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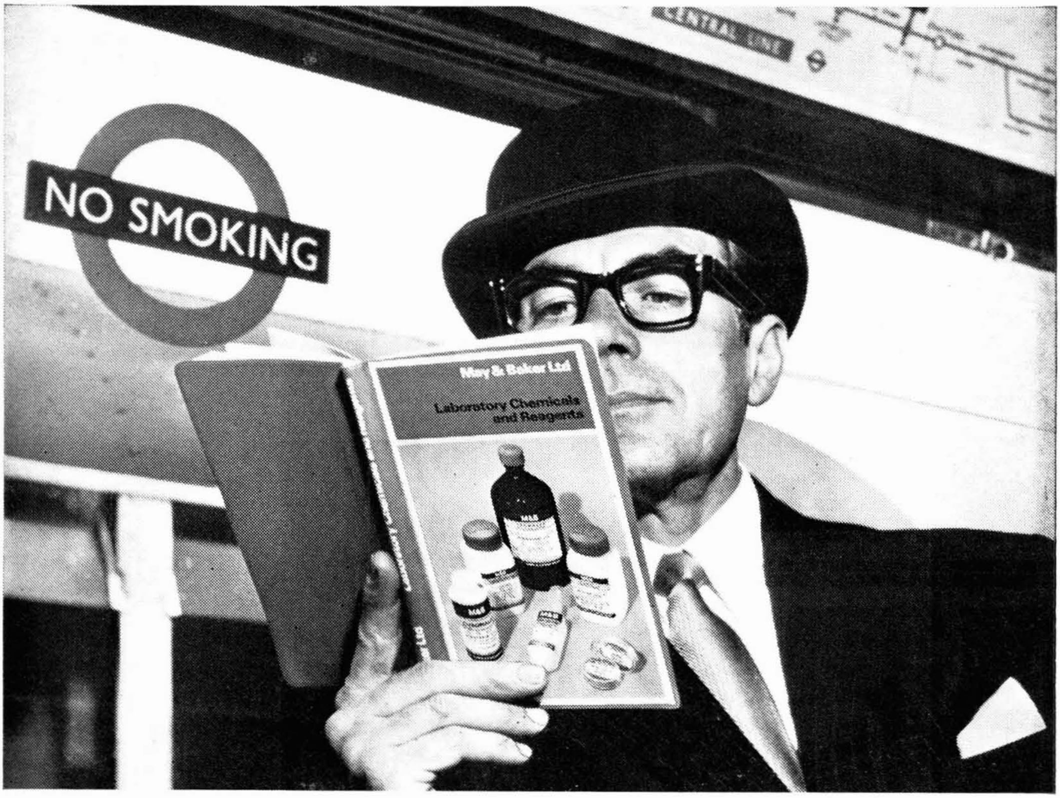
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CHROMATOGRAPHIC SYSTEMS—

System I. Ethyl methyl ketone - dimethylformamide - ammonia solution (sp.gr. 0·90) (13 + 1·9 + 0·1) on silica gel G.

System II. Methanol - chloroform (1 + 1) on alumina G.

System III. Chloroform - methanol - acetic acid (75 + 20 + 5) on silica gel G.

DETECTION REAGENTS—

Reagent A—This consists of the reagents (i) sodium acetate (10 per cent. aqueous), (ii) 2,6-dibromo-*p*-benzoquinone-4-chlorimine (B.D.H. Ltd.) (1 per cent. in ethanol) and (iii) iodine crystals (2 g distributed in two small Petri dishes placed at the bottom of a thin-layer chromatographic tank. [(i) and (ii) remain usable for 5 days if kept in a refrigerator.]

The dried plates were sprayed lightly with (i), then immediately with (ii), carefully avoiding overspray. They were then placed in the iodine tank. Coloured spots appeared promptly. Plates chromatographed in system III were aerated until the acidic background had become dispelled and then sprayed twice with (i) before application of (ii) spray and exposure to iodine vapour.

p-*Dimethylaminobenzaldehyde*.[5]

Modified Procházka reagent.[10]

Potassium iodoplatinate.[11]

GAS CHROMATOGRAPHY

APPARATUS—

A Varian-Aerograph Gas Chromatograph, Model 1520-B, equipped with a Varian-Aerograph Recorder, Model 20, a disc integrator and a hydrogen flame-ionisation detector, was used. It was operated both isothermally and with a matrix multi-linear programmer. Stainless-steel columns, 5 feet × $\frac{1}{8}$ inch, were packed with 5 per cent. silicone rubber S.E. 30 on 60 to 80-mesh Chromosorb W, or 3 per cent. silicone GE X.E 60 on 100 to 120-mesh Aeropak 30. The carrier gas used was nitrogen with a flow-rate of 25 ml per minute at 200° C. The injection port and detector were maintained at temperatures of 50° and 25° C higher, respectively, than that of the column. Gas flow-rates for the flame-ionisation detector were 25 ml per minute for hydrogen and 300 ml per minute for air. The X.E. 60 column was conditioned overnight at 240° C with 10 ml per minute gas flow. The S.E. 30 column was conditioned overnight at 250° C with no flow, then at 240° C with 25 ml per minute gas flow until a stable base-line was obtained.

PROCEDURE—

Samples (0·5 to 4 μl) were injected as free bases in diethyl ether, benzene or methanol solution. Salts of the bases and other solvents, such as chloroform, could also be used, but more frequent cleaning of the flame-ionisation detector was necessary with these. Retention times reported are averages ($\pm$0·1 minute) from six chromatograms of each compound.

REACTION WITH CARBON DISULPHIDE—

Ten to twenty micrograms of free base in diethyl ether (10 to 20 μl) (benzene was used for mescaline) were transferred into a small test-tube and an equal volume of carbon disulphide was added. The solution was left at room temperature (26° C) and, after timed intervals, or after 5 minutes with mixtures, 1 to 4 μl were injected into the gas chromatograph.

RESULTS AND DISCUSSION

THIN-LAYER CHROMATOGRAPHY—

4-Methyl-2,5-dimethoxy-α-methylphenethylamine could be separated from the related compounds in all of the systems (Table I). The low sensitivity of non-phenolic phenylamines towards general alkaloidal reagents, such as Dragendorff's or potassium iodoplatinate, or other non-specific reagents is well known,[10,12,13,14,15] and identification of mescaline has been considerably improved by application of a modified Procházka reagent and observation under ultraviolet light.[10] Strong fluorescence was also observed for the new hallucinogen with

TABLE I

R_F VALUES* IN THREE THIN-LAYER CHROMATOGRAPHIC SYSTEMS AND COLOUR WITH DETECTION REAGENT A

Compound	System I	System II	System III	Colour
Amphetamine	0·58	0·40	0·21	Violet
Methamphetamine	0·14	0·74	0·33	Yellow
4-Methyl-2,5-dimethoxy-α-methylphenethylamine	0·54	0·48	0·33	Yellow
Mescaline	0·49	0·24	0·20	Yellow
NN-Dimethyltryptamine	0·35	0·93	0·10	Orange - brown
Bufotenine	0·15	0·84	0·05	Dark grey

* Average (±0·02) of six measurements.

this reagent, but the reaction was less sensitive than for mescaline (Table II). The formation of isoquinoline derivatives, which has been suggested in the reaction of formalin with mescaline under the conditions of the thin-layer chromatographic spray,[10] could be impeded in 4-methyl-2,5-dimethoxy-α-methylphenethylamine, either because of steric hindrance caused by the α-methyl group or because of the electronic effect of the 5-methoxy group. Detection reagent A produced different colours with the various compounds (Table I) and was, further, the most sensitive detection reagent used in this investigation (Table II). Presence of the indole derivatives, *NN*-dimethyltryptamine and bufotenine, was ascertained by spraying with *p*-dimethylaminobenzaldehyde reagent. Other sprays tried, such as ninhydrin, Fast blue B, dansyl chloride, potassium permanganate, sodium tetraphenylborate - fisetin and *p*-nitroaniline, showed no advantages over those reported under Detection reagents.

TABLE II

LIMIT OF DETECTION (μg) FOR 4-METHYL-2,5-DIMETHOXY-α-METHYLPHENETHYLAMINE

Reagent	Thin-layer chromatographic system	μg
Reagent A	I	0·3
	II	0·03
Modified Procházka reagent	I	0·4
	II	0·1
Potassium iodoplatinate	I	2·0
	II	1·0

TABLE III

GAS-CHROMATOGRAPHIC RETENTION TIMES (MINUTES) OF HALLUCINOGENS AND RELATED BASES ON TWO COLUMNS

	Columns								
	S.E. 30, 5 per cent.				X.E. 60, 3 per cent.				
Temperature, °C	130	180	205	220	110	150	180	210	240
Compounds									
Amphetamine	2·05	0·85	0·7	—	3·1	1·1	—	—	—
Methamphetamine	2·6	0·9	0·8	—	3·2	1·1	—	—	—
4-Methyl-2,5-dimethoxy-α-methylphenethylamine	8·2	2·2	1·1	—	>40	9·2	3·2	1·5	0·8
Mescaline	—	5·5	2·5	—	—	>40	9·0	3·0	1·2
NN-Dimethyltryptamine	—	6·7	3·4	2·1	—	—	12·5	4·5	1·85
Bufotenine	—	—	8·5	5·0	—	—	—	34·5	10·3

GAS CHROMATOGRAPHY—

Results of isothermal gas chromatography of the six compounds on 5 per cent. S.E. 30 and 3 per cent. X.E. 60 are shown in Table III. All of the compounds gave sharp peaks on both columns. For mixtures and temperature-programmed analyses the X.E. 60 column is preferred. 4-Methyl-2,5-dimethoxy-α-methylphenethylamine is well separated from the other compounds (Fig. 1). Adequate separation of amphetamine and methamphetamine can be obtained on the S.E. 30 column at 130° C or on the same column with lower loads of liquid phase[16,17]; 0·02 μg of the new hallucinogen can be detected on both columns.

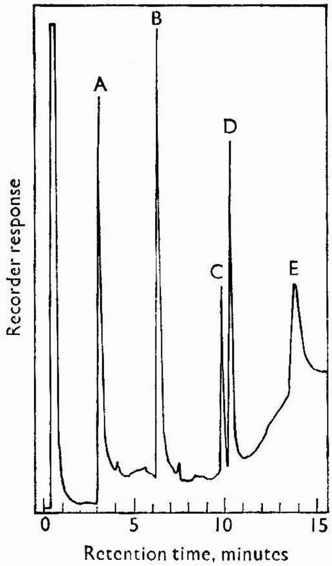

Fig. 1. Programmed gas chromatogram of a mixture of 1 μg each of amphetamine and methamphetamine (A), 2 μg of 4-methyl-2,5-dimethoxy-α-methylphenethylamine (B), 1 μg of mescaline (C), 2 μg of dimethyltryptamine (D) and 2 μg of bufotenine (E); 3 per cent. X.E. 60, single-column operation, flash heater at 220° C, flame-ionisation detector at 250° C, range 1, attenuation 64 and flow-rate of nitrogen, 25 ml per minute. Programme: initial temperature 100° C; 2/20° C; 3/hold; 4/30° C; 6/8° C; 12/15° C; 16/end (numbers before oblique represent minutes after injection, and those after represent the increase in temperature in degrees per minute)

Additional analytical information can be obtained by gas chromatography of derivatives produced by reaction of the primary bases with carbon disulphide at room temperature. Methamphetamine, *NN*-dimethyltryptamine and bufotenine show no reaction, but 4-methyl-2,5-dimethoxy-α-methylphenethylamine, mescaline and amphetamine, after brief treatment with carbon disulphide, yield a derivative generating a distinct peak with higher retention time on either column (Table IV). Formation of the derivative can also be achieved by "on-column reaction gas chromatography," *i.e.*, injection of 1 to 2 μg of the free base, followed, within 10 to 20 seconds, by 3 to 4 μl of carbon disulphide. As retention times obtained by this method are, however, often distorted and conversions incomplete, the procedure as described under Experimental is preferred. Differences were observed in the rate of conversion of the three amines that form derivatives with carbon disulphide. The reaction of mescaline is rapid, being more than 99 per cent. complete after 20 seconds. The reactions of amphetamine and 4-methyl-2,5-dimethoxy-α-methylphenethylamine with carbon disulphide are slower. Approximate conversion rates were determined by comparing the integrated areas for the peaks of the free bases and their derivatives. In this manner, it was established that after 20 seconds, 2·5, 16 and 40 minutes, and 16 hours of contact with carbon disulphide, 51, 56, 71, 87 and 98 per cent. of amphetamine and 47, 53, 59, 67 and 99 per cent. of 4-methyl-2,5-dimethoxy-α-methylphenethylamine were converted into the corresponding derivatives.

TABLE IV

GAS-CHROMATOGRAPHIC RETENTION TIMES (MINUTES) OF ISOTHIOCYANATES ON TWO COLUMNS

	Columns								
	S.E. 30, 5 per cent.				X.E. 60, 3 per cent.				
Temperature, °C..	130	180	205	220	110	150	180	210	240
Compounds									
Amphetamine - carbon disulphide	8·7	2·2	1·5	—	25·5	5·4	2·2	0·8	—
4-Methyl-2,5-dimethoxy-α-methylphenethylamine - carbon disulphide	—	10·7	5·0	—	—	—	11·2	4·0	1·8
Mescaline - carbon disulphide ..	—	15·1	6·9	—	—	—	36·8	10·2	3·1

The reaction of primary amines with carbon disulphide has been applied to the detection of amphetamine in urine,[18] and it has been shown that the product of this reaction is the mustard oil, α-methylphenethylisothiocyanate,[19] which is formed via the dithiocarbamic acid. Mescaline and 4-methyl-2,5-dimethoxy-α-methylphenethylamine probably follow an analogous course of reaction, and the formation of 2,4,5-trimethoxyphenethylisothiocyanate and 4-methyl-2,5-dimethoxy-α-methylphenethylisothiocyanate is likely under the experimental conditions.

We are indebted to the Dow Chemical Company for the gift of a sample, and to Mr. G. Belec for technical assistance.

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Di-2-pyridyl Ketoxime, a New Reagent for the Rapid Gravimetric Determination of Palladium

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Di-2-pyridyl ketoxime is proposed for the gravimetric determination of palladium. The chelate is precipitated over a pH range of between 3 and 11 and weighed as $Pd(C_{11}H_8ON_3)_2$. An extensive study of foreign ions and analytical conditions for precipitation indicates the procedure to be widely applicable, rapid and simple.

NUMEROUS precipitating reagents have been proposed for the gravimetric determination of palladium, and have recently been excellently reviewed by Beamish.[1] The most important reagents for palladium contain the oxime grouping, C=N—OH. Dimethylglyoxime,[2] cyclohexane-1,2-dione dioxime[3] (nioxime) and β-furfuraldoxime[4] are among the well established reagents in this class. More recently 2-selenophene aldoxime,[5] di-2-thienyl ketoxime[6] and 8-mercaptoquinoline[7] have been proposed as new gravimetric reagents for palladium.

The purpose of the present work was to extend the application of di-2-pyridyl ketoxime to other analytical problems. This reagent has been investigated previously, and subsequently proposed for the spectrophotometric determinations of gold,[8] palladium,[9] cobalt[10] and iron.[11] Further studies indicated that over a wide pH range, di-2-pyridyl ketoxime and bivalent palladium formed bis(di-2-pyridyl ketoxime) - palladium(II) in quantitative yield—

$$Pd^{2+} + 2C_{11}H_9ON_3 \longrightarrow Pd(C_{11}H_8ON_3)_2 + 2H^+.$$

In this paper, the above reaction has been applied to the gravimetric determination of bivalent palladium in the presence of many diverse cations and anions.

The palladium chelate is insoluble in hot water, while the reagent is completely soluble. Consequently, filtration from a hot solution, after a brief digestion period, results in a procedure that is rapid, with no loss of accuracy.

EXPERIMENTAL

PREPARATION OF THE REAGENT—

Di-2-pyridyl ketoxime was synthesised by the method outlined in a previous publication.[9] A 1 per cent. solution in 95 per cent. ethanol, which is stable indefinitely, was used as the reagent. Conversion of di-2-pyridyl ketone (available from the Aldrich Chemical Co., Milwaukee, Wisconsin) into the oxime proceeds rapidly and gives a high yield.

PREPARATION OF PALLADIUM SOLUTION—

A stock solution was prepared by dissolving purified palladium(II) chloride in concentrated hydrochloric acid and diluting to 1 litre in a calibrated flask. The concentration of palladium(II) was 1·002 mg per ml, as determined by the dimethylglyoxime method.[12] All other chemicals used were of analytical-reagent quality.

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF PALLADIUM—

Transfer an aliquot of palladium solution, containing up to 50 mg of palladium(II), into a 250-ml beaker. Add about 2·5 ml of 40 per cent. sodium citrate (1 g) and adjust the pH to between 4 and 11. Heat the contents to about 80° C and add an excess of reagent solution (10 to 200 per cent. excess). Digest the hot solution for about 10 minutes, filter through a sintered-glass crucible of medium porosity, and wash the precipitate well with hot water. Dry it at 125° C to constant weight and weigh as $Pd(C_{11}H_8ON_3)_2$. The gravimetric factor for palladium is 0·2116.

EFFECT OF pH ON PRECIPITATION—

The yellow chelate was precipitated from solutions of various pH values according to the procedure outlined, and dilute potassium hydroxide or hydrochloric acid used to make the pH adjustments.

pH of solution	3·0	4·0	5·0	6·0	7·0	9·0	11·0
Palladium taken, mg	8·80	8·80	8·80	8·80	8·80	8·80	8·80
Palladium found, mg	8·82	8·79	8·80	8·79	8·81	8·83	8·76

The results indicate that the optimum pH conditions are between 3 and 11. However, because the precipitate was difficult to filter at pH 3, it is recommended that the pH be maintained above 4·0.

EFFECT OF PALLADIUM CONCENTRATION—

Analyses conducted on a series of different sample weights, as indicated below, showed that palladium could be successfully determined over the range of 4 to 50 mg without co-precipitation of reagent. Because of the voluminous nature of the precipitate, the amount of palladium should not exceed 50 mg.

Palladium taken, mg	4·402	13·21	17·61	22·01	30·81	44·02
Palladium found, mg	4·395	13·19	17·60	22·03	30·83	44·06
Deviation, mg	−0·007	−0·02	−0·01	+0·02	+0·02	+0·04

Each result is the average of six separate analyses.

EFFECT OF REAGENT EXCESS—

Various amounts of di-2-pyridyl ketoxime in excess were added to 13·21 mg of palladium. The results indicated that no co-precipitation occurs, even with 200 per cent. excess of reagent.

EFFECT OF DIGESTION TIME AND TEMPERATURE—

Recoveries of palladium for various digestion temperatures and times indicate that precipitation and filtration can be carried out at room temperature, or at elevated temperatures up to 100° C, with a brief digestion period of 5 to 10 minutes.

DRYING CONDITIONS—

A weighed amount of the chelate was isolated according to the procedure and dried at various oven temperatures and time periods. No significant weight change occurred when the chelate was dried for 1½ hours at temperatures between 118° and 210° C, or for 1¼ hours at 125° C. Drying times of 1 hour, or less, resulted in slightly high results.

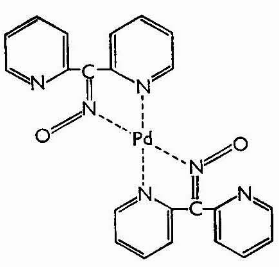
COMPOSITION AND STRUCTURE OF THE PALLADIUM CHELATE—

An aliquot of palladium solution, containing 25·05 mg of palladium(II), was transferred into a 250-ml beaker and the above procedure followed. Results of analyses of the precipitate for carbon, hydrogen and palladium and those calculated for the empirical formula, $Pd(C_{11}H_8ON_3)_2$, are as follows—

	Palladium	Carbon	Hydrogen
Percentage found	21·27	52·60	3·33
Percentage calculated	21·16	52·55	3·21

The palladium was determined gravimetrically by ignition to the metal, a few drops of formic acid being added to eliminate any palladium(II) oxide formed.

A probable structure for the chelate, based on infrared evidence reported previously,[9] is given below.



PRECISION AND ACCURACY—

Pure anhydrous palladium chloride was dried over sulphuric acid for 5 hours and the amount of palladium determined twelve times according to the outlined procedure. The results obtained are listed below. They agree favourably with similar results obtained for dimethylglyoxime reported in a previous publication,[6] in which di-2-thienyl ketoxime was used as a gravimetric reagent for palladium.

Theoretical palladium taken, mg	Palladium found, mg	Relative standard deviation, per cent.
17·97	17·98	0·28
35·98	35·98	0·19

EFFECT OF DIVERSE IONS—

Many foreign ions were studied to make the procedure as diversified as possible. Sodium citrate and EDTA were conveniently used as masking agents. In one series of test solutions 100 mg of a foreign ion were added to 15·03 mg of palladium and the outlined procedure followed. The recoveries gave a standard deviation of 0·02 mg for the following extraneous ions: Zn(II), Mn(II), Cu(II), Ni(II), Fe(II), Co(III), Al(III), Hg(II), Cd(II), Mg(II), Ca(II), Ba(II), Sr(II), Pb(II), Sb(V), Bi(III), As(III), Na, K, Ti(IV), U(VI), Mo(VI), Os(VIII), Ru(III), ammonium, oxalate, vanadate, chloride, pyrophosphate and dichromate. The ions of copper, nickel, cobalt and iron form soluble complexes with di-2-pyridyl ketoxime, and hence consume reagent. This effect was eliminated by masking these metals with 1 g of EDTA.

In another series of test solutions, 100 mg of the following foreign ions were added to 13·21 mg of palladium (the recoveries gave a standard deviation of 0·03 mg): Ag(I), Re(VII), Sn(IV), Te(IV), Ir(III), Zr(IV), Hf(IV), Ga(III), Se(IV), Ce(IV), Th(IV), In(III), Ta(V), Tl(I), iodide, thiourea, nitrite, nitrate, sulphite, sulphate, persulphate, carbonate, phosphate, tungstate, bromide, fluoride, perchlorate and thiocyanate. A silver complex was formed with ammonia at pH 10 to 11, and iridium was masked with 1 g of potassium thiocyanate at pH 8 to 9. The limit for rhodium was 50 mg. There was no interference from 10 mg of platinum in the regular procedure, and up to 50 mg could be tolerated if the precipitation was carried out at room temperature.

Gold interfered but was easily separated by reduction to the metal with sodium nitrite[13] and filtration. Cyanide interfered severely in the procedure and must be absent.

Cations were added as chlorides, nitrates or sulphates, and anions as sodium or potassium salts. Molybdenum, osmium, arsenic, rhenium and selenium were added as their oxides.

DISCUSSION

Di-2-pyridyl ketoxime is recommended for the gravimetric determination of palladium. The reagent has several advantages; it is stable indefinitely and is very water-soluble, thus eliminating co-precipitation, even up to a 200 per cent. excess of reagent. The ketone is commercially available and can readily be converted into the oxime. It is also possible to use the ketone directly and generate the oxime with hydroxylammonium chloride, thus allowing the precipitation of palladium from homogeneous solution. The chelate has a large molecular weight and hence a favourable gravimetric factor, which makes the reagent more sensitive than the classical reagent, dimethylglyoxime. Further, the di-2-pyridyl ketoxime procedure is much faster, producing comparable palladium recoveries in much less time. In the dimethylglyoxime method it is recommended that the precipitate be allowed to cool and stand overnight.[2] The di-2-pyridyl ketoxime palladium precipitate is easy to handle during filtration, thus allowing up to 50 mg of palladium to be accurately determined over a wide pH range of between 3 and 11. There are no isomers to contend with because of the symmetrical structure of this oxime, and there are few interferences in the method. The applicability of this reagent to the determination of palladium was shown in a previous publication,[9] in which trace amounts of the chelate were extracted into chloroform, and the palladium subsequently determined by a spectrophotometric method.

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Application of 1-Phenyl-4-phenylamino-1,2,4-triazolium Chloride to the Determination of Cobalt(II)

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A new reagent, 1-phenyl-4-phenylamino-1,2,4-triazolium chloride, is proposed for the determination of cobalt(II) by extraction into 1,2-dichloroethane and spectrophotometric determination at 626 nm of the ion-association compound formed in the presence of an excess of ammonium thiocyanate. The composition of the species extracted has been determined by applying the continuous variation method to the aqueous - organic phase system, and by determining the chemical composition and molecular weight of the compound precipitated from the aqueous phase.

TERNARY complexes and ion-association compounds formed in the aqueous phase between a transition-metal thiocyanate and an organic base or organic cation have often been used for the extraction of the metal into an organic solvent and its spectrophotometric determination. Among the organic substances proposed as reagents for cobalt(II), tri-iso-octylamine,[1] di(4-antipyryl)methane and its derivatives,[2,3] tetraphenylarsonium[4,5,6] and triphenylmethylarsonium salts[7] have been reported. Recently a derivative of 1,2,4-triazole, nitron, already well known as a precipitation reagent for nitrate ions,[8] has also been proposed for the extraction of various metals from aqueous solutions containing an excess of thiocyanate ions.[9,10,11,12]

In the present paper, the results obtained in the study of a new 1,2,4-triazole derivative, 1-phenyl-4-phenylamino-1,2,4-triazolium chloride ($C_{14}H_{13}N_4Cl$), as a reagent for cobalt(II), are briefly reported.

EXPERIMENTAL

REAGENTS AND APPARATUS—

1-*Phenyl-4-phenylamino*-1,2,4-*triazolium chloride*—Prepare by the method of Runti and Nisi.[13] The thiocyanate was obtained from a concentrated aqueous solution of 1-phenyl-4-phenylamino-1,2,4-triazolium chloride by precipitation with ammonium thiocyanate. Both of the triazolium salts were purified by repeated crystallisation from ethanol - diethyl ether (2 + 1, v/v).

Standard solutions of the triazolium salts were prepared by direct weighing of the compounds previously dried at 60° C under vacuum.

Stock aqueous solution of cobalt(II), $1{\cdot}00 \times 10^{-2}$ F—Prepare from cobalt(II) sulphate heptahydrate, $CoSO_4.7H_2O$, and standardise complexometrically. By using this solution, prepare freshly with de-aerated water more dilute standard solutions as required.

All of the solutions were adjusted to pH 3 by the addition of hydrochloric acid. Other solutions used were prepared with analytical-grade reagents [Erba (Milan, Italy)].

Spectrophotometric results were obtained by using spectrophotometric-grade solvents (Erba) and a Unicam SP500 instrument. The pH of the aqueous phase was determined with a Beckman C pH meter, and the molecular weight with a Hewlett - Packard Mechrolab 302 vapour-pressure osmometer.

PROPERTIES AND STABILITY OF THE TRIAZOLIUM SALTS—

The melting-points and solubilities of the triazolium salts are given below.

Compound	Melting-point, °C	Solubility at 20° C (g per 100 g of solvent)		
		Water	Chloroform	1,2-Dichloroethane
1-Phenyl-4-phenylamino-1,2,4-triazolium chloride	206, 210[13]	4·3	0·45	0·032
1-Phenyl-4-phenylamino-1,2,4-triazolium thiocyanate	136	0·045	1·5	0·28

The absorption spectra of the triazolium salts in chloroform solution show a maximum at wavelength 246 nm (for 1-phenyl-4-phenylamino-1,2,4-triazolium chloride, $\epsilon = 1{\cdot}15 \times 10^{-4}$ litres per cm per mole). In water and 1,2-dichloroethane, only an inflection is observed at 235 nm. The absorption spectrum does not change with varying pH in hydrochloric acid or Britton - Robinson buffer solutions. Buffered solutions of both salts are stable for at least 100 hours in the pH range 0·5 to 6·0. When adjusted with hydrochloric acid to pH 3, the solutions are stable for 2 weeks. Above pH 6·0, the salts are not stable and the hydrolytic oxidative degradation leads to the formation of diphenylformazane as the final product.[13]

SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II)—

Conditions for maximum extraction—The absorption spectrum of the species extracted with 1,2-dichloroethane from an aqueous phase containing $1{\cdot}0 \times 10^{-4}$ F cobalt(II), 0·5 F ammonium thiocyanate and $5{\cdot}0 \times 10^{-3}$ F 1-phenyl-4-phenylamino-1,2,4-triazolium chloride is shown in Fig. 1 (broken-line curve). The spectrum is characterised by a maximum at wavelength 626 nm. Blank tests indicate that the strong ultraviolet absorption is mainly caused by the 1-phenyl-4-phenylamino-1,2,4-triazolium thiocyanate formed with excess of thiocyanate and extracted into the organic layer. Extracts separated from the aqueous phase are stable for several days.

