1-g sample of magnesite, resulted in standard deviations of about 0·08 per cent. As the industrial demand was for an accuracy of at least $\pm$0·1 per cent. these results were clearly of little value. The errors were greatly minimised by increasing the size of the sample to 5 g, at which level the standard deviation dropped to 0·01 to 0·03 per cent. (coefficient of variation about 1 per cent.).

The main disadvantage of the method was the need to use about 40 ml of perchloric acid (60 per cent. w/v) and to heat it to fumes in a glass beaker for at least 30 minutes. The use of perchloric acid in such large amounts introduced an element of danger which, although acceptable from necessity, was nevertheless not desirable. An additional factor was the cost of the perchloric acid which, when used in a duplicate determination, was 40p.

After the discovery that polyethylene oxide coagulated silica in acidic solution,[4] it seemed obvious to investigate the effect of this reagent on the solutions resulting from hydrochloric acid decomposition of magnesites and dolomites. This treatment proved effective

and the residues could be quickly filtered off, provided slight changes were made to the volumes of liquids so as to keep the total volume at the coagulation stage to a reasonable minimum. Perchloric acid attack yielded much smaller residues than those obtained with hydrochloric acid so that there seemed to be a risk of retention of sulphur trioxide after the hydrofluoric acid - sulphuric acid treatment, thus giving rise to low silica figures. In fact, it was demonstrated that the figures obtained for silica when using hydrochloric acid were within 0·01 per cent. of those obtained with perchloric acid decomposition.

The use of a coagulant did, in fact, have one disadvantage. It proved impossible to use the yellow molybdosilicate colour for the determination of the residual silica because of clouding of the solution. However, reversion to the molybdenum-blue method overcame this difficulty.

DETERMINATION OF IRON(III) OXIDE—

No difficulty was experienced in adapting the 1,10-phenanthroline method to magnesites or dolomites. To maintain accuracy it was necessary to prepare a preliminary dilution so as to take a reasonably sized aliquot. This dilution served a second purpose in that it enabled a large aliquot to be taken for the determination of magnesium oxide.

DETERMINATION OF TITANIUM(IV) OXIDE—

No difficulty was experienced in adapting the hydrogen peroxide method. The low level of titanium(IV) oxide in these classes of materials makes this method rather insensitive but the present technological demands of the industry do not require a high order of accuracy, rather a check to ensure that a reasonably low level is maintained. Thus there seemed to be no reason to introduce more sensitive and, probably, more complicated procedures.

DETERMINATION OF MANGANESE(II) OXIDE—

The periodate method offered no difficulties in its application to magnesites and dolomites. It was anticipated that some difficulty might be caused by the low solubility of calcium sulphate and it had been intended to replace the sulphuric acid used for removing chlorides by perchloric acid. In fact, no difficulty was encountered in this respect.

The results show a relatively high coefficient of variation. Measurement against a portion of the same solution reduced with sodium nitrite would probably improve the results. However, the manganese content of these materials is not significant in practice and is usually determined only to ensure that it is not unusually high.

DETERMINATION OF CHROMIUM(III) OXIDE—

The normal diphenylcarbazide procedure was first adopted for this determination but it was found that, at above about 0·1 per cent., the results tended to be low. For this reason the EDTA spectrophotometric method, similar to that used for chrome-bearing materials,[5] was adopted. This proved to be sufficiently sensitive for amounts of chromium(III) oxide greater than about 0·1 per cent. Therefore both methods are included so as to ensure full coverage.

DETERMINATION OF ALUMINIUM(III) OXIDE—

Several techniques were tried in the early stages of development of the present method, *viz.*, gravimetric determination with 8-hydroxyquinoline, spectrophotometric determination with the same reagent and direct titration with EDTA. All of these methods resulted in high figures caused by the interference of magnesium, so it became clear that a separation from magnesium was necessary. Separation was accomplished by precipitation with ammonia solution, which was conducted carefully to ensure complete recovery of aluminium even at the expense of not removing all the magnesium. Thus, if adequate care is taken, the method is not open to the normal objections when crude precipitation is recommended when it is the filtrate that is of prime importance. No attempt is made to oxidise the manganese before the precipitation so that it will escape and need not be corrected for in the EDTA titration. Iron and titanium are, of course, removed in the usual way with a cupferron - chloroform solvent extraction. Chromium, which may be present in moderate amounts (up to 0·75 per cent. in isolated cases), will also be titrated. As it is not possible to determine easily the amount of chromium in the solution after titration, it is necessary either to note its presence or ensure its absence. As it is far more difficult to ensure its absence, it is reduced

and precipitated quantitatively with the alumina. In a recent paper[1] DCTA was used as a replacement for EDTA. The advantage of DCTA lies in the fact that aluminium is complexed in cold solution, whereas chromium is not. Thus, the interference from chromium is eliminated and so are the need and the desirability to reduce the chromium because it is best to allow as much as possible to pass into the filtrate in the form of chromate. In addition, the determination is more rapid in that there is no need to boil and cool the solution. The use of DCTA entails no change in the method as described here except that, to avoid indicator fading, about 2 g of hydroxylammonium chloride must be added to the solution before adding the dithizone.

The results for aluminium(III) oxide show standard deviations for low contents (less than 0·4 per cent.) of about 0·01 per cent. At the higher level of 0·8 to 0·9 per cent. the standard deviation increases to about 0·02 per cent. in the absence of Cr_2O_3 and 0·04 per cent. when 0·75 per cent. of Cr_2O_3 is present. The latter may serve to indicate the increased errors due both to greater problems with the actual titration and also to the errors in the determination of the chromium. Thus the use of DCTA could be expected to improve the accuracy of the aluminium(III) oxide determination.

Determination of lime—

The method used for the determination of lime is similar to an earlier routine method[6] wherein excess of EDTA was added to complex the lime and the magnesium was then precipitated with alkali-metal hydroxide solution. This determination, together with the determination of magnesium oxide, gave the Working Group a large number of problems. Several techniques were tried with various indicators but each gave rise to difficulties in one or more laboratories. Potentiometric methods of determining the end-points were also tried, but without success. In the end it was necessary to revert to a method similar to the original but which included a filtration and the use of screened Calcein as indicator. The speed of this filtration was increased by the use of a partially hydrolysed polyacrylamide coagulant that has been named Magflok.

The substitution of EGTA for EDTA greatly improved the end-point because the superior stability of the calcium complex over that of magnesium is more apparent with EGTA than with EDTA.

The results on the magnesites are very satisfactory; it will be noted that the sample containing 0·75 per cent. of Cr_2O_3 again gives poorer results. This could be caused by background coloration from chromium in the titration solution. The results on the dolomites showed standard deviations (with reference to the ignited material) of 0·13 and 0·18, which is about the level normally obtained in co-operative work on ceramic materials between laboratories for major content determinations.

Determination of magnesium oxide—

Difficulties similar to those with lime were experienced with the end-point for magnesium oxide and, once again, the Working Group tried a number of methods before developing the present procedure. In order to achieve the accuracy desired by the refractories industry it was necessary to take a large aliquot; this was done by using the dilute stock solution made for the iron determination. In the presence of large amounts of magnesium oxide end-points almost inevitably tend to drag and it was therefore desirable to use the most suitable indicator. This precluded the use of the more usual methylthymol blue and the Working Group turned to the Solochrome dyes, preferring, in the end, Solochrome black 6B (blue-black B) to the more usual Solochrome black T. These indicators are easily destroyed and interfering elements such as iron and manganese must be removed. End-points were again shown to be sharper when EDTA was replaced, this time by DCTA.

Since completing the results in the table, it has been demonstrated that aluminium(III) oxide tends to interfere in the determination of magnesium oxide (see Table V).

For accurate work, therefore, if the aluminium(III) oxide content is greater than about 0·50 per cent., it is desirable to include the aluminium(III) oxide separation. For normal work, however, it is possible to allow the presence of up to 1 per cent. of aluminium(III) oxide, as the level of interference is still not greater than the experimental error. The interference was not considered large enough to warrant repeating the analyses reported in the tables. The results are, of course, inferior to those for lime as the magnesium oxide content

TABLE V

INTERFERENCE OF ALUMINIUM(III) OXIDE IN THE DETERMINATION OF MAGNESIUM OXIDE WITH DCTA

Aluminium(III) oxide added, per cent.	Magnesium oxide added, per cent.	Magnesium oxide found, per cent.
0·0	101·1 (≡ 202 mg)	101·1
0·25	101·1	101·1
0·50	101·1	101·1
0·75	101·1	101·25
1·0	101·1	101·25
2·0	101·1	102·1
3·0	101·1	103·0

is obtained by difference so that the errors in the lime determination may add to those in the magnesium oxide titration. This will be most significant in the case of the dolomites. The lime and magnesium oxide contents are usually determined on dolomites to ensure that the CaO - MgO ratio is not abnormal, and in the case of magnesites, prior to the development of this method, a magnesium oxide figure was normally obtained by the difference from 100 per cent. after subtracting the minor constituents. It is therefore clear that both sets of results are, in practice, sufficiently accurate.

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E. W. Orrell	*The Carborundum Co. Ltd.*
J. Sanderson	*Consett Iron Co. Ltd.*
C. E. A. Shanahan ..	*Stewarts and Lloyds Ltd.*
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R. F. Statham	*Samuel Fox and Co. Ltd.*
P. Wilburn	*Simon Engineering Ltd.*
A. K. Wright	*Lysaghts Scunthorpe Works Ltd.*
R. A. Reed (*Secretary*) ..	*The British Ceramic Research Association*

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4-[Bis(carboxymethyl)aminomethyl]-3-hydroxy-2-naphthoic Acid as a Fluorescent Indicator for the Complexometric Titration of Calcium *plus* Magnesium

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4-[Bis(carboxymethyl)aminomethyl]-3-hydroxy-2-naphthoic acid, known also as 1-dicarboxymethylaminomethyl-2-hydroxy-3-naphthoic acid, a spectrofluorimetric reagent for beryllium, has been found to be an effective fluorimetric indicator for the complexometric titration of calcium *plus* magnesium when used in conjunction with a suitable fluorimetric titrimeter. A procedure is described in which the indicator is used in the titrimetric determination of magnesium in silicate rocks.

The synthesis of 4-[bis(carboxymethyl)aminomethyl]-3-hydroxy-2-naphthoic acid, originally named as 1-dicarboxymethylaminomethyl-2-hydroxy-3-naphthoic acid (DHNA), and its use as a spectrofluorimetric reagent for beryllium have been described by Buděšínský and West,[1] who noted that the reagent forms fluorescent complexes with other metals, *e.g.*, it gives a green fluorescence with calcium and blue fluorescence with magnesium. In this paper DHNA is proposed as a fluorescent indicator for the complexometric titration of calcium *plus* magnesium, and a procedure is described for its application in silicate analysis. At pH 10 the fluorescence of the calcium and magnesium complexes of DHNA is progressively quenched by the addition of 1,2-diaminocyclohexane-*NNN'N'*-tetraacetic acid (DCTA), and the disappearance of this fluorescence occurs precisely at the equivalence point. Residual fluorescence of the reagent renders visual detection of the end-point rather difficult, although its detection is possible in a darkened room. The end-point can, however, be observed precisely under normal lighting conditions with the aid of a suitable fluorimetric titrimeter. An instrument of simple construction has been described elsewhere[2] and was used in the present work.

