

# The ANALYST

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# THE ANALYST

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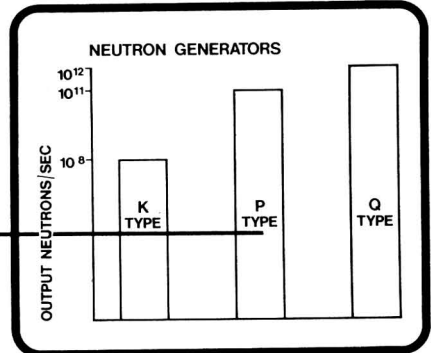
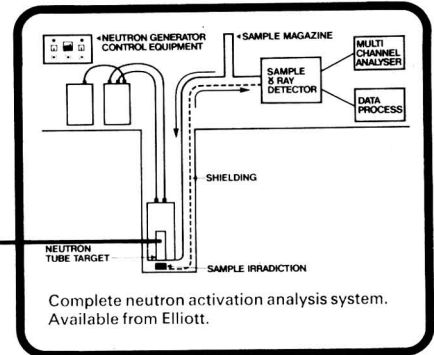
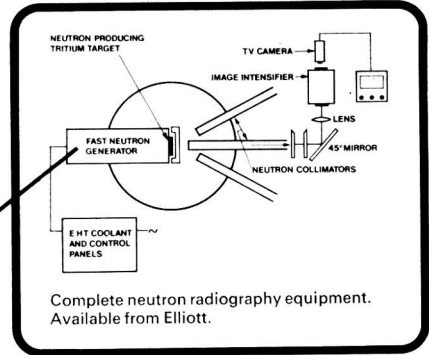
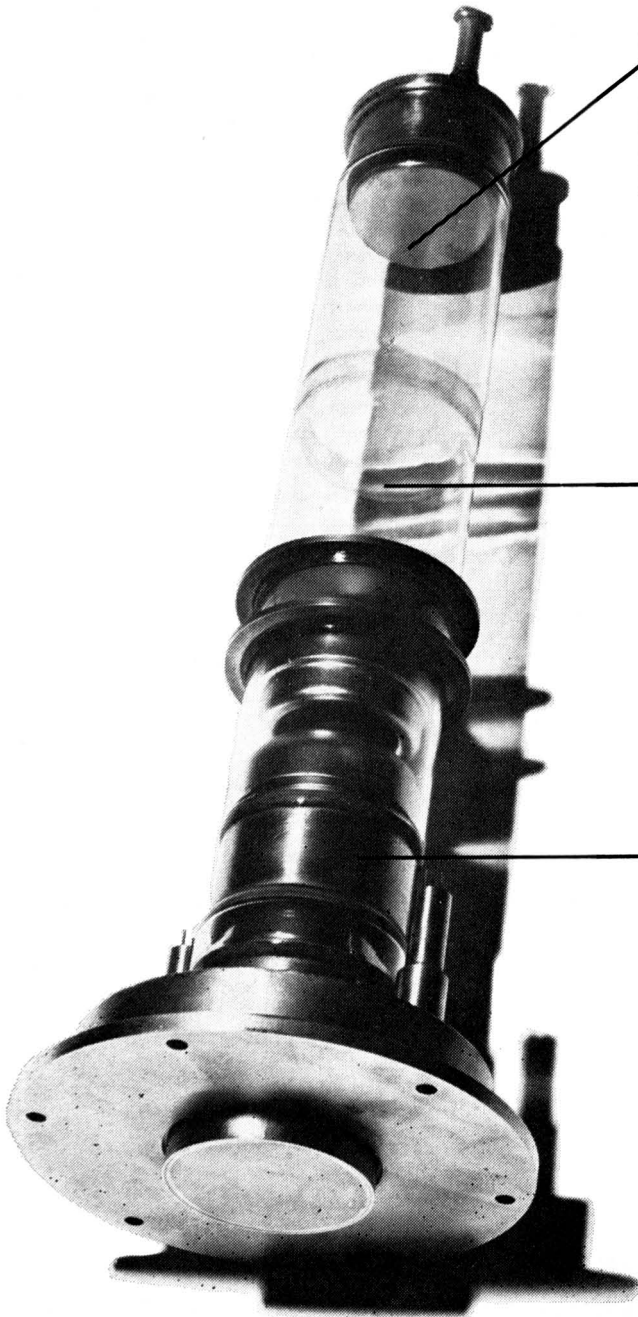
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## Summaries of Papers in this Issue

### The Spectrographic Determination of Impurities in Copper-base Samples of Small Dimensions

Serious problems arise in the point-to-point spectrographic analysis of copper-base materials if only wire or thin-sheet samples are available. In the procedure recommended in this paper, the sample is converted into oxide, transferred to a graphite cup of optimum dimensions, then examined spectrographically. Standard oxide samples are prepared in a similar way (from high-purity reagents) and excited, and resulting reference spectra are used to evaluate the impurities in copper, brass, phosphor and aluminium bronze, cupro-nickel, nickel-silver and Everdur. Densities of the recommended impurity lines for each of these materials are in remarkably close agreement at all comparable impurity levels.

The validity of the proposed method has been substantiated by a comparison with similar analytical results obtained by alternative, often time-consuming, procedures.

A wide range of impurities, down to about the 10 p.p.m. level, can be determined in a single sample within 90 minutes, and several samples can be analysed concurrently.

**W. T. ELWELL and D. M. PEAKE**

Research and Development Department, Imperial Metal Industries Limited, Witton, Birmingham.

*Analyst*, 1971, **96**, 465-474.

### The Spectrophotometric Determination of Tungsten with Thiocyanate

#### Part III. Moderating the Interference by Molybdenum in the Determination of Tungsten in Steel

Molybdenum in excess of 0.3 per cent. w/w interferes in the determination of tungsten in low tungsten steels ( $W < 0.25$  per cent. w/w) with thiocyanate because of a molybdenum - iron inter-element effect. Two procedures are described which overcome this limitation. In the first procedure tungsten(VI) and molybdenum(VI) are extracted into chloroform as benzoin  $\alpha$ -oxime complexes prior to the determination of tungsten. In the second procedure iron is extracted from the tungsten and molybdenum into isobutyl methyl ketone. Up to 4 and 25 per cent. w/w, respectively, of molybdenum in the steel can be tolerated when these procedures are used.

**A. G. FOGG, T. J. JARVIS, D. R. MARRIOTT and D. THORBURN BURNS**

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire.

*Analyst*, 1971, **96**, 475-479.

### The Determination of Lithium, Sodium and Potassium in Geological Materials by Atomic-emission Spectrophotometry with the Nitrous Oxide - Acetylene Laminar-flow Flame

A straightforward method is described for the determination of lithium, sodium and potassium by atomic-emission spectrophotometry on an acidic solution of the sample without separation or concentration. In routine application detection limits of 0.002, 0.01 and 0.01 per cent., respectively, have been obtained with no spectral or chemical interferences. Results are presented for eight standard samples, and long-term relative standard deviations of 2.4 per cent. (lithium), 1.7 per cent. (sodium) and 2.5 per cent. (potassium) have been found on a B.C.S. firebrick.

By using wavelength scanning the determination of trace amounts of lithium has been demonstrated, with a detection limit of about 0.1 p.p.m. in the sample. If blank problems can be controlled the direct determination of sodium and potassium at the parts per million level should be possible even for limestones.

**M. A. HILDON and W. J. F. ALLEN**

Roan Consolidated Mines Limited, Chibuluma Division, RCM Research and Development Department, Kalulushi, Zambia.

*Analyst*, 1971, **96**, 480-487.

# Test Case



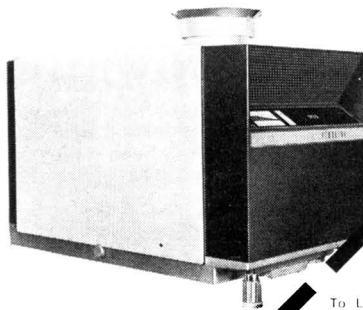
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**Potentiometric Determination of Mercury(II) with Dithiooxamide**

Potentiometric titration with dithiooxamide can be used to determine mercury in the 0.10 to 40.0 p.p.m. range (0.01 mg to 4.00 mg per 100 ml) with a relative standard deviation ranging from 1.50 to 0.26 per cent. and an accuracy of about 0.3 per cent. A silver indicator electrode is used. Several interferences were investigated and found to have little effect. Among these were cadmium, zinc, nickel, iron, lead and cobalt. The interferences of silver and copper in the determination were also investigated and are discussed. Two simple fast modifications to the procedure are suggested when determining mercury in the presence of either silver or copper. The advantages of this method over other methods are outlined.

**GENE E. KALBUS, ROBERT D. WESLEY**

Chemistry Department, California State College at Long Beach, Long Beach, California.

and **LEE H. KALBUS**

Chemistry Department, California State College at San Bernardino, San Bernardino, California.

*Analyst*, 1971, **96**, 488-493.

**Spectrophotometric Determination of Sulphate in Propellants and Nitrocellulose**

An accurate method is proposed for the determination of sulphate in propellants and nitrocellulose that requires only 45 minutes to carry out. The sample is treated with a mixture of nitric acid, perchloric acid and magnesium nitrate, and the solution is evaporated to dryness over a bunsen burner. The salts deposited are heated for 5 minutes with a mixture of hydriodic, hypophosphorous and hydrochloric acids in a simplified distillation apparatus, with nitrogen passing through the system; the hydrogen sulphide that results from the reduction of the sulphate is absorbed into ammonia solution, lead citrate is added, and the brownish yellow lead sulphide colour is measured.

**GEORGE NORWITZ**

Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.

*Analyst*, 1971, **96**, 494-501.

**A Rapid Absorptiometric Method for the Determination of Formates in Corrosion Products Arising from Paints, Lacquers and Woods**

A method has been evolved in which formate ions reduce an excess of silver nitrate to silver under slightly acidic buffered solution conditions. The method is applicable directly to cadmium and zinc corrosion products. Samples of corrosion products from ferrous metals require preliminary separation by distillation from phosphoric acid. The method is also applicable to the study of formic acid vapours evolved from paints, lacquers and woods, the acidic vapour being absorbed in a dilute aqueous solution of an alkali hydroxide. Allowance is made for the presence of residual metallic particles and for chloride interference.

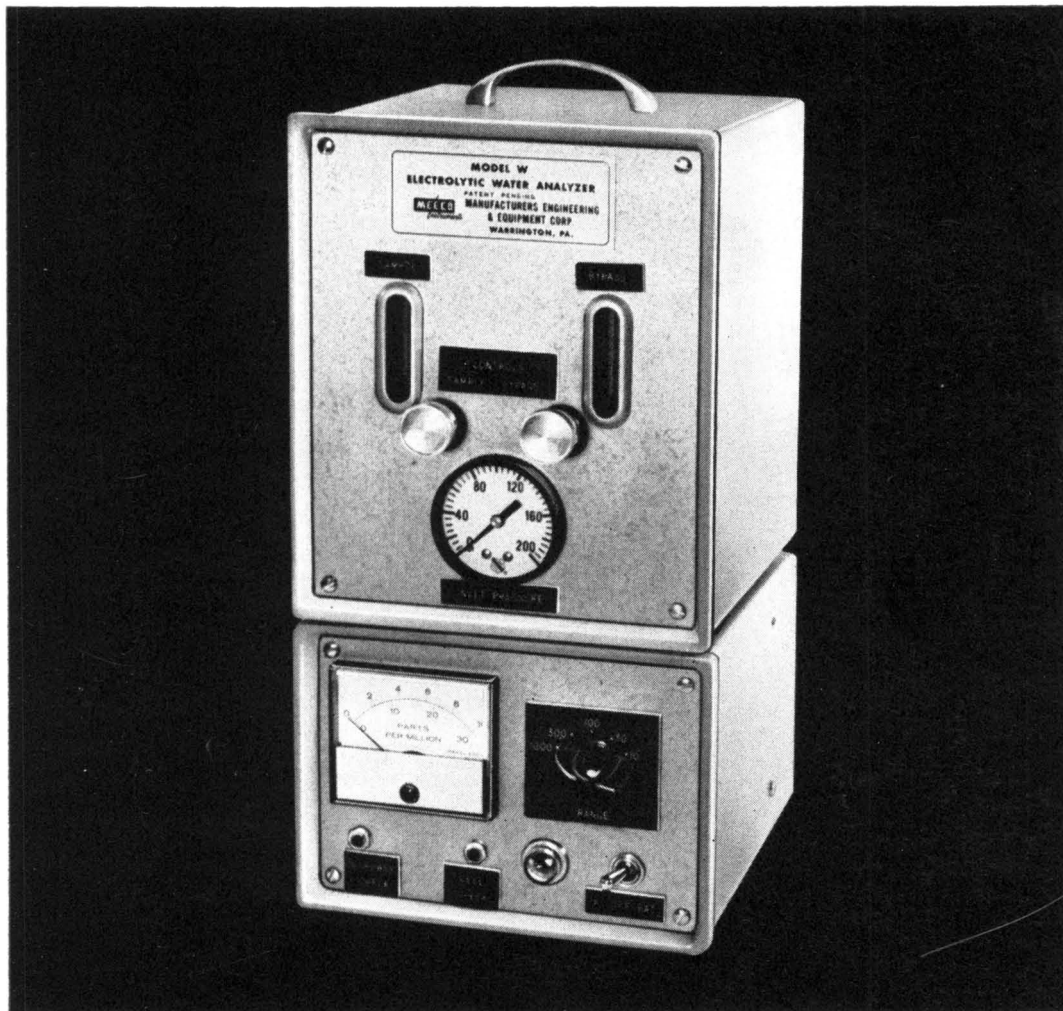
A series of control standards is run concurrently with each batch of samples to compensate for daily changes in sensitivity because of the ageing of the colloid stabiliser. Recovery of formic acid from synthetic mixtures, based on a sample weight of 0.1 g, has been found to be  $\pm 4$  per cent. for aqueous solutions and zinc products and  $\pm 6$  per cent. for cadmium products, with a 95 per cent. confidence limit.