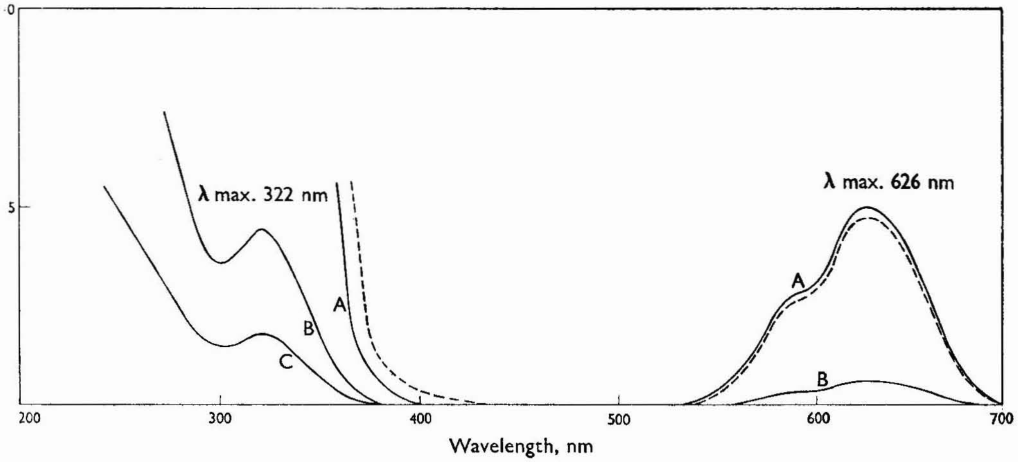

Fig. 1. Broken-line curve: absorption spectrum of the complex extracted with 1,2-dichloroethane (10·0 ml) from an aqueous phase (40·0 ml) containing $1{\cdot}0 \times 10^{-4}$F cobalt (II), 0·5 F ammonium thiocyanate and $5{\cdot}0 \times 10^{-3}$F 1-phenyl-4-phenylamino-1,2,4-triazolium chloride. Continuous-line curves: absorption spectra of the complex in 1,2-dichloroethane: curve A, at concentration $4{\cdot}0 \times 10^{-4}$F; curve B, at $5{\cdot}0 \times 10^{-5}$F; and curve C, at $2{\cdot}0 \times 10^{-5}$F. Optical path length 1 cm

The shapes of the absorption spectra are not changed by varying the concentration of reactants in the aqueous phase, only their intensity changes. At a concentration of $1{\cdot}0 \times 10^{-4}$ F in the aqueous phase, the extraction of cobalt(II) is at a maximum when the concentration of the reagents reaches minimum values of 0·5 F for thiocyanate and $5{\cdot}0 \times 10^{-3}$ F for 1-phenyl-

4-phenylamino-1,2,4-triazolium chloride. Under these conditions, the variation of the pH in the range 0·3 to 4·0 does not affect the absorbance values and, at 626 nm, Beer's law is followed, at least for cobalt(II) in the concentration range 5×10^{-6} to 1×10^{-4} F. At 20° C the apparent specific absorption coefficient is $79{\cdot}2 \pm 0{\cdot}6$ litres per cm per g [with an organic phase-to-aqueous phase (v/v) ratio of 4:1]. This value has been calculated from the regression line of 12 pairs of observations.

Interferences—Only a few interferences have been tested as examples. With the conditions of maximum extraction, copper(II) and iron(III) give coloured extracts, which are orange - brown and red and interfere at concentrations higher than 1×10^{-4} and 5×10^{-6} F, respectively. Iron(II) does not interfere. The interference of iron(III) can be eliminated by using an excess of ammonium fluoride.[5] Manganese(II) and nickel(II) do not give visible absorbing extracts at levels of 1×10^{-3} F, and the absorbance at 626 nm caused by the cobalt(II) is practically unaffected. Among the most common anions considered (fluorides, chlorides, bromides, iodides, sulphates and nitrates), nitrates interfere at concentrations higher than 1×10^{-3} F by causing the precipitation of the sparingly soluble salt, 1-phenyl-4-phenylamino-1,2,4-triazolium nitrate.

PROCEDURE—

A slightly acidic aliquot (less than 10 ml), containing up to 40 µg per ml of cobalt(II), is transferred into a 50-ml calibrated flask, together with 5·0 ml of 4 F ammonium thiocyanate and 20·0 ml of $1{\cdot}0 \times 10^{-2}$ F 1-phenyl-4-phenylamino-1,2,4-triazolium chloride. In the presence of up to 500 µg per ml of iron(III), 2 g of solid ammonium fluoride are added. After diluting the solution to about 38 ml, gently mixing and allowing it to stand for 5 minutes, 10·0 ml of 1,2-dichloroethane are added, the aqueous phase is diluted to the mark and the mixture shaken vigorously for not less than 3 minutes. The contents of the flask are then transferred into a 100-ml separating funnel and, after it has separated, the organic layer is run, dropwise, directly into the spectrophotometric cell. The absorbance is measured at 626 nm against the solvent and corrected for a reagent blank. For an optical path of 1 cm, the working curve lies in the concentration range of 1 to 6 µg per ml of cobalt(II) in the aqueous phase and 1 µg of cobalt(II) per ml is determined, with a standard error of 2 per cent.

CONSTITUTION OF THE EXTRACTED SPECIES—

The method of continuous variations,[14] when applied to the measurement of the extracted compound in 1,2-dichloroethane at 626 nm, shows that the compound contains cobalt(II): thiocyanate: triazolium in the molar ratios 1:2:4, and it probably has the formula $Co(SCN)_4\,(C_{14}H_{13}N_4)_2$. The 500-fold excess of thiocyanate necessary for maximum extraction is about that required for the almost complete formation[15] of the complex $Co(SCN)_4^{2-}$.

When a solution of cobaltothiocyanate (1×10^{-4} F cobalt(II) in 2 F ammonium thiocyanate) is added to a saturated solution of 1-phenyl-4-phenylamino-1,2,4-triazolium thiocyanate in 2 F ammonium thiocyanate, a blue precipitate of waxy appearance is formed, which is purified by re-precipitation with carbon tetrachloride from 1,2-dichloroethane solution and dried under vacuum. Its elemental composition was found to be as follows: C, 50·22 per cent.; H, 3·53 per cent.; N, 22·35 per cent.; S, 16·65 per cent. and Co, 7·72 per cent. (total 100·40 per cent.), which agrees with that calculated for the formula $Co(SCN)_4(C_{14}H_{13}N_4)_2$: C, 50·18 per cent.; H, 3·42 per cent.; N, 21·95 per cent.; S, 16·75 per cent.; and Co, 7·70 per cent. and, in the concentration range 0·05 to 0·3 F in 1,2-dichloroethane, the molecular weight was found to be 752 g per mole, which is in agreement with the value of 765·8 calculated for the proposed formula. The absorption spectrum in the same solvent presents two maxima, at 626 and 322 nm (see Fig. 1, continuous-line curves), and in the visible region it is identical with that observed for the organic extracts. Beer's law is obeyed, with the following molar absorption coefficients: at wavelength 626 nm, $\epsilon = (1{\cdot}256 \pm 0{\cdot}013) \times 10^3$ litres per cm per mole (1×10^{-4} to 1×10^{-3} F); and at wavelength 322 nm, $\epsilon = (8{\cdot}82 \pm 0{\cdot}26) \times 10^3$ litres per cm per mole (1×10^{-5} to 1×10^{-4} F) (the concentration ranges used in this check are given in brackets). From the difference of absorbance at 626 nm between a 1,2-dichloroethane solution and an extract obtained from an aqueous solution containing an equivalent amount of metal, 95 per cent. of the metal is calculated to be extracted under the conditions specified by the proposed method.

CONCLUSIONS

The reagent proposed for the determination of cobalt(II) may be included among those which increase the sensitivity of the classical reaction with thiocyanate by extracting the ion-association compound formed with cobaltothiocyanate into an organic solvent. When compared with those already in use, the procedure suggested is simpler as it involves only one high-efficiency extraction. The sensitivity of the reagent is higher than that given for the tetraphenylarsonium salts.[5] The reagent can be used in media of uncontrolled acidity and no problems arise from instability.

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The Application of Polarography and Related Electroanalytical Techniques to the Determination of Sodium Diethyldithiocarbamate

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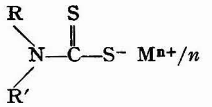
Cathodic stripping analysis has been shown to be an extremely sensitive technique for the determination of compounds that form insoluble mercury salts. The experimental parameters governing the application of this technique have been studied and applied to the determination of sodium diethyldithiocarbamate. The results obtained were compared with those from conventional d.c. polarography, a.c. polarography and linear potential-sweep chrono-amperometry.

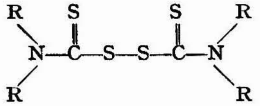
DERIVATIVES of dithiocarbamic acid are widely used as fungicides. The compounds that have been used can be divided into three main types[1]—

simple substituted dithiocarbamic acid salts



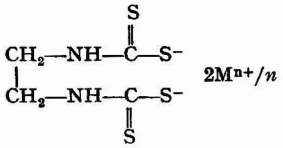
where R $= CH_3$, etc.
R′ $=$ H, CH_3, etc.
M $= Na^+, Fe^{3+}, Zn^{2+}$, etc.

the thiuram disulphides



where R$=$ CH_3, etc.

and salts of ethylenebisdithiocarbamic acid



where M $= Na^+, Zn^{2+}, Mn^{2+}$, etc.

The existing analytical methods for this class of compounds are based on conversion of the sulphur into carbon disulphide, which is then determined colorimetrically, *e.g.*, after reaction with Viles' reagent.[2] The sensitivity of this somewhat lengthy procedure is limited. Moreover, the method is only semi-specific in that it cannot distinguish between dithiocarbamates and thiuram disulphides.

Polarography affords a selective and sensitive technique for the determination of a wide range of organosulphur compounds, but has so far found limited application in pesticide analysis,[3] particularly in regard to the dithiocarbamic acid derivatives. As the dithiocarbamate ion is the fungitoxic species and is also relatively unstable, methods of analysis for this class of compound are more meaningful if the anodic wave of the dithiocarbamate anion, rather than the cathodic wave of the metal ion, is measured. Nangniot has used this approach in the determination of residues of zinc[4] and iron[5] dimethyldithiocarbamates in plants.

This paper describes the study of simple substituted dithiocarbamic acid salts, sodium diethyldithiocarbamate being chosen as the model substance. Simple mono- and dialkyl-substituted dithiocarbamates show anodic waves caused by the formation of insoluble mercury salts.[6] The formation of insoluble films on liquid electrodes has been studied in detail by potentiostatic and a.c. impedance measurements.[7] Most of the detailed polarographic and related studies have been concerned with inorganic anions, in particular the halides.[8,9] Although many organic compounds form insoluble mercury derivatives only a few of these have been studied.[10] This reflects the difficulties associated with elucidation of the electrode process, *e.g.*, determination of *n*, and the isolation of the metastable products of the electrode reaction. At present only a qualitative description of the electrode process for this latter group of compounds is available; this is sufficient basis, however, for the development of an analytical method.

EXPERIMENTAL

REAGENTS—

All reagents used were of analytical-reagent grade.

Sodium diethyldithiocarbamate.

Buffer solution—This was made from 1 M ammonia solution and 1 M ammonium nitrate.

Sodium diethyldithiocarbamate stock solutions, 10^{-2} *to* 10^{-5} M, *aqueous.*

An aliquot of the appropriate stock solution was added to 1 ml of buffer solution and diluted to 10 ml. For a.c. measurements undiluted buffer solution was used as supporting electrolyte. Solutions were de-oxygenated by passage of nitrogen for 3 minutes.

APPARATUS—

Direct current polarograms were recorded on a polarograph, type OH–102 (Metrimpex, Hungary). A Kalousek cell with a separated saturated calomel electrode (S.C.E.) was used. The characteristics of the dropping-mercury electrode, measured at 0·0 volt *versus* S.C.E. in 0·1 M potassium chloride solution were $t = 3{\cdot}82$ s, $m = 2{\cdot}32$ mg s^{-1} at h 65 cm.

Alternating current polarograms were measured with a Univector and general-purpose polarograph (Cambridge Limited, London), with the Metrimpex polarograph being used as the current-output recorder. The connections to the positive cell and negative meter on the general-purpose polarograph were removed and the two terminals short-circuited with a wire. This modification removed the 5-K ohm sensitivity shunt from the output, at the same time eliminating the zero and damping controls. The sensitivity, zero, and damping controls present on the recorder were subsequently used. A Kalousek cell was used in which a platinum-wire counter electrode was placed near the dropping-mercury electrode. The reference and counter electrodes were connected to a 5000-μF capacitor.

Linear potential-sweep chrono-amperometric measurements with a dropping-mercury electrode were made with a K1000 cathode-ray polarograph (Southern Analytical Limited, Surrey). Measurements were also made with a Davis differential cathode-ray polarograph (Southern Analytical Limited, Surrey). In each of these a Kalousek cell was used, as the cells supplied with the instrument have a mercury-pool anode that is unsuitable for studying compounds that react with mercury. The Davis differential polarograph was used in the single cell mode as it was impossible to use two Kalousek cells without major modification of the electrode stand.

Cyclic voltammograms were obtained with the Metrimpex polarograph with a hanging mercury drop electrode in a Kalousek cell. The hanging mercury drop electrode was constructed by cementing a glass capillary tube (0·2-mm bore) into the barrel of an Agla micrometer syringe burette (Burroughs Wellcome Limited, London). Electrical connection was via a platinum wire sealed into the syringe barrel, which was thermally insulated with expanded polystyrene.

For cathodic stripping the Metrimpex polarograph was used to supply both the applied potential for the pre-electrolysis and the voltage sweep for the stripping process. Two types of electrode system were used: a hanging mercury drop electrode and a mercury-coated platinum electrode. The mercury-coated platinum electrode consisted of a platinum wire (10 × 0·5 mm) sealed into a glass tube and coated with mercury by using the method of Joyce and Westcott.[11] The reference electrode was a large current capacity S.C.E. connected by a salt bridge to a micro liquid junction tube (E.I.L. Limited, Surrey). The cell used for the hanging mercury drop electrode was a 25-ml tall-form beaker closed with a rubber bung through which electrodes and gas tubes were passed. For the mercury-coated platinum electrode the cell was made from a B45 socket reduced on to a tube of 3-cm diameter and closed with a flat end. A Perspex cover was machined to fit the ground-glass socket. Solutions were stirred magnetically, a glass-covered rotor being driven by a small magnet attached to a motor. The mercury-coated platinum electrode was mounted in a PTFE stirrer gland (Quickfit and Quartz Limited) and rotated at about 600 r.p.m. by a belt drive from a squirrel cage motor.

RESULTS AND DISCUSSION

DIRECT CURRENT POLAROGRAPHY—

The results of a preliminary survey of the d.c. polarographic behaviour of sodium diethyldithiocarbamate were in agreement with earlier findings[6] and followed the general pattern of insoluble mercury salt formation.

In alkaline solution two anodic waves are observed. The wave at more negative potentials (I) is concentration independent above 10^{-4} M, and shows a linear relationship between current and reservoir height. The wave at more positive potentials (II) begins more or less discontinuously and is only present at concentrations above 10^{-4} M when it is concentration dependent. The first wave (I) has been classified as a Brdicka absorption wave, and arises from the formation of an insoluble monolayer on the drop surface. Further oxidation is then hindered until a more positive potential is reached when the barrier to the charge-transfer reaction is overcome, resulting in a discontinuity in the current - voltage graph.

ALTERNATING CURRENT POLAROGRAPHY—

In alkaline solution sodium diethyldithiocarbamate showed two waves in the concentration range 10^{-3} to 10^{-4} M (Fig. 1) at potentials corresponding to the d.c. waves. The concentration dependence of these two peaks followed the pattern previously observed with d.c. polarography. Peak I was concentration independent over the range 10^{-3} to 10^{-4} M, but linearly dependent in the range 10^{-6} to 10^{-4} M. Peak II showed a rectilinear peak height - concentration relationship over the range 10^{-3} to 10^{-4} M but disappeared below 10^{-4} M. The use of these two peaks gave a rectilinear i_p - concentration dependence over the range 10^{-6} to 10^{-3} M (Tables I and II). Thus the wide concentration range attainable, together with

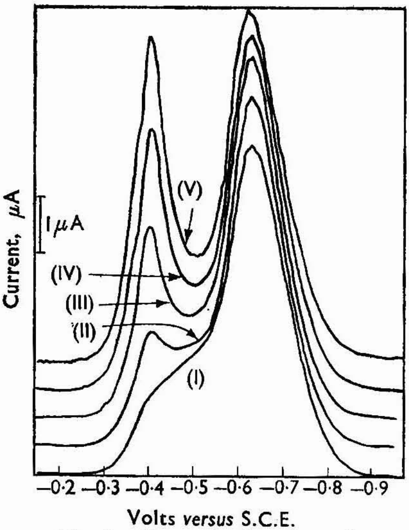


Fig. 1. Concentration dependence of a.c. waves of sodium diethyldithiocarbamate (I) 2 × 10^{-4} M, (II) 4 × 10^{-4} M, (III) 6 × 10^{-4} M, (IV) 8 × 10^{-4} M, (V) 10^{-3} M

TABLE I

COMPARISON OF POLAROGRAPHIC METHODS FOR THE DETERMINATION OF SODIUM DIETHYLDITHIOCARBAMATE

Concentration of sodium diethyldithiocarbamate, M	Currents in μA					
	Direct current polarography		Alternating current polarography		Linear potential-sweep chrono-amperometry*	
	I	II	I	II	I	II
2×10^{-5}	—	—	0·54	—	0·61	—
4×10^{-5}	—	—	1·08	—	1·15	—
6×10^{-5}	—	—	1·60	—	1·74	—
8×10^{-5}	—	—	2·13	—	2·30	—
1×10^{-4}	0·29	0	2·64	0	2·67	0
2×10^{-4}	0·29	0·34	4·54	0·64	3·05	4·9
4×10^{-4}	0·29	1·42	6·30	2·05	3·05	17·6
6×10^{-4}	0·29	2·50	6·43	3·46	3·05	28·8
8×10^{-4}	0·29	4·08	6·40	4·84	—	—
1×10^{-3}	0·29	—	6·40	6·24	—	—

* Cathodic voltage sweep.
I Pre-wave.
II Diffusion controlled wave.

the advantages associated with the derivative type signal obtained, makes this technique ideally suited to the analysis of dithiocarbamate formulations. A concentration of 10^{-6} M must be taken as the lower limit attainable with the apparatus used, as at this level the instrument noise became comparable with the signal. About 1 per cent. a.c. ripple was observed on the rectified output of the Univector unit at twice the applied frequency of about 35 Hz. The recorder that was used (Metrimpex polarograph) incorporated parallel T-filters tuned to frequencies of 1·6, 0·8, 0·8 and 0·4 Hz, which are effective in filtering oscillations caused by drop growth, but do not significantly reduce the 70-Hz ripple. The limit of detection could be extended by the use of an instrument based on solid-state electronics[12] or by incorporating a filter tuned to higher frequencies.

At high concentrations, *e.g.*, 10^{-3} M, when both waves are well developed it is apparent that the width of wave I at half-height, 144 mV, is considerably greater than the corresponding

TABLE II

COMPARISON OF CATHODIC STRIPPING VOLTAMMETRY WITH POLAROGRAPHIC TECHNIQUES FOR THE DETERMINATION OF SODIUM DIETHYLDITHIOCARBAMATE

Concentration of sodium diethyldithiocarbamate, M	Currents in μA			
	Alternating current polarography	Linear potential-sweep chrono-amperometry*	Cathodic stripping	
			Stirred solution	Rotating electrode
2×10^{-8}	—	—	—	0·20†
4×10^{-8}	—	—	—	0·37†
6×10^{-8}	—	—	—	0·56†
8×10^{-8}	—	—	—	0·78†
1×10^{-7}	—	—	—	0·98†
2×10^{-7}	—	—	0·77†	0·56‡
4×10^{-7}	—	—	1·47†	1·18‡
6×10^{-7}	—	—	2·53†	1·87‡
8×10^{-7}	—	—	2·78†	2·38‡
1×10^{-6}	—	—	3·78†	2·88‡
2×10^{-6}	0·03	0·05	0·94§	—
4×10^{-6}	0·07	0·11	1·94§	—
6×10^{-6}	0·10	0·16	2·78§	—
8×10^{-6}	0·14	0·22	4·06§	—
1×10^{-5}	0·17	0·27	4·73§	—

* Cathodic voltage sweep.
† 5 minutes' electrolysis.
‡ 2 minutes' electrolysis.
§ 1 minute's electrolysis.

value for wave II, 88 mV (Fig. 2). Theory predicts that the width of an a.c. wave at half-height is $90{\cdot}5/n$ mV for low frequencies.[13] However, with the apparatus used only the component of the a.c. current in phase with the applied a.c. voltage is rectified and recorded as the a.c. wave. While this results in an increase in sensitivity by eliminating purely capacitative currents, some distortion of the wave shape is inevitable because most faradaic processes have phase angles between 0° and 45°. It is therefore not possible to derive *n* values from this evidence. It is clear, however, that the two processes corresponding to waves I and II both show large in-phase components of the a.c. current, hence both must involve charge-transfer reactions.

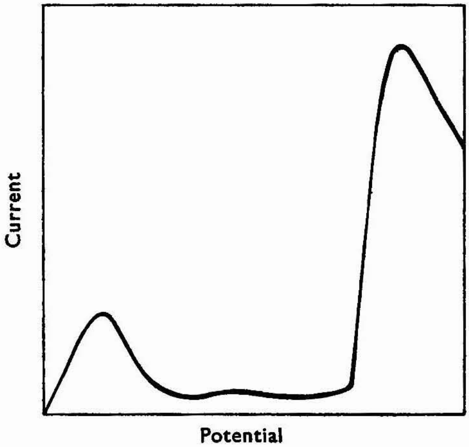


Fig. 2. Cathode-ray polarogram, 5×10^{-4} M sodium diethyldithiocarbamate. Anodic voltage sweep. Sensitivity $7{\cdot}5$ μA f.s.d. Starting voltage $-0{\cdot}7$ volt *versus* S.C.E.

LINEAR POTENTIAL-SWEEP CHRONO-AMPEROMETRY AT A DROPPING-MERCURY ELECTRODE—

Anodic voltage sweeps (from negative to positive potentials) showed two peaks in the concentration range 10^{-3} to 10^{-4} M (Fig. 2). The height of the more negative peak (I) was concentration independent, while peak II showed a rectilinear concentration dependence. Thus peak I clearly corresponds to the d.c. polarographic pre-wave and peak II to the d.c. diffusion wave.

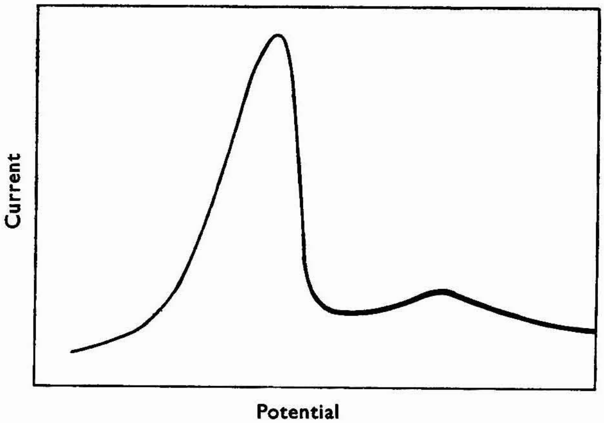


Fig. 3. Cathode-ray polarogram, 5×10^{-4} M sodium diethyldithiocarbamate. Cathodic voltage sweep. Sensitivity 30 μA f.s.d. Starting voltage $-0{\cdot}3$ volt *versus* S.C.E.

Cathodic voltage sweeps (from positive to negative potentials) also showed the same two peaks, but the peak currents obtained were several times greater (Fig. 3). At concentrations above 6×10^{-4} M, peak I (the concentration-independent pre-wave) was obscured by the larger peak II, which required a reduction in the sensitivity control of the instrument to accommodate it. This increase in sensitivity was caused by pre-concentration of the insoluble mercury salt on the drop surface during the 5-second delay period. At concentrations below 10^{-4} M peak II disappeared and peak I became concentration dependent (Table I) over the range 10^{-4} to 10^{-6} M. The consecutive use of the two peaks obtained by cathodic voltage sweeps enabled a rectilinear i_p - concentration dependence to be established over the concentration range 1×10^{-6} to 6×10^{-4} M. The potential-sweep synchronisation circuit of the polarograph requires the use of a dropping-mercury electrode with a drop time of between 6·5 and 7·0 seconds. In the presence of sodium diethyldithiocarbamate the capillary was found to drop erratically, presumably because of the deposition of insoluble material in and around the capillary orifice. This problem was overcome by the use of forced-drop detachment. With the Davis differential cathode-ray polarograph the potential sweep is synchronised with mechanical detachment of the drop. At concentrations below 10^{-6} M peak heights were not reproducible. However, modification of the instrument to allow the use of twin cells with external reference electrodes would result in a decrease in the lower concentration limit.

CYCLIC VOLTAMMETRY—

A cyclic voltammogram of sodium diethyldithiocarbamate in alkaline solution is shown in Fig. 4. A single oxidation - reduction peak is observed at the sweep rates used. The enhancement in peak current during the cathodic sweep compared with the anodic sweep is clearly illustrated. Whenever the electrode potential is more positive than that of the cathodic peak (0·4 volt *versus* S.C.E.), the insoluble mercury - diethyldithiocarbamate compound is formed at the electrode surface. This suggested that cathodic stripping analysis is applicable to the problem. In this technique the electrode is held for a fixed time at a potential at which the insoluble mercury salt is formed, and then a cathodic voltage sweep is applied; the resulting current is recorded as a stripping peak, the height of which is proportional to concentration. Cyclic voltammetry, which allows the direct comparison of the oxidation and reduction processes, was used to determine the potential range available for pre-electrolysis and the optimum sweep rate.

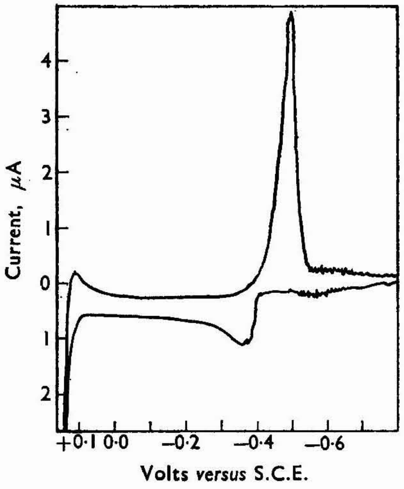


Fig. 4. Cyclic voltammogram, 1×10^{-4} M sodium diethyldithiocarbamate. Single cycle, initial scan anodic. Scan rate 25 mVs^{-1}

The observed separation of anodic and cathodic peak potentials (140 mV) is greater than the expected value of about 60 mV for a reversible one-electron transfer at comparatively slow sweep rates.[14] About 20 to 30 mV of this separation arises through backlash in the polarograph gears. The displacement is still significantly different from the ideal case, and suggests that an activation energy is associated with the stripping process.

CATHODIC STRIPPING ANALYSIS—

There has been considerable work on the technique of anodic stripping[15,16,17] but relatively little work has been done on the converse technique of cathodic stripping. It is not generally realised that cathodic stripping does not suffer from many of the complicating factors encountered in the analogous anodic technique. As the electrolysis is carried out at relatively positive potentials, fewer impurities are plated out. Moreover, the cathodic stripping of an insoluble film from a mercury surface gives an improved peak definition when compared with anodic stripping in which slow diffusion from the bulk of the electrode causes tailing.

Two types of electrode system were studied. Firstly a hanging mercury drop electrode was investigated and subsequently a mercury-coated platinum electrode.

HANGING MERCURY DROP ELECTRODE—

The stripping curve, (*a*), obtained with this type of electrode after pre-electrolysis in unstirred solution is shown in Fig. 5. Peak I corresponds to the pre-wave and peak II to the diffusion controlled wave in Fig. 1. A random dependence of peak current *versus* electrolysis time for peak II was found, while the height of peak I remained constant. When the solution was stirred during the pre-electrolysis an increase in sensitivity was obtained and a rectilinear peak current - electrolysis time relationship was found. Under these conditions the pre-wave was not clearly defined, suggesting that no discrete monolayer was formed as shown in (*b*) in Fig. 5. The magnitude of the stripping peak showed a rectilinear concentration dependence over the range 5×10^{-7} to 10^{-4} M.

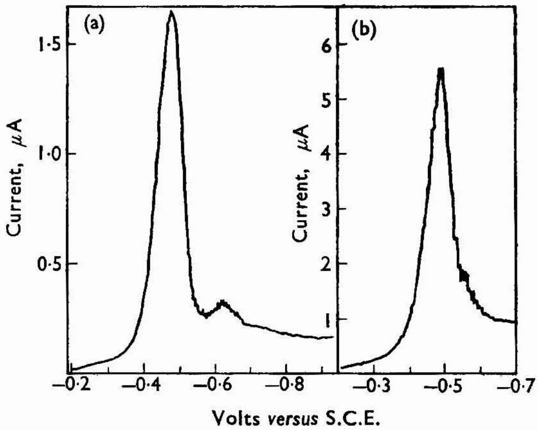


Fig. 5. Stripping peaks at hanging mercury drop electrode, 2×10^{-5}M sodium diethyldithiocarbamate; 4 minutes' electrolysis at 0·0 volt *versus* S.C.E. Scan rate 25 mVs^{-1}: (a) unstirred solution; (b) stirred solution

MERCURY-COATED PLATINUM ELECTRODE—

The two major disadvantages of the hanging mercury drop electrode, *i.e.*, its extreme sensitivity to vibration and the difficulties associated with reproducibility of the drop size are eliminated by using a mercury-coated platinum electrode. Many of the practical difficulties experienced by early workers in the use of this electrode have recently been overcome by Joyce and Westcott.[11] In the present work initial experiments were performed with a stationary electrode in a stirred solution. Results indicated that for a given depolariser concentration, in order to minimise the electrolysis time it was necessary to increase the rate of stirring until just before turbulence occurred. Under these conditions well developed stripping peaks, (*a*) in Fig. 6, were obtained after 2 minutes' electrolysis for concentrations down to 10^{-6} M. At concentrations below this level it was necessary to extend the electrolysis period to 5 minutes to allow the use of a sufficiently low current sensitivity to eliminate instrument noise; under these conditions there was a slight decrease in precision. This problem was overcome by rotating the electrode, at constant speed, during the pre-electrolysis instead of stirring the solution. The stripping peaks, (*b*), obtained after 2 minutes' pre-electrolysis at a rotating electrode were better defined, as shown in Fig. 6(*b*), and allowed the lower concentration level to be extended to 10^{-7} M without loss of precision. The determination of lower concentrations was possible but it was preferable to increase the electrolysis time rather than the instrument sensitivity.