Method

Apparatus—

The simple fluorimetric titrimeter described by Clements and Sergeant[2] is suitable.

An air-bath is also used. This consists of a gas-ring on which stands an open-ended Vitreosil cylinder, 230 mm high and 125 mm in diameter. The PTFE basin is placed over a small flame on a silica triangle supported by the cylinder.

Reagents—

Dilute nitric acid (1 + 1)—Mix equal volumes of concentrated nitric acid (sp.gr. 1·42) and water.

Perchloric acid, 60 *per cent. w/w.*

Hydrofluoric acid, 40 *per cent. w/w.*

Dilute sulphuric acid, approximately 20 N—Add 1 volume of concentrated sulphuric acid (sp.gr. 1·84) cautiously, with stirring, to sufficient water to bring the final volume, when cooled, to 2 volumes.

Triethanolamine solution (1 + 1)—Dilute 1 volume of triethanolamine with an equal volume of water.

Buffer solution, pH 10—Dissolve 67·5 g of ammonium chloride in water, add 570 ml of concentrated ammonia solution (sp.gr. 0·88), and dilute the mixture to 1 litre with water.

1-*Dicarboxymethylaminomethyl*-2-*hydroxy*-3-*naphthoic acid* (*DHNA*) *indicator*—Prepare a mixture of the reagent with sodium chloride containing 0·5 per cent. w/w of the reagent.

Magnesium standard solution—Dissolve 0·603 g of clean magnesium ribbon in about 100 ml of water containing 10 ml of perchloric acid, and dilute the solution to 1 litre with water. This solution contains the equivalent of 1 mg ml^{-1} of magnesium oxide.

DCTA solution, approximately 0·01 M—Dissolve 3·3 g of 1,2-diaminocyclohexane-*NNN'N'*-tetraacetic acid in about 200 ml of water by making small additions of M sodium hydroxide solution. Adjust the pH of the solution to about 10 with acetic acid, and dilute to 1 litre with water. Standardise the solution against standard magnesium solution by titration as described in the procedure given below.

PROCEDURE FOR THE DETERMINATION OF MAGNESIUM IN SILICATE ROCKS—

Transfer 1·0000 g of powdered rock to a platinum or PTFE basin. Add about 20 ml of water followed by 2 ml of dilute nitric acid, 5 ml of perchloric acid and 20 ml of hydrofluoric acid, and allow the rock to digest overnight or longer at room temperature. Complete the decomposition of the sample by evaporating the mixture to dryness on an air-bath, and repeat the evaporation nearly to dryness with three further portions of perchloric acid, to the first of which 2 ml of dilute sulphuric acid have been added. Finally, add 5 ml of perchloric acid and about 50 ml of water, cover the basin and heat it on a water-bath or hot-plate to dissolve the residue. Dilute the solution to 200 ml at room temperature in a graduated flask.

Add, by pipette, to the titration vessel 10 ml of the rock solution followed by about 80 ml of water. Transfer the vessel to the titrimeter and apply magnetic stirring, then add 5 ml of triethanolamine solution, 10 ml of buffer solution and about 30 mg of DHNA indicator. Titrate calcium *plus* magnesium with DCTA solution under filtered ultraviolet illumination (365 nm) by using the fluorimetric titrimeter. A blue gelatine filter is placed over the photocell to improve discrimination; for this purpose the blue component of the Ilford Spectrum Blue-Green 603 filter has been found to be effective. The approach to the titration end-point is characterised by a stepwise reduction in the meter reading for each drop of titrant added, and although the final steps may be fairly small, the end-point is well defined and stable. The magnesium present is calculated from the titration value after making the appropriate deduction for calcium, which may be determined by fluorimetric titration of a further aliquot of solution with ethylene glycol bis(aminoethyl)tetraacetic acid (EGTA) at pH 13 in the presence of triethanolamine, with Calcein as indicator.[3]

RESULTS AND DISCUSSION

In this laboratory the fluorimetric titration of calcium *plus* magnesium, with DHNA as indicator, has now largely replaced the visual titration with Eriochrome black T indicator. The advantages claimed are the elimination of subjective judgment in the assessment of the end-point, and that it is not necessary to convert iron into ferrocyanide in order to mask it sufficiently to prevent interaction with the indicator. A reducing agent such as hydroxylamine is, therefore, not added, and the use of cyanide is required only if significant amounts of elements such as cobalt and nickel are known to be present, which need to be masked. In addition, large amounts of manganese do not interfere except to the extent that the triethanolamine complex reduces the light transmittance of the solution. Of other interferences, barium and strontium have been found to be partially titrated in the presence of calcium and magnesium, but do not themselves form fluorescent complexes with DHNA.

TABLE I

COMPARATIVE FIGURES FOR MAGNESIUM DETERMINATIONS ON ROCK SAMPLES

	MgO, per cent.			
	By method with DHNA indicator			Calcium found (average)
Material analysed	Operator 1	Operator 2	Other figures	CaO, per cent.
Granite, G-1	0·35	0·33	0·38*	1·32
Diabase, W-1	6·68	6·64	6·62*	10·84
Lamprophyre	6·46	6·50	6·54†	4·34
Rhyolitic tuff	0·39	0·40	0·42†	0·37
Chloritic tuff	1·98	1·95	2·08†	0·85
Spilitic tuff	10·75	10·82	—	5·12
Peridotite	30·89	30·71	30·90†	1·11
Norite	18·05	17·98	17·93†	4·69

* From the compilation by M. Fleischer.[4]
† Titration with Eriochrome black T indicator.

In Table I are shown some results of magnesium determinations obtained for several silicate rocks by using the procedure described above.

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Use of the Halphen Reaction for the Determination of the Cyclopropenoid Content of Lipids

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An application to cottonseed oils of a quantitative version of the Halphen test for the determination of cyclopropenoid material has been published by other workers, but for other oils containing higher levels of cyclopropenoids, although the absorption at the 495 nm peak is linearly related to the concentration of each oil examined, the relationship differs among the oils. However, transmethylation of oil before applying the Halphen reaction has been found to give results that are in better agreement with titration with hydrogen bromide for oils with widely differing cyclopropenoid content. The use of pressurised capsules for carrying out the reaction with reduced loss of solvent has proved advantageous, as flatter peaks are obtained when optical absorption is plotted against time. The application of the modified technique to oils containing a wide range of concentrations of total cyclopropenoid material in the component fatty acids is described and discussed.

The Halphen reaction[1] is used either as a qualitative test for cottonseed oil or to detect the presence of this oil in other vegetable oils,[2,3] but its usefulness as a specific test is limited by the positive reactions also given by seed oil from certain other species of the order Malvales.[4] The nature of the red colour developed has not been fully elucidated, but positive Halphen tests have been associated with the occurrence of cyclopropenoid fatty acid[5,6,7] and proportional increases in absorbances, measured at 505 nm, have been reported for mixtures of sterculic acid in corn oil.[8] The relationship between cyclopropenoid contents determined by hydrogen bromide titration and absorbances obtained by using the Halphen reaction has also been reported.[9] Colorimetric methods involving the use of the Halphen reaction have been used for the determination of cyclopropenoid material in cottonseed oil or meal, with crude cottonseed oil or cyclopropenoid-containing oils of unstated origin as standards.[9,10] The

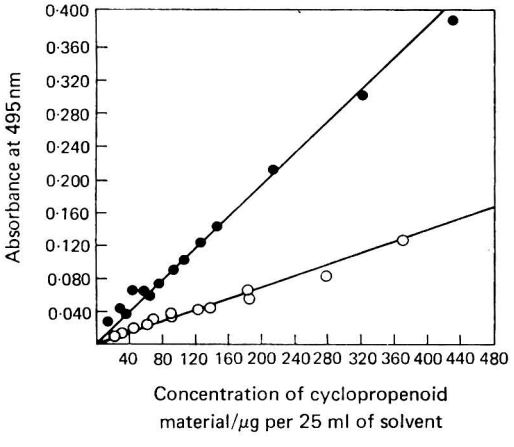

Fig. 1. Values with *Sterculia foetida* oil and its methyl esters by using Bailey and co-workers' method: ○, oil; and ●, methyl esters. (In all figures, open points represent the oils and closed points the methyl esters)

determination of the cyclopropenoid content of rat liver lipid by using a modified Halphen test has also been reported, with methyl sterculate used as a standard.[11]

A variety of reaction conditions has been used to produce the Halphen response from oils or methyl esters, including heating for 2·5 hours at 110 °C,[9,10] or for 1 hour at 48 °C followed by heating for 45 minutes at 108 °C or for 15 minutes at 45 °C followed by heating for 5 minutes at 95 °C and finally for 1 hour at 105 °C.[11] Pentanol has been replaced by pyridine[8,11] or by butanol,[9,10] and morpholine has been used to improve colour stability.[9,10]

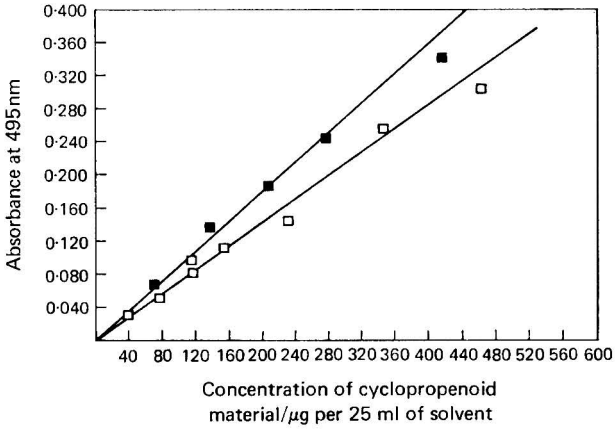

Fig. 2. Values with *Bombacopsis glabra* oil and its methyl esters by using Bailey and co-workers' method: □, oil; and ■, methyl esters

Experimental

By using apparatus and conditions similar to those described by Bailey, Pittman, Magne and Skau,[9] and Levi, Reilich and O'Neill,[10] we have found that absorbances produced by oils of cyclopropenoid content determined by hydrogen bromide titration did not correlate with the absorbances obtained with corresponding concentrations of their methyl esters. This deviation was found to be greatest between *Sterculia foetida* oil (57 per cent. of cyclopropenoids) and its methyl ester (Fig. 1). For *Bombacopsis glabra* oil (34 per cent. of cyclopropenoids) and kapok (*Ceiba pentandra*) oil (14·5 per cent. of cyclopropenoids), the deviation was present to a lesser extent (Figs. 2 and 3). Absorbances produced by the methyl esters of different cyclopropenoid-containing oils were found to have good correlation with cyclopropenoid contents determined by hydrogen bromide titration. These results indicated that the colour development of the Halphen reaction is influenced by the presence of cyclopropenoid glycerides, and that the use of methyl esters (Fig. 4) instead of the parent cyclopropenoid oils (Fig. 5) results in improved absorbance correlation.