**D. G. HIGGS and A. F. CHARLES**

Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks, Kent.

*Analyst*, 1971, **96**, 502-514.





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# THE ANALYST

## The Spectrographic Determination of Impurities in Copper-base Samples of Small Dimensions\*

By W. T. ELWELL AND D. M. PEAKE

(Research and Development Department, Imperial Metal Industries Limited, Witton, Birmingham B6 7BA)

Serious problems arise in the point-to-point spectrographic analysis of copper-base materials if only wire or thin-sheet samples are available. In the procedure recommended in this paper, the sample is converted into oxide, transferred to a graphite cup of optimum dimensions, then examined spectrographically. Standard oxide samples are prepared in a similar way (from high-purity reagents) and excited, and resulting reference spectra are used to evaluate the impurities in copper, brass, phosphor and aluminium bronze, cupro-nickel, nickel-silver and Everdur. Densities of the recommended impurity lines for each of these materials are in remarkably close agreement at all comparable impurity levels.

The validity of the proposed method has been substantiated by a comparison with similar analytical results obtained by alternative, often time-consuming, procedures.

A wide range of impurities, down to about the 10 p.p.m. level, can be determined in a single sample within 90 minutes, and several samples can be analysed concurrently.

In direct point-to-point spectrographic analysis, the provision of a uniformly large (massive) single-piece sample is essential. Serious problems arise if wire or thin-sheet samples are used, because undissipated heat accumulates within the sample when it is excited. The significance of this is that some impurities volatilise more rapidly than others, and the rate of volatilisation can be neither predicted nor controlled.

Alternative methods of determining most of the impurities in these small samples are time-consuming, and experiments were designed to overcome the problems encountered when these materials are analysed spectrographically.

In the following experimental work, a BNF General-purpose Source Unit was used unless otherwise stated.

### EXPERIMENTAL

#### SAMPLE PREPARATION—

Several methods of preparing suitable samples of wire and thin sheet for spectrographic examination were examined.

#### PROVISION OF COMPACTS—

Attempts were made to pressure-weld the sample, and to establish optimum punch and die sizes and pressing loads, but these tests were not successful because all of the samples were seriously contaminated with iron and disintegrated on excitation.

#### EXAMINATION OF SOLUTIONS—

The use of a spectrographic solution method has two outstanding advantages, *viz.*, standards can readily be prepared from high-purity reagents, and the standards and samples are converted into a common matrix.

One expected source of interference in such a method is the OH-band spectrum produced in the region of the bismuth 306.7 nm line by aqueous solutions, and tests in which the "polyethylene-cup" method<sup>1</sup> was used confirmed this. In an attempt to eliminate all water from the solution before excitation, a micro-Bunsen flame was directed between the pick-up

\* Paper presented at the Third SAC Conference, Durham, July 12th to 16th, 1971.

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and excitation regions of a rotating graphite-disc electrode, but this modification failed to achieve the desired effect.

A high-frequency plasma jet can be used to replace the conventional spectrographic discharge; a solution of the sample is nebulised directly into the plasma, and resulting spectra usually have relatively high-density and low-background characteristics. All tests with this alternative source of excitation (by the courtesy of Mr. S. Greenfield, Messrs. Albright & Wilson) failed to eliminate the OH-band spectrum, even after stringent drying of the plasma gas that was thought to be the primary source of OH-band radiation.

#### OXIDE - RESIN METHOD—

This is a standard method of spectrographic analysis, in which the sample, in the form of an oxide powder, is mixed with a Bakelite resin and the cured mixture is excited in the crater of a graphite-rod electrode.<sup>2</sup>

When this method was applied to an essentially copper matrix, the sensitivities obtained for some elements were poor.

#### OXIDE POWDER - CUP PROCEDURE—

In subsequent tests the oxide powder alone was excited in a series of graphite cups of different dimensions, and trial exposures indicated that the method is inherently both sensitive and reproducible; however, cup dimensions were critical. Small cups became very hot and produced a high-background continuum, and when relatively large cups were used the discharge concentrated on the oxide sample, reducing it to the metal, and sensitivities and reproducibilities were poor.

When a graphite cup of the dimensions referred to under Method was used, the discharge circled the lip of the cup, the oxide was drawn directly into the discharge by the vacuum formed and sensitivities and reproducibilities were good.

In further tests to establish the most suitable weight of oxide and optimum excitation conditions to use, it was shown to be a disadvantage to press the oxide firmly into the cup. When the oxide was uniformly distributed within the crater, by lightly tapping the cup, even better reproducibilities and sensitivities were obtained.

Subsequent experimental work was based on the experience gained with this oxide powder - cup procedure in these preliminary tests.

#### PREPARATION OF REFERENCE SOLUTIONS—

It was necessary to provide a series of reference solutions typical of those obtained when copper and certain copper alloys are dissolved in a convenient solvent. Each solution was evaporated to dryness and the residue converted into oxide before applying the method so far developed.

For our immediate purposes, impurities in the following materials were of interest: copper; brasses (Cu 60 and 80 per cent., Zn 40 and 20 per cent.); phosphor bronze (Cu 95, Sn 4.8 and P 0.2 per cent.); aluminium bronze (Cu 90 and Al 10 per cent.); cupro-nickel (Cu 75 and Ni 25 per cent.); nickel-silver (Cu 60, Ni 15 and Zn 25 per cent.); and Everdur (Cu 96, Si 3 and Mn 1 per cent.).

Individual standard solutions were prepared in such a way that when composite solutions were evaporated and the residues were converted into oxides, the dry residues contained the equivalent of 0.5 g of the sample *plus* 0, 10, 50 or 100 p.p.m., 0.05, 0.10, 0.20, 0.30 or 0.50 per cent. of a selection of impurities.

For example, in preparing one of the 60/40 brass standards (see Method), to 6.0 ml of the standard copper solution A were added 4.0 ml of the standard zinc solution B and 3.0 ml of each of the undiluted standard solutions F, G, H, I, J and K. In this way, an oxide was ultimately prepared simulating the composition of the oxide that would be obtained from a 60/40 brass sample containing 0.3 per cent. of each of the following impurities: silver, bismuth, aluminium, manganese, iron, lead, nickel, arsenic, antimony, silicon, tin and phosphorus.

Other standard oxides in the same series were prepared in a similar way; the volumes of the standard copper and zinc solutions were the same but, instead of 3.0 ml of each of the standard solutions F, G, H, I, J and K, equal volumes of each of these solutions (before or after the prescribed dilutions) were used to provide the individual impurities referred to earlier.

This provided nine standard oxides (including a blank) for this particular 60/40 brass series, and similar standard oxides were prepared for each of the other six materials.

Some of the reagents used in preparing the standard solutions dissolved more rapidly in hydrochloric acid than in any other solvent, but tests on the oxide residue from a series of simulated brass (60/40) samples showed that if a large amount of chloride was present, there was a significant loss of arsenic; other impurities were not affected. The use of hydrochloric acid in any stage of the procedure had, therefore, to be circumvented.

Preliminary tests confirmed that none of the elements was lost during conversion of any solution into a dry residue, before excitation, provided the oxides were prepared in accordance with the details given under Method.

#### EXCITATION OF OXIDES—

The oxides were all examined spectrographically (see Method) and resulting spectra were evaluated visually, and independently, by three analysts.

#### METHOD

##### PREPARATION OF STANDARD SOLUTIONS—

Use high-purity reagents and distilled water (including that used for dilutions) throughout.

*Copper solution (A)*—Dissolve 50 g of copper in 500 ml of dilute nitric acid (1 + 1). Warm the solution gently to expel oxides of nitrogen, cool and dilute to 1 litre.

1 ml of solution  $\equiv$  50 mg of copper.

*Zinc solution (B)*—As for copper, but use 50 g of zinc.

1 ml of solution  $\equiv$  50 mg of zinc.

*Nickel solution (C)*—As for copper, but use 25 g of nickel.

1 ml of solution  $\equiv$  25 mg of nickel.

*Aluminium solution (D)*—As for copper, but use 2.5 g of aluminium, a few milligrams of mercury(I) nitrate and 50 ml of dilute nitric acid (1 + 1); the reaction is vigorous. Cool, and dilute the solution to 100 ml.

1 ml of solution  $\equiv$  25 mg of aluminium.

*Manganese solution (E)*—Dissolve 0.5 g of manganese in 10 ml of dilute nitric acid (1 + 1). Warm the solution gently to expel oxides of nitrogen, cool and dilute to 100 ml.

1 ml of solution  $\equiv$  5 mg of manganese.

*Zinc, silver, bismuth, aluminium, manganese, iron, lead and nickel solution (F)*—Dissolve 0.5 g of each of these metals separately in about 5 ml of dilute nitric acid (1 + 1); the presence of about 1 mg of mercury(I) nitrate will aid dissolution of the aluminium. Dilute the combined solutions to 1 litre in a calibrated flask.

1 ml of solution  $\equiv$  0.5 mg of each of the above metals.

*Arsenic solution (G)*—Dissolve 0.165 g of arsenic(III) oxide (dried at 105 °C) in 10 ml of 10 per cent. w/v sodium hydroxide solution. Acidify the solution to litmus with dilute nitric acid (1 + 1), then add an excess of 5 ml of the dilute acid and dilute to 250 ml.

1 ml of solution  $\equiv$  0.5 mg of arsenic.

*Antimony solution (H)*—Dissolve 0.334 g of potassium antimony tartrate (dried at 105 °C) in water and dilute to 250 ml.

1 ml of solution  $\equiv$  0.5 mg of antimony.

*Tin solution (I)*—Dissolve 0.5 g of tin in 50 ml of dilute sulphuric acid (1 + 1). Dilute to 100 ml with the same acid.

1 ml of solution  $\equiv$  5.0 mg of tin.

*Phosphorus solution (J)*—Dissolve 2.195 g of potassium dihydrogen orthophosphate (dried at 105 °C) in water and dilute to 1 litre.

1 ml of solution  $\equiv$  0.5 mg of phosphorus.

*Silicon solution (K)*—Transfer 0.2673 g of calcined silica to a small platinum dish, fuse it with about 1 g of anhydrous sodium carbonate and cool. Dissolve the melt in water, and dilute the solution to 250 ml in a calibrated flask. (It is preferable to make this solution freshly each time it is required, but it can be stored for a few days in a polythene container.)

1 ml of solution  $\equiv$  0.5 mg of silicon.

In making up some of the standard oxides, to avoid taking an inconveniently small aliquot of each of the individual standard solutions F, G, H, I, J and K, dilute, separately, each of these solutions to provide two independent solutions such that with one of them 1 ml is equivalent to 50  $\mu\text{g}$  of the element and with the other 1 ml is equivalent to 5  $\mu\text{g}$  of the element. Use these weaker solutions to prepare the standard oxides containing impurities below about the 0.2 per cent. level.

#### PREPARATION OF COMPOSITE SOLUTIONS—

Make all volumetric measurements as accurately as possible; use a burette.

Make up a series of individual composite solutions to simulate the composition of 0.5-g samples of the parent materials.

On a 0.5-g sample basis, prepare a series of composite solutions of copper, brass (80/20), brass (60/40), phosphor bronze (Cu 95, Sn 4.8 and P 0.2 per cent.), cupro-nickel (Cu 75 and Ni 25 per cent.), nickel-silver (Cu 60, Ni 15 and Zn 25 per cent.) and Everdur (Cu 96, Si 3 and Mn 1 per cent.).