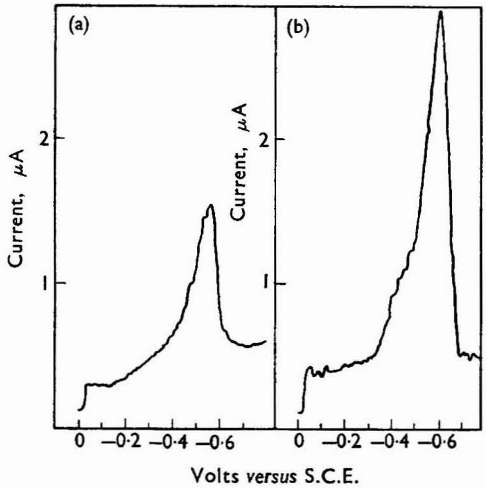


Fig. 6. Stripping peaks at mercury-coated platinum electrode, 8 × 10^{-7} M sodium diethyldithiocarbamate; 2 minutes' electrolysis at 0·0 volt *versus* S.C.E. Scan rate 100 mVs^{-1}: (a) stirred solution; (b) rotated electrode

CONCLUSIONS

The results of the present investigation have shown that of the techniques examined, cathodic stripping proved the most suitable for the determination of trace amounts of sodium diethyldithiocarbamate. Alternating current polarography and potential-sweep chronoamperometry were both applicable to a wide range of concentrations but in both cases the lower limit was 10^{-6} M. The sensitivity of cathodic stripping was limited only by instrument noise, and it is evident that with improved instrumentation by using electronic potential sweeps and oscilloscopic read-out a much lower detection limit could be achieved.

A rotating mercury-coated platinum electrode was found to be the most suitable for cathodic stripping. Its sensitivity and reproducibility were far superior to the hanging mercury drop electrode; in addition it was not affected either by the rate of stirring of the solution or by vibration. Although the present work has been confined to mercury electrodes, it should be noted that certain types of solid electrode, *e.g.*, pyrolytic graphite and carbon paste, might offer some advantages in that the electrode process will involve a true oxidation, rather than mercury salt formation.

We wish to thank the Agricultural Research Council for the provision of a research assistantship to one of us (M. J. D. B.). We would also like to thank Morganite Research and Development Limited for the loan of the K1000 cathode-ray polarograph, and Dr. D. A. Pantony, Metallurgy Department, Imperial College, for the use of the Davis differential cathode-ray polarograph.

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A Field Method for the Determination of Ozone in the Presence of Nitrogen Dioxide

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A method has been developed for the determination of ozone in air in the presence of nitrogen dioxide. Samples of the test atmosphere are drawn, in parallel, through neutral, buffered potassium iodide solutions at 2 litres per minute for 20 minutes. One sample, prior to its passage through the iodide solution, is drawn through a cotton-wool plug. This removes the ozone, and the iodine liberated is a measure of the nitrogen dioxide present, expressed in terms of ozone equivalents. The iodine liberated by the other sample is a measure of the total oxidant, ozone *plus* nitrogen dioxide, also expressed as ozone equivalents. After addition of starch the iodine liberated by each sample is determined visually against prepared colour standards. The difference between the two readings obtained is a measure of the ozone present. The method enables from 0·1 mg m^{-3} (0·05 p.p.m. v/v) of ozone in air, in the presence of up to 9 mg m^{-3} (5 p.p.m.) of nitrogen dioxide, to 0·8 mg m^{-3} (0·4 p.p.m.) of ozone in air, in the absence of nitrogen dioxide, to be determined. The procedure is relatively simple and the time required for a complete analysis is about 30 minutes.

OZONE, which has increasing applications in a variety of industries, is used, for instance, in various chemical syntheses, and as a bleaching agent for textiles. In these processes measures can be taken to minimise the contamination of the working atmosphere by ozone. However, it is less easy to control the ozone formed fortuitously, together with nitrogen dioxide, in the vicinity of high-voltage electrical discharges and during electric arc-welding operations. Ozone is a toxic gas with a current threshold limit value (T.L.V.) in the United Kingdom of only 0·2 mg m^{-3} (0·1 p.p.m. v/v) in air,[1] and it could represent a considerable hazard in an industrial atmosphere. As the T.L.V. for nitrogen dioxide in the United Kingdom is currently set at 9 mg m^{-3} (5 p.p.m. v/v) in air,[1] fifty times that of ozone, it appeared that a need existed for a simple field test for the determination of low concentrations of ozone in the presence of nitrogen dioxide.

The methods already available for the determination of ozone generally either lack specificity or are unsuitable for adaptation to a field test. For example, the reaction of ozone with potassium iodide and subsequent liberation of iodine would be suitable as a basis for a field test except for the interference from oxidising and reducing gases.

Bravo and Lodge[2] reported a method for the determination of ozone by means of its specific reaction with 4,4′-dimethoxystilbene to yield anisaldehyde, which is then determined spectrophotometrically. Besides finding variabilities associated with the source and keeping qualities of the reagents, we considered that the corrosive nature of two of the reagents, trifluoroacetic acid and trifluoroacetic anhydride, precluded the use of this method in the field; similar views have been expressed by other workers.[3]

We found a similar type of method, involving the ozonolysis of 1,2-di-(4-pyridyl)ethylene and subsequent spectrophotometric determination of the pyridyl-4-aldehyde formed,[4] to be much more sensitive than that of Bravo and Lodge. However, under the sampling conditions of at least 2 litres per minute, that we wished to use, somewhat erratic results were obtained. Additionally, the need for a 20-minute heating period during the colour development would be disadvantageous in any field test.

Attempts to develop a field test based on the production of stains on chemically impregnated papers proved unsuccessful. Di- and trihydric phenols, hydroxynaphthalenes, aminophenol, carbazole, "tetra base," indigo carmine and fuchsin were each tried, but the passage of several litres of a 0·2 mg m^{-3} (0·1 p.p.m. v/v) atmosphere of ozone through the respective impregnated papers produced no visible stains.

Better results were obtained from the use of the fluidised-bed technique.[5] Various supports, notably silica gel and activated alumina, were impregnated with each of several compounds known to change colour on exposure to ozone. Best results were obtained with fuchsin on acidic alumina and indigo carmine on silica gel. However, with both systems, insufficient colour differentiation was obtained between 0·1, 0·2 and 0·4 mg m^{-3} ozone levels.

Recently, after we had completed the development of our method, Nash[6] described a procedure for the determination of ozone based on the bleaching effect of the gas on an aqueous solution of diacetyldihydrolutidine. Although we have not investigated this method, the interference of oxides of nitrogen to the extent of 5 per cent. v/v may limit its applicability to the determination of ozone in the presence of nitrogen dioxide.

Other published tests for ozone[7,8] were found to lack the sensitivity required.

In the absence of a more suitable method it was decided to attempt to develop a field test based on the reaction of ozone with neutral potassium iodide solution and incorporating a means of separating ozone from nitrogen dioxide.

EXPERIMENTAL

PREPARATION AND CALIBRATION OF STANDARD ATMOSPHERES—

Atmospheres containing known concentrations of ozone, nitrogen dioxide and mixtures of these gases were required to assess the efficiency of sampling techniques and for the development of a field test.

PREPARATION—

Ozone—A dynamic atmosphere was produced by passing oxygen through a commercial ozoniser (British Oxygen Company, Mark II Ozoniser) at a rate sufficient to give a nominal ozone concentration of 1 per cent. w/w and diluting twice with metered streams of air to the required concentration.

Nitrogen dioxide—A dynamic atmosphere was produced by bubbling nitrogen at a few millilitres per minute through liquid nitrogen dioxide maintained at −5° C and diluting the resultant vapour twice with metered streams of air to the required concentration.

Mixed atmospheres—These were obtained by mixing metered flows of each diluted gas in a suitable mixing chamber.

CALIBRATION—

Ozone—The ozone atmosphere was calibrated by sampling at 20 litres per minute for 40 minutes through three Greenburg - Smith impingers in series, each containing 60 ml of neutral, buffered potassium iodide solution. The total iodine liberated was determined by titration with 0·004 N sodium thiosulphate, and the concentration of ozone in the atmosphere calculated on the basis of a stoicheiometric release of iodine by ozone ($O_3 \equiv I_2$).[9] The use of three bubblers ensured the complete collection of the ozone and eliminated any loss of iodine by carry-over. It would have been desirable to standardise the atmosphere by another method. Although the Bravo and Lodge[2] method gave results comparable with those obtained by the potassium iodide method, the difficulties experienced with the former method meant that little significance could be placed on the results obtained. However, the concentrations of various atmospheres determined by the potassium iodide method agreed closely with those calculated from the graph of ozone output supplied with the ozoniser and by using the appropriate dilution factors. For example, under one set of diluting conditions the calculated and experimentally determined concentrations of the ozone atmosphere after the first dilution stage were 24·6 and 24·5 mg m^{-3}, respectively, and the corresponding figures after the second dilution stage were 0·23 and 0·24 mg m^{-3}.

Nitrogen dioxide—A precisely calibrated atmosphere of this gas was not required but the approximate concentration of nitrogen dioxide in the atmosphere was determined spectrophotometrically with a modified Saltzman[10] reaction.

COLLECTION OF OZONE—

Saltzman and Gilbert[9] have reported on the various aspects of the collection of ozone in potassium iodide solution. Our choice of sampling conditions was based to a considerable extent on this work. In particular, neutral, buffered potassium iodide solution was found suitable as an absorbing solution for ozone. Provided that the solid potassium iodide was fresh, a 2 per cent. solution of this in mixed sodium and potassium hydrogen phosphate buffer was stable and usable for several months.

A comparison was made of the relative merits of sintered and impinger type absorbers. The impingers were found to give more reproducible results and a higher absorption efficiency, thus confirming the previous observations of Hendricks and Larsen.[3] All-glass absorbers of the impinger type shown in Fig. 2 (see page 511) were found suitable and used with 10 ml of absorbing solution.

The minimum sample volume that gave a visually discernible colour with a 0·1 mg m^{-3} ozone atmosphere was 40 litres. With 10 ml of absorbing solution in one absorber it was observed that 2 litres per minute was the maximum sampling rate that could be used without undue loss of liberated iodine. This is discussed more fully later. At higher sampling rates a loss of absorbing solution was also noted. The 20-minute sampling time required under these flow-rate conditions was considered to be compatible with the requirements of a field test.

COLORIMETRIC DETERMINATION OF OZONE—

Previous methods[9,11] for the determination of oxidants or ozone in air with potassium iodide solution have involved spectrophotometric measurements of the liberated iodine. In field testing, visual determination with colour standards is more convenient, especially as scientifically unskilled personnel are likely to be carrying out the test. As the colour of iodine is not suitable for easy colour differentiation, the addition of starch to give the blue starch - iodine complex was found to be the simplest means of improving on this.

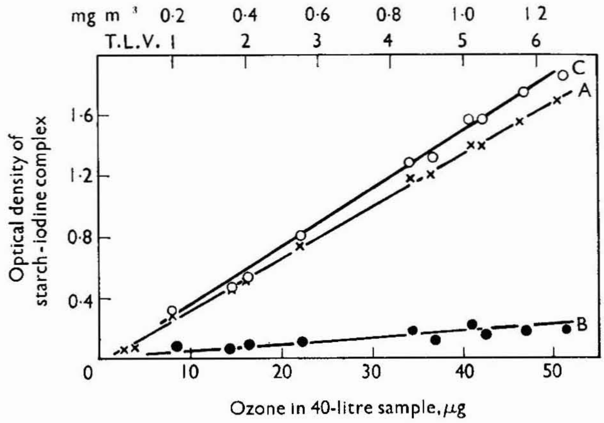


Fig. 1. Relationship between optical density of starch - iodine complex and μg of ozone in a 40-litre atmosphere sample: graph A, sample collected in one absorber; graph B, sample collected in second of two absorbers in series; graph C, sample collected in two absorbers in series

Several methods of producing this blue starch - iodine complex were investigated, including the linear starch reagent proposed by Lambert.[12] This reagent, which contained cadmium iodide, proved unsatisfactory, giving flocculent precipitates in the presence of the phosphate buffer of the absorbing solution. Finally, a 0·25 per cent. w/v aqueous, soluble starch solution, freshly prepared each day, was found to be the most suitable reagent, producing blue colours that were stable for 30 minutes before fading.

It was now necessary to relate the optical density of the colour produced from the released iodine with the weight of ozone in samples of the various standard atmospheres taken under test conditions. Forty-litre samples of standard ozone atmospheres of various concentrations were collected at 2 litres per minute in two all-glass absorbers in series, each containing 10 ml of absorbing solution. Starch was added to each solution and the respective optical densities of the solution in each of the absorbers measured separately at 540 nm with 1-cm cells. Each was plotted against the weight of ozone in the sample. Straight lines, graph A for the first absorber solution and graph B for the second (Fig. 1), were obtained for each. The failure of the lines to pass through the origin of the graph was thought to be caused by a certain small uptake of iodine by the starch without a colour being produced.[12] A correction for this small amount of iodine was made to the optical density of the solution in the second absorber, and the combined optical densities in both absorbers were plotted against weight of ozone in the sample. Graph C (Fig. 1) was obtained and found to be identical with that obtained when 5 ml of starch solution were added to each of a series of 10 ml of buffered potassium iodide solution containing known amounts of iodine and the optical densities of the colours produced plotted against the ozone stoicheiometrically equivalent to the iodine present. This suggests, assuming the $O_3 \equiv I_2$ relationship,[9] that the two absorbers in series were collecting 100 per cent. of the ozone from the various 40-litre samples.

The use of only one absorber was envisaged in the proposed test, and it can be seen from graph A (Fig. 1) that this ensures a reasonably reproducible trapping of 87 per cent. of the ozone in an atmosphere, over a 0 to 1·2 mg m^{-3} ozone concentration range. For the purposes of a field test this was considered to be satisfactory and no extra complication would be introduced, provided the colour standards prepared for the proposed test took this into account. Graph A was used for the calibration of all subsequent work on the development of the field test.

REMOVAL OF NITROGEN DIOXIDE FROM A MIXED OZONE - NITROGEN DIOXIDE ATMOSPHERE—

As previously mentioned, the reaction involving the release of iodine from potassium iodide is not specific for ozone. Nitrogen dioxide, which is likely to be found in certain industrial atmospheres, together with ozone, reacts in a similar manner. The problem of separating the two gases was initially tackled by seeking a means of preferentially trapping the nitrogen dioxide prior to the absorption of the ozone in the potassium iodide solution. Various solutions were tried as traps for nitrogen dioxide: chromic acid, sodium hydroxide (1 per cent. w/v), sodium carbonate (1 per cent. w/v), "nitron" (0·1 per cent. w/v), urea (2 per cent. w/v), sulphuric acid (2 per cent. w/v), alkaline permanganate and alkaline arsenite. None of these solutions completely removed the nitrogen dioxide at the sampling rate required, *i.e.*, 2 litres per minute. Powdered manganese dioxide removed most of the gas but also completely removed the ozone. It was found at this stage that cotton-wool and various man-made fibres could not be used as supports for trapping agents as they themselves removed ozone.

It now seemed unlikely that a simple system could be devised for trapping nitrogen dioxide, therefore it was decided to attempt to remove the ozone from the nitrogen dioxide and determine it by difference. Two parallel sampling systems were envisaged in which one branch would indicate the total oxidant present and the other, containing an ozone trap, would indicate the total oxidant *minus* the ozone. The blue colours obtained in the absorbing solutions on the addition of starch would be a measure of oxidant in terms of an ozone equivalent. The fact that nitrogen dioxide did not give a stoicheiometric release of iodine from potassium iodide solution would not invalidate this, provided it released the same amount of iodine in each branch.

REMOVAL OF OZONE FROM A MIXED OZONE - NITROGEN DIOXIDE ATMOSPHERE—

Ozone was found to be completely removed by a solution of *trans*-stilbene in *sym*-tetrachloroethane. However, carry-over of the solvent into the absorbing solution was a complication. As the use of other solvents did not eliminate this problem, solid-state traps were considered. In particular, the previous findings in connection with attempts to trap nitrogen dioxide suggested that cotton-wool might be used. Preliminary experiments indicated that a plug of cotton-wool would completely remove ozone from a 0·6 mg m^{-3} (0·3 p.p.m. v/v) atmosphere and allow a nitrogen dioxide atmosphere, 9 mg m^{-3} (5 p.p.m.), to pass unaffected. Further investigation showed that the state of the cotton-wool, untreated, washed, dried

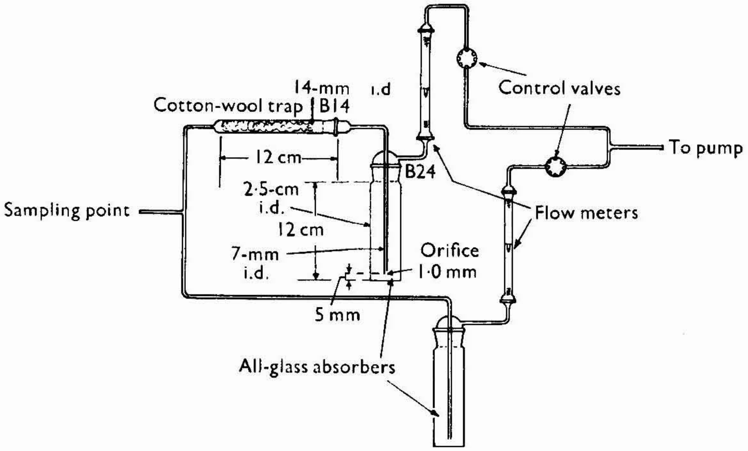


Fig. 2. Field test assembly for the determination of ozone in the presence of nitrogen dioxide

or damp, had no apparent effect as far as the trapping of ozone was concerned. Damp material did, however, remove some nitrogen dioxide. The trap was standardised to the use of 1 g of cotton-wool, washed with tap and then de-ionised water, dried at 105° C and packed in a glass tube (Fig. 2) to a length of about 7 cm. Such a trap absorbed about 40 μg of ozone, *i.e.*, 200 litres of a 0·2 mg m^{-3} atmosphere sampled at 2 litres per minute before breakthrough occurred, as shown in Table I.

TABLE I

REMOVAL OF OZONE FROM ATMOSPHERES WITH COTTON-WOOL

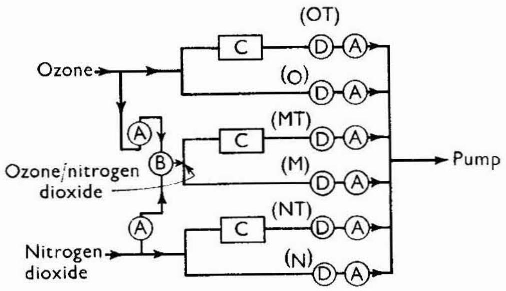
Cotton-wool sample, 1 g	Ozone concentration passed through trap, mg m^{-3}	Equivalent volume of 0·2 mg m^{-3} ozone atmosphere passed, litres		Ozone found after trap, mg m^{-3}
		Per run	Total	
1	0·465	93	93	0
	0·450	90	183	0
	0·445	89	272	0·265
2	0·425	85	85	0
	0·445	89	174	0
	0·440	88	262	0·250
3	0·735	147	147	0
	0·235	94	241	0·100

Fig. 2 shows the proposed field test assembly for the determination of ozone in an atmosphere that also contains nitrogen dioxide.

DETERMINATION OF OZONE IN STANDARD MIXTURES OF OZONE AND NITROGEN DIOXIDE—

In order to assess the validity of the proposed method, a system, represented diagrammatically in Fig. 3, was set up, in which atmospheres of ozone, nitrogen dioxide and a mixture of equal volumes of the ozone and nitrogen dioxide atmospheres could be sampled simultaneously. The sampling rate in each branch of the system was 2 litres per minute.

In Fig. 3, (OT) and (O) represent the amounts of iodine liberated in the absorbing solutions, expressed as ozone equivalents (mg m^{-3}), by 40 litres of the ozone atmosphere with and without a cotton-wool trap in line, respectively. (MT) and (M), and (NT) and (N) represent the iodine liberated by the mixed and nitrogen dioxide atmospheres, respectively, each with and without a similar trap under similar sampling conditions. If the ozone alone is removed by the trap, then (M) *minus* (MT) should represent the ozone concentration in the mixed atmosphere and should be equal to (O)/2 for a mixture of equal volumes of the two gases.



A = Flow meter and control valve
B = Mixing chamber
C = Cotton-wool trap
D = Absorbing solution
O = Iodine liberated by ozone atmosphere without cotton-wool trap
OT = Iodine liberated by ozone atmosphere with cotton-wool trap
N = Iodine liberated by nitrogen dioxide atmosphere without cotton-wool trap
NT = Iodine liberated by nitrogen dioxide with cotton-wool trap
M = Iodine liberated by mixed atmosphere without cotton-wool trap
MT = Iodine liberated by mixed atmosphere with cotton-wool trap

Fig. 3. Diagrammatic representation of the assembly for the analysis of mixed atmospheres of ozone and nitrogen dioxide

A series of determinations was carried out with 1 + 1 v/v mixtures containing concentrations of ozone over the range 0·1 to 0·4 mg m^{-3} and various concentrations of nitrogen dioxide from zero to a maximum of 11·4 mg m^{-3}. Some typical results are shown in Table II.

TABLE II

IODINE, EXPRESSED AS OZONE EQUIVALENTS, LIBERATED IN THE RESPECTIVE ABSORBING SOLUTIONS BY 40 LITRES OF OZONE, NITROGEN DIOXIDE AND MIXED ATMOSPHERES

Actual composition of mixture, mg m^{-3}		Ozone equivalents found in respective absorbing solutions, mg m^{-3}						Ozone found in mixture, (M) - (MT), mg m^{-3}
Ozone	Nitrogen dioxide*	Ozone		Nitrogen dioxide		Mixture ozone + nitrogen dioxide		
(O)/2		Without trap (O)	With trap (OT)	Without trap (N)	With trap (NT)	Without trap (M)	With trap (MT)	
0·118	0	0·235	0	0	0	0·125	0	0·125
0·120	2·9	0·240	0	0·435	0·435	0·335	0·235	0·100
0·110	8·5	0·220	0	1·38	N.D.	0·740	0·645	0·095
0·200	1·7	0·400	0	0·290	N.D.	0·335	0·150	0·185
0·215	2·9	0·430	0	0·480	0·495	0·445	0·255	0·190
0·355	1·7	0·710	0	0·305	0·305	0·475	0·170	0·305
0·395	2·9	0·790	0	0·460	0·475	0·610	0·245	0·365
0·460	5·6	0·920	0	0·970	N.D.	0·890	0·450	0·440
0·405	11·4	0·810	0	>1·5	>1·5	1·580	1·210	0·370

* Nitrogen dioxide concentration determined by a modified Saltzman[10] method.
N.D. Not determined.

The results in Table II show that the cotton-wool trap completely removed the ozone, *i.e.*, (OT) was zero, and also that the nitrogen dioxide concentration was unaffected by the trap, *i.e.*, (N) was equal to (NT).

The average figures for the ozone concentrations found in all the mixtures analysed by the proposed test procedure are summarised in Table III. For ease of presentation the concentrations of ozone in the various mixtures have each been converted into the nearest 0·1 mg m^{-3}. The standard deviations on the mean ozone concentrations found in each set of replicates are also given.

TABLE III

OZONE CONCENTRATIONS IN PREPARED OZONE - AIR MIXTURES, WITH AND WITHOUT ADDED NITROGEN DIOXIDE, AS DETERMINED BY THE PROPOSED PROCEDURE

No. of tests	Nitrogen dioxide concentration in mixture, mg m^{-3}	Ozone concentration in in mixture (O)/2, mg m^{-3}	Mean ozone concentration found in mixture (M) - (MT), mg m^{-3}	Ozone found *minus* ozone added [(M) - (MT)] - (O)/2, mg m^{-3}
2	0	0·1	0·109 ± 0·004	+0·009
5	2·9	0·1	0·080 ± 0·005	−0·020
8	5·6	0·1	0·087 ± 0·021	−0·013
2	8·5	0·1	0·083 ± 0·018	−0·017
11	0	0·2	0·203 ± 0·004	+0·003
4	2·9	0·2	0·174 ± 0·009	−0·026
24	5·6	0·2	0·180 ± 0·028	−0·020
4	11·4	0·2	0·167 ± 0·007	−0·033
2	0	0·4	0·407 ± 0·016	+0·007
4	2·9	0·4	0·372 ± 0·018	−0·028
3	5·6	0·4	0·396 ± 0·039	−0·004

It can be seen from Table III that when nitrogen dioxide was present in the mixture the ozone found, (M) - (MT), was always slightly less than that added, (O)/2. The mean apparent loss of ozone ranged from 0·004 to 0·033 mg m^{-3} in the tests carried out. This would not invalidate the proposed test as it is designed to measure the ozone concentration of an atmosphere only to the nearest 0·05 mg m^{-3} in the 0·1 to 0·2 mg m^{-3} range and to the nearest 0·1 mg m^{-3} in the 0·2 to 0·8 mg m^{-3} range.

This apparent loss of ozone could not have been caused by the interaction of ozone and nitrogen dioxide, as it was found in this series of determinations that within experimental error $\frac{(O) + (N)}{2} = (M)$. Similarly, it could not be attributed to oxidising impurities in the cotton-wool being carried through by the nitrogen dioxide, because experimentally (N) = (NT). One explanation is that an oxidising product is formed by the interaction of ozone with nitrogen dioxide in the presence of cotton-wool resulting in an increase of (MT) and consequently a decrease of (M) - (MT). A possible reaction[13] is $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$, initiated in this reaction by the cotton-wool, with the nitrogen pentoxide having a greater iodine-liberating power than nitrogen dioxide.

COLOUR STANDARDS—

Colour standards that would match the colours produced in the proposed test were required. It was found that 9 mg m^{-3} of nitrogen dioxide was about equal, on a colour intensity basis, to an ozone equivalent of 0·7 mg m^{-3} of ozone (this can be calculated from the figures in Table II). Therefore, a range of standards up to 0·8 mg m^{-3} ozone equivalents would enable the detection of up to 0·2 mg m^{-3} of ozone in the presence of up to 7·5 mg m^{-3} of nitrogen dioxide.

It would have been desirable to prepare and use permanent inorganic colour standards. However, inorganic mixtures such as copper and cobalt solutions did not easily produce colours of suitable intensity and turbidity, therefore it was decided to prepare colour standards based on the starch - iodine complex. As the preparation and use of standard iodine solutions was considered to involve problems too exacting for field work, the liberation of iodine from potassium iodate - potassium iodide solution with standard sulphuric acid and subsequent addition of starch was investigated and found suitable.

The required colours were slightly purple rather than blue. The red component of the standards was found to be dependent on the potassium iodide concentration. The use of a solution 0·00167 M with respect to potassium iodate and 4·5 per cent. w/v with respect to potassium iodide was found suitable.

Aliquots of 0·002 N sulphuric acid over the range 0 to 1 ml were added to 10-ml portions of the potassium iodate - potassium iodide solution. Starch was added to each solution and a graph prepared of optical density against volume of acid used; a straight line was obtained. The optical densities corresponding to 0·1, 0·15, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7 and 0·8 mg m^{-3} ozone equivalents were read from the ozone calibration graph A, Fig. 1. The volumes of acid equivalent to these optical densities were obtained from the graph just prepared. Each of these volumes of acid was that required to be added to potassium iodate - potassium iodide solution to give a series of colour standards for the proposed test.

By using a recording spectrophotometer a check was made on any possible absorption peak or optical density change of the coloured complexes formed in a colour standard and an ozone sample. Over a period of up to 30 minutes neither the standard nor the sample colour exhibited any wavelength shift or significant change in optical density.

The validity and reliability of this series of standards were tested by collecting atmospheres of known ozone concentration in the presence of 0 to 8·5 mg m^{-3} of nitrogen dioxide under the conditions of the proposed test and assessing the ozone concentrations with prepared standards. The results are given in Table IV.

TABLE IV

COMPARISON OF COLOURS PRODUCED FROM MIXED OZONE - NITROGEN DIOXIDE ATMOSPHERES OF KNOWN OZONE CONCENTRATION WITH COLOUR STANDARDS

Actual ozone concentration, mg m^{-3}	0·12	0·16	0·2	0·24	0·34	0·4	0·74	0·81
Ozone concentration indicated by standards, mg m^{-3}	0·1 to 0·15	0·15 to 0·2	0·2	0·2 to 0·3	0·3 to 0·4	0·4	0·7	$>$ 0·8

With some batches of potassium iodide, standards with higher optical densities than expected were obtained. This was thought to be caused by free iodine or acid, or both, in the solid potassium iodide. Accordingly, the potassium iodate - potassium iodide solution was tested before use and samples that gave a trace of blue colour on the addition of starch and 0·02 ml of 0·002 N sulphuric acid were rejected. This amount of acid is not normally sufficient to release enough iodine to produce a colour with starch.

INTERFERENCES—

The effects of several possible interferences likely to be encountered in practice were investigated.

Sulphur dioxide—This gas would react with, and remove, any iodine that had been liberated by ozone or nitrogen dioxide. However, provided that all of the liberated iodine is not removed and that the same amount is removed in each bubbler, *i.e.*, the sulphur dioxide is not trapped by cotton-wool, the test for ozone would still be valid, as has been found experimentally.

Humidity—It was found that the method is not affected by atmospheres with humidities normally occurring in this country. Higher humidities, approaching saturation at room temperature (21° C), had no effect on the removal of ozone by cotton-wool, but some of the nitrogen dioxide was trapped when the wool became damp.

Metal fume—Ozone and nitrogen dioxide are reputed to be formed during electric arc-welding of metals. Tests carried out under factory conditions showed that the presence of iron - iron oxide fume made gas testing difficult. No means of removing this fume was apparent, and any iron oxide trapped on a pre-filter was thought to remove some of the ozone. This latter point was confirmed in laboratory tests when small amounts of iron oxide were found to remove about 20 per cent. of the ozone present in 40 litres of a 0·4 mg m^{-3} ozone atmosphere.

Oxidants—As nitrogen dioxide is the most likely oxidant to be found in an industrial atmosphere together with ozone, the interfering effects of other oxidants on the test were not assessed. However, other oxidants should not invalidate the test, provided that they are not trapped by cotton-wool.

SAMPLING PROBES—

In the field the desired sampling point is often inaccessible, and a length of flexible tube is needed to enable sampling to be carried out. The suitability for this purpose of tubes made of glass and various flexible materials was assessed. Successive 0·4 mg m^{-3} atmospheres of ozone were passed at 2 litres per minute for 20 minutes through 60-cm lengths of each, previously unused, tube and the emergent atmosphere analysed. Table V lists the results obtained. Apart from the glass tube, which seemed to require no conditioning, PVC and nylon appeared to be the most suitable of the flexible materials assessed. Tubes (200 cm in length) of these two latter materials were then evaluated, and from the results (Table V), nylon tubing was selected as the most suitable flexible material to use as a sampling probe.