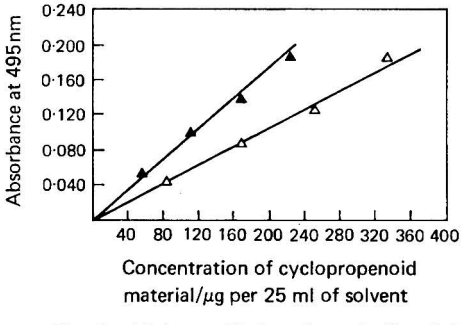

Fig. 3. Values with kapok seed oil and its methyl esters by using Bailey and co-workers' method: △, oil; and ▲, methyl esters

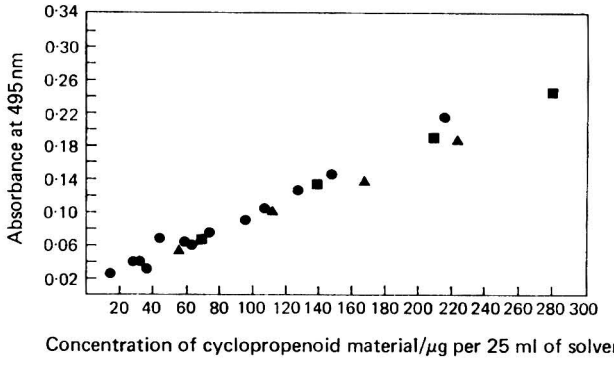

Fig. 4. Values with methyl esters by using Bailey and co-workers' method: ●, *Sterculia foetida* oil esters; ■, *Bombacopsis glabra* oil esters; and ▲, kapok seed oil esters

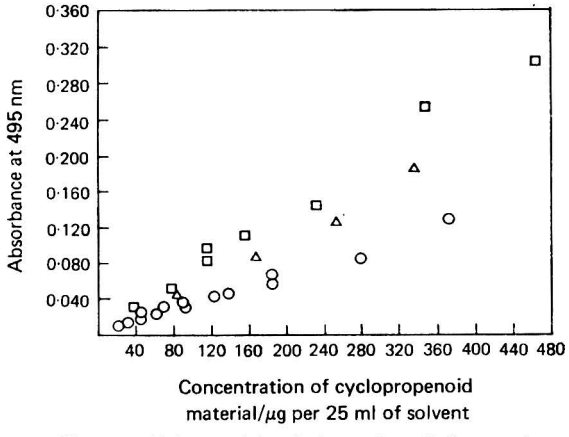

Fig. 5. Values with oil by using Bailey and co-workers' method; ○, *Sterculia foetida* oil; □, *Bombacopsis glabra* oil; and △, kapok seed oil

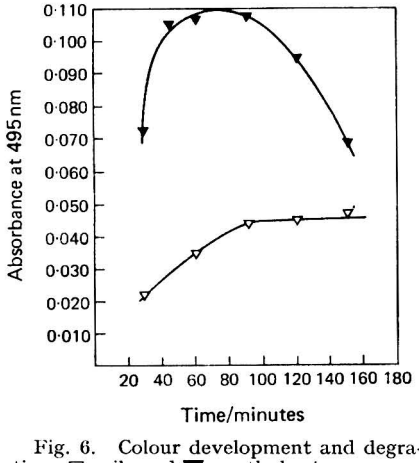

Fig. 6. Colour development and degradation: ▽, oil; and ▼, methyl esters

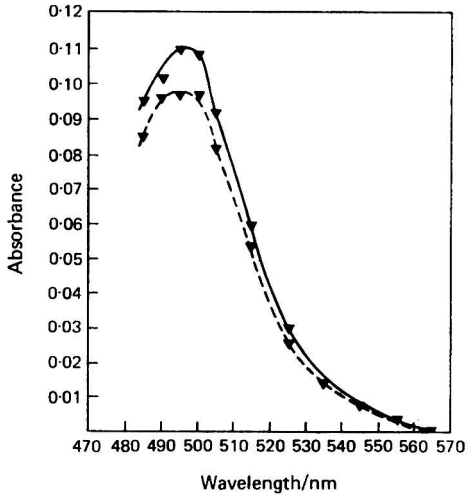

Fig. 7. Halphen colour with methyl esters: ——, with morpholine; and – – – –, without morpholine

VARIATION IN COLOUR DEVELOPMENT—

Although glycerides were found to reach maximum absorbance at 495 nm after 2 to 2½ hours' heating, methyl esters under the same conditions reached maximum absorbance with about 60 to 90 minutes' heating. The colour became less intense if heating was continued for longer than 100 minutes (Fig. 6).

However, the maximum absorbance of methyl esters, which occurred at about 75 minutes, was found not to be reproducible in a specific time. Moreover, the carbon disulphide concentration was found to have an effect on colour development. By allowing the carbon disulphide to boil off quickly at 110 °C, by using open test-tubes, less intense absorbances were produced, while with the use of a water condenser to retain completely the carbon disulphide the reaction temperature was lowered and the colour development unduly slowed down. The use of a small air condenser filled with 5-mm diameter glass spheres to give a fractionation effect was found to improve colour stability. The most reproducible colour development, however, was achieved by using securely stoppered bottles, similar to those described in the Cottonseed Oil Test, British Standard 684 : 1958,[2] with which stabilised colours could be obtained with 90 minutes' heating at 110 °C.

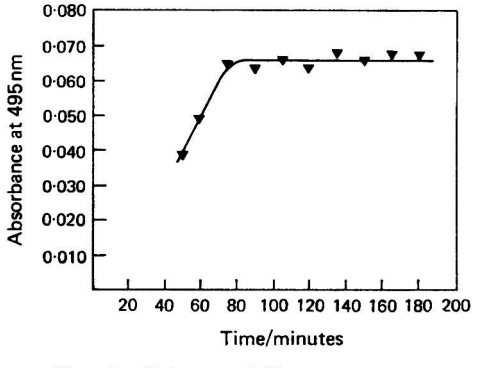

Fig. 8. Colour stability test on methyl esters with morpholine by using universal bottles

The addition of morpholine to the reaction mixture was found not to have a noticeable effect upon the Halphen colour spectrum of methyl esters between 485 and 565 nm, but colour stability was improved by its use (Figs. 7 and 8).

METHOD

APPARATUS—

Oil-bath—This was regulated at 110 ± 1 °C.

Universal bottle—Approximately 20-ml capacity with stout glass walls and metal screw-cap fitted with a rubber seal.

REAGENTS—

Sodium methoxide solution, 0·4 N—Dissolve 9·2 g of freshly cut sodium in 1 litre of re-distilled analytical-reagent grade methanol.

Sulphuric acid - methanol solution, 0·5 N—Dissolve 14 ml of analytical-reagent grade sulphuric acid (sp.gr. 1·84) in 1 litre of methanol.

Petroleum spirit, boiling range 40 *to* 60 °C—Free from aromatic compounds.

Sodium sulphate, anhydrous—Analytical-reagent grade.

Butanol—Analytical-reagent grade.

Morpholine solution, 4 *per cent.*—Dissolve 4 g of general-purpose grade morpholine in 100 ml of analytical-reagent grade butanol.

Sulphur solution, 1 *per cent. in carbon disulphide*—Dissolve 1 g of recrystallised sulphur in 100 ml of analytical-reagent grade carbon disulphide.

PREPARATION OF METHYL ESTER—

Cyclopropenoid-containing oils were extracted by macerating seeds at room temperature with petroleum spirit, filtering the mixture and removing the solvent with the minimum of heating by means of a rotary evaporator.

Methyl esters were prepared by using sodium methoxide in methanol solution[12] in the proportion of 25 ml of solution to 1 g of fat. The flask containing the mixture was warmed by immersing it briefly in a hot water bath at 80 °C, and the solution was shaken continuously until a single phase was obtained. The solution was neutralised with 0·5 N sulphuric acid in methanol, petroleum spirit was added and then distilled water to partition the phases. The petroleum spirit phase was separated and the aqueous layer extracted with a small amount of petroleum spirit, which was combined with the first extract. The combined petroleum spirit extracts were washed with water and dried with anhydrous sodium sulphate. The solvent was then removed completely by using a rotary evaporator with a minimum of heating and the esters were stored in a refrigerator.

TITRATION OF CYCLOPROPENOIDS—

Suitable amounts of methyl esters were weighed and the cyclopropenoid contents were determined at 60 °C by using the Durbetaki titration with hydrogen bromide as described in American Oil Chemists' Society Tentative Method Cd 9–57, but with the glacial acetic acid replaced with 5 per cent. glacial acetic acid in benzene in the preparation of the 0·1 N hydrogen bromide solution.[13] The cyclopropenoid contents were expressed as methyl sterculate (molecular weight 308).

PREPARATION OF STANDARD SOLUTION—

An appropriate amount of the methyl esters was weighed into a 100-ml calibrated flask to produce a stock solution in butanol containing approximately 0·5 mg of cyclopropenoid material per ml of solution. Aliquots of 5 or 10 ml were taken and diluted to 100 ml with butanol in a calibrated flask. The solutions were stored in a refrigerator.

HALPHEN REACTION—

The rubber seal of the universal bottle cap was protected by a disc cut from aluminium-foil sheet with a cork borer of appropriate diameter. Suitable aliquots of cyclopropenoid methyl ester standard solution were introduced by pipette into the bottle, and made up to 5 ml with butanol. Next, 0·1 ml of the 4 per cent. solution of morpholine in butanol was added and the contents were shaken before adding 1·0 ml of a solution of 1 per cent. of sulphur in

carbon disulphide. A solution blank with the cyclopropenoid esters omitted was prepared as reference. The caps were securely tightened to prevent loss of solvent, and the bottles were immersed to one third of their depth for 90 minutes in the oil-bath at 110 °C.

At the end of the reaction time, the bottles were removed from the bath and allowed to cool at room temperature for about 15 minutes. The solution was transferred to a 25-ml calibrated flask and made up to volume with butanol. The absorbance of the solution was measured at 495 nm in a 1-cm cell, with the blank as reference.

Results and discussion

The results are shown in Fig. 9. The Halphen reaction given by the methyl esters, rather than by the original oils, was found to produce better correlation with cyclopropenoid content determined by titration with hydrogen bromide.

The use of a securely stoppered bottle for the Halphen reaction resulted in improved methyl ester colour stability and increased absorbance intensity. The consequent enhancement of the sensitivity and improved reliability of the Halphen reaction extends its usefulness for the determination of low cyclopropenoid concentrations or in the analysis of limited amounts of samples. Further, the reaction is valid for cyclopropenoid-containing oils derived from a variety of seed species.