#### PARENT SOLUTIONS—

These were composed as follows—

Material	Amount of solution/ml					
	A	B	C	D	E	J
Copper .. ..	10.0	—	—	—	—	—
Brass (80/20) .. ..	8.0	2.0	—	—	—	—
Brass (60/40) .. ..	6.0	4.0	—	—	—	—
Phosphor bronze .. ..	9.5*	—	—	—	—	2.0
Aluminium bronze .. ..	9.0	—	—	2.0	—	—
Cupro-nickel (75/25) .. ..	7.5	—	5.0	—	—	—
Nickel-silver .. ..	6.0	2.5	3.0	—	—	—
Everdur .. ..	9.6†	—	—	—	1.0	—

\* Add 30.5 mg of finely divided high-purity tin(IV) oxide to these solutions.

† Add 15 mg of finely divided high-purity silica to these solutions.

#### IMPURITY ADDITIONS—

Impurity level, per cent. .. ..	0.5	0.3	0.2	0.1	0.05	0.01	0.005	0.001
Addition of solution/ml .. ..	5.0*	3.0*	2.0*	1.0*	5.0†	1.0†	5.0‡	1.0‡
	* Containing 0.5 mg ml <sup>-1</sup> .							
	† Containing 50 $\mu\text{g}$ ml <sup>-1</sup> .							
	‡ Containing 5 $\mu\text{g}$ ml <sup>-1</sup> .							

For example, add 7.5 ml of solution A to 5.0 ml of solution C; this combined solution contains the same amount of copper and nickel as a 0.5-g sample of a nominal 75/25 cupro-nickel. Add 5.0 ml of each of the six 50  $\mu\text{g}$  ml<sup>-1</sup> solutions prepared by dilution of the F, G, H, I, J and K solutions.

This combined solution then contains, in addition to the parent metals, the same amounts of zinc, silver, bismuth, aluminium, manganese, iron, lead, arsenic, antimony, silicon, tin and phosphorus as those present in a 0.5-g sample of cupro-nickel containing 0.05 per cent. of these elements.

#### PREPARATION OF OXIDES—

Proceed with each composite solution as follows.

Evaporate the solution to dryness, then heat the residue to 400 °C for 15 minutes and cool it. Transfer the solid residue to a small agate pestle and mortar of the type that is an integral part of a Glen Creston mixing mill, and grind the oxide to a powder in the mill for about 2 minutes.

#### PREPARATION OF STANDARD OXIDE COMPARISON PLATE—

Transfer 0.3 g of each oxide powder, individually, to a standard graphite cup (height 9 mm, o.d. 12 mm, wall thickness 1 mm and base thickness 5 mm, *i.e.*, inside wall height 4 mm). and proceed with each as follows.

Tap the cup lightly several times to ensure uniform distribution of the powder. Place the cup on a graphite pillar (25 mm diameter), and examine spectrographically under the following conditions (expose each set of standards on a separate plate).

Spectrograph	Hilger and Watts Medium Quartz	Inductance	0.06 mH
Source unit	BNF General-purpose	Sample polarity	Negative
Counter electrode	High-purity graphite rod (6 mm diameter), <i>e.g.</i> , Ringsdorff RWO 90° cone	Filter	7 step
Capacitance	250 $\mu$ F	Source-to-slit distance	380 mm
Resistance	10 $\Omega$	Gap	3 mm
		Pre-burn	Nil
		Exposure	15 s
		Plate	Ilford N40

Develop the plate for 2 minutes at  $26 \pm 0.5$  °C by using diluted Johnson's Universal Developer (15 + 85). Rinse the plate, fix and wash it thoroughly, then dry it in a dust-free atmosphere.

#### PROCEDURE—

Transfer about 0.3 g of the sample to a 100-ml squat beaker, add 5 ml of dilute nitric acid (1 + 1), warm until the sample has dissolved, then evaporate the solution to dryness. Heat to 400 °C for 15 minutes, then transfer the solid residue to a small agate pestle and mortar of the type that is an integral part of a Glen Creston mixing mill. Grind the oxide to a powder in the mill for about 2 minutes, then proceed as in Preparation of Standard Oxide Comparison Plate. It is permissible to use a 2-step (0.66) filter and an exposure of 10 seconds.

#### EVALUATION OF SPECTRA—

Compare densities of the lines (Table I) in the sample spectrum with the standard spectra, and evaluate the concentrations of the impurity elements. To reduce the effect of possible interferences, compare three lines for each element whenever possible and record the lowest value. Care should be taken to ensure that spectra of comparable densities are used in this evaluation.

TABLE I  
RECOMMENDED LINES FOR USE WITH PLATE-COMPARISON PROCEDURE

Element	Line, $\lambda$ /nm	Element	Line, $\lambda$ /nm
Tin .. .. .	284.00	Silver .. .. .	338.29
	286.33		241.32
	285.06		237.51
Lead .. .. .	283.31	Antimony .. .. .	231.15
	287.33		217.59
	282.32		259.81
Iron .. .. .	248.81	Bismuth .. .. .	306.77
	296.69		289.80
	297.32		234.98
Nickel .. .. .	305.08	Arsenic .. .. .	286.05
	313.41		234.98
	308.08		288.16
Manganese .. .. .	294.92	Silicon .. .. .	251.61
	288.96		251.43
	423.53		251.43
Aluminium .. .. .	396.15	Zinc .. .. .	330.29
	394.40		334.50
	308.20		253.57
			255.33
		Phosphorus .. .. .	253.40

TABLE IIa: COMPARISON OF RESULTS (PER CENT.)

Sample	Material	Sn	Pb	Fe	Ni	Mn	Al
S281	Copper (D.O.)	<i>0.133</i>	<i>0.115</i>	<i>0.100</i>	<i>0.119</i>	<i>0.076</i>	<i>0.11</i>
		0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	~0.1	~0.1
		0.1-0.2	~0.1	0.1-0.2	0.1-0.2	0.05-0.1	0.1-0.2
		~0.1	~0.1	0.1-0.2	0.1-0.2	~0.1	~0.1
S282		<i>0.044</i>	<i>0.041</i>	<i>0.029</i>	<i>0.041</i>	<i>0.015</i>	<i>0.009</i>
		~0.05	~0.05	~0.05	~0.05	0.01-0.05	~0.01
		~0.05	~0.05	0.01-0.05	~0.05	0.01-0.05	~0.01
		0.01-0.05	0.01-0.05	~0.05	0.01-0.05	~0.01	~0.01
S283		<i>0.011</i>	<i>0.0055</i>	<i>0.0014</i>	<i>0.013</i>	<i>&lt;0.005</i>	<i>0.007</i>
		0.01-0.05	~0.01	0.001-0.005	~0.01	<0.001	~0.001
		0.01-0.05	0.005-0.01	0.001-0.005	0.01-0.05	<0.001	~0.001
		~0.01	0.005-0.01	~0.001	~0.01	<0.001	~0.001
S284		<i>0.003</i>	<i>0.0029</i>	<i>0.0008</i>	<i>0.005</i>	<i>&lt;0.0005</i>	<i>0.003</i>
		0.001-0.005	0.001-0.005	~0.001	~0.005	<0.001	~0.001
		0.005	0.001-0.005	~0.001	~0.005	<0.001	~0.001
		0.001-0.005	0.001-0.005	~0.001	~0.005	<0.001	~0.001
S217	Brass (60/40)	<i>0.122</i>	<i>0.112</i>	<i>0.139</i>	<i>0.136</i>	<i>0.076</i>	<i>0.036</i>
		~0.1	~0.1	0.1-0.2	~0.1	~0.1	~0.05
		0.1-0.2	~0.1	0.1-0.2	0.1-0.2	~0.1	0.01-0.05
		~0.1	~0.1	0.1-0.2	~0.1	~0.1	~0.05
S218		<i>0.038</i>	<i>0.04</i>	<i>0.036</i>	<i>0.047</i>	<i>0.003</i>	<i>&lt;0.002</i>
		~0.05	0.01-0.05	~0.05	0.01-0.05	0.001-0.005	<0.001
		~0.05	0.01-0.05	~0.05	~0.05	0.001-0.005	~0.001
		~0.05	0.01-0.05	0.01-0.05	~0.05	0.001-0.005	~0.001
S219		<i>0.0157</i>	<i>0.0135</i>	<i>0.014</i>	<i>0.0153</i>	<i>0.002</i>	—
		~0.01	~0.01	~0.01	~0.01	0.001-0.005	—
		0.01-0.05	~0.01	0.01-0.05	0.01-0.05	~0.001	—
		~0.01	0.01-0.05	0.01-0.05	~0.01	0.001-0.005	—
S220		<i>0.0037</i>	<i>0.005</i>	<i>0.002</i>	<i>0.006</i>	—	—
		~0.005	~0.005	—	~0.005	—	—
		0.001-0.005	~0.005	~0.005	—	—	—
		0.001-0.005	~0.005	~0.005	—	—	—
S277	85% Copper 15% Zinc	<i>0.144</i>	<i>0.122</i>	<i>0.102</i>	<i>0.120</i>	<i>0.077</i>	<i>0.073</i>
		~0.1	~0.1	~0.1	~0.1	~0.1	0.05-0.1
		0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.05-0.1	0.05-0.1
		0.1-0.2	~0.1	0.1-0.2	0.1-0.2	0.05-0.1	0.05-0.1
S278		<i>0.045</i>	<i>0.044</i>	<i>0.038</i>	<i>0.040</i>	<i>0.024</i>	<i>0.025</i>
		~0.05	~0.05	~0.05	~0.05	0.01-0.05	0.01-0.05
		0.05-0.1	~0.05	~0.05	~0.05	0.01-0.05	0.01-0.05
		~0.05	~0.05	~0.05	~0.05	~0.05	~0.01
S279		<i>0.010</i>	<i>0.012</i>	<i>0.013</i>	<i>0.012</i>	<i>0.007</i>	<i>0.008</i>
		~0.01	~0.01	~0.01	~0.01	~0.005	0.005
		~0.01	~0.01	~0.01	~0.01	~0.005	0.005-0.01
		~0.01	~0.01	~0.01	~0.005	0.005	0.005
S280		<i>0.003</i>	<i>0.0057</i>	<i>0.005</i>	<i>0.005</i>	<i>0.005</i>	<i>0.006</i>
		0.001-0.005	~0.005	~0.005	~0.005	0.001-0.005	~0.001
		0.001-0.005	0.001-0.005	~0.005	~0.005	~0.005	~0.001
		0.001-0.005	~0.005	0.001-0.005	0.001-0.005	~0.001	~0.001
S423	75% Copper 25% Nickel	<i>0.095</i>	<i>0.088</i>	<i>0.080</i>	—	<i>0.014</i>	<i>0.0015</i>
		~0.1	~0.1	~0.1	—	0.01-0.05	~0.001
		~0.1	~0.1	~0.1	—	0.01-0.05	~0.001
		~0.1	~0.1	~0.1	—	0.01-0.05	~0.001
S424		<i>0.030</i>	<i>0.033</i>	<i>0.025</i>	—	<i>&lt;0.001</i>	<i>0.002</i>
		~0.05	~0.05	~0.05	—	~0.001	~0.001
		~0.05	~0.05	0.01-0.05	—	<0.001	~0.001
		0.05	0.05	0.01-0.05	—	<0.001	~0.001
S425		<i>0.012</i>	<i>0.015</i>	<i>0.020</i>	—	<i>0.001</i>	<i>0.002</i>
		0.01-0.05	0.01-0.05	0.01	—	~0.001	~0.001
		0.01	0.01-0.05	0.01	—	<0.001	~0.001
		0.01	0.01	0.01-0.05	—	<0.001	~0.001
S426		<i>0.0065</i>	<i>0.032</i>	<i>0.020</i>	—	<i>0.0015</i>	<i>0.002</i>
		~0.005	0.01-0.05	0.01-0.05	—	~0.001	~0.001
		0.001-0.005	~0.05	0.01-0.05	—	~0.001	~0.001
		~0.005	~0.05	~0.05	—	~0.001	~0.001

First row (italics): results by alternative methods. Second, third and fourth rows: independent results by