TABLE V

COMPARISON OF THE SUITABILITY OF TUBES OF VARIOUS MATERIALS AS SAMPLING PROBES

Tube material	Internal diameter, mm	Length, cm	Ozone passed in successive runs with the same tube, per cent.
Glass	6	60	99, 101, 105, 102, 103
PVC	6	60	87, 91, 99, 96, 95
Silicone rubber ..	4	60	76, 83, 78, 83, 81
Polythene	5	60	93, 95, 91
Nylon	5	60	108, 106, 105
PVC	6	200	86, 86, 89, 92, 93
Nylon	5	200	95, 97, 100, 99, 102

Altshuller and Wartburg,[14] in a study of the interaction of ozone with various materials in a dynamic flow system, found that Teflon passed ozone without loss and also that glass required only a short conditioning period. These workers did not study nylon in this respect.

PROPOSED FIELD METHOD FOR THE DETERMINATION OF OZONE IN THE PRESENCE OF NITROGEN DIOXIDE

APPARATUS—

All-glass absorbers—Two of the type are shown in Fig. 2. These absorbers are obtainable from Glass of Mark Ltd., Jubilee Street, Northwich, Cheshire.

Glass tube—This is of the type shown in Fig. 2.

Glass test-tubes—Optically matched, with 13·5-mm i.d. These tubes are obtainable from Tintometer Ltd.

Flow meters—Two, capable of measuring 2 litres per minute. Suitable flow meters are obtainable from Rotameter Manufacturing Company Ltd.

Control valves—Two, suitable for control at a flow-rate of 2 litres per minute.

Sampling pump—Capable of drawing air through the apparatus at 4 litres per minute.

Remote sampling probe—A length of nylon tubing, 5-mm i.d.

REAGENTS—

Unless otherwise stated, all reagents should be of analytical grade and solutions made with distilled or de-ionised water.

Potassium iodide, neutral, buffered solution—Dissolve 20 g of potassium iodide, 14·2 g of disodium hydrogen phosphate and 13·6 g of potassium dihydrogen phosphate in water and dilute to 1 litre.

Starch solution—Dissolve 0·25 g of soluble starch in about 70 ml of boiling water, cool and dilute to 100 ml. Prepare fresh daily.

Cotton-wool, absorbent, B.P.C.—Wash successively with tap water and distilled or de-ionised water and dry at 105° C. Store in air-tight glass bottles.

Dilute sulphuric acid, 0·002 N.

Potassium iodate solution, 0·0167 M—Test and reject any solution that gives a blue colour with starch solution. (Potassium iodate solution of this concentration is obtainable commercially.)

Potassium iodate - potassium iodide solution—Dissolve 45 g of potassium iodide in water, add 100 ml of the 0·0167 M potassium iodate solution and dilute to 1 litre. Prepare this solution fresh daily and test for the absence of free iodine by adding 0·02 ml of the 0·002 N sulphuric acid and 5 ml of the starch solution to a 10-ml portion. If a blue colour is formed, reject and prepare a new solution with a fresh bottle of potassium iodide.

PROCEDURE—

Pack 1 g of cotton-wool into the glass tube to form a plug about 7 cm long. Pipette 10 ml of neutral, buffered potassium iodide solution into each absorber. In an uncontaminated atmosphere assemble the two branches of the apparatus as shown in Fig. 2. Preferably, use glass ball-and-socket joints. Alternatively, ensure that all glass-to-glass connections are butted and held together with PVC tubing. To prevent water condensing in the flow meters, insert a dried cotton-wool plug between the exit of each absorber and the entry to each flow meter. In the laboratory and before proceeding to field testing, calibrate each flow meter separately on the assembled apparatus to ensure that an equal flow-rate, 2 litres per minute, is obtained in each limb. This can be done either by the use of a third flow meter, open to the atmosphere and connected in series to the flow meter being calibrated, or by any other suitable method, *e.g.*, soap film calibrator.[15] Draw the test atmosphere from a *single* sampling point through each absorber at a rate of 2 litres per minute for 20 minutes. Remove the absorbers from the assembly in an uncontaminated atmosphere, and then the heads from the absorbers, taking care to drain any liquid in the inlet tubes into the main solutions. Pipette 5 ml of the starch solution into each absorber. Mix well and transfer each solution into the optically matched test-tubes and compare the colour produced with the colour standards within 15 minutes.

PREPARATION OF COLOUR STANDARDS—

To each of 9 test-tubes add 10 ml of the potassium iodate - potassium iodide solution and prepare the set of colour standards by adding the appropriate amount of the 0·002 N sulphuric acid to each tube (see Table VI), followed by 5 ml of the starch solution. Mix well and transfer each solution to the optically matched tubes. (The colour standards are stable for 30 minutes.)

TABLE VI

VOLUMES OF ACID REQUIRED TO PREPARE COLOUR STANDARDS

Ozone equivalent, mg m^{-3}	0·1	0·15	0·2	0·3	0·4	0·5	0·6	0·7	0·8
Sulphuric acid, 0·002 N, ml	0·08	0·14	0·20	0·30	0·41	0·52	0·63	0·74	0·85

To obviate the need to prepare a full set of colour standards the following procedure can be adopted. Add 0·1-ml increments of the sulphuric acid to a mixture of 10 ml of the potassium iodate - potassium iodide solution and 5 ml of the starch solution until an approximate match with the sample colour is obtained. Note the volume of acid added and prepare standards equivalent to, and adjacent to, this volume. Match the sample colour with the freshly prepared standards.

If a spectrophotometer is available, a graph of the optical densities of the prepared standards against their respective ozone equivalents can be plotted. From the measured optical densities of the samples in the two absorbers a more precise determination of the ozone concentration in the atmosphere sampled is possible.

As an alternative to the preparation of the above colour standards, a series of permanent standard colours on a comparator disc available from Tintometer Ltd., can be used for this test.

Calculation—

Ozone in sample (mg m^{-3}) = Ozone equivalent in absorber (M) *minus* ozone equivalent in absorber (MT).

APPLICATION OF METHOD—

The proposed method has been assessed under field conditions at various industrial sites where ozone is known, or reputed, to occur as a contaminant in the atmosphere. These included sites where discharge tubes in certain photocopying machines were being tested, plastic sheet was being etched by using high voltage spark discharges and inert-gas shielded arc welding was practised. The field testing in the vicinity of high voltage spark discharges revealed the presence of both ozone and nitrogen dioxide, the concentrations of the latter gas being determined by a *p*-anisidine paper field test method.[16] In the welding process, as already mentioned, the presence of metal fume interfered with the determination of ozone. This fume would presumably interfere with any test that required the drawing of an air sample through an absorber. These few field tests confirmed the results of those tests in the laboratory showing that the proposed method is suitable for detecting up to 0·2 mg m^{-3} of ozone in the presence of up to 7·5 mg m^{-3} of nitrogen dioxide. In the absence of nitrogen dioxide up to 0·8 mg m^{-3} of ozone can be determined.

The apparatus required for the test is portable and requires only an external electrical power supply to operate the pump. The complete assembly can be mounted in a box 8 × 12 × 15 inches. A complete determination takes about 30 minutes.

As we prefer to determine nitrogen dioxide in any atmosphere by a specific field test method,[10] no attempt was made in the present work to develop a method for the determination of this gas on the basis of its reaction with potassium iodide and subsequent release of iodine. However, an approximate estimate of nitrogen dioxide concentration in a mixed ozone - nitrogen dioxide contaminated atmosphere, containing no other oxidant, can be made by converting the intensity of the colour in the absorber (MT), expressed as ozone equivalents, into mg m^{-3} of nitrogen dioxide. This is done by multiplying this ozone equivalent figure by 13, as it was observed in this work that 9 mg m^{-3} of nitrogen dioxide gave about the same colour intensity as 0·7 mg m^{-3} of ozone.

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Molecular-emission Spectroscopy in Cool Flames

Part III.* The Emission Characteristics of Tin in Diffusion Flames

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Tin can be determined in the range 3 to 3000 p.p.m. by molecular-band emission from the SnH species in a nitrogen - hydrogen diffusion flame. The emission at 609·5 nm, which is almost line-like, gives a limit of detection of 1·5 p.p.m. of tin. Spectral interference from sodium is eliminated by use of a didymium filter. The presence of oxygen gives rise to a much broader spectrum, caused by tin(II) oxide formation, with a visual limit of detection of 5 p.p.m. of tin. Atomic emission can be observed only in the presence of alcohols, *e.g.*, isopropyl alcohol, but a high concentration of ground-state tin atoms exists in the diffusion flame. Mechanisms are discussed to explain the production of tin atoms, SnH and the resonance-line emission.

TIN is an example of an element that is difficult to excite thermally in conventional pre-mixed flames. Herrmann and Alkemade,[1] for example, state that only in an oxy-cyanogen flame are the tin lines intense enough to be used analytically. In other flames, weak resonance emission can only be observed in the inner reaction zones. However, the cool diffusion flames of nitrogen and hydrogen used in earlier papers in this series for the determination of sulphur[2] and phosphorus[3] have been found to promote emission from molecular species not encountered in most other flames. The purpose of this paper is to report the results of a study involving tin in diffusion flames, which is of both analytical and spectroscopic interest.

The diffusion flame obtained by burning a mixture of hydrogen and nitrogen in air at atmospheric pressure yields an intense red colour in its cool inner region when a tin(II) chloride solution is sprayed into it. A thin blue outer mantle may also be observed when there is a high enough concentration of oxygen to form the tin oxide species.

SPECTRAL CHARACTERISTICS

BAND EMISSION—

The spectrum, recorded on a Unicam SP900A flame spectrophotometer, consisted of a sharp peak at 609·5 nm and a much weaker band with a maximum at 621 nm (Fig. 1 (*b*)). Sodium is included to show the line-like nature of the Sn–H emission. The former peak is listed by Herrmann and Alkemade[1] and corresponds to the SnH species. Pearse and Gaydon[4] also list the weaker band at 621 nm, which has only been observed previously in a tin arc operating in a hydrogen atmosphere.

The emission at 609·5 nm is not very dependent on hydrogen pressure or on the position of measurement in the flame, although it reaches a maximum about 1 cm above the top of the burner head. The intensity of the emission is directly proportional to the concentration of tin(II) and also to the square of the slit width (which is to be expected for a band-emission signal).

Linear calibration graphs may be obtained over the range 3 to 3000 p.p.m. of tin with a detection limit of about 1·5 p.p.m. (signal-to-noise ratio = 1). The effects of extraneous cations and anions were not investigated but, unless a monochromator of fairly high resolution is used, spectral interference may be expected from sodium. However, in this instance a didymium filter interposed between the flame and monochromator slit was found to reduce the sodium emission at 589 nm by 99·5 per cent., while at the same time transmitting about 60 per cent. of the emission caused by SnH at 609·5 nm.

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* For details of earlier parts of this series, see reference list, p. 521.

Because the flame temperature is low[2] (down to 280° C) there is little thermal emission, even from the most easily excited elements. The noise level caused by the flame is also low because the flame exhibits negligible background, even over the OH band region. Some matrix effects caused by aluminium and magnesium have been observed in former studies[5] with this flame, and they were overcome then by introducing a small volume of oxygen through an auxiliary jet in the burner stem[6] to increase the flame temperature. In this instance this would not be possible, as the presence of a small amount of oxygen replaces the red colour of the SnH species by a blue coloration. The recorded spectrum of the latter showed a continuum with superimposed bands from 360 to 540 nm, with a maximum intensity at 484 nm, and corresponded to the tin(II) oxide species,[1] *cf.* Fig. 1 (*a*). No analytical use can be made of the blue colour with the Unicam SP900A spectrophotometer because of the absence of sharp bands, but it is sensitive visually with a limit of detection of about 5 p.p.m. of tin.

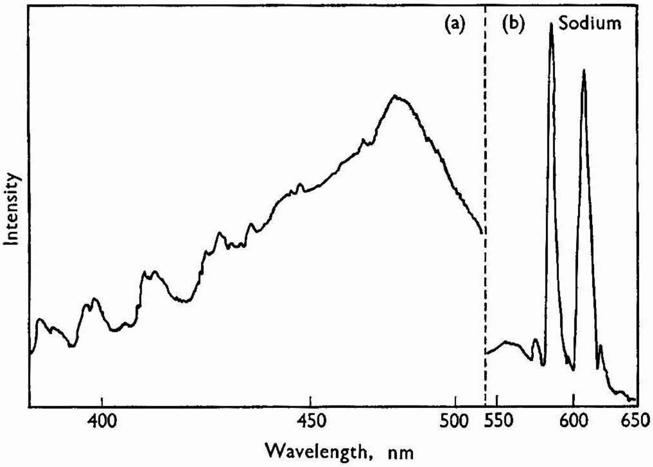

Fig. 1. Emission spectrum of Sn-O and Sn-H species: (a), spectrum of 3×10^{-2} M tin(II) (0·5 M hydrochloric acid) in the nitrogen - air - hydrogen flame. Slit, 0·03 mm, gain 3,10, bandwidth 1; (b) spectrum of 3×10^{-2} M tin(II) (0·5 M hydrochloric acid) in the nitrogen - hydrogen flame. Slit, 0·03 mm, gain 3,10, band width 1

Solutions of tin(IV) chloride produced an exactly similar spectrum [*i.e.*, SnH and tin(II) oxide], but the emission was about 60 per cent. more intense at 609·5 nm than that obtained with tin(II) chloride. The increased response to tin(IV) is probably caused by the greater volatility of its chloride, which would be more in evidence in a cool flame than in a hot one.

As a result of these observations it may be concluded that a substantial number of elements whose salts do not break down at the temperature of this flame (about 280° to 400° C) would cause matrix effects and thus interfere although in many instances it should be possible to produce calibration graphs of lesser gradient if the amount present were approximately known. Anionic interference might be more marked, however.

The emission characteristics of the SnH species were also observed in the air - hydrogen separated flame.[2] However, under these conditions, the emission signal was only about half of that in the diffusion flame. Further, concentrated solutions of tin caused severe staining of the quartz separator, and the flame exhibited a higher background than the diffusion flame.

The SnCl and SnBr bands[4] are not observed in these flames, unless the halogen concentration is high, *e.g.*, 0·1 M in hydrochloric or hydrobromic acids. Under these latter conditions a thin dark blue cone appears when chloride is present and a similar shaped green cone when bromide is present. Each cone extends about 1 cm above the top of the burner head in the coolest portion of the flame. The red SnH bands were present as before, extending much higher in the flame. It would seem that the SnCl and SnBr bands arise from the chemiluminescent reduction of tin chloride and bromide clotlets by hydrogen.

LINE EMISSION—

No thermal emission of tin at the principal resonance lines 284 and 286·3 nm was observed from aqueous solutions of tin(II) or tin(IV) salts in any diffusion flame. However, a 1000 p.p.m. tin solution, 40 per cent. w/v in isopropyl alcohol, gave not only strong emission signals at 284 and 286·3 nm, but also many other tin lines extending far into the ultraviolet region. The major lines observed were at 286·3, 284, 270·6, 254·7, 243, 235·5, 226·9 and 224·6 nm. These lines have previously been observed by Gilbert from isopropyl alcohol solutions of tin in air - hydrogen flames with a total-consumption burner.[7] The chemiluminescence emission from the diffusion flame is clearly observable at 284 nm even in the presence of 1 per cent. isopropyl alcohol.

For emission at the 224·6-nm line, an excitation energy of 5·5 eV is required which is considerably greater than that available in the diffusion flame. Although tin atoms are produced in the diffusion flame from aqueous solutions [from atomic-absorption studies of tin in diffusion flames (R. M. Dagnall, K. C. Thompson and T. S. West, unpublished work)], no emission can be observed as excitation does not occur. It was not possible to determine whether the emission from the isopropyl alcohol solutions emanated from the relatively cool oxygen-free central flame regions or from the outer reaction zone.

As a result of these observations we are led to conclude that the production of tin atoms in such diffusion flames must arise as the result of chemical reaction rather than thermal decomposition of tin(II) oxide or tin(II) chloride. In the presence of isopropyl alcohol the tin atoms most probably undergo excitation by decomposition products of isopropyl alcohol, *e.g.*, CH. Gibson, Grossman and Cooke[8] have suggested a three-body reaction to account for this emission from isopropyl alcohol solutions in an air - hydrogen flame, *viz.*:

$$\mathrm{Sn} + \mathrm{CH} + \mathrm{OH} \longrightarrow \mathrm{Sn}^* + \mathrm{CO} + \mathrm{H_2}.$$

The emission observed in our studies extended throughout the flame and was quite intense, being as high as 4 cm above the burner head. When air was supplied to the diffusion flame through an auxiliary jet in the burner base,[6] the emission higher up in the flame decreased with increasing air pressure, while the emission just above the burner head increased. The presence of air created an inner (*i.e.*, primary) reaction zone from which the tin emission emanated.

Ethanol, methanol and acetone gave emission signals similar in intensity to isopropyl alcohol. Although the emission increased with increasing alcohol concentration, it was not linear, the emission for a 40 per cent. w/v isopropyl alcohol - tin solution being only 50 per cent. higher than a 20 per cent. w/v solution. Glycerol gave only slight emission at 284 nm from a 1000 p.p.m. tin solution, but this could have been caused by increased viscosity.

EXPERIMENTAL

APPARATUS—

A Unicam SP900A atomic-absorption - flame-emission spectrophotometer was used in its emission mode of operation, coupled to a 0 to 10-mV Servoscribe recorder. The normal EMI 9529B photomultiplier was replaced by a more ultraviolet-sensitive EMI 9601B photomultiplier.

FLAME CONDITIONS—

The nitrogen - hydrogen diffusion flame was obtained with an acetylene jet in the standard burner base, with the 1·8 × 7·5-cm air - acetylene emission head supplied. The nitrogen pressure was set at 15 p.s.i., and the hydrogen pressure corresponded to a reading of 16 cm on the dibutyl phthalate filled manometer gauge. The top of the burner head was set about 0·5 cm below the bottom of the monochromator slit.

REAGENTS—

The reagents used were of analytical-reagent grade; we found that reagents conforming to AnalaR specifications were suitable.

Tin(II) solution, 2000 p.p.m.—Dissolve 2 g of tin metal in 200 ml of concentrated hydrochloric acid and dilute to 1 litre with distilled water.

PREPARATION OF CALIBRATION CURVE (20 TO 200 P.P.M. OF TIN)—

Transfer by pipette 1 to 10 ml of a 2000 p.p.m. tin(II) solution into a series of 100-ml calibrated flasks and dilute to volume with distilled water. Nebulise into the nitrogen - hydrogen diffusion flame by using a slit width of 0·15 mm, gain 3,10 and band width 3, and measure the emission at 609·5 nm. No background correction is necessary.

The readings should be taken soon after solution preparation because a decrease in response is obtained on standing (*e.g.*, overnight). This is probably caused by the hydrolysis of the tin(II) chloride. Other concentration ranges can be prepared by suitable dilution and appropriate adjustment of the slit and gain controls.

CONCLUSION

Although the SnH species, which are shown to be prevalent in diffusion flames of nitrogen and hydrogen, provide a sensitive method of analysis for tin, the mechanism of their production is perhaps of even greater interest. The cool diffusion flame (burning on a Perkin-Elmer triple-slot burner) is known to provide as good an atom reservoir for tin as an air - hydrogen pre-mixed flame for atomic-absorption studies (R. M. Dagnall, K. C. Thompson and T. S. West, unpublished work). The production of tin atoms, and subsequently SnH, presumably occurs via an exothermic reduction process involving hydrogen and tin(II) chloride. The thermal energy of the diffusion flame is insufficient to dissociate tin(II) oxide (dissociation energy 5·7 eV), and hence the breakdown must be caused by the highly reducing nature of the flame and the almost complete absence of molecular or atomic oxygen. We have suggested this type of breakdown in a previous paper to explain the dissociation of certain metal phosphates.[3] The air - hydrogen pre-mixed flame gives more than twice the absorbance at the major tin resonance lines of the nitrous oxide - acetylene or air - acetylene flames and this again could be caused by a lower concentration of atomic oxygen.

The emission produced from alcoholic tin solutions in the diffusion flame appears to favour a reaction mechanism involving a carbonaceous species such as the CH radical, but not the CN radical as this species is not observed in the flame spectrum. Support is given to this theory because there is insufficient thermal energy available to give excitation at wavelengths as low as 224·6 nm. In addition, resonance-line emission can be observed from aqueous solutions of tin in the nitrogen - acetylene diffusion flame maintained on the same burner system as before. This flame exhibits a light blue region extending 2 to 3 cm above the burner top and is completely luminous above this. The tin emission may be observed in the lower light blue region that shows only CH and C_2 emission. In general, the emission intensities are only about 10 per cent. of those observed from the inner reaction zones of a slightly fuel-rich air - acetylene flame maintained on the same burner. There is negligible emission above the inner cones of the pre-mixed flame.

One of us (K.C.T.) wishes to thank the Science Research Council for the award of a grant. We also thank Unicam Instruments Limited for the loan of the spectrophotometer used in this study.

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The Determination of Beryllium by Thermal-emission and Atomic-fluorescence Spectroscopy in a Separated Nitrous Oxide - Acetylene Flame

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The determination of beryllium by thermal-emission and atomic-fluorescence spectroscopy in a separated nitrous oxide - acetylene flame has been investigated. The high temperature, reducing nature and low background of this type of flame permit the determination of down to 0·25 and 0·03 p.p.m. of beryllium in aqueous solution by measurement of thermal emission and atomic fluorescence, respectively. A beryllium microwave-excited, electrodeless discharge tube was used for excitation of the atomic fluorescence. The optimum conditions for both techniques have been investigated, and the effects of other cations and anions studied.

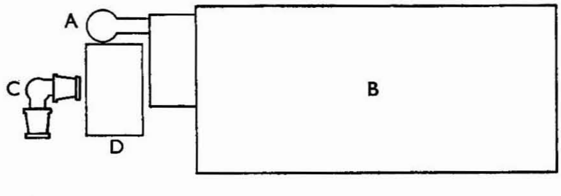
THE growing utilisation of beryllium in nuclear reactor technology, and as an alloying element, has resulted in the need for sensitive methods for the determination of this element. Thus its determination by flame-spectrophotometric procedures in hot flames has recently been investigated by several workers. Gilbert,[1] for example, has reported its detection by emission in an oxygen-sheathed, fuel-rich, oxy-acetylene flame burning at a total-consumption nebuliser burner. The limit of detection at 234·86 nm was 0·4 p.p.m. for an aqueous solution and 0·1 p.p.m. for a methanolic solution. Beryllium has also been detected in emission down to 1 p.p.m. in an oxy-cyanogen flame.[2] The determination by atomic-absorption spectroscopy in oxy-acetylene and nitrous oxide - acetylene flames has recently been described by Ramakrishna, Robinson and West.[3] These authors report sensitivities of 0·09 p.p.m. for 1 per cent. absorption in oxy-acetylene and 0·02 p.p.m. in nitrous oxide - acetylene, both at 234·86 nm. We also observe a sensitivity of 0·024 p.p.m. at 234·86 nm for atomic-absorption spectroscopy in a 5-cm nitrous oxide - acetylene flame. Koirtyohann[4] reports a detection limit of 0·2 p.p.m. for the atomic emission of beryllium at 234·86 nm in a nitrous oxide - acetylene flame. The determination of beryllium by atomic-fluorescence spectroscopy does not appear to have been investigated.

The hot, reducing pre-mixed nitrous oxide - acetylene flame provides good sensitivity in the determination of refractory elements by flame-emission spectroscopy, although it exhibits high background emission and noise levels. In an earlier communication from this laboratory, we have described the separation of this flame by using a silica tube.[5] In this device, the primary and secondary reaction zones of the flame are mechanically separated, so that it is possible to view the hot, reducing interconal zone without interference from the radiation produced by the secondary "diffusion" zone. Thus the flame-background emission is severely depressed, and the separator tube prevents ingress of atmospheric oxygen to the interconal zone. The reducing nature of this zone is thereby protected, so that high populations of free atoms of the refractory elements are more efficiently maintained than in the unseparated flame. This paper describes the sensitive determination of beryllium by flame-emission spectroscopy in the separated nitrous oxide - acetylene flame, and an investigation of its atomic-fluorescence spectroscopic behaviour in this flame by using a beryllium microwave-excited, electrodeless discharge-tube source.

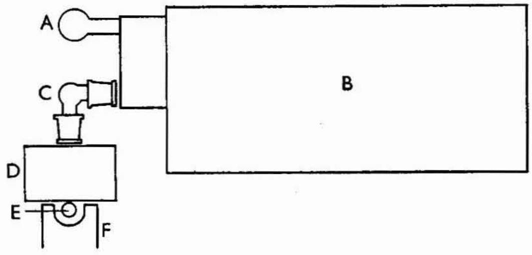
EXPERIMENTAL

APPARATUS—

The experimental arrangement used is shown diagrammatically in Fig. 1. The monochromator, B, and photomultiplier, A, used were those of the Techtron AA4 flame spectrophotometer (Techtron Pty. Ltd., Melbourne, Australia). The monochromator was fitted with a wavelength-scanning motor (1 nm per minute), and the analytical signals were displayed on a Sargent SRL recorder. A beryllium electrodeless discharge tube, E, (transparent Vitreosil tubing, i.d. 8 mm, length 70 mm) was prepared at an argon-filler gas pressure of 0·03 mm of mercury and contained about 1 mg of pure powdered metallic beryllium and a slightly smaller amount (less than 1 mg) of elemental iodine. Other beryllium halide tubes were prepared containing varying proportions of beryllium and chlorine or bromine, but only sources prepared with excess of beryllium and a small amount of iodine gave the required stability of output (±1 per cent. per hour) and intensity. The discharge was maintained with a Microtron 200 microwave generator at a Model 214 L discharge cavity, F [Electro-Medical Supplies Ltd. (Greenham) London, W.1]. In the Techtron AA4 flame spectrophotometer a 285-Hz amplification system is used. Consequently, for flame-emission spectroscopy measurements it was necessary to modulate the signals at this frequency by using a 285-Hz modulating chopper, D, between the flame, C, and monochromator entrance slit. Likewise for the atomic-fluorescence spectroscopy measurements, modulated fluorescence signals were obtained by placing this modulating device, D, immediately in front of the electrodeless discharge tube source, which was itself arranged so that its radiation was focused on the interconal zone of the separated flame, C, along an axis at 90° to the burner - monochromator axis. The radiation was focused on the flame with a quartz lens of 64-mm focal length attached to the modulating chopper.



Thermal emission



Atomic fluorescence

Fig. 1. Details of experimental arrangement used (lettered parts of the apparatus are referred to in the text)

Burner arrangement—The burner and separator used in this study are shown in Fig. 2. The burner head is similar to that previously described,[5] and consists of a stainless-steel head with a circular slot 0·75 mm wide and 11-mm internal diameter. The central steel plug of the burner head is held centrally in position by three steel grub-screws (6 B.A.) inserted at 120° intervals at the same height through the burner barrel. The base of the burner head was provided with a copper water-cooling jacket. This serves to minimise the deposition of carbon on the burner head when nitrous oxide - acetylene flames are used. A silica separator tube of 24-mm internal diameter and length 5 cm was found most suitable for the maintenance of stable separated flames with this burner. Two short silica side-arms were fused to the separator tube at the same height and at 90° to each other. These were fitted with B19 cones, to which B19 ground-glass sockets fitted with optical quality silica end-windows were attached.

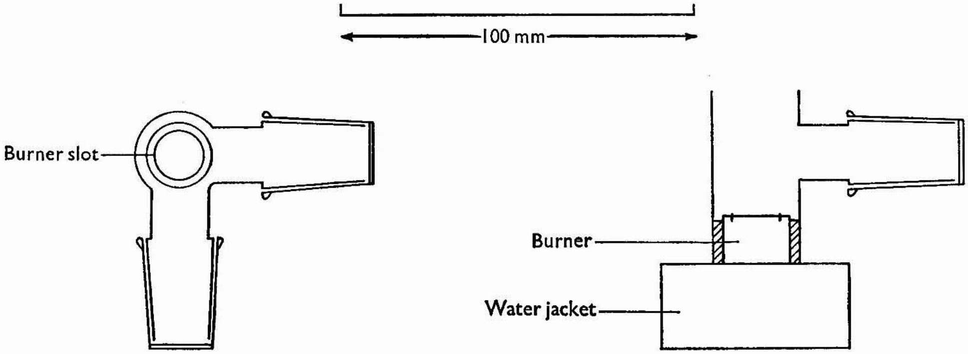


Fig. 2. Burner and separator assembly

Nitrous oxide and acetylene pressures, and flow-rates, were controlled by the gas control unit on the Techtron flame spectrophotometer. The indirect nebuliser of the Techtron flame spectrophotometer was used, so that sample solutions were nebulised on nitrous oxide.

The separated flame was supported at an operating pressure of 15 p.s.i. of nitrous oxide (flow-rate about 7 litres per minute). A stable primary reaction zone was then obtained at the slot of the burner head. The diffusion zone, where the carbon monoxide and hydrogen produced in the primary zone burn with support from the atmosphere, is maintained at the top of the separator tube. The interconal zone of the flame, which contains the hot, reducing region of analytical interest, is then at the same height as the side-arms and observation windows.

REAGENTS—

Beryllium stock solution—Pure beryllium metal, 0·100 g (Imperial Metal Industries Limited), was dissolved in 10 ml of aqua regia and the solution diluted to 100 ml with distilled water. This 1000 p.p.m. solution was diluted with distilled water as required to 10 or 1 p.p.m.

All other reagents used were of analytical-reagent grade.

RESULTS

THERMAL-EMISSION CHARACTERISTICS—

The background-emission spectrum of the interconal zone of the separated nitrous oxide - acetylene flame has been described in a previous paper from this laboratory.[5] The OH bands and the continuum emission due to the combustion of carbon monoxide is virtually absent in the interconal zone, and the only significant background arises from the CN species, which is chiefly responsible for the reducing atmosphere of the zone. The variation of background emission of CN and OH with fuel flow-rate for the separated and unseparated (conventional) flames is shown in Fig. 3 (*a* and *b*).