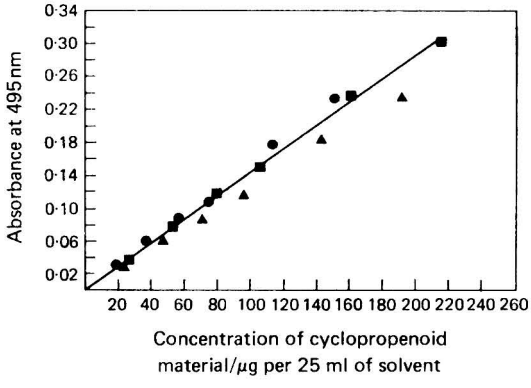

Fig. 9. Values with methyl esters by using universal bottle: ●, *Sterculia foetida* oil esters; ■, *Bombacopsis glabra* oil esters; and ▲, kapok seed oil esters

We thank Miss G. Felber for experimental assistance, and Mr. G. Shone of Kingston Polytechnic for supplying samples of *Sterculia foetida* seeds.

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Determination of Clamidoxic Acid in Serum by Gas-Liquid Chromatography

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A method has been developed for the determination of clamidoxic acid [2-(3,4-dichlorobenzamido)phenoxyacetic acid] in serum by using gas chromatography with electron-capture detection. Clamidoxic acid is extracted from acidified serum into toluene and returned to an aqueous sodium hydroxide phase. The amide is hydrolysed to 3,4-dichlorobenzoic acid which, after acidification, is extracted into toluene containing an internal standard. The acid is converted into its methyl ester by the addition of a solution of diazomethane in diethyl ether, excess of diazomethane is destroyed with acetic acid, and an aliquot analysed.

CLAMIDOXIC ACID [2-(3,4-dichlorobenzamido)phenoxyacetic acid] has been shown to have anti-inflammatory activity and low toxicity in animal tests. Pilot trials on human volunteers and patients with rheumatoid arthritis have been carried out. The compound is now undergoing controlled trials in patients suffering from rheumatoid arthritis and painful uncomplicated osteo-arthritis of the hip.

For the initial tests it was decided to administer 50 mg of clamidoxic acid to a volunteer with an expected serum level of 1 μg ml^{-1} of clamidoxic acid. In order to study the kinetics of the decline in the blood level of clamidoxic acid a highly sensitive and specific method was required. Gas - liquid chromatography of the methylated clamidoxic acid resulted in decomposition at the high temperatures required for volatilisation and elution. However, hydrolysis in 2 N sodium hydroxide produced 3,4-dichlorobenzoic acid, which was converted into its methyl ester. Gas - liquid chromatography of methyl 3,4-dichlorobenzoate on a 3·8 per cent. S.E.30 column with an electron-capture detector system indicated that this compound has a high electron affinity and showed no decomposition.

METHOD

INSTRUMENTATION—

A Hewlett-Packard, Model F & M 810, gas chromatograph fitted with a 200-mCi titanium tritide electron-capture detector and a 1-mV Honeywell recorder, and a 4-foot column of 3·8 per cent. S.E.30 on 60 to 80-mesh HMDS-treated[1] Embacel contained in $\frac{1}{4}$-inch glass tubing were used.

The carrier gas consisted of argon containing 5 per cent. of methane, which was passed through a molecular sieve before entering the column, with a flow-rate of 45 ml minute^{-1} and purge gas (argon *plus* 5 per cent. of methane) to give a total flow-rate of 170 ml minute^{-1}.

OPERATING CONDITIONS—

Oven temperature, 140 °C; injection port temperature, 165 °C; detector temperature, 190 °C; recorder chart speed, 15 inches hour^{-1}; pulse for optimum response, 150 μs; and range and attenuation, 10 × 32.

The retention time for methyl 3,4-dichlorobenzoate was 5·2 minutes and for methyl-$\beta\beta\beta$-trichloroethyl succinate 6·6 minutes.

REAGENTS—

Sulphuric acid, 17 and 2 N.
Sodium hydroxide solution, 2 N.
Toluene.
Diethyl ether.
Glacial acetic acid.

All of the above reagents and solvents were of analytical-reagent grade quality.

Diazomethane, approximately 0·15 M, *in diethyl ether*—Diazomethane was prepared according to the method of De Boer and Backer[2] and the container was always kept surrounded by solid carbon dioxide when in the laboratory. The solution was stored at −10 °C and a fresh solution prepared after 72 hours.

Internal standard—A solution of about 0·3 μg ml^{-1} of methyl-βββ-trichloroethyl succinate in toluene.

Standard solution of clamidoxic acid containing 2 μg ml^{-1} *in water*—2-(3,4-Dichlorobenzamido)phenoxyacetic acid was prepared by the method of Drain, Daly, Davy, Horlington, Howes, Scruton and Selway[3] and gave the following elemental analysis: C, 52·95; H, 3·44; and N, 4·33 per cent. $C_{15}H_{11}Cl_2NO_4$ requires C, 52·94; H, 3·24; and N, 4·12 per cent. Its purity was further verified by thin-layer chromatography.

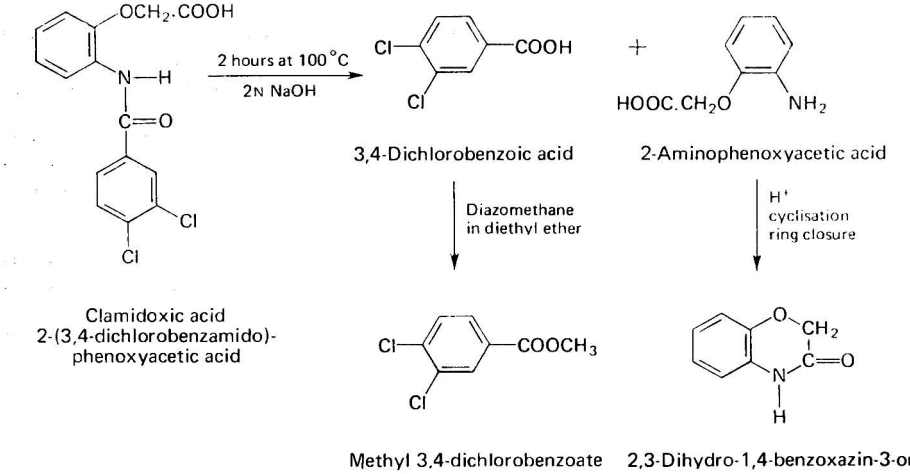
PROCEDURE—

Place the sample of serum containing clamidoxic acid into a 50-ml glass-stoppered tube and make the volume up to 10 ml with distilled water, then add 1 ml of 2 N sulphuric acid. Add 25 ml of toluene to the mixture and shake it for 10 minutes on a horizontal mechanical shaker. Centrifuge it at 2000 r.p.m. for 10 minutes, then transfer 20 ml of the toluene layer into a second 50-ml glass-stoppered tube, followed by 6 ml of 2 N sodium hydroxide, and shake the mixture for 10 minutes. Transfer 5 ml of the aqueous phase to a 1-inch diameter polyethylene centrifuge tube and cover the tube loosely.

Heat the tube on a boiling water bath for 2 hours. After cooling, transfer the contents to a 20-ml separating funnel, washing the tube with two 2·5-ml portions of water and adding the washings. Add 1 ml of 17 N sulphuric acid, shake the funnel and allow the solution to cool, then add 1 ml of toluene containing the internal standard. Extract by shaking the mixture for 30 s and allowing the phases to separate. Run off the aqueous phase and dry the separator stem below the tap with a tissue.

Transfer the toluene to a 5-ml stoppered vial and allow it to cool to 0 °C by standing it for 15 minutes in a box containing solid carbon dioxide. Add 1 ml of diazomethane solution in ether and allow the mixture to stand at room temperature for 15 minutes before adding 0·1 ml of glacial acetic acid to destroy excess of diazomethane.

Standards and a blank serum sample are carried through the above procedure. A constant volume of sample (about 5 μl) is applied to the column. Determine the concentration of clamidoxic acid from the calibration graph by using peak height ratios.



DETERMINATION OF STANDARD GRAPH FOR CLAMIDOXIC ACID—

2-(3,4-Dichlorobenzamido)phenoxyacetic acid was dissolved in water to give a stock solution containing 2 μg ml^{-1}. Suitable volumes of this solution were added to serum and taken through the extraction procedure to yield calibration graphs in the range 0·2 to 2·0 μg

per 5 ml of serum. After column conditioning, samples of about 5 μl of the final toluene extract were injected into the chromatograph and a graph of peak height ratio (methyl 3,4-dichlorobenzoate to internal standard) *versus* micrograms of clamidoxic acid was drawn by using the Bravais - Pearson coefficient of linear correlation. Peak heights were measured from a base-line, constructed with the aid of a flexible curve, across the chromatogram following the solvent tailing. A standard graph was determined each time samples were analysed to allow for variations in column performance and detector response.

Results and discussion

Development of method—

Because of the excellent response of the electron-capture detector system to methyl 3,4-dichlorobenzoate it was decided to develop a method in which reproducible extractions rather than quantitative extractions were used. It was found that the relatively small losses on extraction still allowed ample sensitivity to be achieved and the reduction in the number of extractions per step resulted in a more rapid procedure, with the facility for a greater number of samples to be analysed. The investigations into the various steps, which were carried out by gas - liquid chromatography, involved the preparation of a calibration graph under the same conditions with known amounts of methyl 3,4-dichlorobenzoate and internal standard.

Esterification—

The methylation of 3,4-dichlorobenzoic acid was found to be quantitative (98·5 to 100·2 per cent.). However, samples that had been methylated and allowed to stand at room temperature for long periods in the presence of excess of diazomethane tended to produce several interfering peaks on being chromatographed. To prevent these undesirable products from being formed on standing, excess of diazomethane was destroyed by the addition of glacial acetic acid. This had a slight disadvantage in that solvent tailing occurred. Various dilutions of acetic acid in diethyl ether were used to reduce solvent tailing, and although the sensitivity of the method was slightly increased no over-all change in precision was noted.

Hydrolysis—

Hydrolysis of clamidoxic acid to 3,4-dichlorobenzoic acid with 2 N sodium hydroxide was found to be complete after 2 hours at 100 °C. The investigation of this step was carried out by determining the 2-aminophenoxyacetic acid content colorimetrically. The amine is diazotised and coupled with *N*-1-naphthylethylenediamine and the colour intensity measured at wavelength 570 nm. A blank is carried out on each sample by heating an aliquot with hydrochloric acid prior to the diazotisation and coupling procedure. This cyclises the amine to 2,3-dihydro-1,4-benzoxazin-3-one, which gives no colour in the reaction. An aqueous solution of sodium 2-aminophenoxyacetate was used to give a calibration graph at a concentration of about 20 μg ml^{-1}.