## FOR COPPER AND SOME COPPER-BASE ALLOYS

Ag	Sb	Bi	As	Si	P	Zn	Sample
<i>0.062</i>	<i>0.01</i>	<i>0.012</i>	<i>0.113</i>	<i>0.064</i>	<i>0.133</i>	<i>0.153</i>	S281
~0.05	~0.01	~0.01	0.1-0.2	0.05-0.1	~0.1	0.1-0.2	
0.05-0.1	~0.01	~0.01	0.1-0.2	0.05-0.1	0.1-0.2	0.1-0.2	
~0.05	0.01-0.05	~0.01	0.1-0.2	~0.1	~0.1	~0.1	
<i>0.022</i>	<i>0.003</i>	<i>0.004</i>	<i>0.038</i>	<i>0.008</i>	<i>0.058</i>	<i>0.055</i>	S282
~0.01	~0.005	0.001-0.005	~0.05	~0.01	~0.05	0.05-0.1	
~0.05	<0.005	0.001-0.005	~0.05	0.005-0.01	~0.05	0.05-0.1	
0.01-0.05	0.001-0.005	0.001-0.005	0.01-0.05	0.005-0.01	~0.05	0.01-0.05	
<i>0.008</i>	<i>0.0008</i>	<i>0.001</i>	<i>0.013</i>	<i>0.005</i>	<i>0.019</i>	<i>0.0068</i>	S283
~0.005	<0.005	~0.001	0.01-0.05	<0.001	~0.01	~0.005	
~0.01	<0.005	~0.001	0.01-0.05	<0.001	~0.01	0.01-0.05	
~0.005	<0.005	~0.001	0.01-0.05	<0.001	~0.01	~0.005	
<i>0.003</i>	<i>&lt;0.0005</i>	<i>0.0005</i>	<i>0.0047</i>	<i>&lt;0.005</i>	<i>0.023</i>	<i>0.0038</i>	S284
~0.001	<0.005	<0.001	~0.005	<0.001	0.01-0.05	<0.005	
0.001-0.005	<0.005	<0.001	~0.005	<0.001	~0.01	0.001-0.005	
0.001-0.005	<0.005	<0.001	~0.005	<0.001	~0.01	~0.005	
<i>0.043</i>	<i>0.012</i>	<i>0.0096</i>	<i>0.116</i>	<i>0.061</i>	<i>0.125</i>	—	S217
0.01-0.05	~0.01	~0.01	~0.1	0.05-0.1	~0.1	—	
0.01-0.05	0.01-0.05	0.005-0.01	0.1-0.2	0.05-0.1	0.1-0.2	—	
0.01-0.05	0.01-0.05	~0.01	~0.1	0.05-0.1	0.1-0.2	—	
<i>0.018</i>	<i>0.004</i>	<i>0.0028</i>	<i>0.039</i>	<i>&lt;0.001</i>	<i>0.024</i>	—	S218
0.01-0.05	~0.005	0.001-0.005	~0.05	<0.005	0.01-0.05	—	
0.01-0.05	<0.005	0.001-0.005	~0.05	<0.001	0.01-0.05	—	
0.01-0.05	~0.005	<0.005	~0.05	~0.001	~0.01	—	
<i>0.005</i>	<i>0.0012</i>	<i>0.0012</i>	<i>0.013</i>	<i>0.0016</i>	<i>0.065</i>	—	S219
~0.005	<0.005	~0.001	~0.01	<0.005	~0.05	—	
0.005-0.01	<0.005	~0.001	~0.01	<0.001	~0.05	—	
0.005-0.01	<0.005	~0.001	~0.01	<0.001	~0.05	—	
—	<i>0.0003</i>	<i>0.0005</i>	<i>0.0042</i>	<i>&lt;0.005</i>	<i>0.0004</i>	—	S220
—	<0.005	<0.001	<0.005	<0.005	<0.005	—	
—	<0.005	<0.001	<0.005	<0.001	<0.001	—	
—	<0.005	<0.001	<0.005	<0.001	<0.001	—	
<i>0.061</i>	<i>0.011</i>	<i>0.009</i>	<i>0.121</i>	<i>0.068</i>	<i>0.132</i>	—	S277
0.05-0.1	0.01-0.05	~0.01	~0.1	~0.1	~0.1	—	
~0.1	0.01-0.05	0.005-0.01	0.1-0.2	~0.1	0.1-0.2	—	
~0.1	~0.01	~0.01	~0.1	~0.1	0.1-0.2	—	
<i>0.022</i>	<i>0.004</i>	<i>0.003</i>	<i>0.039</i>	<i>0.019</i>	<i>0.042</i>	—	S278
0.01-0.05	~0.005	0.001-0.005	0.01-0.05	~0.01	0.01-0.05	—	
~0.05	0.001-0.005	0.001-0.005	~0.05	~0.01	~0.05	—	
0.01-0.05	0.001-0.005	0.001-0.005	~0.05	0.01-0.05	~0.05	—	
<i>0.007</i>	<i>0.0009</i>	<i>0.0009</i>	<i>0.0114</i>	<i>0.005</i>	<i>0.013</i>	—	S279
0.005-0.01	<0.005	~0.001	0.01-0.05	~0.005	~0.01	—	
~0.005	<0.005	<0.001	0.005-0.01	0.001-0.005	~0.01	—	
0.005-0.01	<0.005	~0.001	0.005-0.01	0.001-0.005	~0.01	—	
<i>0.003</i>	<i>0.0005</i>	<i>0.0004</i>	<i>0.004</i>	<i>&lt;0.0005</i>	<i>0.004</i>	—	S280
~0.005	<0.005	<0.001	~0.005	<0.001	<0.005	—	
0.001-0.005	<0.005	<0.001	<0.005	<0.001	<0.005	—	
0.001-0.005	<0.005	<0.001	0.001-0.005	~0.001	<0.005	—	
<i>0.053</i>	<i>0.0095</i>	<i>0.009</i>	<i>0.096</i>	<i>0.0025</i>	<i>0.088</i>	<i>0.11</i>	S423
0.05-0.1	~0.01	~0.01	0.1-0.2	~0.005	0.05-0.1	~0.1	
0.05-0.1	~0.01	~0.01	~0.1	~0.005	0.05-0.1	0.1-0.2	
~0.05	~0.01	~0.01	~0.1	~0.005	~0.1	0.05-0.1	
<i>0.024</i>	<i>0.003</i>	<i>0.003</i>	<i>0.031</i>	<i>0.0015</i>	<i>0.009</i>	<i>0.023</i>	S424
0.01-0.05	~0.005	0.001-0.005	~0.05	~0.001	0.005-0.01	~0.05	
0.01-0.05	~0.005	0.001-0.005	~0.05	~0.001	~0.01	~0.05	
~0.05	~0.005	~0.005	~0.05	~0.001	~0.01	0.01-0.05	
<i>0.012</i>	<i>0.001</i>	<i>0.001</i>	<i>0.012</i>	<i>0.0015</i>	<i>0.003</i>	<i>0.015</i>	S425
0.01-0.05	~0.001	0.001-0.005	0.005-0.01	~0.001	0.001-0.005	~0.01	
0.01-0.05	~0.001	~0.001	~0.01	~0.001	0.001-0.005	~0.01	
0.01-0.05	~0.001	~0.001	~0.01	~0.001	<0.005	~0.01	
<i>0.004</i>	<i>0.0015</i>	<i>0.0002</i>	<i>0.004</i>	<i>0.0010</i>	<i>0.003</i>	<i>0.21</i>	S426
~0.005	~0.001	<0.001	0.001-0.005	0.001-0.005	~0.005	~0.2	
~0.005	~0.001	<0.001	~0.005	0.001-0.005	0.001-0.005	~0.2	
~0.005	~0.001	<0.001	~0.005	~0.001	0.001-0.005	~0.2	

recommended spectrographic method with three independent analysts.

## RESULTS AND CONCLUSIONS

Adequate sensitivities were obtained, and line densities of the spectra showed a gradual increase with increase in impurity content at the wavelengths used. The blank in no instance exceeded 10 p.p.m. of the element to be determined.

When densities of the selected impurity lines for any of the seven materials were compared, all were in remarkably close agreement at all impurity levels. A possible explanation for this agreement is that all of the finely divided oxide entering the plasma is completely excited. This observation implies that the impurity-line intensities are independent of matrix composition, the significance of which is that a single calibration for all of the types of materials examined is adequate. It is, therefore, reasonable to speculate that other copper-base alloys would respond in the same way.

Typical standards of known composition are a prerequisite of most spectrographic analyses, and the recommended method of preparing oxides with known levels of impurities meets this requirement in the analysis of samples of small dimensions.

Results in Tables II*a*, II*b*, II*c* and III show the level of agreement obtained by the three analysts, who reported, independently, their visual interpretation of the same spectra, and also a comparison of their results with those obtained by alternative, often time-consuming, non-spectrographic procedures.

It is not recommended that small samples should be supplied for spectrographic analysis when massive samples can be made available, because the recommended method takes much longer than any established spectrographic procedure for analysing massive samples. The

TABLE II*b*  
COMPARISON OF RESULTS (PER CENT.) FOR 95 PER CENT. COPPER, 4.8 PER CENT. TIN,  
0.2 PER CENT. PHOSPHORUS ALLOYS

Sample	Zn	Pb	Fe	Ni	Bi	As	P
S135	0.10						
	~0.1	—	—	—	—	—	—
	~0.1	—	—	—	—	—	—
	~0.1	—	—	—	—	—	—
S136	0.006						
	~0.005	—	—	—	—	—	—
	~0.005	—	—	—	—	—	—
	~0.005	—	—	—	—	—	—
S137		0.005			0.001		
	—	~0.005	—	—	~0.001	—	—
	—	~0.005	—	—	~0.001	—	—
	—	~0.005	—	—	~0.001	—	—
S138		0.004			0.0013		
	—	~0.005	—	—	~0.001	—	—
	—	~0.005	—	—	~0.001	—	—
	—	0.001-0.005	—	—	~0.001	—	—
S139		0.002			0.0008	<0.005	0.012
	—	~0.001	—	—	<0.001	0.001-0.005	~0.01
	—	~0.001	—	—	<0.001	0.001-0.005	~0.01
	—	~0.001	—	—	<0.001	0.001-0.005	~0.01
S140		0.005			0.0027	0.005	0.018
	—	~0.005	—	—	0.001-0.005	0.001-0.005	0.01
	—	~0.005	—	—	0.001-0.005	0.001-0.005	0.01
	—	~0.005	—	—	0.001-0.005	0.001-0.005	0.01
S143		0.06	0.01	0.02		0.015	0.14
	—	~0.1	0.01-0.05	0.01-0.05	—	0.01-0.05	0.1-0.2
	—	0.05-0.1	0.01-0.05	0.01-0.05	—	0.01-0.05	0.1-0.2
	—	~0.05	~0.01	0.01-0.05	—	~0.01	0.1-0.2
S144							0.18
	—	—	—	—	—	—	0.1-0.2
	—	—	—	—	—	—	0.1-0.2
	—	—	—	—	—	—	0.1-0.2
S555							0.05
	—	—	—	—	—	—	0.05
	—	—	—	—	—	—	0.05
	—	—	—	—	—	—	0.05

recommended method does, however, enable samples of wire and thin sheet, and other samples of similar small dimensions, to be analysed spectrographically to meet the requirements made on the laboratory for the determination of specified impurity levels in certain grades of copper and in a range of copper-base materials.

It cannot be claimed that the method is as accurate as some alternative procedures but, provided its limitations are appreciated and the analytical results obtained are adequate, a wide range of impurity elements can be determined in a single sample within 90 minutes, and several samples can be analysed concurrently.

The authors thank members of the IMI Research and Development Department staff who were responsible for most of the experimental results and, in particular, Mr. A. G. Gofton,\* who did much of the development work.

\* Now with the Central Electricity Generating Board.

TABLE IIc

COMPARISON OF RESULTS (PER CENT.) FOR 76 PER CENT. COPPER, 22 PER CENT. ZINC, 2 PER CENT. ALUMINIUM ALLOYS

Sample	Sn	Pb	Fe	Ni	As	Si
S552	0.08 ~0.1 ~0.1 ~0.1	— — — —	— — — —	— — — —	0.042 ~0.05 ~0.05 ~0.05	— — — —
S553	0.13 0.1-0.2 0.1-0.2 0.1-0.2	— — — —	— — — —	— — — —	0.042 ~0.05 ~0.05 ~0.05	— — — —
S554	0.18 0.1-0.2 0.1-0.2 ~0.2	— — — —	— — — —	— — — —	0.044 ~0.05 ~0.05 ~0.05	— — — —
S587	— — —	0.0095 ~0.01 ~0.01 ~0.01	— — — —	— — — —	— — — —	— — — —
S588	— — —	— — —	0.019 0.01-0.05 0.01-0.05 0.01-0.05	— — — —	— — — —	— — — —
S589	— — —	— — —	— — —	— — —	0.016 0.01-0.05 0.01-0.05 0.01-0.05	— — — —
S590	— — —	— — —	— — —	— — —	— — —	0.004 0.005 0.005 0.005
S591	— — —	— — —	— — —	— — —	— — —	0.007 0.005-0.01 0.005-0.01 ~0.01
S592	0.0045 ~0.005 ~0.005 ~0.005	— — — —	— — — —	0.07 0.05-0.1 0.05-0.1 0.05-0.1	— — — —	— — — —
S593	0.018 0.01-0.05 0.01-0.05 0.01-0.05	— — — —	— — — —	— — — —	0.044 0.01-0.05 ~0.05 0.01-0.05	— — — —
S594	0.038 ~0.05 0.01-0.05 ~0.05	— — — —	— — — —	— — — —	— — — —	— — — —

TABLE III  
ADDITIONAL RESULTS (PER CENT.)