The atomic emission of beryllium introduced into the flame was examined relative to the flame background in the visible and ultraviolet region between 200 and 600 nm. The only intense atomic emission observed was from the beryllium resonance line at 234·86 nm, which results from the $^1P_1 \rightarrow {}^1S_0$ transition. Against the low background of the separated flame it was possible to observe emission from the unresolved non-resonance beryllium triplet at 332·1 nm ($^3S_1 \rightarrow {}^3P_{2,1,0}$) when strong beryllium samples were nebulised. The variations in the intensity of the beryllium emission at 234·86 nm, and that of the flame background, with acetylene flow-rate, are shown in Fig. 4(*a*) for both the separated and unseparated (conventional) flames. In both flames, the background is minimal in the slightly fuel-rich

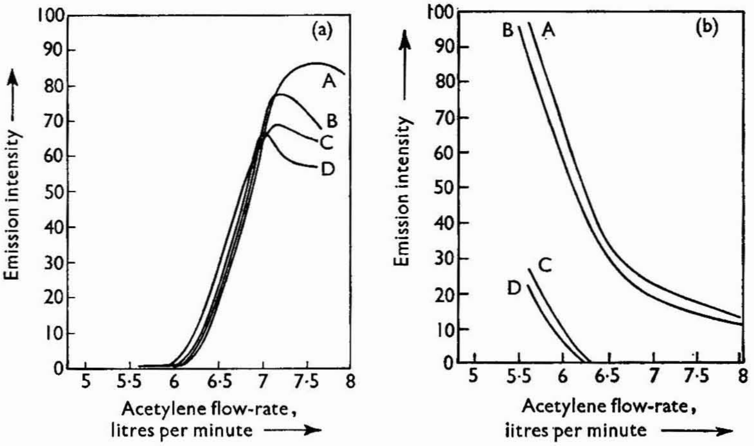


Fig. 3. Effect of acetylene flow-rate on: (*a*), CN emission at 388·3 nm; (*b*), OH emission at 306·4 nm. Curve A, unseparated flame alone; curve B, unseparated flame, water nebulised; curve C, separated flame alone; and curve D, separated flame, water nebulised

flame, while the beryllium emission reaches a maximum in the same flame. A flame burning at this mixture strength was used for all other investigations. The observed variation in the beryllium emission can be explained by the need for a fuel-rich, reducing flame for the efficient maintenance of the free beryllium atom population, and the decrease in its emission in very rich flames by a slight drop in flame temperature under these conditions. Fig. 4(*a*) also shows that the background-emission intensity and noise level obtained in the slightly fuel-rich, separated flame is lower than in the conventional flame at 234·86 nm, whereas the beryllium emission is slightly more intense in the separated flame than in the unseparated flame despite the slightly lower temperature of its interconal zone. This may be attributed to the more efficient maintenance of a population of atoms by the protected reducing atmosphere in this zone, and to its extended size.

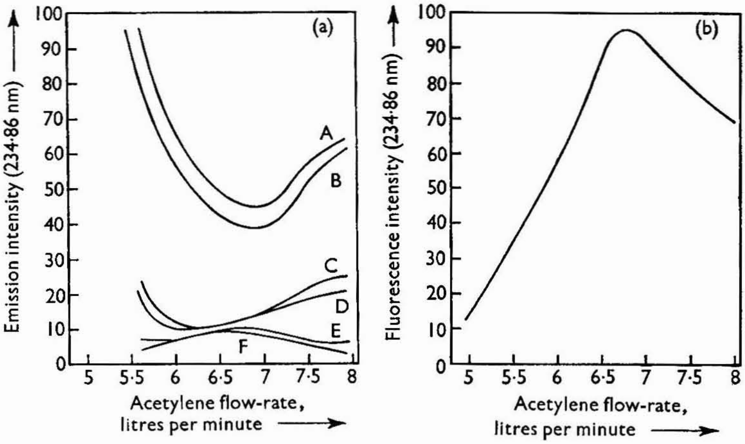


Fig. 4. Effect of acetylene flow-rate: (*a*) on beryllium thermal emission and background emission at 234·86 nm; curve A, flame background, unseparated; curve B, flame background, unseparated, water nebulised; curve C, flame background, separated; curve D, flame background, separated, water nebulised; curve E, beryllium emission for 1 p.p.m. in separated flame; and curve F, beryllium emission for 1 p.p.m. in unseparated flame; (*b*), on atomic-fluorescence emission for 1 p.p.m. beryllium solution at 234·86 nm

SENSITIVITY AND PRECISION—

Linear calibration graphs were obtained for the beryllium emission at 234·86 nm in the slightly fuel-rich flame over the range 0·3 to 10 p.p.m., with an optimised slit width of 200 μm (0·66-nm band width). The limit of detection, which is defined as that concentration producing a signal-to-noise ratio of 1 : 1, was 0·1 p.p.m. The limit of practical measurement with the experimental arrangement used was considered to be about 0·25 p.p.m. In a conventional fuel-rich flame (unseparated), the high noise levels result in a detection limit of about 2 p.p.m. of beryllium. Repetitive introduction (10 times) of a 3 p.p.m. beryllium solution into the separated flame under the optimal conditions used to obtain calibration values indicated a relative standard deviation in the emission intensity of 1·3 per cent.

EFFECT OF DIVERSE IONS—

The effect of 100 and 1000-fold excesses by weight of a range of cations and anions on the emission intensity produced by 3 p.p.m. of beryllium under optimised conditions by using a 200-μm slit width was investigated. The following elements did not interfere (*i.e.*, they produced a variation in emission intensity of not greater than twice the standard deviation) when present in 1000-fold excess: Bi, Cd, Cu, Fe(III), Hg(II), K, Mg, Mn(II), Na, Pb, Se(IV), Te(IV), U(VI), Zr and PO_4^{3-}. No interference was observed when beryllium was aspirated in the presence of 5 per cent. sulphuric acid or 10 per cent. nitric, hydrochloric and hydrofluoric acid solutions. On the other hand, 1000-fold excesses of the following ions produced interference, frequently by obstruction of the burner slit by deposition of solid, but the presence of 100-fold excesses caused no interference: Al, As(V), Ca, Cr(VI), Mo(VI), Nb(V), Ti(IV), W(VI) and borate. A 100-fold excess of the following ions produced the error in the beryllium emission given in parentheses: Co(II) (+20 per cent.), Ni(II) (+95 per cent.), Si(IV) (+22 per cent.), Sn(II) (+27 per cent.) and V(V) (+50 per cent.). It is difficult to assign the cause of these interferences unequivocally, although it seems that the effect of tin(II), nickel and cobalt(II) is possibly due to spectral interference from their nearby atomic lines. Substantial emission is in fact observed from the introduction of tin(II), nickel and cobalt(II) solutions in the absence of beryllium. An indication of the potential of the measurement of the beryllium thermal emission, under the recommended conditions, was obtained by determination of the beryllium content of a beryllium - copper alloy. Analysis of the alloy sample by this method gave a result corresponding to 1·86 ± 0·03 per cent. of beryllium. Independent analysis of the sample by atomic-absorption spectroscopy in a conventional 5-cm nitrous oxide - acetylene flame gave a result of 1·75 ± 0·03 per cent. of beryllium.

ATOMIC-FLUORESCENCE MEASUREMENTS—

The experimental arrangement used for the fluorescence measurements is shown in Fig. 1. The beryllium microwave-discharge tube was placed immediately behind the modulating chopper, and the radiation was focused into the interconal zone of the flame through the entrance window and side-arm of the separator. The flame and separator were positioned so that the exit window was only about 2 mm from the monochromator entrance slit. The discharge tube was operated at 50 watts with moderate air-cooling of the exterior of the cavity. The modulated flame emission was observed in the presence of dilute beryllium solutions. As for the thermal emission, the only intense fluorescence emission observed was that from the resonance line at 234·86 nm. Thus the photomultiplier receives both the unmodulated beryllium thermal emission and the modulated fluorescence emission at 234·86 nm, but the tuned amplification system amplifies only the fluorescence emission efficiently. The effect of the acetylene flow-rate on the beryllium fluorescence emission in the separated flame is shown in Fig. 4(*b*). The maximum emission is again found to coincide with the use of a slightly fuel-rich flame.

Linear calibration graphs were obtained for the fluorescence emission in the range 0·03 to 1 p.p.m., with an optimised slit width of 300 μm (0·99 nm band width). Higher concentrations were also examined, and linear calibration graphs were obtained between 1 and 20 p.p.m. The limit of detection, which is defined as that concentration producing a signal-to-noise ratio of 1 : 1, was 0·01 p.p.m. Repetitive introduction of a 0·5 p.p.m. beryllium solution into the flame under the optimal conditions gave a relative standard deviation in fluorescence of 3 per cent.

EFFECT OF DIVERSE IONS—

The effects on the intensity in atomic-fluorescence spectroscopy produced by 0·5 p.p.m. of beryllium of 100 and 1000-fold excess by weight of those ions examined for interference in thermal emission were investigated. As expected, ions that produced no interference in the thermal emission also did not affect the atomic-fluorescence signal. In addition, no interference was observed for cobalt(II), nickel and tin(II). Interference was again observed from solutions containing very high concentrations (1000-fold excess) of the ions aluminium, calcium and molybdenum(VI), whereas the presence of a 100-fold excess of these ions caused no interference.

DISCUSSION

The slightly fuel-rich, separated nitrous oxide - acetylene flame provides an "atom reservoir" of high temperature and reducing properties. The reducing atmosphere serves to maintain a high population of free ground-state atoms of beryllium, which otherwise have a pronounced tendency to form a refractory (BeO) species in more conventional flames. The high flame temperature provides sufficient energy for the excitation of the beryllium resonance line at 234·86 nm, which requires 5·28 eV. High sensitivity is thus obtainable in the determination of beryllium by thermal-emission spectroscopy in this relatively low background flame, and the protection afforded to the interconal zone in the separated flame results in a reducing atmosphere of extended physical dimensions. Consequently, even higher sensitivity should result from the use of a monochromator of greater light-gathering power than that used in this study. The selectivity obtainable in the determination by thermal spectroscopy is high, as the hot flame suppresses the tendency for compound formation between beryllium and other compounds introduced into the flame.

Because of the maintenance of a high population of beryllium atoms in the flame used, the sensitivity of the atomic-fluorescence spectroscopic determination of beryllium is also high. When an intense beryllium source is used, such as the beryllium microwave-excited, electrodeless discharge tube used in this study, the sensitivity obtainable in atomic fluorescence, with the same instrumentation, is about one order of magnitude greater than that obtained in thermal emission. The selectivity of the determination of beryllium by atomic fluorescence, with a modulated source, is also an improvement on that of the determination by thermal emission. There is no significant overlap of d.c. atomic emission from other elements on the a.c. beryllium fluorescence and they are not excited by the beryllium source.

We are grateful to Murex Ltd. (Rainham, Essex), for the provision of equipment, and for granting study leave to one of us (D. N. H.).

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Spectrophotometric Determination of Iron(III) Ions with 2,4-Dihydroxybutyrophenone

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The colour reaction between iron(III) and 2,4-dihydroxybutyrophenone has been studied to determine the optimum conditions for the analytical use of this reagent. The strongest colour developed at pH 2·9 to 3·0, and the complex exhibits an absorption maximum at 470 mμ. The composition of the complex is 1 to 1, as indicated by mole-ratio studies. The absorbance of the solution at 470 mμ obeys Beer's Law in the iron(III) concentration range 1·0 to 56·0 p.p.m. and the sensitivity is 0·074 μg per ml of the iron(III) solutions. The reagent is fairly selective for iron.

2,4-DIHYDROXYBUTYROPHENONE has not so far been investigated as an analytical reagent. This paper deals with a study of the reaction between iron(III) ions and 2,4-dihydroxybutyrophenone, and the use of the latter as a specific reagent for the spectrophotometric determination of iron.

EXPERIMENTAL

APPARATUS—

A Unicam SP500 spectrophotometer was used, with matched 1-cm silica cells, for absorbance measurements. A Beckman pH meter, Model H2, was used for all pH determinations.

REAGENTS—

2,4-Dihydroxybutyrophenone was synthesised by condensing resorcinol (1 gram mole) with butyric acid (1 gram mole) in the presence of freshly distilled phosphorus oxychloride (2 gram moles).[1] The reaction was allowed to proceed at room temperature for 24 hours, and the reaction mixture then poured on to a mixture of 400 g of crushed ice and 200 ml of 50 per cent. hydrochloric acid. A yellow mass separated which, on recrystallisation from chloroform, gave colourless plates of 2,4-dihydroxybutyrophenone (m.p. 67° C,[2] yield 85 per cent.).

A solution of 2,4-dihydroxybutyrophenone in 40 per cent. ethanol was used in all of the experiments.

PROPERTIES OF THE IRON(III) - 2,4-DIHYDROXYBUTYROPHENONE CHELATE—

The complex has a reddish violet colour between pH 2·0 and 3·0, which is stable, and a reddish brown colour above pH 3·0. The optimum pH range is 2·9 to 3·0, and the complex exhibits a maximum absorbance at 470 mμ. The absorption spectra of the reagent, iron(III) nitrate and the iron(III) - 2,4-dihydroxybutyrophenone complex are given in Fig. 1. The colour of the complex is formed instantaneously and is stable for 3 hours. The sequence of adding the reactants has no effect on the absorbance of the complex and Beer's law is obeyed between 1·0 and 56·0 p.p.m. of iron.

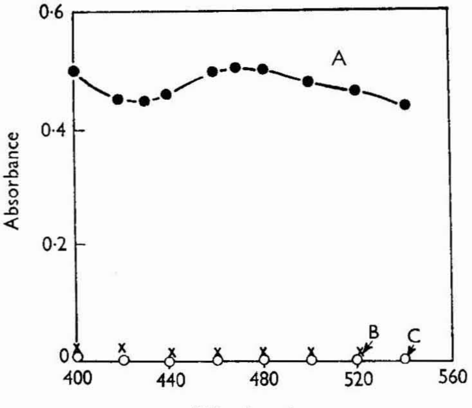

Fig. 1. Absorption spectra of 2,4-dihydroxybutyrophenone, iron(III) nitrate and iron(III) - 2,4-dihydroxybutyrophenone complex: graph A, 2 ml of 0·01 M iron(III) nitrate + 20 ml of 0·01 M 2,4-dihydroxybutyrophenone; points × for graph B, 2 ml of 0·01 M iron(III) nitrate; and points ○ for graph C, 20 ml of 0·01 M 2,4-dihydroxybutyrophenone. Final volume 50 ml; pH 2·95

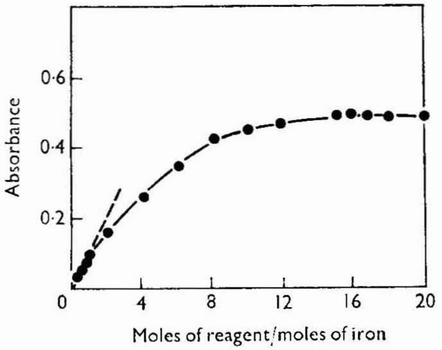

Fig. 2. Composition of the iron(III) - 2,4-dihydroxybutyrophenone complex by the mole-ratio method at 470 mμ. $\mu = 0·1$ $NaClO_4$ (2 ml of 0·01 M iron (III) nitrate + varying amounts of 2,4-dihydroxybutyro phenone; final volume 50 ml); pH 2·95

MOLE-RATIO STUDIES—

A study of the composition of the complex by the mole-ratio method[3] (Fig. 2), the method of continuous variation[4,5,6] (Fig. 3), the slope-ratio method[7] (Fig. 4) and the Bent and French method[8] (Fig. 5) indicates that the complex has a 1 to 1 composition.

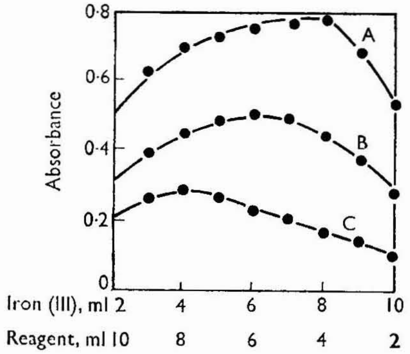

Fig. 3. Composition of the iron (III) - 2,4-dihydroxybutyrophenone complex at pH 2·95 by Job's method of continuous variation at 470 mμ. x ml of 0·01 M iron(III) nitrate + $(12 - x)$ ml of 2,4-dihydroxybutyrophenone (graph A, 0·02 M reagent; graph B, 0·01 M reagent; and graph C, 0·005 M reagent) + 5 ml of M $NaClO_4$; final volume 50 ml

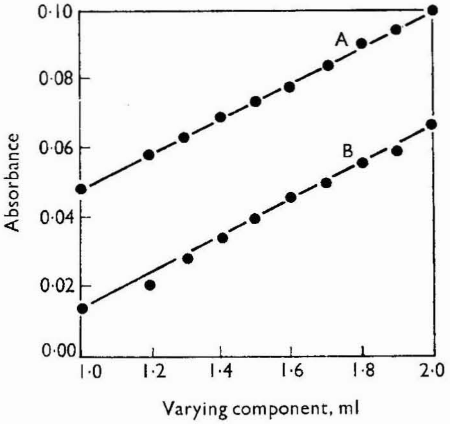

Fig. 4. Composition of the iron(III) - 2,4-dihydroxybutyrophenone complex at pH 2·95 by the slope-ratio method at 470 mμ. $\mu = 0·1$ $NaClO_4$ (graph A, 10 ml of 0·01 M reagent + varying amounts of 0·002 M iron (III) nitrate; and graph B, 10 ml of 0·01 M iron (III) nitrate + varying amounts of 0·002 M reagent; final volume 50 ml)

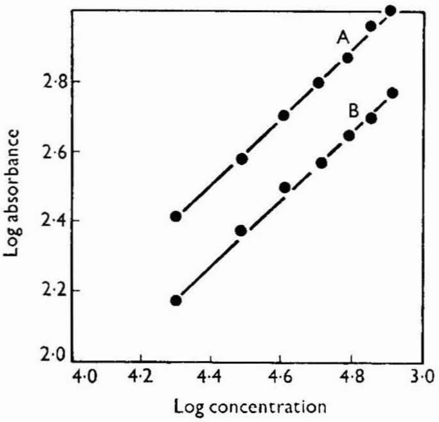

Fig. 5. Composition of the iron(III) - 2,4-dihydroxybutyrophenone complex at pH 2·95 by the logarithmic method of Bent and French at 470 mμ. μ = 0·1 $NaClO_4$ (graph A, 5 ml of 0·01 M reagent + varying amounts of 0·002 M iron(III) nitrate; and graph B, 5 ml of 0·01 M iron(III) nitrate + varying amounts of 0·002 M reagent; final volume 50 ml)

RECOMMENDED PROCEDURE FOR PREPARATION OF CALIBRATION CURVES—

Transfer 0·25, 0·50, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of a standard iron(III) solution (0·01 M) into 50-ml calibrated flasks, add 7·5 ml of 0·1 M solution of the reagent in 40 per cent. ethanol, mix well and adjust the pH to 2·95. Make up to volume with distilled water and mix thoroughly. The series contains 2·8, 5·6, 11·2, 22·4, 33·6, 44·8 and 56·0 p.p.m. of iron, respectively, when diluted to 50 ml. Measure the absorbance at 470 mμ after half an hour, with an iron(III) solution of corresponding concentration as blank. Plot the absorbance as a function of iron concentration.

SENSITIVITY AND OPTIMUM CONCENTRATION RANGE—

The sensitivity of the reaction is 0·074 μg per ml of Fe^{3+} at 470 mμ, *i.e.*, 0·74 part of iron(III) ion in 10^7 parts of the solution. The spectrophotometric error[9] is at a minimum in the absorbance range 0·2 to 0·7. This corresponds to an optimum concentration of 7·4 to 26·1 p.p.m.

REPRODUCIBILITY—

Six aliquots of 2 ml, corresponding to 11·2 p.p.m. of iron at the final dilution, were analysed by the recommended procedure. The standard deviation was $\pm$0·0025 unit of absorbance, *i.e.*, 1 per cent.

EFFECT OF DIVERSE IONS—

The effect of 37 ions was investigated. At an iron concentration of 11·2 p.p.m., 1000 p.p.m. concentrations of Al^{3+}, Ba^{2+}, Be^{2+}, Cd^{2+}, Cs^{+}, Ca^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, K^{+}, Sr^{2+}, Th^{4+}, UO_2^{2+}, Zn^{2+}, Zr^{4+}, NH_4^{+}, Cl^{-}, ClO_4^{-}, NO_3^{-} and SO_4^{2-}, 750 p.p.m. of Br^{-} and Co^{2+}, 500 p.p.m. of Cr^{3+}, Pb^{2+} and Ag^{+}, 150 p.p.m. of I^{-}, 60 p.p.m. of Pd^{2+}, 25 p.p.m. of V^{4+}, 15 p.p.m. of Cu^{2+} and 5 p.p.m. of molybdate and tellurate could be tolerated; PO_4^{3-}, F^{-}, citrates, oxalates and vanadates interfered at all levels.

APPLICATIONS—

Eight samples were prepared containing known concentrations of diverse ions. These were analysed for iron according to the recommended procedure. The results are shown in Table I.

An indigenous iron ore, with the following percentage composition: Fe_2O_3 92·8, Al_2O_3 1·54, SiO_2 3·07, CaO 0·3, TiO_2 0·01, MgO 0·28, P 0·10 and S 0·03, was also analysed. A sample of the ore (0·4752 g) was brought into solution by the standard method and diluted to 1 litre. Two 2-ml aliquots of the solution were then analysed according to the proposed procedure. The absorbance values were 0·270 and 0·275, which corresponded to 12·22 and 12·45 p.p.m. of iron, respectively. The results are in good agreement with the calculated amount of iron, which is 12·24 p.p.m.

TABLE I

ANALYSIS OF SYNTHETIC SOLUTIONS

Sample, p.p.m.	Absorbance	Fe^{3+} found, p.p.m.
Fe^{3+} 11·2 + Sr^{2+} 1000 + Mn^{2+} 1000 + Ca^{2+} 1000	0·250	11·32
Fe^{3+} 11·2 + Sr^{2+} 1000 + Pb^{2+} 250 + Ca^{2+} 1000	0·250	11·32
Fe^{3+} 11·2 + Ca^{2+} 1000 + Zn^{2+} 1000 + K^+ 1000 + Al^{3+} 1000 ..	0·245	11·09
Fe^{3+} 11·2 + Cu^{2+} 10 + Ni^{2+} 250	0·249	11·27
Fe^{3+} 11·2 + Cr^{3+} 250 + Ni^{2+} 250	0·252	11·41
Fe^{3+} 11·2 + Cr^{3+} 250 + Ni^{2+} 250 + Na^+ 1000	0·252	11·41
Fe^{3+} 11·2 + Na^+1000 + K^+ 1000 + Ba^{2+} 1000	0·249	11·27
Fe^{3+} 11·2 + Cu^{2+} 5 + Cr^{3+} 100 + Zn^{2+} 100 + Ca^{2+} 100 + Sr^{2+} 100 + Al^{3+} 100 + Cd^{2+} 100	0·24	10·86

DISCUSSION

The proposed method is not as sensitive as some methods for the spectrophotometric determination of iron, but its optimum range of 7·4 to 26·1 p.p.m. is a distinct advantage and should be useful for the determination of large amounts of iron.[10] It is reasonable to expect that the concentration-range limit could be extended significantly by the use of longer cells. This is especially promising, as the reagent does not absorb light in the visible region. The tolerance of diverse ions shown suggests that 2,4-dihydroxybutyrophenone can be used as a specific reagent for iron(III) ions at a relatively high concentration level in the presence of large amounts of other ions.

According to Sandell,[11] one great advantage of *o*-phenanthroline over some other reagents for iron is that it can be used in slightly acidic solutions, so that metal hydroxides are not precipitated. As the optimum pH for the 2,4-dihydroxybutyrophenone reagent is 2·9 to 3·0, this requirement is met. Moreover, the absorbance values of the complex formed are almost constant in the spectral range 460 to 480 mμ, thus giving rise to a 20-mμ wide spectrophotometric absorption plateau, which enables this reagent to be adapted for colour measurements with filter photometers.

We thank Professor B. K. Vaidya for his kind interest, and the Gujarat University for the award of a research scholarship to one of us (M.H.G.).

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The Determination of Iron(II) Sulphide in Soil in the Presence of Iron(III) Oxide

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Hydrogen sulphide is partially oxidised by iron(III) when soils containing sulphide and iron(III) oxide are acidified. Satisfactory recoveries of hydrogen sulphide are obtained by using a solution of tin(II) chloride in hydrochloric acid to decompose the sulphide.

In studying the reduction of sulphate in waterlogged soil it was necessary to determine the amount of iron(II) sulphide that was produced as one of the reaction products. Attempts to determine this as the iron(II) iron liberated when the soil was treated with a solution of a mercury(II) salt were unsuccessful. The difficulties of this method are aggravated by the need to correct for soluble iron compounds, also formed during anaerobic incubation, and the determination of this quantity is uncertain, particularly under the conditions imposed by the requirements of the main experiment.

The only alternative seemed to be to determine iron(II) sulphide as hydrogen sulphide liberated on acidification. As iron(III) oxide would also be present in the reaction mixture, we determined the extent to which this would interfere, according to the reaction $2Fe^{3+} + S^{2-} = 2Fe^{2+} + S$, with calcium sulphide as the source of sulphide.

The apparatus used is illustrated in Fig. 1.

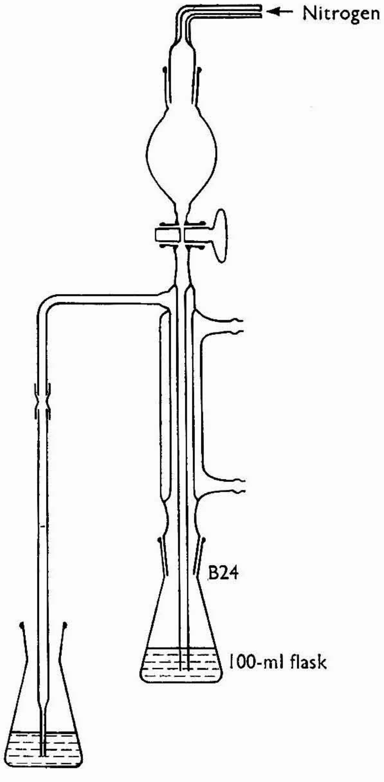

Fig. 1. Details of apparatus

METHOD

REAGENTS—

Ammoniacal zinc sulphate solution—Dissolve 50 g of zinc sulphate, $ZnSO_4.7H_2O$, in 250 ml of water. Add 250 ml of concentrated ammonia solution, allow to stand overnight in a stoppered container and filter.

Potassium iodate solution, 0·1 N.

Potassium iodide solution, 1 *per cent. w/v, aqueous*—Freshly prepared.

Hydrochloric acid (1 + 1 *v/v*).

PROCEDURE—

About 0·1 g of calcium sulphide and various amounts of hydrated iron(III) oxide were weighed into the conical flask (Fig. 1) and the apparatus flushed with nitrogen. About 25 ml of dilute hydrochloric acid were added from the dropping funnel, and the liberated hydrogen sulphide swept out with a gentle stream of nitrogen. When the initial vigorous effervescence had ceased, the contents of the reaction flask were heated to boiling. The hydrogen sulphide evolved was absorbed in about 5 ml of the ammoniacal zinc sulphate solution diluted with 25 to 30 ml of water. When all of the hydrogen sulphide was expelled, 2 to 3 ml of potassium iodide were added to the receiver, followed by starch solution and by dilute hydrochloric acid to dissolve the precipitate of zinc sulphide; the hydrogen sulphide thus liberated was titrated immediately with 0·1 N potassium iodate to the first appearance of a permanent blue colour.

TABLE I

THE EFFECT OF IRON(III) OXIDE ON THE RECOVERY OF HYDROGEN SULPHIDE

Sulphide taken, mg	Iron(III) oxide added, mg	Sulphide recovered, mg	Recovery, per cent.
30·8	20	30·6	99·4
28·3	60	26·9	95·1
29·7	140	22·1	74·4
28·8	200	17·5	60·8
28·5	400	14·4	50·5
28·8	900	13·9	48·3
29·7	50*	24·9	88·2
28·7	100*	21·7	76·9
28·8	500*	15·7	55·6

* Added as subsoil.

The iron(III) oxide used to obtain the results given in Table I was a synthetic goethite that dissolved readily in dilute acid, and it might therefore have caused a bigger proportional error than the less readily soluble iron(III) oxide of a soil. However, when subsoil from the Rothamsted farm was substituted for the laboratory preparation, the loss of sulphide was not appreciably smaller.

The error caused by iron(III) oxide is thus considerable; the failure of Chaudhry and Cornfield[1] to recover more than 60 per cent. of sulphide added to air-dried soil can presumably be ascribed to this effect.

Because of the lack of any method for determining the iron(II)-to-iron(III) ratio in a reduced soil it is impossible to generalise, but the few determinations we have made of the sulphide contents of field samples suggest that the largest iron(III) oxide-to-sulphide ratios in Table I are probably those most relevant to actual soils.

As the concentration of iron(III) oxide decreases during the anaerobic incubation of a soil, the extent of the error would vary throughout our experiments, and the results obtained by this method would be quite meaningless.

Attempts to limit the interference by adding metallic zinc or tin to the sulphide before acidification failed, but by adding tin(II) chloride to the acid used to decompose the sulphide (about 2 g per 25 ml), the loss of sulphide was largely overcome (Table II).

When water was added to the sulphide - iron(III) oxide mixture, satisfactory recoveries were obtained when the concentration of the acid used to decompose the sample was increased to give a final value of about 5 N.

TABLE II

THE RECOVERY OF HYDROGEN SULPHIDE IN THE PRESENCE OF IRON(III) OXIDE WITH TIN(II) CHLORIDE - HYDROCHLORIC ACID

Sulphide taken, mg	Iron(III) oxide taken, mg	Sulphide recovered, mg	Recovery, per cent.
30·6	45	30·4	99·5
29·2	100	28·9	99·0
29·2	200	29·2	100·0
29·4	900	28·6	97·5
28·7	50*	28·4	99·0

* Added as subsoil.