Table I

Recovery of 3,4-dichlorobenzoic acid from 2 N sodium hydroxide after extraction into internally standardised toluene and conversion into methyl 3,4-dichlorobenzoate

3,4-Dichlorobenzoic acid added/μg	3,4-Dichlorobenzoic acid, as determined by gas - liquid chromatography, recovered/μg	Recovery, per cent.
0·206	0·164	79·6
0·412	0·342	83·0
0·515	0·434	84·2
—	0·414	80·3
1·029	0·788	76·5
—	0·805	78·2

Mean 80·3 $\pm$ 2·9 per cent.

FINAL TOLUENE EXTRACT—

Various amounts of 3,4-dichlorobenzoic acid (50 to 1000 ng) were added to 5 ml of 2 N sodium hydroxide. After dilution to 10 ml with water, and acidification, the samples were extracted with 1 ml of toluene containing internal standard. By shaking each sample for exactly 30 s a recovery of 80·3 ± 2·9 per cent. (Table I) was obtained for samples containing more than 200 ng of 3,4-dichlorobenzoic acid, determined as methyl 3,4-dichlorobenzoate by gas - liquid chromatography. Extraction with double the amount of internally standardised toluene gave an additional recovery of about 3 per cent., with a further loss in sensitivity that did not justify its use. Samples containing less than 200 ng of 3,4-dichlorobenzoic acid were detectable; however, the peak heights involved were so small that large variations in recovery were observed, which tended to cause the 3,4-dichlorobenzoic acid to be overestimated.

TABLE II

RECOVERY OF CLAMIDOXIC ACID FROM 2 N SODIUM HYDROXIDE AFTER HYDROLYSIS TO 3,4-DICHLOROBENZOIC ACID, EXTRACTION INTO INTERNALLY STANDARDISED TOLUENE AND CONVERSION INTO METHYL 3,4-DICHLOROBENZOATE

Clamidoxic acid added/μg	3,4-Dichlorobenzoic acid calculated/μg	Methyl 3,4-dichlorobenzoate, as determined by gas - liquid chromatography, recovered/μg	Percentage hydrolysis
0·199	0·112	0·080	71·4
—	—	0·078	69·6
0·398	0·223	0·174	78·0
—	—	0·170	76·2
1·393	0·782	0·562	71·9
1·990	1·118	0·858	76·7
—	—	0·773	69·1

Mean 73·3 ± 3·6 per cent.

The hydrolysis of clamidoxic acid (0·2 to 2·0 μg) in 2 N sodium hydroxide gave a recovery of 73·3 ± 3·6 per cent. when determined by gas - liquid chromatography (Table II); this represents a loss of about 7 per cent. on hydrolysis. The extractions of clamidoxic acid from acidified serum into toluene followed by extraction into 2 N sodium hydroxide were not studied as separate stages. However, preliminary experiments by using the spectrophotometric method previously indicated had shown that for larger amounts of clamidoxic acid

TABLE III

RECOVERY OF CLAMIDOXIC ACID ADDED TO 5 ml OF SERUM

Clamidoxic acid added/μg	Peak height ratio	3,4-Dichlorobenzoic acid calculated/μg	3,4-Dichlorobenzoic acid recovered/μg	Recovery, per cent.
0·000	—	—	0·000	—
0·199	0·045[a]	0·112	0·049	43·7
—	0·043[b]	—	0·046	41·1
—	0·043[c]	—	0·046	41·1
0·398	0·086[b]	0·223	0·094	42·1
—	0·091[c]	—	0·100	44·8
0·796	0·181[a]	0·446	0·198	44·4
1·393	0·310[a]	0·782	0·336	43·0
—	0·278[b]	—	0·302	38·6
—	0·301[c]	—	0·328	41·9
1·990	0·416[a]	1·118	0·450	40·2
—	0·428[b]	—	0·464	41·5
—	0·438[c]	—	0·476	42·6

Mean 42·1 ± 1·8 per cent.

Bravais - Pearson coefficient of linear correlation for clamidoxic acid (μg per 5 ml of serum) as abscissa and peak height ratio as ordinate.

Set a: slope = 0·2113, intercept = 0·0054, correlation coefficient = 0·9988.
Set b: slope = 0·2106, intercept = −0·0006, correlation coefficient = 0·9988.
Set c: slope = 0·2187, intercept = 0·0005, correlation coefficient = 0·9999.

(up to 100 μg per ml of serum) an over-all recovery of 89 to 92 per cent. was obtained. Almost total extraction from acidified serum into toluene and then into 2 N sodium hydroxide must take place when only 1 ml of serum is used.

TABLE IV

EFFECT OF SERUM VOLUME ON THE SLOPE OF THE CALIBRATION GRAPH

Clamidoxic acid	Peak height ratio	
Added, μg per 2·5 ml of serum—		
0·000	—	
0·414	0·256	
0·818	0·574	Slope = 0·6590
1·242	0·848	Intercept = 0·0022
1·656	1·027	Correlation coefficient = 0·9972
2·070	1·394	
Added, μg per 1 ml of serum—		
0·000	—	
1·035	0·715	Slope = 0·7676
2·070	1·605	Intercept = −0·0225
5·175	3·946	Correlation coefficient = 0·9997

RECOVERY EXPERIMENTS—

Clamidoxic acid was added to serum, extracted and determined as methyl 3,4 dichlorobenzoate by gas - liquid chromatography. For the range 0·2 to 2·0 μg of clamidoxic acid added to 5 ml of serum the recovery was 42·1 ± 1·8 per cent. (Table III).

Allowing for the incomplete use of the initial toluene extract and the 2 N sodium hydroxide extract this represents a true recovery of 63·0 ± 2·6 per cent. When losses on

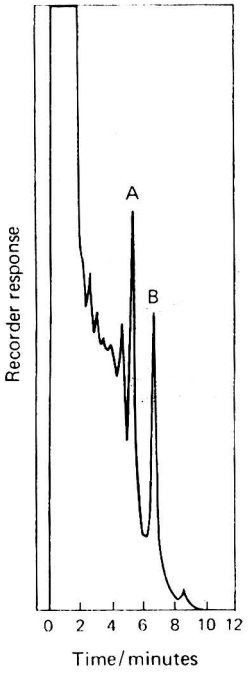


Fig. 1. Gas chromatogram of clamidoxic acid from serum recovered as methyl 3,4-dichlorobenzoate (A) and internal standard (B)

hydrolysis and extraction into the internally standardised toluene are considered, an initial extraction efficiency from serum into toluene of about 86 per cent. is indicated. The loss on hydrolysis is unexplained; however, the reproducibility of the complete procedure is within practical error and linear calibration graphs were always obtained. It would appear that the over-all loss of about 14 per cent. arises in the initial extraction from 5 ml of serum as extractions from 1 ml of serum were almost quantitative. Further evidence supporting this is the increase in peak height ratios noted when the range was extended to include 6 μg of clamidoxic acid per ml of serum, by using smaller volumes of serum for extraction (Table IV). Even when extending the range to cover the higher serum levels linear calibration graphs were obtained. Amounts of 90 to 180 ng of clamidoxic acid per 5 ml of serum were detectable, although the accuracy of measurement at this level was not within the reproducibility shown at the higher levels.

GAS - LIQUID CHROMATOGRAPHY—

The use of a non-polar 3·8 per cent. S.E.30 column proved to be adequate for this work. Although both methyl 3,4-dichlorobenzoate and the internal standard were eluted on a sloping base-line (Fig. 1), measurement of peak heights provided linear calibration graphs (Table III) in the range 0·2 to 2·0 μg of clamidoxic acid per 5 ml of serum.

Subsequent work on serum levels in man involved the extension of this range, with a different internal standard concentration, to include levels of 6 μg per ml of serum (by dilution) with no loss in linearity of the calibration graphs (Table IV). To achieve this linearity it was necessary to condition the column by the injection of two or three 5-μl samples of the final toluene extract before proceeding to run samples for quantitative measurement. A constant injection volume of about 5 μl was used throughout and, rather than alter this volume, any sample that was too concentrated was diluted with diethyl ether prior to undergoing chromatography.

In general, both the methyl 3,4-dichlorobenzoate and internal standard peaks were found to be unaffected by serum extractables. However, a blank extraction was carried out on serum obtained from volunteers before administration of clamidoxic acid and any component that had the same retention time was allowed for in the ensuing calculations. Day-to-day variations in response of the electron-capture detector were noted (Table III) and each set of determinations was accompanied by a set of standards.

The column was used at irregular intervals over a period of 2 years before any drastic reduction in sensitivity was observed. Care was taken to seal the column ends on removal from the oven and it was stored horizontally while not in use.

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Residues of Prophylactics in Animal Products

Part I. The Determination of Sulphaquinoxaline in Eggs and Poultry by Gas - Liquid Chromatography

By S. CRISP

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A procedure for the detection and determination of residues of sulphaquinoxaline in eggs and poultry is described. Sulphaquinoxaline is extracted from the sample with acetonitrile and, after a partition clean-up process, is hydrolysed to 2-aminoquinoxaline. The trifluoroacetyl derivative of this amine is a suitable compound for determination by gas - liquid chromatography with electron-capture detection. The method is applicable to residues at concentrations in the range 0·1 to 5 mg kg^{-1}.

SULPHAQUINOXALINE is a coccidiostat and can be incorporated in poultry feed at concentrations up to 100 mg kg^{-1}.[1] In order to be able to assess the amounts of sulphaquinoxaline that could occur in eggs or meat from treated poultry, a method capable of determining this compound at concentrations down to the level of 0·1 mg kg^{-1} was required. A procedure[2] for determining sulphanilamide in human tissues has been applied to the determination of sulphaquinoxaline in feeding stuffs.[3] The extracted material is diazotised, coupled with *N*-1-naphthylethylenediamine, and determined spectrophotometrically. This method suffers from interference from tryptophan and other hydrolysis products, which arise during extraction with an aqueous solution of alkali. Extraction of feeding stuffs with hot dimethylformamide and cold chloroform[1] avoids this type of interference but can lead to difficulties with emulsion formation unless great care is taken. Attempts to apply this latter extraction procedure to eggs and poultry meat led to the formation of extremely stable emulsions, and attempts to use this spectrophotometric procedure for tissue residues were therefore abandoned. After the completion of this work by the Prophylactics in Animal Feeds Sub-Committee of the Analytical Methods Committee of the Society for Analytical Chemistry, the application of the spectrophotometric method to eggs and poultry meat with a modified extraction procedure[4] was described.[5] The concentrations studied ranged up to 10 mg kg^{-1} and the detection limit was claimed to be 0·1 mg kg^{-1}.

Thin-layer chromatographic methods are available for detecting sulphaquinoxaline[6] in pharmaceutical combinations[7] and feeding stuffs.[8,9] These methods are claimed to detect 1 μg of sulphaquinoxaline, and include visualisation by any one of four chemical reagents or by ultraviolet light. The sensitivity of the methods approaches that required for detecting residues in tissues, but the clean-up of samples of eggs and poultry meat would be difficult and the determination would be only approximate. A method for determining sulphaquinoxaline by infrared spectrophotometry is available,[10] but similar clean-up problems would be encountered.