Sample	Material	Added	Element			
			Found by			
			Alternative method	Recommended method		
S135	Phosphor bronze 95% Cu, 4.8% Sn, 0.2% P	Zinc	0.10	~0.1	~0.1	~0.1
S136		Zinc	0.006	~0.005	~0.005	~0.005
S137		Lead	0.005	~0.005	~0.005	~0.005
		Bismuth	0.001	~0.001	~0.001	~0.001
S138		Lead	0.004	~0.005	~0.005	~0.001-0.005
		Bismuth	0.0013	~0.001	~0.001	~0.001
S139		Lead	0.002	~0.001	~0.001	~0.001
		Bismuth	0.0008	<0.001	<0.001	<0.001
		Arsenic	<0.005	0.001-0.005	0.001-0.005	0.001-0.005
		Phosphorus	0.012	~0.01	~0.01	~0.01
S140		Lead	0.005	~0.005	~0.005	~0.005
		Bismuth	0.0027	0.001-0.005	0.001-0.005	0.001-0.005
		Arsenic	0.005	0.001-0.005	0.001-0.005	0.001-0.005
		Phosphorus	0.018	~0.01	~0.01	~0.01
S143		Lead	0.06	0.05-0.1	~0.1	~0.05
		Iron	0.01	0.01-0.05	0.01-0.05	~0.01
		Nickel	0.02	0.01-0.05	0.01-0.05	0.01-0.05
		Arsenic	0.015	0.01-0.05	0.01-0.05	~0.01
		Phosphorus	0.14	0.1-0.2	0.1-0.2	0.1-0.2
S144		Phosphorus	0.18	0.1-0.2	0.1-0.2	0.1-0.2
S555		Phosphorus	0.05	~0.05	~0.05	~0.05
S552	Alumbro 76% Cu, 22% Zn, 2% Al	Tin	0.08	~0.1	~0.1	~0.1
		Arsenic	0.042	~0.05	~0.05	~0.05
S553		Tin	0.13	0.1-0.2	0.1-0.2	0.1-0.2
		Arsenic	0.042	~0.05	~0.05	~0.05
S554		Tin	0.18	0.1-0.2	0.1-0.2	0.2
		Arsenic	0.044	~0.05	~0.05	~0.05
S587		Lead	0.0095	~0.01	~0.01	~0.01
S588		Iron	0.019	0.01-0.05	0.01-0.05	0.01-0.05
S589		Arsenic	0.016	0.01-0.05	0.01-0.05	0.01-0.05
S590		Silicon	0.004	~0.005	~0.005	~0.005
S591		Silicon	0.007	0.005-0.01	0.005-0.01	~0.01
S592		Tin	0.0045	~0.005	~0.005	~0.005
		Nickel	0.07	0.05-0.1	0.05-0.1	0.05-0.1
S593		Tin	0.018	0.01-0.05	0.01-0.05	0.01-0.05
		Arsenic	0.044	~0.05	0.01-0.05	0.01-0.05
S594		Tin	0.038	~0.05	~0.05	0.01-0.05

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# The Spectrophotometric Determination of Tungsten with Thiocyanate

## Part III. Moderating the Interference by Molybdenum in the Determination of Tungsten in Steel

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Molybdenum in excess of 0.3 per cent. w/w interferes in the determination of tungsten in low tungsten steels ( $W < 0.25$  per cent. w/w) with thiocyanate because of a molybdenum-iron inter-element effect. Two procedures are described which overcome this limitation. In the first procedure tungsten(VI) and molybdenum(VI) are extracted into chloroform as benzoin  $\alpha$ -oxime complexes prior to the determination of tungsten. In the second procedure iron is extracted from the tungsten and molybdenum into isobutyl methyl ketone. Up to 4 and 25 per cent. w/w, respectively, of molybdenum in the steel can be tolerated when these procedures are used.

In Part II<sup>1</sup> a procedure in which tetraphenylarsonium thiocyanatotungstate(V) is extracted into chloroform was recommended for the determination of tungsten in steel. Precise results were obtained with this procedure in determining tungsten in a wide range of steels when either hydrochloric acid or orthophosphoric acid was used with nitric acid to dissolve the steel samples. The use of orthophosphoric acid is preferred by steel analysts, however, as its complexing action makes the hydrolysis of the tungsten less likely. One of the major advantages that the new procedure has over the existing British Standards' procedure<sup>2</sup> is that vanadium interference is eliminated completely. The tolerance to molybdenum, however, is the same as in the British Standards' procedure. For steel samples containing more than 0.25 per cent. of tungsten, molybdenum does not seriously interfere, as at least 3 per cent. of molybdenum in the steel can be tolerated.

The extent of interference by molybdenum is largely a function of the iron-to-molybdenum ratio in the sample, and interference occurs when the sample weight is increased to obtain an acceptable sensitivity in the tungsten-thiocyanate reaction at low tungsten levels. For steel samples containing less than 0.25 per cent. of tungsten, when a large weight of sample had to be taken, only about 0.3 per cent. of molybdenum could be tolerated in the direct procedure.

The present paper describes the development of modified procedures in which interference by molybdenum in the determination of tungsten in low tungsten steels is greatly reduced. Several approaches to the elimination of molybdenum interference are possible, including the prior precipitation of molybdenum as its sulphide, as has been suggested by Bush and Higgs.<sup>3</sup> The present work has been concerned with methods that reduce the concentration of iron in the solution from which the tungsten-thiocyanate complex is extracted, *viz.*, prior solvent extraction of the tungsten and molybdenum from the iron and prior solvent extraction of the iron from the tungsten and molybdenum.

Benzoin  $\alpha$ -oxime has been suggested previously<sup>4,5</sup> as a reagent for extracting tungsten(VI) and molybdenum(VI) from iron, and this procedure, with certain modifications, has been applied satisfactorily in the present work. Luke,<sup>6</sup> on the other hand, extracted iron(III) from concentrated hydrochloric acid-water solution (1 + 1 v/v) into isobutyl methyl ketone in the determination of tungsten with thiocyanate; this procedure has also been adapted in the present work.

METHOD I. EXTRACTION OF TUNGSTEN AND MOLYBDENUM WITH BENZOIN  $\alpha$ -OXIME AS PART OF THE PROCEDURE FOR THE DETERMINATION OF TUNGSTEN IN STEEL

The extraction of tungsten(VI) and molybdenum(VI) with benzoïn  $\alpha$ -oxime into chloroform has been used previously, in conjunction with thiocyanate in the determination of tungsten in steel.<sup>7,8</sup> In these procedures the solid tungsten and molybdenum-benzoïn  $\alpha$ -oxime complexes were wet oxidised prior to the determination of tungsten. In the present investigation, however, satisfactory results were obtained without wet oxidising the benzoïn  $\alpha$ -oxime complexes. After evaporating the chloroform extract nearly to dryness, the residue was treated directly with concentrated hydrochloric acid and tin(II) chloride. Attempts to back-extract the tungsten quantitatively from the chloroform solution into a 2 per cent. w/v solution of tin(II) chloride in concentrated hydrochloric acid were unsuccessful.

Orthophosphoric acid interfered with the extraction of the tungsten-benzoïn  $\alpha$ -oxime complex, and this precluded its use in the dissolution of steel samples. Steel samples were dissolved in a mixture of hydrochloric and nitric acids, as indicated previously (Dissolution of steels (*i*) in Part II).

In the procedure described below the tolerance to molybdenum is increased to 4 per cent. w/w in the steel. When more molybdenum is present the amount of benzoïn  $\alpha$ -oxime used is insufficient to extract all of the molybdenum and tungsten. This difficulty cannot be overcome by adding more reagent, as the increased amount of reagent interferes with the extraction of the tungsten(V) - thiocyanate complex.

REAGENTS—

*Hydrochloric acid, concentrated, sp.gr. 1.16 to 1.18.*

*Nitric acid, sp.gr. 1.42.*

*Orthophosphoric acid, sp.gr. 1.75.*

*Chloroform.*

The above reagents should be of analytical-reagent grade.

*Standard sodium tungstate solution, 25  $\mu\text{g ml}^{-1}$ , in concentrated hydrochloric acid*—Dissolve 2.2432 g of analytical-reagent grade sodium tungstate dihydrate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in water, and dilute the resulting solution to 500 ml with water in a calibrated flask. Dilute 5.00 ml of this solution to 500 ml in a calibrated flask with concentrated hydrochloric acid.

*Benzoïn  $\alpha$ -oxime solution, 0.15 per cent. w/v, in chloroform*—Dissolve 1.5 g of benzoïn  $\alpha$ -oxime in ethanol and dilute to 100 ml with ethanol. Dilute 10 ml of this solution to 100 ml with chloroform as required.

*Ammonium iron(II) sulphate solution, 20 per cent. w/v*—Dissolve 20 g of ammonium iron(II) sulphate in water and dilute the resulting solution to 100 ml with water. Prepare fresh daily.

*Tin(II) chloride solution, 10 per cent. w/v, in concentrated hydrochloric acid*—Dissolve 20 g of tin(II) chloride dihydrate in 180 ml of concentrated hydrochloric acid. This solution should be prepared fresh weekly.

*Sodium thiocyanate solution, 2 M*—Dissolve 117 g of sodium thiocyanate dihydrate in water, and dilute to 500 ml with water. This solution is stable for about 3 weeks, but should be discarded if a pink colour develops.

*Tetraphenylarsonium chloride solution, 0.025 M*—Dissolve 1.05 g of tetraphenylarsonium chloride in 100 ml of water. This solution should be prepared fresh every 2 or 3 weeks.

*Chloroform containing 0.08 per cent. w/v of quinol*—Prepare a 1 per cent. w/v solution of quinol in absolute ethanol, and dilute 20 ml of this solution to 250 ml with chloroform. The ethanol solution is stable for about 1 week when stored in the dark, but should be discarded if a pink colour develops. The chloroform solution should be prepared fresh daily.

*Ammonium hydrogen difluoride.*

*Hydrochloric acid, approximately 6 M*—Dilute 258 ml of concentrated hydrochloric acid to 500 ml with water.

DISSOLUTION OF THE STEEL—

Dissolve 0.5 g of the steel in 25 ml of concentrated hydrochloric acid and the minimum amount of nitric acid (5 to 10 drops). For more rapid dissolution warm the mixture gently. When the steel is dissolved, boil the solution for 5 minutes to remove oxides of nitrogen. Dilute the solution to 50 ml in a calibrated flask with concentrated hydrochloric acid.

No difficulties were experienced with this dissolution procedure. If a small residue remains it should be filtered off and treated with a small amount of an orthophosphoric acid - nitric acid mixture (2 + 1, v/v). The resulting solution should then be returned to the main sample solution immediately after the solvent-extraction stage has been completed. For the routine analysis of a particular steel, the residue insoluble in hydrochloric acid - nitric acid should be examined spectrographically for tungsten. If absent, the residue in these instances can be discarded, with consequent saving in time.

PROCEDURE—

With a safety pipette, add 10 ml of the steel solution to 35 ml of water in a 100-ml separating funnel. Add 5 ml of ammonium iron(II) sulphate solution and mix thoroughly. Extract the tungsten and molybdenum with four 10-ml portions of benzoic  $\alpha$ -oxime solution in chloroform, then combine the extracts in a 100-ml conical flask and evaporate the chloroform solution nearly to dryness. Add 16 ml of concentrated hydrochloric acid and 4 ml of tin(II) chloride solution. Simmer the solution just below its boiling-point for 5 minutes.\* Cool the solution, preferably in an ice-bath.

Transfer the solution to a 100-ml separating funnel fitted with a Teflon tap and use two 10-ml portions of 6 M hydrochloric acid solution to wash the solution remaining in the conical flask into the separating funnel. With a safety pipette, add 1 ml of tetraphenylarsonium chloride solution, swirl the solution, add 3 ml of sodium thiocyanate solution from a safety pipette, swirl the solution again, and extract the tetraphenylarsonium tungsten(V) - thiocyanate complex successively with 9, 8 and 7-ml amounts of chloroform containing quinol, adding 10 drops of tetraphenylarsonium chloride solution before each of the last two extractions.