The effect of the tin(II) chloride reagent on other sulphur compounds present, or likely to be present, in the incubated reaction mixture was tested. Thiosulphate was reduced quantitatively to sulphide, but the effect on sulphate and elemental sulphur was negligible. Pyrite reacts slowly, thus causing a positive error. It is unlikely that pyrite is formed in our experiments, but, as it is often the chief sulphur compound in sulphidic soils, it could cause serious error when dealing with a natural soil. In testing sulphate, sulphur and pyrite, the hydrogen sulphide was absorbed in sodium hydroxide solution and titrated with 0·001 N mercury(II) acetate, with dithizone as indicator.[2]

The tin(II) chloride reagent has been used for several years in our work on sulphate reduction. The iodate method described above is unsuitable for the amounts with which we are concerned; instead, hydrogen sulphide is absorbed in 25 ml of 0·05 N hypochlorite solution (0·4 N with respect to sodium hydroxide), and the excess of hypochlorite determined iodimetrically.

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A Titrimetric Method for Determining Total Sulphur in Mineral Soils

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A rapid method for the determination of total sulphur in mineral soils is described. The various sulphur compounds in soil are first oxidised to sulphate by potassium dichromate in phosphoric acid, and the sulphate thus formed is then reduced to sulphur dioxide by heating with activated charcoal. The evolved sulphur dioxide is trapped in hydrogen peroxide, barium perchlorate added to the resulting sulphuric acid to precipitate barium sulphate, and the excess of barium determined by titration against standard potassium sulphate, with sulphonazo III as indicator. The proposed method gave acceptable results when tested on pure compounds and on soils of known sulphur content. No interferences are to be expected from normal soil constituents.

WHEN soils containing charcoal are strongly heated with phosphoric acid, sulphur dioxide is evolved from any sulphates that may be present. A new method, based on this observation, was developed for determining total sulphur in soil that compares favourably, both in speed and simplicity, with other current chemical techniques for this determination.[1,2,3]

Inorganic sulphur is often present in soil as sulphate, held by anion exchange, but can be found, particularly in soils from arid regions, as calcium and magnesium sulphates; it occurs as sulphides in certain soils developed under waterlogged conditions. Some of the organic sulphur in soil is combined in sulphur-containing α-amino-acids, and some as ester sulphate, but the chemical nature of much of the soil organic sulphur is obscure; for a review see Freney.[4] In all chemical methods for determining total sulphur in soil, the different sulphur compounds are first quantitatively converted into a single form; the sulphur in this is then isolated from the soil residue for determination. Analytical methods for determining total sulphur in soil have been briefly discussed by Bloomfield[2] and by Bardsley and Lancaster.[1]

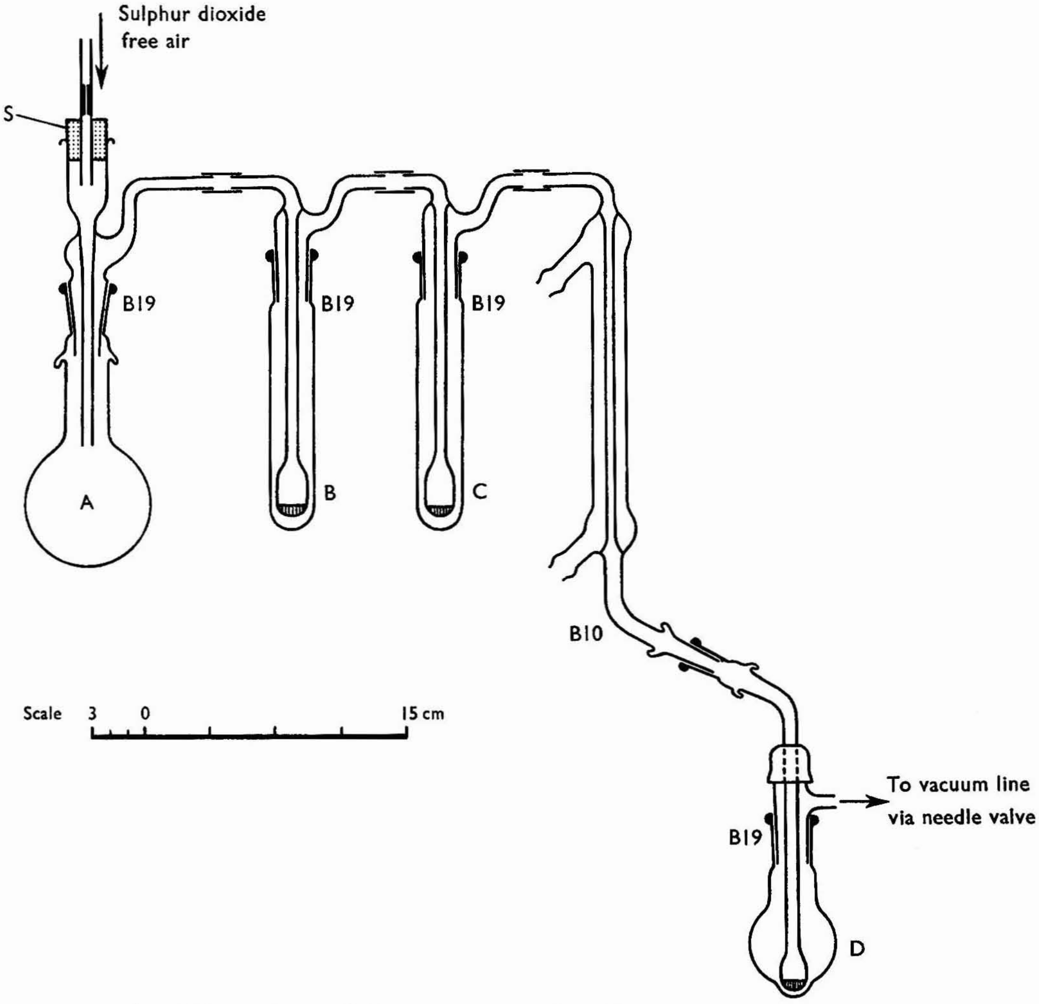
The proposed method is in three steps: organic and inorganic soil sulphur are oxidised to sulphate by refluxing with potassium dichromate and dehydrated phosphoric acid (oxidation step); the sulphate thus formed is reduced to sulphur dioxide by heating with activated charcoal in phosphoric acid (reduction step); the evolved sulphur dioxide is oxidised to sulphuric acid by hydrogen peroxide, barium perchlorate added to precipitate barium sulphate, and the excess of barium determined by titration against standard potassium sulphate solution, with sulphonazo III as indicator.[5] Back-titration is used rather than direct titration because of the erratic colour changes that sometimes occurred at the beginning of direct titrations, caused, most probably, by the absence of barium sulphate precipitation nuclei.

Preliminary work showed that it was essential to pre-treat the phosphoric acid by heating to 370° C with activated charcoal if low blank values were to be obtained. During this pretreatment the orthophosphoric acid is dehydrated, giving a mixture of ortho, pyro and metaphosphoric acids. The charcoal and the dehydrated acid are then both used as reagents in the determination. Use of the dehydrated acid has an incidental advantage in that excess of dichromate remaining after oxidation of the organic matter during the first step is decomposed at the temperature of reflux (about 305° C). If, for example, 88 per cent. orthophosphoric acid is used in the oxidation step, the reflux temperature is lower (about 170° C), excess of dichromate remains in the reaction mixture and then reacts violently when heated with charcoal during the reduction step.

METHOD

APPARATUS—

This is shown in Fig. 1. The gas stream carrying sulphur dioxide from the 150-ml flask, A, is sucked through traps, B and C, each containing a sintered-glass thimble (porosity No. 2, diameter 14 mm) to stop acid spray, before going through a water condenser and into the absorption trap, D. The absorption trap also contains a sintered-glass thimble of the same size and porosity as those in traps B and C. The sintered-glass thimble in the absorption trap, D, must fit snugly into the dimple in the absorption flask, almost touching the bottom. Construction of the absorption flask is simplified if, as in Fig. 1, a screw-thread adaptor with a PTFE washer (Quickfit and Quartz Ltd.) is used to connect the tube carrying the sinter to the B19 cone. Connections are as short as possible and made with poly(vinyl chloride) tubing. The incoming air is passed through a U-tube containing self-indicating soda lime



A = 150-ml reduction flask

B and C = Traps containing a sintered-glass thimble (porosity No. 2, diameter 14 mm)

D = Absorption trap

S = Stopper

Fig. 1. Details of the apparatus

to remove oxides of sulphur. To facilitate control of the gas flow, a length of capillary tubing (1 cm long, 0·25-mm i.d.) is inserted between the U-tube containing soda lime and flask A. Except for the 50-ml absorption flask (D, Fig. 1), all the glassware is available commercially.

REAGENTS—

Phosphoric acid—Heat 750 ml of 88 per cent. analytical-reagent grade orthophosphoric acid with 15 g of activated charcoal (Merck's Pro Analysi grade) in a distillation flask connected to a water condenser. Collect 200 ml of the distillate, then allow the suspension to cool to about 150° C, and filter under suction through a No. 3 glass sinter, discarding the first few millilitres of filtrate. Traces of suspended charcoal in the filtered phosphoric acid can be disregarded. Any crystals that appear on standing can be re-dissolved by keeping the acid overnight in an oven at 80° C. A burette, 3 cm in diameter with a tap and "jet" of 6-mm i.d., is convenient for dispensing the viscous acid.

Active charcoal—Wash the charcoal remaining on the sinter with three 250-ml portions of boiling distilled water, making sure that the charcoal is well dispersed in each wash, and dry overnight at 105° C.

Barium perchlorate—A 0·03 N solution of barium perchlorate trihydrate (general-purpose reagent grade) in water.

Standard sulphate solution—Dissolve 0·2717 g of analytical-reagent grade potassium sulphate, dried overnight at 105° C, in water and make up to 1 litre; 1 ml of this solution contains 0·05 mg of sulphur.

Indicator—A 0·1 per cent. solution of sulphonazo III in water.

Potassium dichromate—Analytical-reagent grade.

Hydrogen peroxide, 100 *vol*—Microanalytical-reagent grade.

Acetone—Analytical-reagent grade.

PROCEDURE—

Weigh 1 g (less if the sulphur content exceeds 500 p.p.m.) of air-dried soil (ground to pass a 30-mesh sieve or finer) into the dry reaction flask. Moisten with 1 ml of water, add 2 g of potassium dichromate and add 25 ml of phosphoric acid. Connect the flask to a water-cooled reflux condenser, bring the solution to the boil, swirl the flask, and heat it under steady reflux for 10 minutes. Allow to cool, add 0·5 g of activated charcoal and 4 ml of water and connect the flask to the apparatus as shown in Fig. 1. Place 0·2 ml of hydrogen peroxide in the absorption trap, D. Adjust the stream of air passing through the apparatus to give a steady rapid flow of bubbles in the absorption trap. Heat the reduction flask on a bunsen burner: if foaming occurs when the mixture begins to boil, momentarily remove the flame. After the mixture has come to the boil, heat for 5 minutes. The rate of heating should be such that steam reaches the top of the water condenser between $2\frac{1}{2}$ and $3\frac{1}{2}$ minutes after coming to the boil. Two minutes after the burner is turned off, remove stopper, S, then disconnect the absorption trap and wash the sinter inside and out with 15 ml of acetone, adding the washings to the absorption flask. Add 3 drops of indicator and run in 1 ml of barium perchlorate by using a Van Slyke pipette. If the solution remains purple add a further 1 ml of perchlorate. Titrate against the standard potassium sulphate solution, with a 10-ml burette. The colour change is from blue to purple. Carry out a blank determination, omitting the soil, with the same volume of barium perchlorate solution.

Sulphur, mg = (ml of potassium sulphate solution required by blank − ml of potassium sulphate solution required by sample) × 0·05.

Between determinations, empty the water collected in traps B and C. If the reduction mixture is allowed to cool in the flask it solidifies: to avoid this pour it out while still liquid and then wash the flask with hot water.

RESULTS AND DISCUSSION

Table I gives the sulphur contents of some organic and inorganic compounds as found by the proposed method, together with the calculated values. For analysis, 2 g of potassium dichromate and 25 ml of phosphoric acid were added to 1 ml of an aqueous solution of the compound containing about 0·4 mg of sulphur. The rest of the determination was as described above. Results were quantitative, within ±2 per cent. In Table I and subsequent tables results are means of triplicate determinations unless otherwise indicated.

TABLE I

SULPHUR CONTENTS OF SOME ORGANIC AND INORGANIC COMPOUNDS

Compound*	Sulphur calculated, per cent.	Sulphur by proposed method, per cent.
Sulphamic acid†	33·0	32·9
S-Benzylthiuronium chloride†	15·8	15·7
Sulphanilic acid‡	18·5	18·7
Methionine	21·5	21·3
Cystine	26·7	26·7
Copper(II) sulphate pentahydrate‡	12·8	13·0
Potassium sulphate‡	18·4	18·1

* All dried over anhydrous magnesium perchlorate.
† Microanalytical-reagent grade.
‡ Analytical-reagent grade.

TABLE II

SULPHUR CONTENTS OF SOME ANALYSED MATERIALS

Material*	Sulphur nominal, per cent.	Sulphur by proposed method, per cent.
Basic slag†	0·16	0·197
Anthracite†	2·33	2·25
Iron pyrites	44·6	35·6 (44·0)‡
Portland cement†	1·21	1·23
Shale	5·07	5·24

* All results (except pyrites) on oven-dried (24 hours at 80° C) basis.
† Obtained from the Bureau of Analysed Samples Ltd.
‡ Result in parenthesis is after hydrogen peroxide treatment.

Table II gives the sulphur contents of five analysed materials. The nominal sulphur contents of the basic slag, anthracite and Portland cement were those given by the Bureau of Analysed Samples Ltd.; those given for pyrites and shale were obtained by the gravimetric procedure described by Vogel.[6] Acceptable agreement was obtained, except with pyrites. Unchanged pyrites crystals were found in the reaction mixture at the end of the dichromate oxidation stage. The more coarsely ground the pyrites, the less was oxidised. Hydrogen peroxide in the cold will oxidise pyrites.[7] More sulphur was recovered (see Table II) from pyrites if, instead of moistening with 1 ml of water before oxidation, 1 ml of 100-vol hydrogen peroxide was added, the mixture left to stand overnight, and the analysis then continued as above. This peroxide treatment is probably only necessary with soils containing much coarsely crystalline pyrites.

TABLE III

SULPHUR CONTENTS OF SOME ROTHAMSTED SOILS

Soil No.*	Sampling depth, inches	pH	Organic carbon, per cent.	Carbonate carbon, per cent.	Nitrogen, per cent.	Clay, per cent.	Sulphur by proposed method, p.p.m.	Sulphur by Bloomfield's method, p.p.m.
1	0 to 6	7·8	2·43	0·14	0·246	18	511	492
2	0 to 6	8·1	0·97	0·16	0·107	18	200	187
3	0 to 9	7·8	2·89	0·19	0·261	24	419	411
4	9 to 18	7·9	0·81	0·04	0·098	50	157	149
5	18 to 27	7·7	0·55	0	0·075	62	108	115
6	0 to 9	4·5	1·98	0	0·168	20	326	330

* All results on oven-dried (24 hours at 80° C) basis.

Table III gives the sulphur contents of a range of Rothamsted soils as determined by Bloomfield's method[2] and by the proposed method. Agreement was close. Table IV gives the sulphur contents of some Australian soils as found by the proposed method and that of Steinbergs, Iismaa, Freney and Barrow; with these, discrepancies between the two methods were slightly greater than with the Rothamsted soils, but neither method gave values consistently higher than those by the other.

INTERFERENCES—

The addition of 1000 p.p.m. of Fe^{3+}, Pb^{2+}, Al^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Sn^{2+}, Sr^{2+}, Zn^{2+},Mg^{2+}, Ba^{2+}, NH_4^+, K^+, Na^+, SeO_4^{2-}, F^-, Cl^-, Br^-, $B_4O_7^{2-}$, NO_3^- or NO_2^- to soil 2 (Table III) did not significantly alter the value found by the proposed method for the sulphur content of this soil (200 p.p.m.). Of the cations and anions tested, iodide alone interfered; in the presence of 1000 p.p.m. of iodide (as potassium iodide) the sulphur content of soil 2 was found to be 171 p.p.m. Iodine concentrations as large as this are most unlikely in soils.

PRECISION—

Table IV gives the sulphur contents of six soils; each value is the mean of four determinations. The standard errors of these means range from ±2 to ±9 p.p.m., so that the method is precise enough for most soil work.

TABLE IV

SULPHUR CONTENTS OF SOME AUSTRALIAN SOILS

Soil No.*	Type	Sampling depth, inches	pH	Organic carbon, per cent.	Nitrogen, per cent.	Sulphur by proposed method, p.p.m.	Sulphur by Steinbergs, Iismaa, Freney and Barrow's method,[3] p.p.m.
1	Red-brown earth	0 to 4	5·9	0·65	0·043	68 ± 3·2†	67
2	Red-brown earth	0 to 4	6·8	2·23	0·135	168 ± 3·1	167
3	Red-brown earth	0 to 4	5·9	2·70	0·152	209 ± 2·1	199
4	Podsol	0 to 2	5·6	3·89	0·306	326 ± 1·9	343
5	Alpine humus	0 to 4	4·9	7·50	0·409	442 ± 3·9	473
6	Kraznozem	0 to 2	6·1	7·71	0·675	954 ± 9·4	928

* All results on oven-dried (24 hours at 80° C) basis.

† Standard error of mean (four replicates).

CONCLUSIONS

The proposed method is rapid and may be of value when the number of determinations to be carried out does not warrant more complex apparatus. It is convenient to perform the oxidation step in batches of six and to duplicate the apparatus in Fig. 1, so that two reductions can be done at the same time. Six determinations then take 1½ hours. The sensitivity is adequate for the range of sulphur contents common in mineral soils. If needed, the sensitivity could probably be increased by abandoning the titrimetric finish, collecting the sulphur dioxide in sodium tetrachloromercurate instead of hydrogen peroxide, and determining the sulphur dioxide colorimetrically by the rosaniline method.[8] A disadvantage is that the hot phosphoric acid attacks the glass reaction flask, A: flask life is limited to twenty to fifty determinations. Buděšinský and Krumlová have recently shown that dimethyl sulphonazo III is a slightly better indicator than sulphonazo III for the titration of sulphate with barium perchlorate.[9] This reagent could probably be used as an alternative to sulphonazo III in the proposed method.

I thank Dr. C. H. Williams for supplying the Australian soils, together with the results in Table IV characterising them, and also British Drug Houses Ltd. and Dr. B. Buděšinský for samples of sulphonazo III.

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Determination of Total Sulphur in Soil by Using High-frequency Induction Furnace Equipment

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A method is described for the determination of total sulphur in soils and silicate minerals by combustion in a high-frequency induction furnace. Oxides of sulphur are absorbed in a solution of sodium hydroxide giving sulphate and sulphite. Reduction subsequently converts these into hydrogen sulphide, which is determined by a colorimetric methylene-blue method. Preliminary tests with soils showed that if the only combustion product determined is sulphur dioxide, then low and inconsistent values are obtained.

Values for soils and several mineral reference samples are compared with those obtained by an acid-digestion method.

SULPHUR is present in soils in rather small amounts, generally below 0·2 per cent. w/w, and often much less. It occurs in both organic (*e.g.*, amino-acid) and inorganic (*e.g.*, sulphide) forms, and to determine the total sulphur content it is necessary to convert these into soluble forms (usually sulphate) for quantitative determination. As this is often effected by fusion with alkaline fluxes or digestion with oxidising acids, the determination of sulphate is usually carried out in the presence of relatively large amounts of salts, and for this reason such methods tend to be time consuming and frequently unreliable.

Methods involving the use of sodium peroxide as flux and oxidant have been perhaps the most widely used in the past, although they have by no means enjoyed unqualified support.[1,2] In the A.O.A.C.[3] method, a sodium carbonate - sodium peroxide fusion is used with a nickel crucible at temperatures up to 900° C; at such temperatures the crucible is severely attacked, and a very pure grade of nickel is required to avoid high and irregular blanks. For the determination of total sulphur in silicate rocks, Ricke[4] used a sodium peroxide fusion in a corundum crucible at 650° C; after removal of cations (including aluminium) by an ion-exchange column, and of insoluble material by filtration, sulphate was determined by titration with barium chloride. Although Rafter[5] showed that platinum could be used for peroxide fusions of minerals, provided the temperature is kept below 550° C, this procedure could be unsafe with materials with a high organic-matter content.[6] Gravimetric determination of barium sulphate is usual with the peroxide method, although a turbidimetric procedure can also be used. Neither of these procedures is entirely satisfactory, as the precipitation of small amounts of sulphate may be inhibited by the excess of salts present, while the turbidimetric method, in particular, requires close control of the conditions of precipitation.[1,7]

In their proposed method for total sulphur in soils, Butters and Chenery[1] heated the sample overnight with magnesium nitrate at 300° C, digested it with nitric acid, and then determined sulphate in the filtered digest turbidimetrically as barium sulphate. Although they obtained good recovery of added organic and soluble sulphate sulphur, they provided no evidence for the recovery of sulphur from refractory minerals. Chaudhry and Cornfield[8] compared results obtained by this method, and a similar method in which potassium chlorate was used,[9] with results they obtained by heating the soil with potassium nitrate and nitric acid at 550° C. They found that their method (potassium nitrate *plus* nitric acid) gave slightly higher results for total soil sulphur than either of the other two.

Little[10] briefly reviewed a range of published oxidation and reduction methods for the determination of total sulphur and proposed a reduction method for total sulphur in soils, in which sulphur was reduced to sulphide by heating the soil with ferrum reductum at between 700° and 900° C in specially constructed heating blocks. The hydrogen sulphide evolved by a subsequent acid treatment was then determined iodimetrically. Here again, the presumed accuracy of the method would appear to be based mainly on the recovery of various organic and soluble inorganic compounds, and with this method there is the disadvantage that very pure ferrum reductum metal of low sulphur content is required, which is not always readily available.

Bloomfield[11] proposed a combustion method in which the soil is ignited in a current of nitrogen, with vanadium pentoxide and hot copper(II) oxide as oxidising agents. The combustion gases are then passed over hot metallic copper to convert sulphur trioxide into sulphur dioxide, which is then determined colorimetrically. Results for soils were comparable with those obtained by the two methods of Steinbergs, Iismaa, Freney and Barrow,[2] the first of which involves reduction with magnesium and determination of the resulting hydrogen sulphide, and the second oxidation by sintering with sodium carbonate and silver oxide at 550° C, followed by the reduction of sulphate and its determination by the Johnson and Nishita[12] procedure.

In a method for determining total sulphur in silicates, Wilson, Sergeant and Lionnel[6] used wet oxidation with aqua regia and perchloric acid, combined with dissolution of silicates with hydrofluoric acid in a polytetrafluoroethylene basin. Addition of vanadium pentoxide, together with perchloric acid, after the first digestion, was found to expedite the oxidation of organic matter and pyrite. Sulphate was finally determined by a gravimetric barium sulphate method following extraction of iron and titanium by cupferron. Although still time consuming, this method appears to provide a reliable alternative to fusion methods, particularly for minerals containing appreciable organic matter and of high sulphur content.

The high-frequency induction furnace method is attractive in principle because of its speed and convenience, and it is surprising that it has received so little attention as a method for determining total sulphur in soils, sediments and silicate minerals. Kaplan, Emery and Rittenberg,[13] in studies of sulphur in marine sediments, obtained higher values by wet combustion with bromine and aqua regia than by the use of a Leco* induction furnace (with determination of liberated sulphur dioxide by automatic titration with iodine solution). Low and poorly reproducible results for surface sediments were always obtained by the Leco method, and this was attributed to incomplete combustion of the organic matter, which produced smoke and interfered with the operation of the automatic photoelectric titrator.

In this laboratory, two methods for soils have been used with success, the sodium hydrogen carbonate fusion method of Steinbergs, Iismaa, Freney and Barrow,[2] and Collie's triple acid-extraction method (T. W. Collie, unpublished work), in which is an adaptation of the Bethge[14] extraction method used for the digestion of wood products. Collie's method involves digestion with orthophosphoric, nitric and perchloric acids, followed by destruction of nitric acid with formic acid and determination of sulphate in an aliquot of the digest by the Johnson and Nishita procedure,[12] and has given accurate results on referee and standard samples. In the main, Collie's results by this method have been used as a check on the induction furnace method described below.

Analysis with an induction furnace involves the measurement or analysis of gases evolved when a sample is heated in a stream of oxygen. The heat is produced by a high-frequency electrical flux induced in the sample itself, or, with poor conductors such as soils, in the sample mixed with a conducting matrix of iron powder. According to the method recommended by Leco, sulphur is determined as sulphur dioxide, which is collected in acid and titrated with standard potassium iodate. This method was originally intended for rapid sulphur analysis of ferrous metals, but so far there has been only limited research into the application of this technique to the analysis of poorly conductive and readily oxidisable materials. This paper outlines a simple, rapid and reasonably accurate method for the determination of total sulphur in soils by using a high-frequency induction furnace.

EXPERIMENTAL

In preliminary experiments, it was found that catalytic oxidants must be used to obtain temperatures sufficiently high for complete combustion. It was also found that under these conditions recovery of sulphur from soils as sulphur dioxide is not reliably quantitative (see Table I).

These findings agree with those of Green,[15] who considered that catalytic oxidants favoured the formation of sulphur trioxide, and that to obtain results approaching total recovery of sulphur from cast iron, it was necessary to retain the sulphur trioxide formed.

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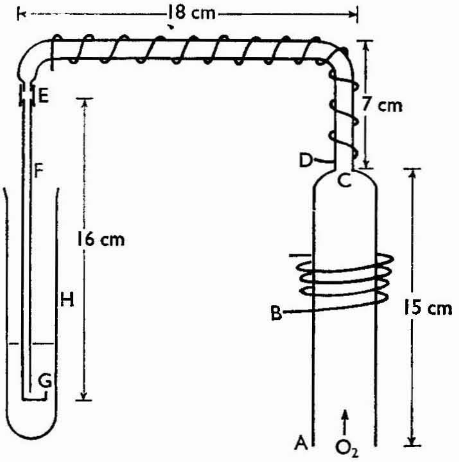
TABLE I

TOTAL SOIL SULPHUR VALUES BY LECO SULPHUR DIOXIDE TITRATOR AND BY A TRIPLE ACID METHOD*

	Sulphur, per cent.	
Sample	Triple acid extraction	Sulphur dioxide titrator (replicates)
7535 F	0·027	0·009, 0·025
7585 A	0·046	0·014, 0·038
7638 C	0·063	0·030, 0·033
7592 B	0·103	0·099, 0·025
7640 F	0·083	0·057, 0·015

* T. W. Collie, Soil Bureau (personal communication).

To determine both sulphur dioxide and sulphur trioxide evolved from soils during combustion, the gases were bubbled into N sodium hydroxide and the resulting solution was analysed for sulphur by a modified Johnson and Nishita[12] method. In this method, 2 ml of sample solution are boiled for 15 minutes with 6 ml of acidic reducing mixture (hypophosphorous, formic and hydriodic acids); sulphate and sulphite are reduced to hydrogen sulphide, which is collected in zinc acetate solution and determined colorimetrically by the methylene-blue reaction.[16]



A = Leco silica combustion tube, i.d. 3·1 cm
B = Furnace induction coil
C = Combustion tube narrows to delivery tube, i.d. 0·8 cm
D = "Electrothermal" heating tape
E = PVC connection between silica delivery tube and removable glass tube
F = Glass tube, i.d. 0·3 cm
G = Sintered-glass bubbler, porosity 2
H = 25-ml graduated collecting vessel containing 15 ml of N sodium hydroxide

Fig. 1. Modified combustion and delivery tube

During collection of the combustion gases, losses of sulphur occurred, and it was noted that the delivery tube from the furnace to the collection vessel became coated with moist dust particles. When the delivery tube was washed it was found that the washings contained small but significant amounts of sulphur compounds. Washing the delivery system after each ignition proved to be slow and inefficient, as the entire tube could not be washed without removal from the apparatus, consequently it was decided to minimise the losses by restricting the amount of cool surface area on which dust and moisture could accumulate. This was done by shortening the length of the delivery tube from the outlet end of the combustion tube, and by bending it at right angles as close as possible to the furnace. The delivery tube was wrapped in heating tape to keep the system at about 100° C, and connected to a removable sintered-glass bubbler that was immersed in the collecting solution (Fig. 1). By heating the tube adsorption of sulphur trioxide on to the glass was eliminated, but some trouble was experienced with dust blocking the sintered bubbler. The worst effects of this were eliminated by using porous covers on top of the crucibles. As the standards for soils are within the range 0 to 25 μg of sulphur per 2 ml, it is necessary to ensure that the sulphur concentration in the sample solution is within the range 0 to 12·5 p.p.m. of sulphur. This may be accomplished by variation of the sample weight and volume of final solution. The rate of heating of crucibles is affected by varying the sample weight, but for most soils it was found that 0·25 g of sample allowed a satisfactory heating rate.

Standards for the complete procedure (induction furnace combustion, followed by Johnson and Nishita[12] distillation) were prepared by weighing appropriate portions of analytical-reagent grade aluminium potassium sulphate into crucibles, heating them in the furnace and collecting the combustion gases in sodium hydroxide solution, which was then made up to volume. Aluminium potassium sulphate was chosen because large amounts of the salt represented small amounts of sulphur, thus enabling weights of reasonable magnitude to be used.

Manganese dioxide and vanadium pentoxide proved to be efficient catalysts, but they contained sufficient sulphur, even in pure reagent form, to give inconveniently high blanks. Molybdenum trioxide and chromium trioxide were substituted, and experiments showed that the best recovery of sulphur was obtained when these catalysts were used in combination, and that when used in conjunction with low-sulphur iron powder the blank value was reduced to an acceptable level.