These methods were found to be unsuitable for application to eggs and poultry meat; therefore it was decided to seek a method based on gas - liquid chromatography. With an electron-capturing derivative of sulphaquinoxaline a high sensitivity can be achieved, while any other drugs of a similar chemical constitution in the tissue can be separated by the appropriate choice of column support and stationary phase.

Sulphaquinoxaline can be hydrolysed to 2-aminoquinoxaline, from which a trifluoroacetyl derivative can be prepared that is suitable for gas - liquid chromatographic determination with electron-capture detection. Four hydrolysis procedures were compared: heating with 6 M hydrochloric acid,[11] warming with an aqueous solution of bromine,[12,13] boiling with 40 per cent. v/v sulphuric acid[14] and heating with 85 per cent. v/v sulphuric acid.[15] The last procedure was found to give the most consistent results with extracts of eggs and of poultry meat.

2-Aminoquinoxaline was confirmed to be the hydrolysis product by an infrared spectrophotometric comparison of the compound isolated from the hydrolysis reaction with a sample of 2-aminoquinoxaline synthesised by the method of Petering and van Giessen[16] and by elemental analysis of the trifluoroacetyl derivative.

METHOD

REAGENTS—

Analytical-grade reagents should be used whenever possible.
Acetone—Re-distil before use.
Ethanol, absolute.
Pyridine—1 per cent. v/v solution in toluene.
Sodium carbonate, saturated solution.
Sodium hydroxide solution, N.
Sodium sulphate, anhydrous, granulated.
Sulphuric acid, sp.gr. 1·84.
Trifluoroacetic anhydride—Re-distil before use.

PREPARATION OF STANDARD SOLUTION OF QUINOXALIN-2-YL TRIFLUOROACETATE—

Dissolve 0·1 g of 2-aminoquinoxaline in 10 ml of diethyl ether, add 2 drops of a 1 per cent. v/v solution of pyridine in toluene and then 0·5 ml of trifluoroacetic anhydride, and reflux the mixture for 30 minutes. Evaporate the ether and excess of reagent, and remove the last trace of reagent by blowing a gentle stream of air into the flask. Recrystallise at least twice from aqueous ethanol, using charcoal if required to remove colouring material. Dry the product in a desiccator and check the melting-point, which should be 150 °C. Dissolve 10 mg of the compound in acetone and adjust the volume to 100 ml in a calibrated flask. Store this stock solution in the dark.

GAS - LIQUID CHROMATOGRAPHIC CONDITIONS—

A glass column, 4 mm i.d., 125 cm long, was packed with acid-washed silanised Chromosorb W, mesh size 100–120, supporting 5 per cent. of neopentylglycol succinate. The carrier gas, oxygen-free nitrogen, had a flow-rate of 4 ml s^{-1} measured at room temperature without the detector. A tritium-foil electron-capture detector, applied voltage 10 V, was used and the oven temperature was 190 °C.

PROCEDURE—

For samples of poultry meat, remove the flesh from the bones with a scalpel, and mince it. Weigh 10 g of meat into a 150-ml vortex beaker for analysis.

For samples of eggs, blend by stirring in a beaker. Weigh 10 g into a 150-ml vortex beaker for analysis.

Macerate the 10-g sample in a vortex beaker with 50 ml of acetonitrile by using a high-speed mixer, decant on to a column (330 mm long and 22 mm o.d.) of granulated anhydrous sodium sulphate supported on a sintered disc of porosity 0, and collect the eluate in a 500-ml flask fitted with a B34 neck. Repeat these operations with two further 50-ml portions of acetonitrile. Evaporate the combined acetonitrile extracts in the same flask to dryness in a rotary evaporator heated on a water-bath at 60 to 80 °C, and wash the residue into a 250-ml separating funnel with several portions of N sodium hydroxide solution, making a total volume of 50 ml. Add 20 ml of chloroform, shake the mixture for one minute, allow it to stand for 10 minutes, and discard the chloroform layer. Wash the aqueous solution first with 20 ml of chloroform and then with 20 ml of diethyl ether, discard the washes and add 5 ml of glacial acetic acid to the solution. Extract the solution with two 20-ml portions of chloroform, and evaporate the combined extracts to dryness on a boiling water bath in a 150-ml beaker covered with a watch-glass. Add 6 ml of 85 per cent. v/v sulphuric acid to the residue and heat the mixture on the water-bath for 2 hours. Add the resulting solution to 50 ml of water in a 250-ml separating funnel and cool the contents to room temperature. Wash the solution with 25 ml of diethyl ether, add it cautiously to 100 ml of saturated sodium carbonate solution, and extract it with two 25-ml portions of diethyl ether. Add the ethereal extract to a column (300 mm long and 15 mm o.d.) of granulated anhydrous sodium sulphate on a plug of cotton-wool, wash the column with an additional 25 ml of diethyl ether and collect the solution in

a 150-ml conical flask. Evaporate the ethereal solution to dryness on a water-bath at 60 °C. Dissolve the residue in about 20 ml of diethyl ether and add successively two drops of a 1 per cent. v/v solution of pyridine in toluene and 1 ml of trifluoroacetic anhydride. Evaporate the reaction mixture to dryness and remove the excess of reagent by passing a gentle stream of air into the flask. Wash the mixture with 5 ml of acetone into a graduated 10-ml test-tube fitted with a B14 stopper.

Dilute 50 μl of stock solution with 6·25 ml of acetone to give a solution equivalent to 1 μg ml^{-1} of sulphaquinoxaline. Inject 5 μl of the standard and test solutions consecutively on to the gas - liquid chromatographic column.

PREPARATION OF CALIBRATION CURVE—

Prepare a series of standard solutions from the stock solution of the trifluoroacetyl derivative at concentrations of 0·2 to 2·0 μg ml^{-1} and inject them on to the gas - liquid chromatographic column. Divide the peak height by that obtained for the 0·8 μg ml^{-1} solution and plot this ratio against mass of derivative added to the column. Use this curve for samples with residues of 0·1 to 1·0 mg kg^{-1} of sulphaquinoxaline; for more concentrated samples dilute the test solution so that its sulphaquinoxaline content falls within this concentration range. Under the specified conditions the derivative has a retention time of 4 to 5 minutes.

DISCUSSION

Sulphaquinoxaline is readily soluble in chloroform, methanol, ethyl methyl ketone, and acetonitrile: of these, acetonitrile was found to be the most efficient solvent for extracting sulphaquinoxaline from eggs and poultry meat. Attempts were also made to extract sulphaquinoxaline as its sodium salt with sodium hydroxide solution, but this led to the formation of emulsions in the clean-up stage and a gelatinous precipitate on acidifying the aqueous solution. Consequently, the method was difficult to manipulate and gave low (less than 20 per cent.) and erratic recoveries. In the present method only a moderate amount of fat is extracted by the acetonitrile so that stable emulsions are avoided in the clean-up stage. It is essential to clean up the sample before hydrolysis otherwise an emulsion will be formed.

For hydrolysis of sulphaquinoxaline and derivative formation, the over-all yield for these reactions was 91 per cent. (2 runs) on 10 mg of material and 93 per cent. (4 runs) on 5 μg of material. Over the same concentration range the derivative formation was observed to be 98 per cent. complete. The over-all efficiency of the method was assessed by adding 5-μg and 50-μg amounts of sulphaquinoxaline to 150 ml of acetonitrile and proceeding as described in the method. The recoveries were 86 $\pm$ 12 per cent. (12 runs) and 69 $\pm$ 7 per cent. (10 runs), respectively. The lower results are thought to arise through losses at the evaporation stages. Recovery experiments were run with spiked eggs and poultry meat and the results are shown in Table I.

TABLE I

RECOVERIES OF SULPHAQUINOXALINE FROM EGGS AND POULTRY MEAT

Sample	Sulphaquinoxaline added/ mg kg^{-1}	No. of experiments	Mean sulphaquinoxaline recovered/ mg kg^{-1}	Standard deviation/ mg kg^{-1}	Blank/ mg kg^{-1}	Mean recovery/ mg kg^{-1}	Mean extraction efficiency, per cent.
Poultry meat	0·5	5	0·37	$\pm$0·04	0·07	0·30	70
	5·0	9	3·8	$\pm$0·4	0·07	3·7	107
Eggs	0·5	7	0·25	$\pm$0·04	Nil	0·25	58
	5·0	8	3·3	$\pm$0·5	Nil	3·3	96

$$\text{Extraction efficiency} = \frac{\text{Percentage recovery of sulphaquinoxaline from 10 g of sample}}{\text{Percentage recovery of sulphaquinoxaline from 150 ml of acetonitrile}}$$

The last column expresses the recoveries as a percentage of the over-all efficiency of the method and is hence a measure of the extraction efficiency. For samples with 5 mg kg^{-1} of added sulphaquinoxaline the extraction appears to be very efficient; for samples with 0·5 mg kg^{-1} of added sulphaquinoxaline the extraction is less efficient, but a correction factor can be applied. A few 50-g samples spiked at 0·1 mg kg^{-1} were analysed and the clean-up was found to be adequate; the recoveries were about 70 per cent.

In this work a peak of 70 per cent. of full-scale deflection was obtained with 4 ng of standard on the 3×10^{-8} A amplifier range with a straight base-line. If the injection volume was reduced to 2 μl, 16 pg of the derivative were detected on the 10^{-9} A range with a signal-to-noise ratio of 4·5.

Conclusion

The method is specific for the determination of sulphaquinoxaline in eggs and poultry meat and has been established over the concentration range 0·1 to 5·0 mg kg^{-1}. The method is capable of detecting sulphaquinoxaline at much lower levels, but the corresponding extraction efficiency has not been investigated.

Permission to publish this paper has been given by the Government Chemist, Department of Trade and Industry.

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Colorimetric Method for the Determination of Iron in Pyrethrum Extracts

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It has been shown that pyrethrum extract is contaminated with iron during processing and that it is necessary to destroy the organic matter before determining the metal. Wet oxidation has been carried out with a mixture of sulphuric and nitric acids, but this treatment may lead to the precipitation of an iron complex. It was found that addition of potassium sulphate prior to oxidation prevented the precipitation of this complex. The iron can be determined spectrophotometrically at 480 nm by use of its thiocyanate complex. Nitrous acid residues from the oxidation must be removed by boiling with water and nitric acid added to oxidise iron(II) ions. The resultant method for determining microgram amounts of iron is both rapid and precise with small weights of extract, but when weights greater than 0·1 g are digested loss of sulphuric acid by evaporation causes small errors.

A NEED exists for a method for determining trace amounts of iron in refined pyrethrum extract for quality control during its manufacture. A method has been put forward that depends on extracting the iron by shaking a solution of the extract in light petroleum with dilute hydrochloric acid, followed by development of the colour formed with thiocyanate. Some difficulty was experienced in obtaining reproducible results with this method as troublesome emulsions were sometimes formed, and there was doubt as to whether the iron was quantitatively recovered (Dr. L. O. Hopkins, The Pyrethrum Board of Kenya, Nakuru, Kenya, private communication).