Transfer the extracts to a second 100-ml separating funnel fitted with a Teflon tap. Add 10 ml of water from a measuring cylinder and 1.5 to 2 g of ammonium hydrogen difluoride, and shake the mixture. Pass all of the chloroform layer through a No. 1 Whatman filter-paper directly into a 25-ml calibrated flask. Wash the aqueous fluoride layer with 1 ml of chloroform containing quinol, and pass the chloroform through the filter-paper into the flask. Wash the filter-paper with a small amount of chloroform containing quinol, and dilute the chloroform extracts to 25 ml with the same chloroform. Mix the solution thoroughly and measure the absorbance at 402 nm against chloroform by using 1-cm cells.

METHOD 2. USE OF ISOBUTYL METHYL KETONE TO EXTRACT IRON

It was considered that a procedure by which iron could be extracted from tungsten and molybdenum would be simpler than the benzoic  $\alpha$ -oxime procedure. Luke<sup>6</sup> used isobutyl methyl ketone for the extraction of iron(III) from hydrochloric acid - water (1 + 1, v/v) solution in the determination of tungsten with thiocyanate. The procedure described below was developed in the present work. By dosing a hydrochloric acid solution of British Chemical Standards steel No. 322 with sodium molybdate, it was found that molybdenum in concentrations up to 25 per cent. w/w in the steel could be tolerated. When molybdenum was present in greater concentrations the red colour of the molybdenum(V) - thiocyanate complex was observed in the measured solutions and the absorbance values obtained were high.

As in the benzoic  $\alpha$ -oxime procedure, orthophosphoric acid cannot be used to dissolve the steel in this case, because of its complexing action on the iron(III), which prevents the extraction of the iron into isobutyl methyl ketone.

PROCEDURE—

Prepare a concentrated hydrochloric acid solution of the steel as described in the benzoic  $\alpha$ -oxime method above.

With a safety pipette, transfer 10 ml of this solution into a 100-ml separating funnel containing 10 ml of water and 20 ml of isobutyl methyl ketone. Immediately shake the mixture vigorously to extract the iron and run the lower aqueous layer into a 100-ml conical flask. Extract the isobutyl methyl ketone layer with two 4-ml portions of 6 M hydrochloric acid solution, adding the aqueous layer on each occasion to the conical flask.

Evaporate the aqueous layer nearly to dryness and immediately add carefully 16 ml of concentrated hydrochloric acid and 4 ml of tin(II) chloride solution. Complete the analysis as described in the benzoic  $\alpha$ -oxime method from "Simmer the solution just below its boiling-point for 5 minutes. . . ."

\* The procedure described hereafter is also used in Method 2 below.

## RESULTS

The extent of molybdenum interference in the benzoin  $\alpha$ -oxime procedure, described in Method 1, was investigated by using standard solutions of sodium tungstate and sodium molybdate; the iron was added as iron(III) chloride. The results given in Table I were obtained under conditions simulating those for the analysis of a low-tungsten sample and indicate that up to 4 per cent. w/w of molybdenum could be tolerated in such a steel sample. Serious molybdenum interference, when it occurred, could be detected by visual examination of the chloroform extract; when tungsten alone was present the chloroform solution was straw-coloured, whereas with a trace amount of the molybdenum(V) - thiocyanate complex present it was tinged with red.

TABLE I  
MOLYBDENUM TOLERANCE OF THE BENZOIN  $\alpha$ -OXIME PROCEDURE

Molybdenum, per cent. w/w, in the steel equivalent to molybdate added	0	1	2	3	4	5	6
Absorbance*	0.487	0.466	0.473	0.472	0.465	0.428	0.262

\* 150  $\mu$ g of tungsten level with 50 mg of iron.

The extent of molybdenum interference in the isobutyl methyl ketone procedure, described in Method 2, was investigated by determining the tungsten in British Chemical Standards steel No. 322, by dosing the sample aliquots with various amounts of sodium molybdate. The results obtained with this procedure are compared in Table II with those obtained with the direct procedure given in Part II. With the isobutyl methyl ketone procedure up to 25 per cent. w/w of molybdenum in the steel can be tolerated, whereas the direct procedure clearly gives high results with molybdenum contents above 0.5 per cent. w/w.

TABLE II  
EFFECT OF ADDED MOLYBDATE ON THE DETERMINATION OF TUNGSTEN IN B.C.S. 322 STEEL BY USING THE DIRECT AND ISOBUTYL METHYL KETONE PROCEDURES

Molybdenum, per cent. w/w, in the steel equivalent to molybdate added*	Apparent tungsten content of B.C.S. 322, per cent. w/w	
	Direct procedure <sup>1</sup>	Isobutyl methyl ketone procedure
0	0.049	0.049
0.5		0.050
5	0.074	0.051
10		0.052
15		0.053
20		0.052
25	0.114	0.053
30		0.054
40		0.057
50		0.062
100	0.122	0.070

\* B.C.S. 322 contains 0.045 per cent. w/w of molybdenum. The amount of iron present remained constant; in practice, the amount of iron present would decrease as the amount of molybdenum increased and the tolerance would be somewhat greater.

The results of analyses of three steels with tungsten contents of less than 0.25 per cent., and molybdenum contents of greater than 0.3 per cent., are given in Table III. Molybdenum was expected to interfere in the determination of tungsten in these three steels when using the direct thiocyanate procedure, but this was found not to be so because of the high concentration of other alloying elements present in these steels, which effectively decreases the amount of iron present in the aliquot taken. Nevertheless, these three steels were also analysed by using the benzoin  $\alpha$ -oxime and the isobutyl methyl ketone procedures. The results agree well with those obtained with the direct thiocyanate procedure and with the dithiol method.



TABLE III  
COMPARISON OF THE DIRECT AND MODIFIED PROCEDURES IN THE DETERMINATION  
OF TUNGSTEN IN STEEL SAMPLES

Sample No.	Spectrographic values, per cent. w/w*					Dithiol* method	Direct procedure	Benzoin $\alpha$ -oxime procedure	Isobutyl methyl ketone procedure
	Cr	Ni	Ti	Mo	W				
1	18	8	—	2.6	<0.1	0.055	0.052	0.054	0.053
2	18	8	0.5	0.5	<0.1	0.05	0.046	0.044	0.044
3	18	8	—	0.6	0.15	0.12	0.121	0.115	0.121

\* Spectrographic and dithiol values from Firth-Brown Limited.

#### DISCUSSION

The benzoin  $\alpha$ -oxime and isobutyl methyl ketone extraction modifications to the direct colorimetric procedure for determining tungsten with thiocyanate allow its extension to the determination of tungsten in steel samples containing amounts of molybdenum that would normally interfere. Unfortunately orthophosphoric acid interferes in both of these modifications to the procedure, and therefore this acid cannot be used in the dissolution of the steel. This disadvantage will detract from the use of these modifications by steel analysts who are conscious of the possibility that tungsten(VI) will hydrolyse in the absence of orthophosphoric acid. Orthophosphoric acid can be used to treat residues insoluble in hydrochloric acid; the resulting solution is added after the extraction stage.

Difficulties arising from the hydrolysis of tungsten(VI) were experienced in the present work only in the isobutyl methyl ketone extraction procedure when the tungsten was kept for longer than 5 minutes in concentrated hydrochloric acid - water (1 + 1 v/v) solution. Delay at the iron extraction stage should be avoided; once the concentrated hydrochloric acid is diluted in the separating funnel, the extraction of the iron and the transfer of the aqueous layer to the conical flask should be made as rapidly as possible.

In many instances the direct procedure involving orthophosphoric acid dissolution can be extended to low tungsten steels containing relatively high molybdenum contents by taking a smaller sample weight than that recommended and either accepting a lower absorbance reading or using cells with a longer path length, or both. For example, if the recommended sample weight and aliquot volumes were taken in determining tungsten in a steel containing 0.1 per cent. of that element, then the final chloroform extract would contain 100  $\mu$ g of tungsten. An absorbance value of 0.32 would be obtained, and at least 0.3 per cent. of molybdenum could be tolerated. If one fifth of this sample weight were taken the absorbance reading would be 0.060<sub>4</sub> and 12 per cent. of molybdenum could be tolerated.<sup>1</sup> The use of cells with a longer path length would give a more acceptable absorbance value without reducing the molybdenum tolerance. The exact amount that could be tolerated would depend on the percentage of other alloying metals present in the steel, as has been shown in this paper. The presence of other alloying metals reduces the amount of iron present in the sample weight taken, and reduces the interference of molybdenum.

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NOTE—Reference 1 is to Part II of this series.

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# The Determination of Lithium, Sodium and Potassium in Geological Materials by Atomic-emission Spectrophotometry with the Nitrous Oxide - Acetylene Laminar-flow Flame

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A straightforward method is described for the determination of lithium, sodium and potassium by atomic-emission spectrophotometry on an acidic solution of the sample without separation or concentration. In routine application detection limits of 0.002, 0.01 and 0.01 per cent., respectively, have been obtained with no spectral or chemical interferences. Results are presented for eight standard samples, and long-term relative standard deviations of 2.4 per cent. (lithium), 1.7 per cent. (sodium) and 2.5 per cent. (potassium) have been found on a B.C.S. firebrick.

By using wavelength scanning the determination of trace amounts of lithium has been demonstrated, with a detection limit of about 0.1 p.p.m. in the sample. If blank problems can be controlled the direct determination of sodium and potassium at the parts per million level should be possible even for limestones.

In a recent review Pickett and Koirtyohann<sup>1</sup> have drawn attention to the increasing applicability of atomic-emission spectrophotometry to chemical analysis by using instruments equipped with high resolution grating monochromators and laminar-flow burner systems. The determination of the alkali metals was the earliest application of flame photometry but it has usually involved the use of simple filter instruments and total-consumption burners. Often cool, air - town gas or air - propane or air - butane flames have been used. As a result both chemical and spectroscopic interferences are common, leading most workers to recommend careful matrix matching or separation procedures to remove major constituents.<sup>2,3,4,5</sup> However, ionisation interferences remain from the effect of other alkali metals on the analyte and these can require complex correction methods.<sup>3</sup>

Thus several authors have suggested the use of atomic-absorption spectrophotometry.<sup>6,7,8</sup> With this technique spectral interferences are avoided but chemical and ionisation effects can still cause difficulties.

The laminar-flow air - acetylene flame has been used for the atomic-emission spectrophotometric determination of the alkali metals in combination with buffers to suppress interferences. Thus Sulcek and Rubeska<sup>7</sup> used aluminium nitrate as a buffer in the determination of lithium. In a study of the applicability of the nitrous oxide - acetylene flame in emission analysis, Pickett and Koirtyohann<sup>9,10</sup> have shown that the lithium determination is extremely sensitive (detection limit  $3 \times 10^{-5}$  p.p.m.), but they did not investigate chemical or spectroscopic interferences. No work has been published on the determination of sodium or potassium in this flame.

This paper describes the investigation and use of the nitrous oxide - acetylene laminar-flow flame in the analysis of siliceous and similar materials to determine lithium, sodium and potassium.

## EXPERIMENTAL

### INSTRUMENTAL AND APPARATUS—

A Techtron, Model AA5, atomic-absorption spectrophotometer, fitted with a Jarrell-Ash, Model 82-025, scanning monochromator, a 285-Hz chopper and the Standard Techtron burner assembly, was used. Spectra were recorded on a Servoscribe potentiometric recorder. The

monochromator was equipped with a variable, curved jaw, slit assembly (10 to 400- $\mu$ m aperture) and a grating blazed at 400 nm. The reciprocal dispersion was 1.6 nm in the first order. A Wratten No. 8 coloured glass filter was used to remove second-order interferences. For the sodium ( $\lambda = 589.0$  nm) and lithium ( $\lambda = 670.8$  nm) determinations, a Hamatsu R136 photomultiplier tube was found most suitable, while a R196 tube was used for potassium ( $\lambda = 766.5$  nm).

The use of glassware was kept to a minimum. Solutions were stored in plasticware and decomposition of materials was effected in PTFE beakers.

#### REAGENTS—

*Primary standards, 1 000 p.p.m.*—For lithium, dissolve 2.661 9 g of lithium carbonate (Johnson Matthey Specpure) in the minimum volume of hydrochloric acid and make the volume up to 500 ml with water; for sodium, dissolve 1.271 0 g of analytical-reagent grade sodium chloride in water and make the volume up to 500 ml; and for potassium, dissolve 0.953 3 g of analytical-reagent grade potassium chloride in water and make the volume up to 500 ml.

*Caesium buffer, 4 per cent. w/v*—Dissolve 50.8 g of caesium chloride (Hopkin and Williams AnalaR grade) in water and make the volume up to 1 litre.