The choice of combustion crucible is important to the success of the method. Several grades of "carbon and sulphur-blank free," zircon-base, refractory ceramic crucibles are supplied by the furnace manufacturers. Under the rather severe operating conditions (high plate-current) prevailing in the present work, it was found that Catalogue No. 528–25 crucibles invariably failed before maximum heat could be applied, while No. 528–35 crucibles (green) also failed quite frequently after sustained heating. No. 528–120 crucibles (white), although immune to heat failure, were insufficiently pervious to oxygen to permit complete combustion of the sample. Eventually, it was found that maximum heating without risk of crucible failure could be obtained by using a Leco Catalogue No. 528–35 crucible with a porous cover (No. 528–42) placed between the pedestal and crucible.

METHOD

APPARATUS—

Furnace—A Leco high-frequency induction furnace, Catalogue No. 521, or similar instrument. The furnace operates at a frequency of 14·6 MHz.

Purifying train—A Leco 516–000, or equivalent. The inflowing oxygen is passed successively through concentrated sulphuric acid, Ascarite and Anhydrone absorbents, and finally a flow meter.

Combustion tube—A Leco 550–120, modified as shown in Fig. 1.

Crucibles—Leco 528–35, with 528–42 porous covers.

REAGENTS—

Molybdenum trioxide—Analytical-reagent grade.

Chromium trioxide—Analytical-reagent grade.

Iron powder—Low-sulphur, Leco 501–78.

RECOMMENDED PROCEDURE—

Samples—Samples are normally air-dried at about 35° C and ground to pass a 2-mm sieve, as in the usual procedure for soil analysis. A representative sub-sample is then ground to pass a 60-mesh sieve. Oven-drying of the sample has not been found necessary. A scoop delivering about 1 g of iron powder is used to load the crucible and the charge, in order of addition, is 1 scoop of low-sulphur iron powder (about 1 g), 1 scoop of analytical-reagent grade molybdenum trioxide powder (about 0·5 g), soil sample (generally 0·25 g), 1 scoop of analytical-reagent grade chromium trioxide crystals (dried) (about 0·5 g) and 1 scoop of low-sulphur iron powder (about 1 g).

The mixture is stirred thoroughly with a glass rod, a further scoop of iron powder is added and a porous cover placed on top of the crucible, which rests upon a similar porous cover on top of the ceramic pedestal. A graduated 25-ml tube containing about 15 ml of N sodium hydroxide is used as a collection vessel and is clamped into position so that the sintered bubbler at the end of the delivery tube is well immersed in the solution. By raising the pedestal mechanism, the heating and oxygen flow (0·8 litres per minute) is started, and this treatment is allowed to proceed for 2 minutes after the plate-current reaches 400 mA. The reaction is stopped by lowering the pedestal, the sintered bubbler rinsed with de-ionised water, the rinsings being collected in the graduated tube, and the resulting solution made up to volume; the tube is stoppered and shaken.

Standards—Standards are prepared by using the same amounts of iron powder, molybdenum trioxide and chromium trioxide as for the samples. Weighed amounts of aluminium potassium sulphate, which should cover the range 0 to 92·5 mg of $AlK(SO_4)_2.12H_2O$ per litre (2 ml of solution $\equiv$ 0 to 25 μg of sulphur), are placed in the crucibles, ignited in the furnace and the gases collected in 15 ml of N sodium hydroxide, which is then made up to 1 litre with de-ionised water.

Blanks—These are determined by adding similar amounts of iron powder, molybdenum trioxide and chromium trioxide, as used for the samples and standards, and, after ignition in the furnace, the combustion gases are collected in 15 ml of N sodium hydroxide. The solution is then made up to the same final volume as the samples (25 ml). Blank values of between 2 and 3 μg of sulphur in 2-ml aliquots should be obtained.

Solutions obtained from samples, standards and blanks are then analysed by the Johnson and Nishita[12] method, the absorption being measured at 673 mμ, with a 4-cm cell.

CALCULATION—

Assuming that 0·25 g of soil is used and that the absorbing solution is made up to 25 ml, then a 2-ml aliquot corresponds to 0·02 g of soil.

Supposing this 2-ml aliquot contains $x + b$ μg of sulphur (from standard graph) where the blank value is b μg of sulphur for a 2-ml aliquot,

$$\text{then 100 g of soil contains } \frac{100}{0{\cdot}02}\cdot(x+b) - b = \frac{100x}{0{\cdot}02}\,\mu\text{g of sulphur,}$$

$$\text{so that the percentage of sulphur in soil} = \frac{100x}{0{\cdot}02 \times 10^6} = 0{\cdot}005x$$

where x is the number of micrograms of soil sulphur in a 2-ml aliquot of a 25-ml extract from 0·25 g of soil.

RESULTS AND DISCUSSION

In Table II, results for total soil sulphur by the triple acid and induction furnace methods are compared for a wide range of soils; these show generally satisfactory agreement. Table III

TABLE II

COMPARISON OF TOTAL SOIL SULPHUR VALUES OBTAINED BY ACID EXTRACTION AND COMBUSTION

	Sulphur, per cent.		
		Induction furnace method	
Sample	Triple acid method*	Mean	Standard deviation
7535 F	0·027	0·029	±0·0026
7536 B	0·032	0·036	±0·0025
7585 A	0·046	0·049	±0·0021
7592 B	0·103	0·094	±0·0045
7597 B	0·123	0·119	±0·0098
7597 C	0·097	0·096	±0·0084
7604 A	0·041	0·042	±0·0019
7604 D	0·007	0·008	±0·0005
7638 C	0·060	0·063	±0·0035
7640 F	0·083	0·089	±0·0057
7641 B	0·028	0·022	±0·0034
7671 D	0·096	0·095	±0·0032
7698 A	0·234	0·261	±0·0119

* T. W. Collie, Soil Bureau (personal communication).

shows results for total sulphur obtained for standard substances by the same two methods. These again show good agreement with each other, but in some instances are not in accord with the quoted sulphur contents. This is especially true for the bauxite sample (N.B.S. No. 69a) which, according to the data sheet, contains 0·040 per cent. of sulphur trioxide (sulphur = 0·016 per cent.). The method of analysis was not stated, however, and, because of the good agreement between the other methods, it would appear that either the N.B.S. result is in error or it represents only a particular (sulphate-S) fraction of the total sulphur.

TABLE III

COMPARISON OF TOTAL SULPHUR RESULTS OBTAINED BY TRIPLE ACID AND INDUCTION FURNACE METHODS FOR STANDARD SUBSTANCES

	Sulphur, per cent.			
			Induction furnace method	
Nature of sample	Quoted	Triple acid method	Mean	Standard deviation
British Chemical Standards—				
Liberian iron ore No. 175/1	0·034	0·032	0·031	±0·0049
Basic slag No. 174/1	0·160	[0·180]*	0·196	±0·0093
Basic slag No. 249/1	0·300	0·285	0·291	±0·0258
National Bureau of Standards—				
Bauxite No. 69a	0·016	0·036 [0·034]†	0·036	±0·0012
Argillaceous limestone No. 1a	0·266	0·292	0·306	±0·0233

* Result (average of five determinations) by using digestion procedure of Wilson, Sergeant and Lionnel,[6] followed by Johnson and Nishita[12] distillation.

† Mean of two determinations by T. W. Collie (personal communication) by using the sodium hydrogen carbonate procedure of Steinbergs, Iismaa, Freney and Barrow,[2] followed by Johnson and Nishita[12] distillation.

Determination of total sulphur in soils presents problems, both in decomposing the sample without loss of sulphur and in determining the sulphur released in the presence of relatively large amounts of other substances produced or introduced during the decomposition procedure. The present work shows that, provided account is taken of sulphur trioxide evolved with the sulphur dioxide, acceptable results may be obtained by combustion in the high-frequency induction furnace, followed by absorptiometric determination of sulphur as methylene blue.

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Potentiometric Micro Determination of the Sulphate Ion

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In the measurement of fast neutrons, the amount of sulphur dispersed in the special films used is important. To determine their sulphur content a potentiometric titration has been studied in which sulphate ions, obtained by oxidation, are titrated with standard lead nitrate solution. The standard deviation in the titration value for 10-μg amounts of sulphur is lower than 1 per cent. As constant potential is rapidly attained after each addition of titrating solution, an automatic titration is carried out.

THIS method was developed for the determination of micro amounts of sulphur contained in special films used at the Centro Studi Nucleari della Casaccia del Comitato Nazionale per l'Energia Nucleare, Roma, for measuring fast neutrons. These films consist of poly(vinyl alcohol), in which sulphur is homogeneously dispersed[1]; the amounts of sulphur to be determined may be as low as a few tens of micrograms, and the error in their determination must be less than ± 1 per cent.

We have, therefore, modified a method reported in the literature,[2] which consists in titrating the sulphate ion solution with a lead nitrate solution, after addition of potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III), with a platinum wire as measuring electrode and a silver reference electrode.

At the equivalence point, lead hexacyanoferrate(II) precipitates, with a resulting sharp change in the potential of the platinum electrode; the titration is carried out in a water - ethanol (1 + 1) solution.

The modifications introduced into this method, which are discussed below, have resulted in the rapid stabilisation of the electromotive force of the cell after each addition of titrating solution; this has made it possible to perform the titration automatically and to determine very small amounts of sulphur.

EXPERIMENTAL

APPARATUS AND REAGENTS—

A Metrohm E336 Potentiograph (supplied by Metrohm A.G., Herisau, Switzerland) connected with a 1-ml automatic Metrohm E336 microburette was used.

The measuring electrode consists of a 12 × 12-mm platinum plate, which is washed in concentrated nitric acid and heated to whiteness with a blow lamp before use; the reference electrode consists of a silver rod, 1·7 mm in diameter, which is cleaned by abrasion, washed with distilled water and immersed for 4 hours in a freshly prepared solution containing 126 mg of potassium hexacyanoferrate(II) [$K_4Fe(CN)_6.3H_2O$] and 82·2 mg of potassium hexacyanoferrate(III) [$K_3Fe(CN)_6$] in 100 ml; this electrode is washed and kept dry. An electrode prepared in this manner was used for fifteen titrations carried out within 3 days of its preparation.

All of the reagents used were of recognised analytical grade, except the Specpure sulphur (Johnson Matthey Ltd.) used for the determination of the titre of the lead nitrate solution.

PROCEDURE—

The titre of the standard lead nitrate solution is determined by carefully weighing about 10 mg of sulphur into a 1-ml Pyrex-glass ampoule; 0·05 ml of 99 per cent. nitric acid is added and the ampoule sealed after drawing out into a capillary. The ampoule is heated for 10 minutes at 200° C, the sulphur being thus oxidised to sulphuric acid. After cooling, the ampoule is inserted, capillary downwards, into a 25-ml cylinder containing 7 to 8 ml of distilled water; the capillary at the bottom of the ampoule is broken, so that the gas bubbles through the water; the ampoule itself is then broken. The solution and washings from the cylinder are transferred into a dish, a slight excess of ammonia solution is added and the solution evaporated to dryness; the residue is dissolved in distilled water, which is made up to a suitable volume in a calibrated flask.

An aliquot containing the equivalent of between 40 and 100 µg of sulphur is introduced into the titration cell and the volume made up to 18 ml with distilled water, 40 ml of isopropyl alcohol are added, the solution is stirred and the electrodes are introduced. The potential difference is immediately stabilised, and the automatic titration is carried out with a solution containing about 1 g per litre of lead nitrate. The titration rate is about 0·1 ml per minute; the potential drop, at the equivalence point, ranges between 30 and 60 mV. After each titration, the silver electrode is carefully washed with distilled water, dried and stored.

The amount of sulphur contained in a film is determined in the same way. A disc of film whose area is 1 cm^2, which contains an amount of sulphur ranging between a few tens of micrograms and 500 µg, with an organic-matter content of about 1000 µg, is used; if the amount of sulphur present is small enough, 18 ml of distilled water and 40 ml of isopropyl alcohol are added, and the titration is carried out as indicated above.

RESULTS

The results obtained for the standardisation are shown in Table I.

TABLE I

DETERMINATION OF THE STANDARD DEVIATION OF THE METHOD

Amount of sulphur taken, µg	Volume of lead nitrate consumed, ml	Amount of sulphur corresponding to 1 ml of titrating solution, µg per ml
30·24	0·343	88·16
50·40	0·555	90·81
58·20	0·638	91·22
70·56	0·770	91·64
82·15	0·897	91·58
82·50	0·899	91·77

As can be seen, when using amounts of sulphur between 38 and 83 µg, the relative standard deviation of the titre of the standard lead nitrate solution is ±0·6 per cent. We have not determined the relative standard deviation for the film analyses, because the lack of homogeneity of the film gives rise to a greater deviation than that of the analysis; on the other hand, the nitric acid oxidises the poly(vinyl alcohol) to carbon dioxide and water, which do not interfere. Therefore, assuming that the relative standard deviations of the standardisation of the titrating solution and of the titration value for the film solution are equal, then the relative standard deviation is $\pm \sqrt{2 \times 0{\cdot}6^2}$ or ±0·8 per cent. for the determination of sulphur in the film. This value relates to the amount of sulphur contained in the portion of the film destroyed during the analysis; it is therefore strictly applicable only if the disc of film used for measuring the fast neutrons is analysed.

If the piece of film used as a detector has to be preserved, two adjacent discs are cut from the film; one is used as the detector and the other is destroyed in the course of the analysis. The amounts of sulphur found in two adjacent 1-cm^2 discs differ by less than 1 per cent. when films prepared according to the method described[1] are used. The results of the potentiometric determination thus obtained were fully consistent with results obtained from experimental measurements with fast neutrons carried out at the Laboratorio Fisica e Calcolo Reattori of CNEN, C.S.N., Casaccia, Rome.

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Comments on "Determination of Sulphate in the Presence of Soluble Silicate"

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On precipitating barium sulphate in the presence of different amounts of soluble silicate it has been proved that dimethylformamide has no hold-back carrier effect for the silicate as postulated in a previous paper by Azeem.

THE possibility of determining sulphate by precipitation of barium sulphate in the presence of soluble silicate was recently described by Azeem.[1] According to the author, dimethylformamide, used as "a hold-back carrier for the silicate," forms a soluble complex of the type $Si(OH)_4(\text{dimethylformamide})_x$. We have tested the procedure for the possible application of this method to silicate analysis. In his work, Azeem used mixtures of sulphate with "the equivalent amount of sodium silicate." It seemed reasonable to investigate the precipitation of barium sulphate in the presence of different amounts of silicate.

METHOD

All reagents used were of analytical-reagent grade. The weights and glassware used were calibrated. The respective concentrations of the standard solutions of sodium sulphate and sodium silicate were determined by standard methods.[2] The procedure given by Azeem[1] was closely adhered to, the only difference being that tests were carried out to determine the influence of different concentrations of dimethylformamide.

RESULTS

The results obtained on precipitating barium sulphate from solutions containing different amounts of silicate are given in Table I. They were compared by means of the Pseudo-*t*-test[3] by using the range instead of standard deviation. The presence of systematic error was established in experiments 2, 3 and 4, when $t' > t, P = 0{\cdot}95$ and $f = 3$, whereas no systematic error was proved in experiment 1 and, most probably, experiment 5, when $t' < t$, $P = 0{\cdot}95$ and $f = 5$ [where $t' = \frac{(\bar{x} - \mu_o)}{R}$, t is Student's coefficient of distribution, $\bar{x}$ the mean value, μ_o the true value, R the range, P the confidence probability and f the number of degrees of freedom]. It can be concluded from these results that dimethylformamide in the concentration used has no "hold-back carrier" effect if the ratio of sodium sulphate to sodium silicate is 1:10 or higher. Further, there is no difference in results obtained whether dimethylformamide is present or not (see experiments 1 and 5, or 3 and 4).

TABLE I

PRECIPITATION OF SULPHATE FROM SOLUTIONS WITH DIFFERENT SULPHATE-TO-SILICATE RATIO

Sample number	Ratio (w/w) Na_2SO_4: Na_2SiO_3	Na_2SO_4 given, g	Dimethyl-formamide, ml	Na_2SO_4 found, g	Error, per cent.	Number of experi-ments	Range	t'
1	1: 1	0·1890	2	$0{\cdot}1889_5$	− 0·03	6	0·0019	0·03
2	1:10	0·0976	2	$0{\cdot}1012_7$	+ 3·76	4	0·0009	4·1
3	1:60	0·0155	2	$0{\cdot}0184_1$	+18·77	4	0·0005	5·8
4	1:60	0·0155	0	$0{\cdot}0183_6$	+18·45	4	0·0005	5·7
5	1: 1	0·1890	0	$0{\cdot}1907_6$	+ 0·93	6	0·0038	0·46

The influence of increased concentration of dimethylformamide has also been investigated (see Table II). It can be concluded from the results that the amount of barium sulphate precipitated is not affected by the amount of dimethylformamide present (in the range tested).

If the assumption that the complex Si(OH)$_4$(dimethylformamide)$_x$ is formed is correct, then when the dimethylformamide concentration is increased an increased amount of silica would be complexed, which would be shown by the decreased positive error in the amount of barium sulphate. This, however, has not been observed; on the contrary, silica was precipitated from the solutions if 20 ml of dimethylformamide were added.

TABLE II

INFLUENCE OF DIMETHYLFORMAMIDE CONCENTRATION ON THE DETERMINATION OF SULPHATE IN THE PRESENCE OF SILICATE

Weight of Na_2SO_4 is 0·0155 g, ratio of Na_2SO_4 to Na_2SiO_3 is 1 : 60 and volume of solution before precipitation is 200 ml

Dimethyl-formamide, ml	Sodium sulphate Found, g	Sodium sulphate Error, per cent.	Number of experiments
2	0·0184$_1$	+18·77	4
5	0·0179	+15·48	2
10	0·0182	+17·42	2
15	0·0181	+16·77	2
20	Precipitation of silica		

Therefore, it can be concluded that the determination of sulphate in the presence of soluble silicate is made possible, not by the use of dimethylformamide but by the known colloidal properties of silica. The direct determination of sulphate in silicates based on these properties has already been described.[4]

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Rapid X-ray Fluorescence Analysis of a Standard Plant Material

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BOWEN[1] has published an interlaboratory study of the elemental analysis of a standard dried kale powder, by using a variety of analytical techniques. As this study appears to have overlooked the potential of X-ray fluorescence methods for this work, we wish to show how some elements can be readily determined by using published methods[2,3] or simple adaptations of them.

OUTLINE OF METHODS

CALCIUM, POTASSIUM AND SULPHUR[3]—

One gram of appropriately dried powder was dissolved in analytical-reagent grade nitric acid (sp.gr. 1·42), filtered and made up to 50 ml with water. Peak intensities were compared with appropriate aqueous standard intensities.

STRONTIUM, RUBIDIUM AND ZINC[2]—

The dried powder was pressed into a 1-inch diameter disc. Peak and background intensities were measured and compared with those from appropriate aqueous standards. Scattering factors[2] were determined for this sample, and for water at each wavelength used.

RESULTS

The mean of duplicate measurements on a single sample is quoted below, together with the mean and standard deviation reported by Bowen.[1]

Element	X-ray fluorescence method, p.p.m.	Bowen's mean and standard deviation, p.p.m.
Calcium	42,370	41,400 ± 2230
Potassium	24,770	24,630 ± 1218
Sulphur	18,000	16,010 ± 2648
Rubidium	57	52·8 ± 6·25
Strontium	101	84·1 ± 10·7
Zinc	35	31·88 ± 4·82

The X-ray results agree with the mean of different methods within one standard deviation of that mean with the exception of strontium where the difference is about 1·5 standard deviations. This relatively large difference is difficult to explain on the basis of errors in the X-ray determination, as this technique has been well tested previously.[2] Further, the X-ray determination of strontium is closely analogous to that of rubidium, where excellent agreement was obtained.

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Complicating Rôle of Reactions Induced by Isomeric Transitions in Neutron-activation Analysis for Bromine-82 and Iodine-130

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NEUTRON-ACTIVATION analysis has been generally used for the determination of numerous elements in a large variety of inorganic, organic, biological and pharmaceutical materials.[1,2,3,4]

In activation analysis, the sample is exposed to a thermal or fast-neutron flux, and the element to be determined acquires a radioactive label. The instances in which the activated atoms are generated in metastable isomeric states and decay to longer-lived isotopes are the principal concern of this paper.

In the analysis for bromine-82 and iodine-130, which have isomeric states,[5,6,7] it is important to take cognisance of possible isomeric-transition induced reactions of the bromine-82 and iodine-130 in the sample (and possibly the sample container), and with solvent and solute, if the sample must be transferred from the sample vessel in which it was irradiated to carry out wet-chemical procedures for the removal of interferences. Although numerous analytical techniques have been developed for the determination of bromine and iodine,[1,2,3,4,8] it is now apparent, and necessary, that the analyst should consider the possible influence of isomeric-transition induced reactions on his results. Radiative neutron-capture by bromine-81 results in 91 per cent. of the activated atoms being generated as bromine-82*m* (half-life 6 minutes), which decays by isomeric transition to bromine-82 (half-life 35·3 hours). As an example, the scheme of Belkas and Souliotis[8] for the simultaneous determination of iodine and bromine in urine by neutron-activation analysis may be considered. If bromine-82 separation is begun immediately after removal of the sample from the reactor, considerable bromine-82 activity may be discarded before the assay because of isomeric-transition reactions of bromine-82 with the carbon tetrachloride used in subsequent solvent extractions. That is, hot-atom isomeric-transition reactions may incorporate halogen into chemical forms that do not lend themselves to desirable chemical separation. The hot-atom chemistry of bromine-82 and iodine-130 reactions in several organic solvents has been discussed,[9,10,11,12] and evidence is clearly presented to indicate that at least 50 per cent. of the activity resulting from bromine-82*m* to bromine-82 isomeric-transition reactions at dilute bromine concentrations will react with carbon tetrachloride. However, by waiting until the short-lived metastable isotope has decayed (about 10 half-lives) before performing any chemical operations with the sample, complicating isomeric-transition induced reactions are eliminated. With long-lived metastable isomers, *e.g.*, bromine-80*m* (half-life 4·5 hours), contributions from isomeric-transition reactions are minimised by performing operations with the sample in a time interval that is short compared with the half-life of the metastable species being analysed.

The neutron-activation analysis of fission-produced iodine-129 in the atmosphere, and in biological systems, as a result of atomic testing fall-out, has been of recent interest. As the subjection of iodine-129 to a neutron flux results in 61 per cent. of the activated atoms being generated as iodine-130*m* (half-life 9 minutes), many of the techniques developed for the neutron-activation analysis of iodine-128 (formed directly by neutron-capture) may not be applicable without making proper modification to the analysis of iodine-130 (half-life 12·4 hours).

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552 *Analyst*, August, 1968, Vol. 93, *pp*. 552–554

Communications

Manuscripts are *not* subjected to the usual examination by referees. Inclusion of a Communication is at the Editor's discretion; a manuscript not accepted as a Communication may, if the author wishes, be submitted to the Editorial Committee as a possible paper and subjected to the usual scrutiny by referees.

MEASUREMENT OF GAS FLOW-RATES AND CALIBRATION OF FLOW METERS FOR FLAME SPECTROSCOPY

RECENT interest in analytical flame emission and absorption spectroscopy as methods of trace analysis has resulted in extensive additions to the literature on the subject. Unfortunately, in much of the recently reported work the amounts of fuel and oxidant gases used are quoted in such a manner that the values are both arbitrary and meaningless to other workers. Although Mansfield and Winefordner[1] have attempted to clarify the situation, there appears to be no simple, practical description available of the reliable and economical measurement of gas flow-rates by the flame spectroscopist so that they may be of immediate value to other workers. Flame-spectroscopy textbooks devote little space to the subject, and texts and journals on flow measurement itself are usually written for the engineer. The gas-metering devices most commonly used in analytical flame spectroscopy are pressure gauges or rotameters, or a combination of both. When used correctly, and in conjunction with each other, these two components can provide all the information required on gas flow-rates. It is our experience, however, that it may not always be apparent how and when the calibrations marked on a rotameter are applicable, and why the correct positioning of the rotameter in the flow-line is important. We would like to outline how simple and inexpensive apparatus may be used most economically to obtain reliable flow-rate results of use to other analytical chemists engaged in flame spectroscopy.

Simple laboratory rotameters (such as those supplied by the Rotameter Co. Ltd., Croydon, Surrey, and with commercial flame spectrophotometers) usually consist of a vertically mounted tapered glass tube containing a metal float. Needle valves may be integrally mounted at one or both ends of the tube. The gas-flow velocity (volumetric flow-rate) is measured from the height the float attains in the tube when the upward drag of the gas on the float and its buoyancy force balance the downward force of gravity on the float. The rotameter tube usually carries calibration markings (in litres per minute). This calibration only applies for a particular gas at a given pressure and temperature. This has led to a common supposition that different rotameters must be purchased for use with different gases, and that calibration curves must be prepared to allow for variations in temperature and pressure of the gas being used. In fact, change in the nature, pressure or temperature of the gas merely alters the density and viscosity of the fluid passing through the rotameter, and it is possible to calibrate one instrument so that it may be used over a wide range of densities and viscosities.[2] In practice this is rather tedious, as a calibration graph is required for each reading on the scale because of the taper of the tube. Results that are almost as accurate, however, and are equally useful for the purposes of analytical flame spectroscopy, can be obtained by the simpler method outlined below.

1. When there are several commercial flame spectrophotometers in the laboratory, each with its own set of valves and uncalibrated gauges supplied with the instrument, it is very useful to purchase a set of auxiliary rotameters calibrated at a pressure of one atmosphere for, *e.g.*, air at 15° C, and covering a suitable range of flow-rates (*e.g.*, 0 to 2, 1 to 10 and 2 to 20 litres per minute). These can then be used to calibrate the existing flow-lines simply by attaching them to the end of the system (*i.e.*, to the burner), leaving the upper end of the rotameter open to the atmosphere, and with the manufacturers' specific-gravity correction graphs for gases other than air. Any temperature corrections necessary may be made as described below, but in our experience the temperature for most gases is usually within 5° to 10° C of the calibration temperature. The error introduced by variation in temperature would then probably be within the accuracy of the rotameter calibration.

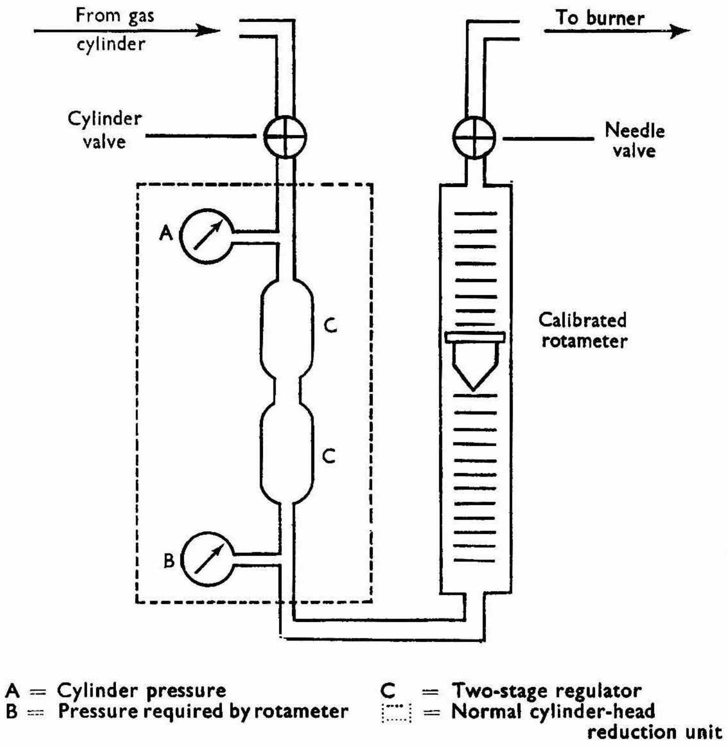

Fig. 1. Recommended rotameter arrangement for use in the flow-line to an atomiser or burner

2. When rotameters must be purchased on installation of a flame spectrophotometer, it is most convenient to purchase calibrated rotameters that can be left permanently in the flow-line to the burner, and the pressure specified for the calibration must be chosen carefully with respect to the flow-rates likely to be required. We have found 5 p.s.i.g. and 25 p.s.i.g. suitable for fuel and oxidant gases, respectively. *Although the pressure at the atomiser or burner jets will vary with the gas flow-rate used, it is possible to isolate the rotameter in each line behind a valve so that the calibration pressure is always maintained at the rotameter.* In this way the tedious correction for different pressures is avoided. The rotameter can then be used for any gas at any flow-rate within its range by simple reference to a single manufacturer's specific-gravity correction graph to allow for a change of gas from the calibration gas. A simple but wholly adequate arrangement is shown in Fig. 1. It will be seen that, apart from a rotameter and needle valve, the only equipment required is the cylinder-head reduction-valve regulator assembly usually used with cylinder gases. This conventional two-stage reduction-valve assembly (as supplied by British Industrial Gases Ltd., Enfield, Middlesex) not only has the required pressure gauge so that the rotameter calibration pressure may be accurately set, but is also fitted with an "automatic" diaphragm, which will maintain the rotameter pressure at the required value no matter what flow-rate is set by using the needle valve. Note that—

(*a*) There should be no valves between the regulator and the rotameter, as this would prevent the regulator maintaining a constant pressure at the rotameter.

(*b*) With this arrangement the line pressure after the needle valve may be any value up to that for which the rotameter is calibrated. The highest value required should therefore be known when a calibrated rotameter is to be acquired.

(*c*) A rotameter fitted with a needle valve at the top (outlet) is most convenient; a needle valve at the inlet cannot be used with this arrangement, because any adjustment to alter the flow-rate will also alter the pressure at the rotameter.

(*d*) Most rotameters are calibrated in "free litres per minute," *i.e.*, the volume that the gas would occupy at atmospheric pressure rather than the calibration pressure. These units could be used for all published values of gas flow-rates. The pressure at which the oxidant gas is supplied to the atomiser should also be quoted. This is facilitated by the fact that most instruments are equipped with a suitable pressure gauge that can be used for all gases and temperatures.