A method has therefore been devised in which the organic matter in the pyrethrum extract is destroyed by wet oxidation, followed by colorimetric determination of the iron as the thiocyanate complex.[1] Several complications came to light during the investigation of the method, which have not been adequately described in the literature. Although the present work has been confined to the determination of iron in pyrethrum extract it is believed that it may be of general interest, as the method involving wet oxidation has frequently been used for the determination of iron in other organic materials.

STUDY OF THE METHOD—

The requirement was for a method that would enable iron to be determined down to 20 p.p.m. with a precision of ± 5 per cent. It was found that amounts of up to 1 g of 50 per cent. pyrethrum extract could be oxidised with nitric acid in the presence of 2 ml of sulphuric acid without much difficulty. Dilution of the 2 ml of concentrated sulphuric acid with 10 ml of water was found to give a solution of suitable acidity for development of the iron(III) thiocyanate colour. Lower concentrations of acid gave less intense colour (see below) while higher concentrations resulted in rapidly fading colours and in decomposition of the thiocyanate.

However, when samples of pyrethrum extract were digested with 2 ml of sulphuric acid and the product diluted with 10 ml of water, strong colours of variable intensity were given with thiocyanate. These irregularities were caused by residual nitrous acid produced during the wet oxidation. Nitrous acid formed by adding a dilute solution of sodium nitrite to sulphuric acid gives a red colour with thiocyanate, which is distinguished from that of iron only by its rapid fading. Elimination of all of the nitrous acid was therefore essential, and this was achieved by adding water to the sulphuric acid after completion of the wet-oxidation stage and re-heating the solution until the sulphuric acid fumed strongly. This step is repeated in the method to ensure its complete removal.

For iron to react with thiocyanate it must be present in the iron(III) state. An oxidising agent is therefore added prior to the colour development; dilute nitric acid was chosen for

this purpose. Instead of adding 10 ml of water to the final 2 ml of sulphuric acid, 10 ml of N nitric acid are used, the action of which has been shown to be quantitative by tests carried out with ammonium iron(II) sulphate. Dilute nitric acid has a second beneficial effect as it renders the colour produced with thiocyanate stable for at least 15 minutes. In the absence of the nitric acid, the intensity of the red colour decreases slowly from the moment the thiocyanate is added.

The results obtained by the method after the difficulties caused by nitrous acid had been eradicated were still very erratic. It was noticed, however, that with some samples after the digestion, the sulphuric acid contained a small amount of a white precipitate that did not dissolve completely on dilution with N nitric acid; this precipitate was shown to contain iron. A solid of similar appearance can in fact be obtained by dissolving pure iron wire in dilute sulphuric acid, evaporating off the water and boiling the concentrated acid for a few minutes. Mason[2] also obtained erratic results, which he ascribed to the formation of a soluble iron complex, and decomposed it by heating it on a water-bath with a complexing agent. It has been found that the addition of potassium sulphate in the correct proportion prior to digestion prevents the formation of any precipitate if iron is present in the expected concentration. It is therefore recommended that 2 ml of a 25 per cent. w/v solution of potassium sulphate in concentrated sulphuric acid is used for this digestion instead of sulphuric acid alone.

METHOD

REAGENTS—

Potassium sulphate - sulphuric acid solution—Dissolve 25 g of analytical-reagent grade potassium sulphate in concentrated sulphuric acid, cool, make the solution up to 100 ml with the same acid and filter it through sintered glass.

Potassium thiocyanate solution—Dissolve 20 g of analytical-reagent grade potassium thiocyanate in distilled water, warm to room temperature, make the solution up to 100 ml and filter it.

Nitric acid, N—Dilute 64 ml of analytical-reagent grade concentrated nitric acid to 1 litre.

PROCEDURE—

Weigh, by difference, an amount of pyrethrum extract (not more than 0·1 g if an accurate result is required) containing 5 to 30 μg of iron into a Kjeldahl flask. With a pipette, introduce into the flask 2 ml of potassium sulphate - sulphuric acid solution, allowing 30 s for the pipette to drain. Digest the sample by adding portions of nitric acid as required to the heated flask until a clear, yellow or colourless solution is obtained. (CAUTION—Initially, small amounts of nitric acid should be added to the cold flask to avoid the risk of an explosive reaction.) Heat the mixture until the sulphuric acid distils into the neck of the flask, cool it and add 5 ml of distilled water. Heat until the sulphuric acid starts to distil again and cool. The solution should now be colourless or almost so; if not, add further portions of nitric acid. After heating, add a further 5 ml of distilled water and evaporate it off as before. With a pipette, introduce 10 ml of N nitric acid into the cooled residual sulphuric acid solution and shake the mixture. After again cooling, remove an aliquot of 5 ml and mix it with 1 ml of 20 per cent. potassium thiocyanate solution. Measure the absorbance of the red colour on a spectrophotometer at wavelength 480 nm in a 1-cm cell within 15 minutes of mixing the solutions. If the colour is too intense, take a smaller aliquot of the dilute nitric acid solution and make it up to 5 ml with a solution consisting of 1 volume of potassium sulphate - sulphuric acid solution and 5 volumes of N nitric acid. Then treat the new 5-ml portion with 1 ml of 20 per cent. potassium thiocyanate solution. Carry out a blank on the reagents.

Iron content of extract in parts per million =

$$\frac{(\text{Absorbance of test solution—absorbance of blank}) \times 77{\cdot}17}{\text{Weight of extract in grams}}$$

RESULTS

The method was checked by using a solution of ammonium iron(III) sulphate in N nitric acid with potassium sulphate - sulphuric acid solution. The intensity of the thiocyanate colour was shown to obey the Beer - Lambert law. The factor given in the equation above was obtained from these results and was used throughout this work.

Ten different samples of about 0·15 g of an extract rich in iron were each digested with 2 ml of concentrated nitric acid, and the iron content determined by the standard method was found to be 328 p.p.m. The standard deviation was $\pm 0{\cdot}5$ p.p.m.; the relative error (1σ confidence level) was therefore $\pm 0{\cdot}2$ per cent.

The results are not nearly so satisfactory, however, when different weights of the same extract are used. Table I shows the figures for the iron content of the extract when weights of from 0·05 to 1·3 g are analysed separately. The second column of this table gives the dilution necessary when the larger weights of extract are taken. The results show that the greater the weight of extract taken initially the greater is the iron content determined, the difference between the extremes being 6 per cent.

TABLE I

DETERMINATION OF THE IRON CONCENTRATION OF DIFFERENT WEIGHTS OF THE SAME EXTRACT

Weight of extract/g	Dilution	Iron concentration/p.p.m.	Error, per cent.
0·05	—	324	0·0
0·07	—	324	0·0
0·16	—	331	2·2
0·32	×2·5	338	4·3
0·62	×5	339	4·6
1·32	×10	343	5·9

The error is caused by evaporation or destruction of sulphuric acid during digestion; for instance, 62 per cent. of the sulphuric acid was lost when 1 g of extract was oxidised. This loss decreases the total volume and hence increases the iron concentration. Its effect is, however, partly offset by the corresponding decrease in acidity, which causes a fall in the iron(III) thiocyanate absorbance (Table II). It is therefore necessary to limit the technique to weights of extract up to about 0·1 g if an accurate result is required. If a larger weight of extract must be digested, then the digestate can be made up to a standard volume and an aliquot titrated against a solution of alkali. The sulphuric acid lost can then be replaced on making up to a new standard volume.

TABLE II

EFFECT OF THE SULPHURIC ACID CONCENTRATION ON THE IRON(III) THIOCYANATE ABSORBANCE

Sulphuric acid per 25 ml of solution/ml	Optical density at 480 nm	Change in absorbance, per cent.
4	0·393	0·0
3	0·382	−2·8
2	0·373	−5·1
1	0·362	−7·9
0·3	0·359	−8·6

Frequent reagent blanks were carried out throughout this work and the optical density was normally found to be about 0·035. However, anomalous readings were obtained occasionally, which were as high as 0·060, and as they did not result from the presence of iron in the acids, it was assumed that they were caused by etching of the Pyrex glass of the flasks by potassium hydrogen sulphate.

Decolorised pyrethrum extract prepared in glass and polythene apparatus was digested with potassium sulphate - sulphuric acid solution containing standard amounts of ammonium iron(III) sulphate. The resultant optical densities were identical with a blank that contained only the acid mixture and a standard amount of ammonium iron(III) sulphate. It was therefore concluded that the iron normally found in pyrethrum extract is picked up during the processing or storage. Therefore, to check whether other ions could be derived in a similar way and interfere in the above method, salts of the elements in common constructional use, *viz.*, aluminium, copper, zinc, nickel, cadmium, cobalt, manganese, tin, chromium and lead, were added to standard iron(III) solutions in the ratio of 10 mole to 1 mole and the colours developed. The absorbances obtained did not differ significantly from that obtained with iron(III) ions alone.

Conclusion

The wet oxidation of pyrethrum extract is best carried out with nitric acid and a potassium sulphate - sulphuric acid mixture. The iron can then be determined accurately by means of its thiocyanate complex. The method is sufficiently rapid and precise to be recommended for quality control of pyrethrum extract and could probably be used in other similar industries.

The author thanks Mr. J. Ward, P.O. Box 4517, Nairobi, Kenya, for his advice and assistance, and the directors of Mitchell Cotts (Holdings) Ltd. for permission to publish this work.

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1. Vogel, A. I., "A Text-Book of Quantitative Inorganic Analysis," Third Edition, Longmans, Green & Co. Ltd., London, 1961, p. 786.
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Book Reviews

ADVANCES IN ACTIVATION ANALYSIS. VOLUME 1. Edited by J. M. A. LENIHAN and S. J. THOMSON. Pp. x + 223. London and New York: Academic Press. 1969. Price £3·25.

The field of activation analysis is not well covered by comprehensive, up-to-date publications so the appearance of the first volume of a new series will be of considerable interest to those concerned with or interested in the technique. The aim of the series is stated as being "to provide a single source for authoritative accounts of recent advances in this subject normally only available in the literature of such diverse disciplines as nuclear physics, biology, engineering and chemistry." This first volume contains seven chapters by different authors: Activation Analysis—Some Basic Principles, by W. Schulze; Reactors as Neutron Sources, by V. P. Guinn; Automation and Electronic Data Handling, by R. E. Wainerdi; Standard Materials and Intercomparisons, by H. J. M. Bowen; Activation Analysis Techniques for Dosimetry and Hazard Control with High Energy Radiations, by L. Sklavenitis; γ-Ray Spectroscopy by Means of Germanium Lithium-Drifted Detectors in Activation Analysis, by F. Girardi and G. Guzzi; and Clinical Application of Activation Analysis, by D. Comar.