*Interference solutions*—These were generally prepared from the analytical-reagent grade chlorides (cerium was used as ammonium cerium nitrate and lead and aluminium were used as their nitrates) and were stored as 2 per cent. w/v solutions.

*Acids*—Analytical-reagent grade concentrated acids were used without further purification.

Laboratory de-ionised water was further purified by passage through a mixed-bed de-ioniser.

#### PROCEDURE—

Weigh 0.500 0 g of sample into a 150-ml PTFE beaker. Add 5 ml of nitric acid (sp.gr. 1.42), 1 ml of sulphuric acid (sp.gr. 1.84) and 5 ml of 40 per cent. w/v hydrofluoric acid. Heat the mixture on an asbestos covered hot-plate until fumes of sulphur trioxide appear. Remove the beaker from the hot-plate, cool, and add the same amounts of these acids again. Heat to fumes and add the same amounts of acids for a third time. Heat the mixture to fumes and leave to fume on the hot-plate overnight. Cool. Add 10 ml of hydrochloric acid (sp.gr. 1.18) and 20 ml of water and heat to dissolve salts. Transfer the solution to a 100-ml flask (preferably polypropylene), add 10 ml of a 4 per cent. w/v caesium solution and make up to volume. Store in plasticware. Duplicate reagent blanks should be run routinely.

Alkali-metal standards are prepared by dilution of the 1 000 p.p.m. primary standards. They should be matched with 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid.

Samples are compared with the standards by using the instrumental conditions shown in Table I.

TABLE I

#### INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF THE ALKALI METALS WITH THE NITROUS OXIDE - ACETYLENE FLAME

Element	Lithium	Sodium	Potassium
Wavelength/nm .. .. .	670.8	589.0	766.5
Photomultiplier tube .. .. .	R 136	R 136	R 196
Spectral half-band width/nm .. .. .	0.08	0.08	0.16
Slit height/mm .. .. .	20	3	20
Burner* .. .. .	AB 50	AB 50	AB 50
Burner height/mm .. .. .	10 to 12	8 to 10	9 to 11
Flame adjustment† (red "feather")/mm ..	3	1	1
Typical working range, p.p.m. .. .. .	0 to 2	0 to 50	0 to 150
Typical gain setting .. .. .	2	1	11

\* Aligned at right angles to light path.

† Adjusted to give maximum emission signal when aspirating a standard solution.

## RESULTS

All work was carried out at the primary emission wavelength for each element, which were 670.8 nm for lithium, 589.0 nm for sodium and 766.5 nm for potassium.

## AIR - ACETYLENE FLAME—

An initial investigation was made into the effectiveness of various levels of aluminium nitrate, lanthanum chloride and caesium chloride in removing interferences from up to 2 000 p.p.m. (equivalent to 40 per cent. in the sample) of some common elements in the determination of sodium and potassium in the air - acetylene flame. A 100-mm slot, AB51, burner (Techtron) was used with the slot aligned parallel to the optical path. The flame and burner heights were adjusted to provide maximum signal strength for each element. The solutions contained 50 p.p.m. of the analyte and 10 per cent. v/v of hydrochloric acid in addition to the interferent and buffer. With no buffer present the most serious effects were observed from the other alkali metals, iron and calcium. It is apparent from the results shown in Table II that none of the buffers reduced interferences to a tolerable level.

## NITROUS OXIDE - ACETYLENE FLAME—

Koirtyohann and Pickett<sup>10</sup> have shown that lithium is ionised to a considerable extent in the nitrous oxide - acetylene flame. This was confirmed and 4 000 p.p.m. of caesium were used as an ionisation buffer for the three alkali metals; 4 000 p.p.m. of caesium were used in all subsequent measurements. The same authors have demonstrated that self-absorption can cause bending of the analytical curves when the burner slot is aligned parallel to the optical path. As the sensitivity for the three alkali metals is more than adequate for requirements, the burner was turned at right angles to the optical path. Some curvature was still found, which was more pronounced at high concentrations, but the working curves were nevertheless satisfactory.

TABLE II  
RECOVERY OF SODIUM AND POTASSIUM IN THE AIR - ACETYLENE FLAME  
SHOWING THE ACTION OF VARIOUS BUFFERS

Interferent (2 000 p.p.m.)	Apparent concentration of sodium, p.p.m., in the presence of			
	No buffer	2 000 p.p.m. of aluminium	10 000 p.p.m. of lanthanum	4 000 p.p.m. of caesium
None .. .. .	50.0	50.0	50.0	50.0
Iron .. .. .	50.0	53.0	50.0	53.0
Calcium .. .. .	51.5	51.0	51.5	53.5
Magnesium .. .. .	48.5	49.5	49.5	51.0
Aluminium .. .. .	49.0	50.0	50.0	51.0
Manganese .. .. .	50.0	52.5	50.5	53.0
Cobalt .. .. .	50.0	52.0	50.0	52.0
Copper .. .. .	48.0	49.5	50.0	51.5
Nickel .. .. .	49.0	49.0	50.0	52.0
Potassium .. .. .	52.5	54.5	53.5	52.0

Interferent (2 000 p.p.m.)	Apparent concentration of potassium, p.p.m., in the presence of			
	No buffer	2 000 p.p.m. of aluminium	10 000 p.p.m. of lanthanum	4 000 p.p.m. of caesium
None .. .. .	50.0	50.0	50.0	50.0
Iron .. .. .	46.0	47.0	46.5	46.5
Calcium .. .. .	46.0	48.0	45.5	47.5
Magnesium .. .. .	47.5	48.5	47.5	49.5
Aluminium .. .. .	49.5	50.0	49.5	48.5
Manganese .. .. .	50.5	50.0	50.0	49.5
Cobalt .. .. .	48.0	47.5	48.0	48.5
Copper .. .. .	48.5	50.0	48.5	49.5
Nickel .. .. .	49.0	48.5	49.0	49.0
Sodium .. .. .	57.0	57.0	54.0	48.0

All solutions contained 10 per cent. v/v of hydrochloric acid. The flame and burner heights were adjusted to give maximum emission intensity for the buffered solution with no interferent present.

The effects of flame and burner height adjustment for the three elements are shown in Figs. 1 and 2. Burner heights are measured in millimetres by using the scale on the Techtron burner unit. On this scale the zero corresponds to the position when the burner top is at the centre of the optical axis. When the instrument is used in the atomic-absorption mode the light beam from a hollow-cathode lamp intercepts the burner top at a height of 5 mm. For the burner height study the flame was adjusted to give maximum signal strength (Table I). In all work a nebulisation pressure of  $175 \text{ kNm}^{-2}$  (25 p.s.i.) was used, which produced a nitrous oxide flow of 7 to 8 l minute<sup>-1</sup>. For the flame adjustment study the burner height was optimised (Fig. 1). The flame showing the highest signal strength had a trace of red "feather," and the lithium flame was noticeably richer than that of sodium or potassium. Under these optimised conditions the emission intensity for each element was compared with that obtained in an optimised air - acetylene flame with the 100-mm slot burner also aligned at right angles to the optical path. The nitrous oxide - acetylene flame was more sensitive for all three elements (Table III). The relative intensities for lithium are in reasonable agreement with previous results.<sup>10</sup>

TABLE III  
COMPARISON OF THE EMISSION INTENSITIES IN THE AIR - ACETYLENE AND  
NITROUS OXIDE - ACETYLENE FLAMES

Element	Concentration, p.p.m.	Emission intensity	
		Air - acetylene*	Nitrous oxide - acetylene†
Lithium .. .. .	2	8	100
Sodium .. .. .	50	15	100
Potassium .. .. .	50	45	100

All solutions contained 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid.

\* AB51, 100-mm slot burner at right angles.

† AB50, 60-mm slot burner at right angles.

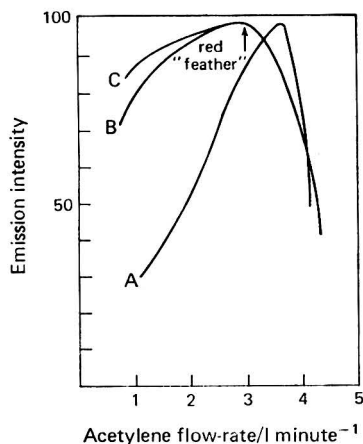


Fig. 1. Effect of acetylene flow-rate on emission intensity. Other parameters as shown in Table I. A, lithium 2 p.p.m.; B, sodium 50 p.p.m.; and C, potassium 50 p.p.m.

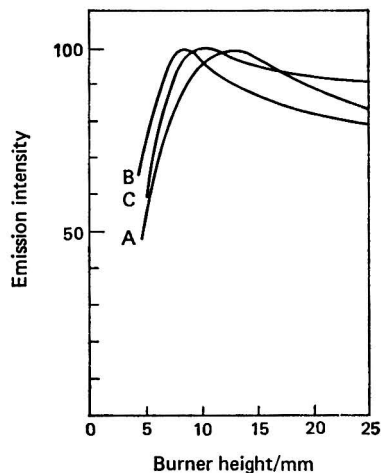


Fig. 2. Effect of burner height on emission intensity. Other parameters as shown in Table I. A, lithium 2 p.p.m.; B, sodium 50 p.p.m.; and C, potassium 50 p.p.m.

#### INTERFERENCES—

All interference studies were made by using the standard flame and burner height conditions shown in Table I.

Spectral interferences were investigated by aspirating a 2 000 p.p.m. solution of all common cations and scanning the wavelength for each analyte. Usually the reagents contained sufficient alkali-metal impurity to indicate the wavelength. Chemical and ionisation

interferences were investigated by preparing sets of solutions containing the same concentration of analyte and the different interferents at the 200 and 2 000 p.p.m. levels. When necessary, corrections were made for spectral interferences and alkali-metal impurity in the interferent, as indicated by the wavelength scan.

*Lithium*—The gain was adjusted to bring 0.1 p.p.m. of lithium to full scale. No detectable increase in background was observed for the following elements: sodium, potassium, vanadium, chromium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, lead, bismuth, aluminium and magnesium. Barium, lanthanum and cerium caused a slight increase in background (Fig. 3). The effect from calcium was more pronounced and was such that an apparent concentration of 0.000 5 per cent. of lithium oxide would be found in a limestone sample (0.5 per cent. w/v sample concentration) if none was present. Strontium hydroxide band interference on lithium is well known. The effect observed here was such that a concentration of 1 200 p.p.m. of strontium produced a signal equivalent to that from 0.1 p.p.m. of lithium. Thus a strontium oxide concentration of 1 per cent. in a sample would cause an apparent 0.000 15 per cent. of lithium oxide to be reported if no wavelength scan were made.

It can be seen that none of these effects are likely to be important in analytical applications unless very low levels of lithium (less than 0.002 per cent.) are required in limestones

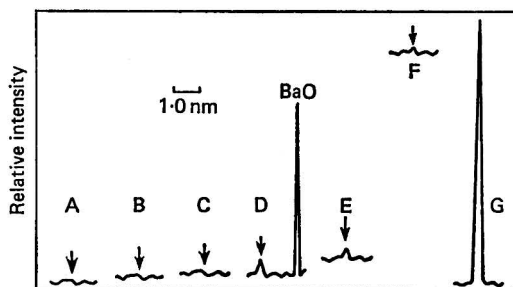


Fig. 3. Spectral interference on lithium. Wavelength scans at 670.8 nm, 0.08 nm spectral half-band width. All solutions contain 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid: A, water; B, 2 000 p.p.m. of lanthanum; C, 2 000 p.p.m. of cerium; D, 2 000 p.p.m. of barium; E, 2 000 p.p.m. of calcium; F, 1 000 p.p.m. of strontium; and G, 0.1 p.p.m. of lithium

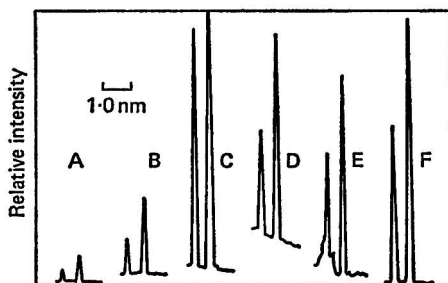


Fig. 4. Spectral interference on sodium. Wavelength scans at 589.0 nm, 0.08 nm spectral half-band width. All solutions contain 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid: A, water; B, typical scan of 2 000 p.p.m. of chromium, manganese, iron or barium; C, 2 000 p.p.m. of strontium; D, 2 000 p.p.m. of calcium; E, 2 000 p.p.m. of lanthanum; and F, 1 p.p.m. of sodium

or samples high in strontium. In this event the effect can be completely allowed for by scanning the wavelength and subtracting the background signal.