Temperature correction—It is our experience that most compressed cylinder gases attain a temperature of 15° to 25° C at the rotameter, so that a rotameter calibrated at 15° C is adequate for most purposes. If a correction for temperature is required, however, the method suggested by Ower and Pankhurst[3] is simple to use and sufficiently accurate with most common gases and flow-rates. These authors point out that with modern rotameter designs and nearly all gases, the rotameter reading is virtually independent of the viscosity of the gas, and it is only the density of the gas that changes with the temperature. Further, it may be shown that for any given rotameter—

$$\frac{Q_1}{Q_2} = \sqrt{\frac{d_2}{d_1}}$$

where Q_1 and Q_2 are the volumetric flow-rates and d_1 and d_2 are the densities of the gases. Therefore, if the reading on the rotameter is Q with a gas of density d_2 and the instrument was calibrated at density d_1—

$$\text{true flow-rate} = Q.\sqrt{\frac{d_1}{d_2}}\ .$$

The change of density with temperature may readily be found in the literature for most common gases. Finally, we would mention that if only occasional flow-rate measurements are necessary, and no calibrated flow meter is available, the "soap-film" method described by Barr[4] and Gooderham[5] is suitable for most laboratory purposes. This method is easily followed, and requires no special equipment other than a suitable glass tube and a stop-clock.

Some uniformity in the manner in which meaningful gas flow-rate data are obtained and reported in analytical flame spectroscopy is clearly desirable. It is our hope that these observations will be of interest to analytical chemists engaged in this work.

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Book Reviews

EXTRA PHARMACOPOEIA (MARTINDALE). Twenty-fifth Edition. Edited by R. G. TODD. Pp. xxviii + 1804. London: Pharmaceutical Press. 1967. Price 50s.

This twenty-fifth edition of "Martindale" departs from the more recent practices of the Extra Pharmacopoeia in being issued in one volume, much of the type of information previously appearing in Volume II of earlier editions having been omitted. It is intended to publish a series of Extra Pharmacopoeia Companion Volumes that will deal with the subjects omitted, and particularly with analytical and biochemical matter relating to the substances given in the Extra Pharmacopoeia.

The volume has been designed primarily for the immediate needs of practising physicians and pharmacists, and although analytical information does not now appear, it would be difficult to imagine that the analyst engaged in the examination of drugs and galenicals could possibly manage without the Extra Pharmacopoeia as a reference book, for which it is primarily intended.

The book was published in February, 1967, and yet, by continuous planning, abstracts as late as the last quarter of 1966 and details of proprietary products as recent as November, 1966, have been included. Eighty per cent. more material has been added in this new edition, and the page size has been increased by more than fifty per cent. The master index, very thoroughly referenced and cross-referenced, occupies more than one tenth of the number of pages.

The format, size of pages and thickness of paper have been very carefully chosen to produce a volume, not too unwieldy in size for so much information, yet legible and enduring.

There are three main parts to the book. Part 1 contains some 2600 monographs of substances, and is divided into 169 chapters, which are arranged in order of substances with the same pharmacological action, therapeutic or pharmaceutical use, under the title of a typical member of the group. Part 2 consists of a series of short monographs on some 600 drugs and ancillary substances, together with a Supplementary List of Proprietary Preparations and a list of Proprietary Test Substances, which, for a number of reasons, are not included in Part 1.

The formulae of 1600 proprietary medicines of the type advertised to the public, and usually supplied over the counter on demand, make up Part 3.

Botanical names follow the International Rules of Botanical Nomenclature, chemical names are in accordance with the current practice in Great Britain and generally follow the recommendations of the Chemical Society.

In addition to indicating the inclusion of a substance in the British Pharmacopoeia and the British Pharmaceutical Codex, many foreign pharmacopoeias and related publications have been examined and a list given of those in which a substance appears.

Among other information given are chemical and physical properties, incompatibilities and stability of a drug. Pharmacological and therapeutic information on the toxic effects, antidotes, contra-indications and uses of a drug are elaborated and expanded by abstracts of original papers and reviews; where this would be too lengthy, references are given. There is extremely wide coverage of drugs and galenicals, British and foreign, new and old. Products that have long disappeared from pharmacopoeias, those which have not yet been included and even some that have been marketed after the publication of the Extra Pharmacopoeia are given.

Since the analyst of drugs in consultancy or industry works for a purpose and not in a vacuum, this publication is likely to be of considerable use. The editor and his staff are to be congratulated on what The Pharmaceutical Press rightly claims "Martindale" to be: "The world's most comprehensive guide to drugs and medicines in current use complete in one volume. . . ."

H. E. BROOKES

SEPARATION TECHNIQUES IN CHEMISTRY AND BIOCHEMISTRY. Edited by ROY A. KELLER. Pp. xvi + 415. New York: Marcel Dekker Inc. 1967. Price 115s.

In June, 1966, the Nineteenth Annual Summer Symposium on Analytical Chemistry, entitled "Separation Techniques," was held, outside the United States for the first time, at the University of Alberta, Edmonton, Alberta, Canada.

A total of 28 papers was presented during the two and a half days of the symposium. This book is the collected proceedings of that symposium, which was sponsored by the Division of Analytical Chemistry of the American Chemical Society and *Analytical Chemistry*. Most of the papers have already been published in issues of *Separation Science*, and perhaps it is thus unfortunate that this book has been published so long after the symposium. However, this is a criticism that can be levelled at a great many books containing symposium proceedings, often not being a fault of the publishers and printers, either.

Naturally the book reflects the importance of chromatography in separation techniques because 24 of the papers deal with the former technique, including both theory and practice.

However, as this book is really the report of a conference, one cannot, justifiably, pass criticism on its contents.

This book can be recommended to those who do not have access to the journal *Separation Science*. However, if access is possible, then this is a high price to pay for a conference report.

G. NICKLESS

PRACTICAL CLINICAL BIOCHEMISTRY. By HAROLD VARLEY, M.Sc., F.R.I.C. Fourth Edition. Pp. x + 802. London: William Heinemann Medical Books Ltd.; New York: Interscience Books Inc. 1967. Price 70s.

"Varley" is well known to clinical biochemists, it is their bench Bible and, far from depending on reviews for their guidance, many will have placed their orders at the time this new edition was first advertised.

The practical problems of clinical chemistry are, almost exclusively, analytical. Not only are methods required for some rather unusual substances (*e.g.*, galactose, acetoacetic acid, creatine, creatinine, fibrinogen, uric acid, five varieties of lactate dehydrogenase, pregnanetriol) in quantities varying from micrograms to grams, but these methods must be free from interference from a wide range of known substances in health and an even wider range of largely unknown substances in the presence of disease. Other analysts, to whom the book may be of considerable help, may, however, be less well acquainted with it, and may even have been discouraged by the title from opening it. While the precise circumstances may not be repeated in other fields of analysis, the same problems exist in several.

Clinical chemists, too, have been prominent in developing automatic methods of analysis and several (for albumin, calcium, chloride, glucose, sodium, potassium and urea) are included in this edition and the introductory chapters, which have always been valued by new technicians for their succinct presentation of analytical apparatus and techniques, now describe aids to multiple analysis such as the AutoAnalyzer, automatic pipettes and diluters.

Scientifically, clinical chemistry was once viewed with reserve and, although it is a long time since this was justified, it is interesting to note that the methods developed 40 years ago are those most in need of replacement (*e.g.*, the picrate method for creatinine, diazo methods for bilirubin and molybdophosphate methods for glucose). In the case of glucose a newer orthotolidine method is offered, but recent warnings of the carcinogenic nature of this and other reagents came too late to be included in this edition. On the other hand, many methods developed in recent years (such as calcium by chelometric titration, sodium and potassium by flame photometry and some enzyme and specific protein determinations) are much more satisfactory.

Harold Varley retires this year from his post as Biochemist to the Manchester Royal Infirmary. If his leisure is to be spent in preparing a further edition, he should try to preserve the nice balance between methodology and interpretation that characterises the book. Perhaps he may find the courage to discard the old Esbach method for protein in urine and fermentation and osazone tests for sugars, to make room for the new. If he is sentimental, perhaps these may be included in a chapter on the development of clinical chemistry, a topic on which he (and the reviewer) has discoursed elsewhere.

There is no serious English competitor to this book and its American rival is three times as costly; the success of this new edition is assured.

D. N. RAINE

ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGION. Edited by DR. L. LANG. Volume VIII. Pp. vii + 7–416. Budapest: Akademiai Kiado. 1967. Price 135s.

ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGION. Edited by DR. L. LANG. Volume IX. Pp. vi + 7–416. Budapest: Akademiai Kiado. 1967. Price 135s.

Volume VIII contains curves for many aminoanthraquinones, barbituric acid derivatives, benzoylacetic acid derivatives, hydantoins and silicon-organic compounds. There are also numerous curves for pyridine, pyrimidine, triazine, triazole and thiazole and thiohydantoin derivatives. In this volume pharmaceutical products are again prominent.

Volume IX begins with spectra for chromium-, molybdenum- and tungstenhexacarbonyls and hexamethylbenzene tungstentricarbonyl. This is followed by a large number of fairly simple substitution products of benzene. Numerous curves appear for phenylsilanes, siloxanes, pyridine, pyridone, pyridylamine and pyridine-carboxylic acid derivatives. There are also groups of pyrimidine, pyrimidone, quinoxaline, triazine and thiazole derivatives.

The two volumes follow the established pattern for the series and record with considerable accuracy the ultraviolet absorption curves for a mixed bag of 400 compounds. R. A. MORTON

Summaries of Papers in this Issue

Chromatographic Methods for the Identification of the New Hallucinogen, 4-Methyl-2,5-dimethoxy-α-methylphenethylamine, and Related Drugs

Thin-layer and gas-chromatographic methods are described for the detection of 4-methyl-2,5-dimethoxy-α-methylphenethylamine in the sub-microgram range. Chromatographic criteria of identity for this new hallucinogen and for the related amines, amphetamine, methamphetamine and mescaline, and the hallucinogens, dimethyltryptamine and bufotenine, are also reported.

K. GENEST and D. W. HUGHES

Research Laboratories, Food and Drug Directorate, Ottawa, Ontario, Canada.

Analyst, 1968, **93**, 485–489.

Di-2-pyridyl Ketoxime, a New Reagent for the Rapid Gravimetric Determination of Palladium

Di-2-pyridyl ketoxime is proposed for the gravimetric determination of palladium. The chelate is precipitated over a pH range of between 3 and 11 and weighed as $Pd(C_{11}H_8ON_3)_2$. An extensive study of foreign ions and analytical conditions for precipitation indicates the procedure to be widely applicable, rapid and simple.

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Analyst, 1968, **93**, 490–493.

Application of 1-Phenyl-4-phenylamino-1,2,4-triazolium Chloride to the Determination of Cobalt(II)

A new reagent, 1-phenyl-4-phenylamino-1,2,4-triazolium chloride, is proposed for the determination of cobalt(II) by extraction into 1,2-dichloroethane and spectrophotometric determination at 626 nm of the ion-association compound formed in the presence of an excess of ammonium thiocyanate. The composition of the species extracted has been determined by applying the continuous variation method to the aqueous - organic phase system, and by determining the chemical composition and molecular weight of the compound precipitated from the aqueous phase.

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Analyst, 1968, **93**, 494–497.

The Application of Polarography and Related Electroanalytical Techniques to the Determination of Sodium Diethyldithiocarbamate

Cathodic stripping analysis has been shown to be an extremely sensitive technique for the determination of compounds that form insoluble mercury salts. The experimental parameters governing the application of this technique have been studied and applied to the determination of sodium diethyldithiocarbamate. The results obtained were compared with those from conventional d.c. polarography, a.c. polarography and linear potential-sweep chrono-amperometry.

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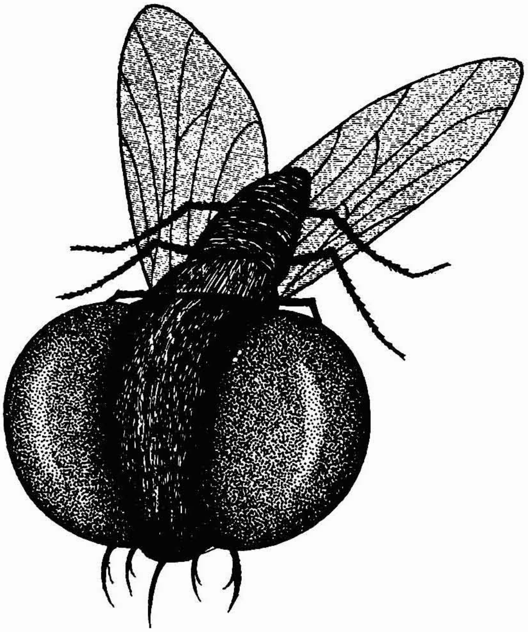
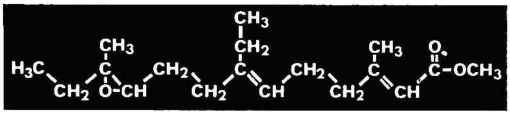
Chemistry Department, Imperial College of Science and Technology, London, S.W.7.

Analyst, 1968, **93**, 498–506.





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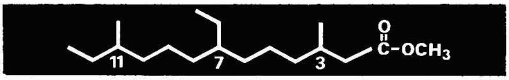

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A Field Method for the Determination of Ozone in the Presence of Nitrogen Dioxide

A method has been developed for the determination of ozone in air in the presence of nitrogen dioxide. Samples of the test atmosphere are drawn, in parallel, through neutral, buffered potassium iodide solutions at 2 litres per minute for 20 minutes. One sample, prior to its passage through the iodide solution, is drawn through a cotton-wool plug. This removes the ozone, and the iodine liberated is a measure of the nitrogen dioxide present, expressed in terms of ozone equivalents. The iodine liberated by the other sample is a measure of the total oxidant, ozone *plus* nitrogen dioxide, also expressed as ozone equivalents. After addition of starch the iodine liberated by each sample is determined visually against prepared colour standards. The difference between the two readings obtained is a measure of the ozone present. The method enables from 0·1 mg m^{-3} (0·05 p.p.m. v/v) of ozone in air, in the presence of up to 9 mg m^{-3} (5 p.p.m.) of nitrogen dioxide, to 0·8 mg m^{-3} (0·4 p.p.m.) of ozone in air, in the absence of nitrogen dioxide, to be determined. The procedure is relatively simple and the time required for a complete analysis is about 30 minutes.

I. C. COHEN, A. F. SMITH and R. WOOD

Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, **1968**, **93**, **507–517.**

Molecular-emission Spectroscopy in Cool Flames

Part III. The Emission Characteristics of Tin in Diffusion Flames

Tin can be determined in the range 3 to 3000 p.p.m. by molecular-band emission from the SnH species in a nitrogen - hydrogen diffusion flame. The emission at 609·5 nm, which is almost line-like, gives a limit of detection of 1·5 p.p.m. of tin. Spectral interference from sodium is eliminated by use of a didymium filter. The presence of oxygen gives rise to a much broader spectrum, caused by tin(II) oxide formation, with a visual limit of detection of 5 p.p.m. of tin. Atomic emission can be observed only in the presence of alcohols, *e.g.*, isopropyl alcohol, but a high concentration of ground-state tin atoms exists in the diffusion flame. Mechanisms are discussed to explain the production of tin atoms, SnH and the resonance-line emission.

R. M. DAGNALL, K. C. THOMPSON and T. S. WEST

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

Analyst, **1968**, **93**, **518–521.**

The Determination of Beryllium by Thermal-emission and Atomic-fluorescence Spectroscopy in a Separated Nitrous Oxide - Acetylene Flame

The determination of beryllium by thermal-emission and atomic-fluorescence spectroscopy in a separated nitrous oxide - acetylene flame has been investigated. The high temperature, reducing nature and low background of this type of flame permit the determination of down to 0·25 and 0·03 p.p.m. of beryllium in aqueous solution by measurement of thermal emission and atomic fluorescence, respectively. A beryllium microwave-excited, electrodeless discharge tube was used for excitation of the atomic fluorescence. The optimum conditions for both techniques have been investigated, and the effects of other cations and anions studied.

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

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

Analyst, **1968**, **93**, **522–527.**

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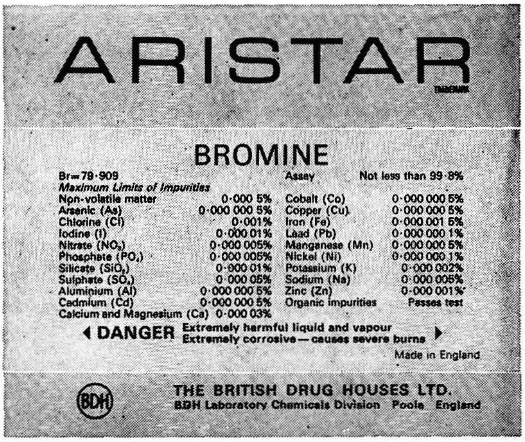

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Spectrophotometric Determination of Iron(III) Ions with 2,4-Dihydroxybutyrophenone

The colour reaction between iron(III) and 2,4-dihydroxybutyrophenone has been studied to determine the optimum conditions for the analytical use of this reagent. The strongest colour developed at pH 2·9 to 3·0, and the complex exhibits an absorption maximum at 470 mμ. The composition of the complex is 1 to 1, as indicated by mole-ratio studies. The absorbance of the solution at 470 mμ obeys Beer's Law in the iron(III) concentration range 1·0 to 56·0 p.p.m. and the sensitivity is 0·074 μg per ml of the iron(III) solutions. The reagent is fairly selective for iron.

Miss M. H. GANDHI and MAHENDRA N. DESAI

Chemistry Department, University School of Sciences, Gujarat University, Ahmedabad 9.

Analyst, 1968, **93**, 528–531.

The Determination of Iron(II) Sulphide in Soil in the Presence of Iron(III) Oxide

Hydrogen sulphide is partially oxidised by iron(III) when soils containing sulphide and iron(III) oxide are acidified. Satisfactory recoveries of hydrogen sulphide are obtained by using a solution of tin(II) chloride in hydrochloric acid to decompose the sulphide.

G. PRUDEN and C. BLOOMFIELD

Rothamsted Experimental Station, Harpenden, Herts.

Analyst, 1968, **93**, 532–534.

A Titrimetric Method for Determining Total Sulphur in Mineral Soils

A rapid method for the determination of total sulphur in mineral soils is described. The various sulphur compounds in soil are first oxidised to sulphate by potassium dichromate in phosphoric acid, and the sulphate thus formed is then reduced to sulphur dioxide by heating with activated charcoal. The evolved sulphur dioxide is trapped in hydrogen peroxide, barium perchlorate added to the resulting sulphuric acid to precipitate barium sulphate, and the excess of barium determined by titration against standard potassium sulphate, with sulphonazo III as indicator. The proposed method gave acceptable results when tested on pure compounds and on soils of known sulphur content. No interferences are to be expected from normal soil constituents.

D. S. JENKINSON

Pedology Department, Rothamsted Experimental Station, Harpenden, Herts.

Analyst, 1968, **93**, 535–539.

Determination of Total Sulphur in Soil by Using High-frequency Induction Furnace Equipment

A method is described for the determination of total sulphur in soils and silicate minerals by combustion in a high-frequency induction furnace. Oxides of sulphur are absorbed in a solution of sodium hydroxide giving sulphate and sulphite. Reduction subsequently converts these into hydrogen sulphide, which is determined by a colorimetric methylene-blue method. Preliminary tests with soils showed that if the only combustion product determined is sulphur dioxide, then low and inconsistent values are obtained.

Values for soils and several mineral reference samples are compared with those obtained by an acid-digestion method.

P. L. SEARLE

Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt, New Zealand.

Analyst, 1968, **93**, 540–545.

Potentiometric Micro Determination of the Sulphate Ion

In the measurement of fast neutrons, the amount of sulphur dispersed in the special films used is important. To determine their sulphur content a potentiometric titration has been studied in which sulphate ions, obtained by oxidation, are titrated with standard lead nitrate solution. The standard deviation in the titration value for 10-μg amounts of sulphur is lower than 1 per cent. As constant potential is rapidly attained after each addition of titrating solution, an automatic titration is carried out.

G. C. CORTELLESSA

Laboratorio Fisica e Calcolo Reattori - CNEN - C.S.N., Casaccia C.P. 2400, Roma, Italy.

and C. A. NAPOLI

Gruppo Diffrazione e Spettroscopia dei Neutroni CNEN - CCR Euratom - Ispra (Varese), Italy.

Analyst, **1968**, **93**, 546–547.

Comments on "Determination of Sulphate in the Presence of Soluble Silicate"

On precipitating barium sulphate in the presence of different amounts of soluble silicate it has been proved that dimethylformamide has no hold-back carrier effect for the silicate as postulated in a previous paper by Azeem.

F. VLÁČIL and J. KOUCKÝ

Department of Analytical Chemistry, Institute of Chemical Technology, Praha 6, Czechoslovakia.

Analyst, 1968, **93**, 548–549.

Rapid X-ray Fluorescence Analysis of a Standard Plant Material

Results are reported for six elements by methods not included in Bowen's inter-method survey. With the exception of strontium, all results are within one standard deviation of Bowen's mean.

K. P. CHAMPION and R. N. WHITTEM

Australian Atomic Energy Commission Research Establishment, Sutherland, New South Wales, Australia.

Analyst, 1968, **93**, 550.

Complicating Rôle of Reactions Induced by Isomeric Transitions in Neutron-activation Analysis for Bromine-82 and Iodine-130

In the neutron-activation analysis for bromine-82 and iodine-130, which have isomeric states, it is necessary to take cognisance of possible isomeric transition reactions of the bromine-82 and iodine-130 in designing wet-chemical procedures for the removal of interferences.

R. M. LAMBRECHT and E. P. RACK

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508.

Analyst, 1968, **93**, 550–551.

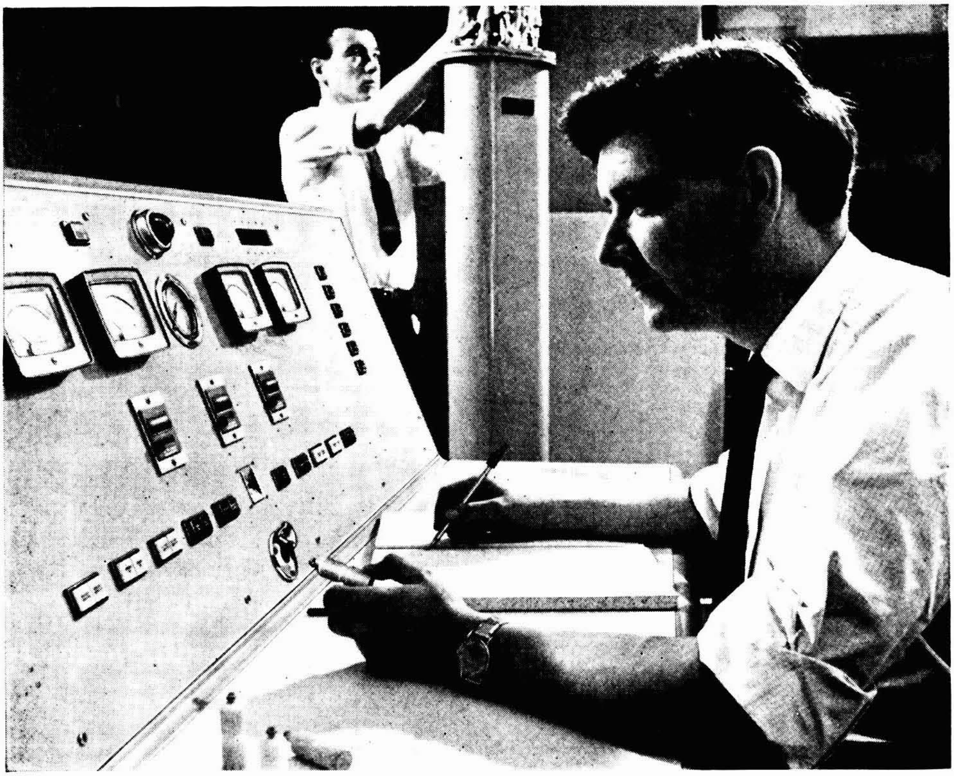
Measurement of Gas Flow-rates and Calibration of Flow Meters for Flame Spectroscopy

Communication

G. F. KIRKBRIGHT and M. SARGENT

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

Analyst, 1968, **93**, 552–554.



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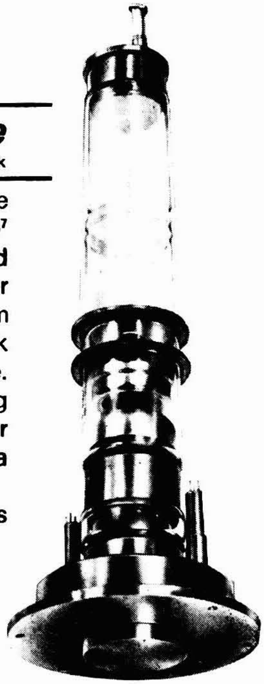

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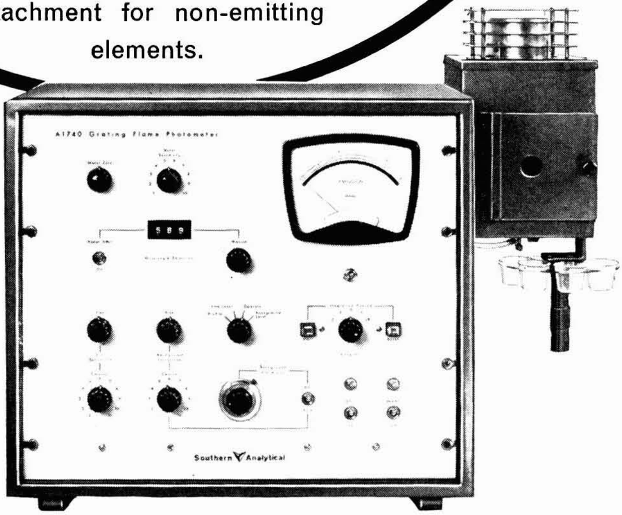
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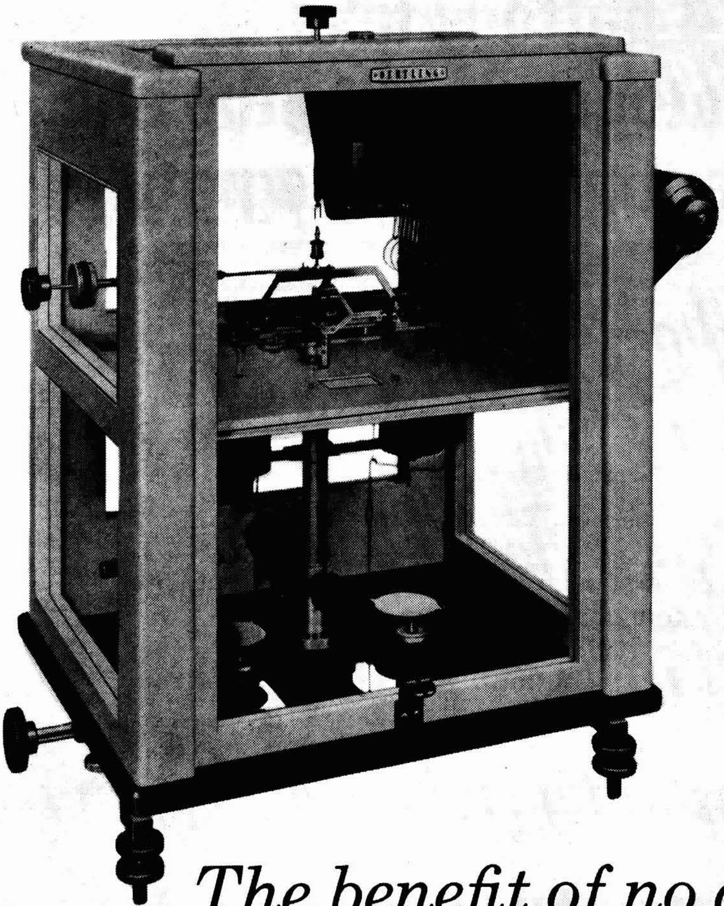

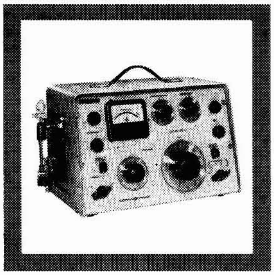

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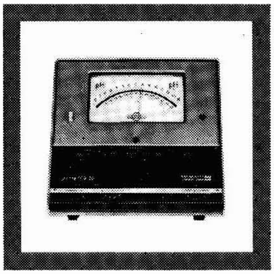

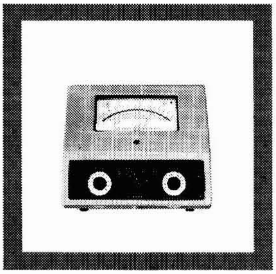

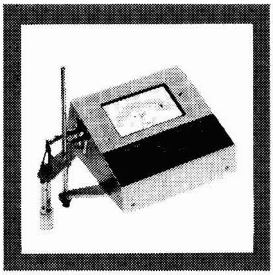

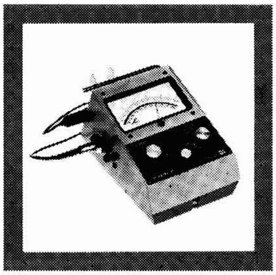

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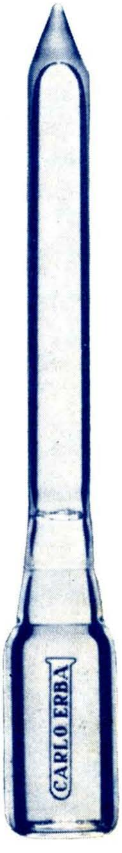
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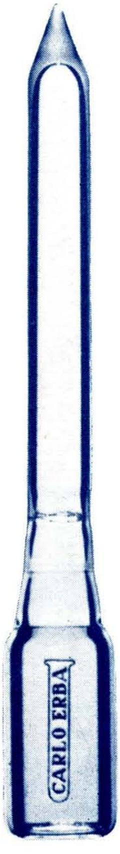
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THE ANALYST

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