The short first chapter on basic principles is concerned with the mechanism of the production of radioactivity by irradiation with thermal and fast neutrons, charged particles and γ-photons, and includes data likely to be used as the basis for activation analyses. Guinn underlines the value and versatility of the nuclear reactor as a neutron source and provides a useful summary of both reactor characteristics and analytical techniques available, but the chapter is primarily concerned with one type of reactor. The implications of automation in activation analysis are discussed by Wainerdi and examples are given of large instrumental installations, but the rôle of the small, cheap computer in activation analysis has not been considered. Bowen's chapter summarises some results obtained by different laboratories for the analysis of standard materials, particularly standard kale, while Sklavenitis' discussion of the use of activation analysis for dosimetry and hazard control, while not of direct relevance to the experimental programmes of many workers, provides interesting background information. The applications considered in the final two chapters, the use of germanium counters and clinical applications of activation analysis, will be of more general interest, particularly the chapter concerned with germanium counters in view of the importance these new detectors are assuming in instrumental analysis.

A problem, naturally associated with any book that makes no pretence of approaching a subject, particularly one with as broad a scope as activation analysis, in a systematic way, but is made up of a number of specialist chapters, is to decide at what level the individual chapters should be pitched. Not all chapters will be of direct relevance to the work of any one reader and a detailed exposition may not be suitable for background reading. In general, the chapters in this book do not attempt to treat subjects in depth but are informative and make easy reading. They are therefore more likely to appeal to those anxious to improve their general understanding of activation analysis than to the expert wishing to extend further specialist knowledge.

T. B. PIERCE

ATOMIC ABSORPTION SPECTROSCOPY. By R. J. REYNOLDS and K. ALDOUS. Pp. x + 201. London: Charles Griffin & Co. Ltd. 1970. Price £4·50

The increasing use and versatility of atomic-absorption spectroscopy as an analytical tool is evident from the number of books and other publications that have appeared on the subject over the past decade. This is really not surprising, and in this review it would be invidious to assess the relative merits of the available books and to draw comparisons between their purchase prices, though this is likely to be done by individuals with limited financial resources.

With the appearance of this book, it may be reasoned that progress in the field in recent years has been so rapid that a new presentation of relevant facts, together with updated information, surveyed and assessed by completely independent authors, could soon justify any additional expense that might be involved.

The first three chapters deal with the fundamental principles of atomic absorption, procedural considerations (interferences, selection of wavelength, flame systems, sensitivities, etc.), and general principles of measurement. The next two chapters provide essential reference data on characteristics of the elements to be determined, and describe the application of atomic-absorption spectroscopy to specific fields of analysis.

In later chapters, the theoretical principles of atomic-fluorescence spectroscopy are outlined in sufficient detail to enable the reader to appreciate what is involved in this related and somewhat newer technique and how its potentialities compare with those of atomic-absorption spectroscopy.

Information on the characteristics of certain commercial units and some of the techniques and hardware that may ultimately be associated with future equipment is included in later chapters.

In the final pages of the text, Chapter VIII, Dr. K. C. Thompson is to be congratulated on his contribution under the heading Theory.

The book is certainly up-to-date, it is free from any obvious technical or typographical errors, the selected supporting references, nearly 300, are well chosen, and the price, by present-day standards, is not unreasonable. W. T. ELWELL

INSTRUMENTAL ANALYSIS MANUAL. MODERN EXPERIMENTS FOR THE LABORATORY. By GEORGE G. GUILBAULT and LARRY G. HARGIS. Pp. xii + 444. New York: Marcel Dekker Inc. 1970. Price $7.75.

This interesting compilation of instructive and ingenious laboratory experiments deserves to be read by all concerned with the teaching of any aspect of modern instrumental analysis: few will fail to acquire useful new ideas for modernising or extending their present range of demonstrations and teaching experiments.

Chapters are devoted to each of the following nineteen techniques, the number of experiments embodied in each chapter being indicated in parentheses: molecular absorption (5), molecular emission (5), atomic absorption and emission (4), electron spin resonance (2), nuclear magnetic resonance (2), electronics (4), potentiometry (4), conductance (1), amperometry (3), coulometry (3), polarography (4), gas chromatography (3), electrophoresis (1), ion exchange (2), thin-layer chromatography (1), gel filtration (1), radiochemistry (2), mass spectrometry (2) and thermometric titrations (1). There are therefore instructions for fifty laboratory experiments, and it is stated that "when they are properly prepared in advance by the laboratory instructor" almost all of them can be completed in a single period of 3 to 4 hours.

The relevant basic theory is summarised in each chapter. In turn, each experiment includes a brief discussion of the basic principle involved together with sufficient detail for the experiment to be undertaken, although the student is deliberately left with a bit of thinking to do; there are a few suggestions for supplementary reading, and each experiment ends with a useful list of questions designed to test the student's knowledge of the details and principles involved.

Following the main text there are fifteen appendices that extend over 40 pages and give useful information, *e.g.*, dipole moments, polarographic half-wave potentials, dielectric constants, common reference electrodes, stability constants, oxidation potentials, ionisation constants, atomic-absorption wavelengths, etc.

This manual reveals a strong practical approach throughout, and there are useful suggestions for the construction of low-cost home-made apparatus, *e.g.*, apparatus for disc polyacrylamide gel electrophoresis at a cost of "less than 10 dollars."

The book in its present format (paperback, reproduction of typed pages) is a "preliminary edition," brought out to allow thorough evaluation of the experiments by a wider range of teachers

and students over a trial period. The authors' intention is to reprint eventually in a "final edition." Although a few typist's errors exist, this production is remarkably free from serious misprints or blemishes. At its present price, adoption of this manual for laboratory class work is a proposition that should be considered seriously by institutions in which the instrumental analysis course is not completely up-to-date. When the "final edition" is produced, it is to be hoped that its binding or presentation will not be made more "glossy" if an increase in price would result. What is wanted is a reasonably priced bench handbook; the present production provides this.

D. M. W. ANDERSON

THE CHEMICAL ANALYSIS OF FOOD. Sixth Edition. By DAVID PEARSON. Pp. xii + 604. London: J. & A. Churchill. 1970. £6.

The latest edition of "The Chemical Analysis of Foods" retains very little, apart from the format, of the original work of H. E. Cox. The author has undertaken an extensive revision to provide useful pertinent information on analytical methods, legislation and compositional data relating to broad classes of foods, including sugars and preserves, cereals, fruit and vegetable products, beverages, fermentation products, meats, dairy products and oils and fats. The sixth edition is considerably enlarged. The greater type area and the 140 additional pages compared with the fifth edition are some measure of the additional information now provided. Among the new commodities included are sugar confectionery, biscuits, marzipan, canned cereals, milk puddings, pickles and sauces, peanut butter, vodka and monosodium glutamate.

Alternative methods of analysis are provided for many determinations, either as an abstract or by reference. The methods preferred by the author are given in detail with clear working instructions. Throughout the book the relationship between the analysis and the legal requirement is emphasised and may account for what appears to be a bias towards enforcement methods. The provision of alternative methods does provide the food analyst with a choice of methods, but many of the recent developments in techniques and instrumental analysis do not feature as prominently in the selected methods as their current use would justify. Equally there is a significant omission of international reference methods developed by international organisations.

A considerable part of the analytical data has been updated and new appendices include useful information on various food additives, energy calculations, S.I. units and recent legislation. The book is well produced, contains few typographical errors, and includes a comprehensive index. The whole is a valuable source of information on methods of food analysis and the relevant legislation, and should prove an excellent laboratory handbook for the food chemist with the minimum need for recourse to other publications.

A. W. HUBBARD

UNDERGRADUATE INSTRUMENTAL ANALYSIS. By JAMES W. ROBINSON. Pp. xx + 379. New York: Marcel Dekker Inc. 1970. Price £5·50.

This book is intended only as an introduction to instrumental techniques of analysis. Its aim is to make the student aware of the principal features of the techniques discussed. This is accomplished by the adoption of a general, largely non-mathematical approach, which is, nevertheless, informative and adequate for this purpose. The volume is introduced by a section concerned with concepts of analytical chemistry and statistics, and the most frequently encountered instrumental techniques are then dealt with chapter by chapter. Ten chapters are devoted to spectroscopic techniques, and the remaining chapters deal with chromatography, thermal analysis, mass spectrometry and electrochemistry. At the conclusion of each chapter, elementary experiments and sample problems concerning the technique are presented. The material of each chapter is quite up-to-date (1968–69), and for many of the techniques quite recent innovations are described. For example, the application of ion-selective electrodes and some of the recent work that has revived interest in flame-emission spectroscopy are discussed briefly. However, some quite important instrumental techniques, such as solution fluorimetry and phosphorimetry, are not dealt with; this is surprising in view of the statement made in Chapter 2, which deals with the general principles of spectroscopy, that molecular fluorescence is a very important analytical field.

The present reviewer feels that students will find this book very easy to read; the basic concepts of the techniques are readily assimilated in the manner in which they are presented. By the nature of its approach, whereby an over-all view is presented, the student is encouraged to see the "wood" of instrumental analysis before others persuade him to climb the individual "trees" of the various techniques.

G. F. KIRKBRIGHT

Residues of Prophylactics in Animal Products
Part I. The Determination of Sulphaquinoxaline in Eggs and Poultry by Gas - Liquid Chromatography

A procedure for the detection and determination of residues of sulphaquinoxaline in eggs and poultry is described. Sulphaquinoxaline is extracted from the sample with acetonitrile and, after a partition clean-up process, is hydrolysed to 2-aminoquinoxaline. The trifluoroacetyl derivative of this amine is a suitable compound for determination by gas - liquid chromatography with electron-capture detection. The method is applicable to residues at concentrations in the range 0·1 to 5 mg kg^{-1}.

S. CRISP

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Analyst, 1971, **96**, 671–674.

Colorimetric Method for the Determination of Iron in Pyrethrum Extracts

It has been shown that pyrethrum extract is contaminated with iron during processing and that it is necessary to destroy the organic matter before determining the metal. Wet oxidation has been carried out with a mixture of sulphuric and nitric acids, but this treatment may lead to the precipitation of an iron complex. It was found that addition of potassium sulphate prior to oxidation prevented the precipitation of this complex. The iron can be determined spectrophotometrically at 480 nm by use of its thiocyanate complex. Nitrous acid residues from the oxidation must be removed by boiling with water and nitric acid added to oxidise iron(II) ions. The resultant method for determining microgram amounts of iron is both rapid and precise with small weights of extract, but when weights greater than 0·1 g are digested loss of sulphuric acid by evaporation causes small errors.

R. A. G. MARSHALL

Department of Chemistry, Thames Polytechnic, London, S.E.18.

Analyst, 1971, **96**, 675–678.

Reprints of Review Papers

REPRINTS of the following Review Papers published in *The Analyst* since January, 1963, are available from The Society for Analytical Chemistry, Book Department, 9/10 Savile Row, London, W1X 1AF (not through Trade Agents). Orders MUST be accompanied by a remittance for the correct amount made out to "Society for Analytical Chemistry."

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HAP Erba (Hydrated Antimony Pentoxide)
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TDO Erba (Tin Dioxide)
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CARLO ERBA Divisione Chimica Industriale / Via C. Imbonati 24 / 20159 Milano

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