Chemical and ionisation interferences were studied at the 1 p.p.m. level for all those interfering elements listed above, with the exception of strontium. When the solutions were aspirated under the standard conditions  $1.00 \pm 0.01$  p.p.m. of lithium was found in all instances.

*Sodium*—For the wavelength scan the gain was adjusted to bring 1 p.p.m. of sodium to full scale. No increase in background was observed for the following elements: lithium, potassium, vanadium, molybdenum, cobalt, copper, zinc, cadmium, lead, bismuth, aluminium, magnesium and cerium. Slight increases in background were observed for chromium, manganese, iron and barium and more definite effects from strontium, lanthanum and calcium (Fig. 4). The greatest effect was from calcium and was such that an apparent concentration of 0.003 per cent. of sodium oxide would be found in a limestone sample if none was present. In routine application this will not be significant as reagent blanks equivalent to 0.01 per cent. are usual.

Chemical and ionisation interferences were studied at the 50 p.p.m. level for all those elements listed previously. After correction for sodium impurity in the interference solutions,  $50 \pm 0.5$  p.p.m. of sodium were found in all instances.

*Potassium*—Spectral interferences were again studied at the 1 p.p.m. level; the only effects observed were slight background signals from calcium and strontium and stronger signals from barium and lanthanum (Fig. 5). No chemical or ionisation effects on 50 p.p.m. of potassium were observed even from 2 000 p.p.m. of sodium (ionisation potential 5.12 eV), when corrections had been made for potassium in the reagents.

These results indicate that spectral, chemical and ionisation effects should not cause any errors in the routine analysis of a very wide range of materials for alkali metals.

#### ROUTINE APPLICATION—

The main interest of this laboratory in alkali metals is the analysis of feldspars of typical composition: potassium oxide, 1 to 11 per cent.; sodium oxide, 0.5 to 3 per cent.; and lithium oxide, 0.005 to 0.05 per cent. The sample-to-solution concentration was 0.5 per cent. w/v and the working ranges were 0 to 150 p.p.m. for potassium, 0 to 50 p.p.m. for sodium and 0 to 2 p.p.m. for lithium. One great advantage of atomic-emission spectrophotometry is that the working range can easily be adapted to suit specific applications. Thus, if low potassium figures were required a working range of 0 to 25 p.p.m. was used. In preference to aspirating high concentrations (greater than 200 p.p.m.), when curvature of the calibration graphs would become serious, samples at high concentrations were diluted four times. The range thus covered is shown in Table IV. Instrumental conditions have already been tabulated (Table I). The only possible spectral interference within this routine working range would occur for

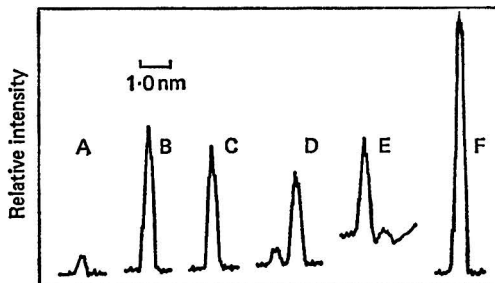


Fig. 5. Spectral interference on potassium. Wavelength scans at 766.5 nm, 0.32 nm spectral half-band width. All solutions contain 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid: A, water; B, 2 000 p.p.m. of strontium; C, 2 000 p.p.m. of calcium; D, 2 000 p.p.m. of barium; E, 2 000 p.p.m. of lanthanum; and F, 1 p.p.m. of potassium

TABLE IV  
TYPICAL ROUTINE WORKING RANGES

Element	Standards, p.p.m.	Metal oxide in sample,* per cent.	
		Range on direct solution	Range on 4 × diluted solution
Lithium .. .. .	0 to 2	0.002 to 0.09	0.09 to 0.35
Sodium .. .. .	0 to 50	0.01 to 1.35	1.35 to 5.40
Potassium .. .. .	0 to 25 0 to 150	0.01 to 0.60 0.60 to 3.60	— 3.60 to 14.4

\* Assuming a 0.5 per cent. w/v sample concentration.

the lithium determination on samples containing more than 10 per cent. of strontium. Levels of calcium up to those resulting from the dissolution of pure limestone do not interfere.

Table V shows results obtained on several British and American standard materials. All of the sodium and potassium results and the lithium results on samples Nos. 315, 269 and 1016, were obtained by using the routine method. The sodium on sample 99a was obtained on a 10-fold dilution of the original solution. Lithium was determined in the spodumene on a 20-fold dilution of the original solution, by using standards in the range 0 to 10 p.p.m. With the routine method results of less than 0.002 per cent. of lithium oxide were reported for samples 1b, 70a, 99a and 319. The determination of trace amounts of lithium is considered later.

The agreement obtained with the standard figures was in most instances excellent. Sodium and potassium could not be detected above the reagent blank for the magnesite sample (319) and the lithium oxide concentration was less than 0.002 per cent. The errors in the accepted figures for this sample are an indication of the difficulties in determining trace levels of the alkali metals by conventional flame photometry. Strelow, Toerien and Weinert<sup>8</sup> have also found that the values given in the literature for several international rocks are over one order of magnitude too high at the trace level for sodium and potassium.

The B.C.S. firebrick 269 was used as an analytical control over a period of 2 months while a batch of five hundred feldspars was being analysed. The relative standard deviations obtained (thirty-six observations) were as follows: lithium 2.4 per cent., sodium 1.7 per cent. and potassium 2.5 per cent.

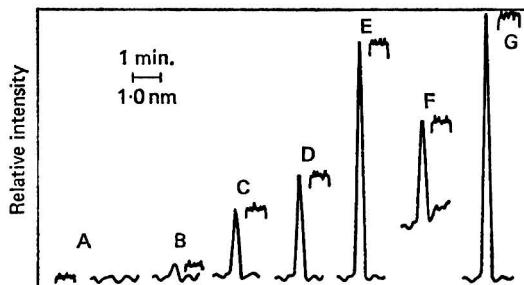


Fig. 6. Determination of trace amounts of lithium. Wavelength and time scans 670.8 nm, 0.08 nm spectral half-band width. A, water. All other solutions contain 4 000 p.p.m. of caesium and 10 per cent. v/v of hydrochloric acid: B, "0" p.p.m. standard and reagent blank; C, N.B.S. 99a; D, N.B.S. 70a; E, B.C.S. 319; F, N.B.S. 1b; and G, 0.05 p.p.m. of lithium standard

#### DETERMINATION OF TRACE AMOUNTS OF ALKALI METALS—

One of the greatest problems in the determination of trace amounts of alkali metals arises from adventitious contamination. When using analytical-reagent grade acids, twice de-ionised water and PTFE decomposition vessels we found typical sodium and potassium reagent



TABLE V  
RESULTS OBTAINED ON STANDARD MATERIALS

Number	Description	Lithium		Sodium		Potassium	
		This method	Certified	This method	Certified	This method	Certified
B.C.S. 315	Firebrick	0.093	0.09	0.10	0.13	0.49	0.52
B.C.S. 269	Firebrick	0.124	0.13*	0.38	0.37	2.52	2.62
B.C.S. 319	Magnesite	0.0018	0.02*	<0.01	0.04	<0.01	0.02
N.B.S. 1b	Argillaceous limestone	0.0009	—	0.04	0.04	0.26	0.25
N.B.S. 1016	Portland cement	0.018	0.012*	0.52	0.55	0.04	0.04
N.B.S. 70a	Feldspar	0.0008	—	2.50	2.55	11.6	11.8
N.B.S. 99a	Feldspar	0.0005	—	6.1 <sub>7</sub>	6.2	5.1 <sub>1</sub>	5.2
N.B.S. 181	Spodumene	6.3 <sub>6</sub>	6.3 <sub>9</sub>	0.88	0.8*	0.27	0.3*

The results are means of triplicates and are given as percentage of metal oxide.

\* Preliminary results only.

blanks of 50 to 100  $\mu\text{g}$ . Strelow, Toerien and Weinert<sup>8</sup> used ultra-pure acids and obtained blanks of 0.5 to 3  $\mu\text{g}$ . The limitation then appeared to be from atmospheric contamination.

In this work lithium blanks were not found to be troublesome and lithium could not be detected in reagent blanks (probably less than 0.01  $\mu\text{g}$ ). About 0.15  $\mu\text{g}$  of lithium was found in the caesium buffer and a "0" p.p.m. standard was therefore used. Wavelength scans for lithium were made for samples Nos. 1b, 70a, 99a and 319, the gain being adjusted to bring 0.05 p.p.m. of lithium to full scale; these are shown in Fig. 6. It can be seen that there is no background emission whatsoever for samples 99a and 319 and only a negligible increase for sample 70a, which is in agreement with the predictions from the spectral interference study. The correct results for these samples would therefore be obtained from a simple measurement of peak height at 670.8 nm. Definite background emission is, however, observed for sample 1b and this must be subtracted from the peak height in the calculation. The results for these four samples obtained from the wavelength scan are shown in Table V.

These results show that if the blank problem can be controlled this method could be used for the determination of trace amounts of sodium and potassium down to the parts per million level without the need for prior separation of the analyte. It should be emphasised that the sensitivity for all three alkali metals is more than adequate for requirements, as indicated by the fact that all of the work reported was performed with the burner slot aligned at right angles to the light path. At low concentrations, when self-absorption should not be serious, enhancements of from five to ten times could be obtained by aligning the burner slot parallel to the light path.

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# Potentiometric Determination of Mercury(II) with Dithiooxamide

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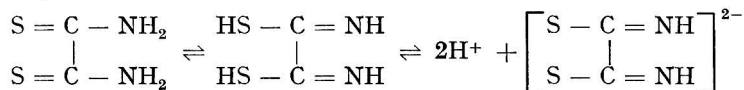
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Potentiometric titration with dithiooxamide can be used to determine mercury in the 0.10 to 40.0 p.p.m. range (0.01 mg to 4.00 mg per 100 ml) with a relative standard deviation ranging from 1.50 to 0.26 per cent. and an accuracy of about 0.3 per cent. A silver indicator electrode is used. Several interferences were investigated and found to have little effect. Among these were cadmium, zinc, nickel, iron, lead and cobalt. The interferences of silver and copper in the determination were also investigated and are discussed. Two simple fast modifications to the procedure are suggested when determining mercury in the presence of either silver or copper. The advantages of this method over other methods are outlined.

THE determination of mercury at the microgram level is of considerable importance because of the increasing concern associated with the use of various mercury-containing fungicides, insecticides, pharmaceuticals, etc., and the resulting possible health hazards. Several methods for determining mercury are available, but most of them suffer from one or more of the following disadvantages: (i) need for lengthy preliminary separations, (ii) need for careful pH control, (iii) necessity for using very pure solvents, (iv) lack of sensitivity and numerous interferences, (v) instability of reagents, (vi) lack of suitable precision or accuracy, or both, and (vii) need for elaborate, expensive equipment.<sup>1 to 12</sup> The method described in this paper involves the use of equipment that is available in almost every laboratory and may in many instances, depending on the interferences present, accuracy desired and equipment available, provide a faster or more convenient method for the determination of trace amounts of mercury than those currently available.

Potentiometric titrations of copper and silver with dithiooxamide (rubeanic acid) have already been described<sup>13,14</sup>; in both instances, a silver electrode was used as the indicator electrode and was found to produce a high degree of accuracy, precision and selectivity. In the present investigation, the determination of mercury by this method was thoroughly examined and its accuracy and precision evaluated.

Dithiooxamide was first used as a precipitation reagent by Ray and Ray.<sup>15</sup> It exists in solution in equilibrium with its tautomeric form<sup>16</sup>—



It reacts with metals such as zinc, copper, palladium, cobalt and nickel to form 1:1 chelates, which are stable at room temperature. The salts are probably polymeric compounds of dithiooxamide.<sup>17</sup> Iron(II), iron(III), ruthenium, silver, cadmium and mercury ions form unstable compounds, which rapidly decompose to yield sulphides. Gold and platinum salts are reduced to the metals.<sup>18</sup> By correct pH control and by complexation with fluoride and EDTA the reagent can be made more selective.

## METHOD

### APPARATUS—

A Beckman "Zeromatic" pH meter with a silver indicator electrode and glass reference electrode was used in all titrations. Titrant was added from a 10-ml burette and continuous stirring was provided with a magnetic stirrer.

## REAGENTS—

All reagents should be of analytical-reagent grade if possible.

*Mercury stock solution*—Prepare a standard mercury (II) nitrate solution containing 0.100 0 mg ml<sup>-1</sup> of mercury by weighing 100.0 mg of triple-distilled mercury metal, dissolving it in 1 to 2 ml of 6 N nitric acid and diluting the solution to 1 litre with conductivity water.

*Dithiooxamide solution*—Prepare the dithiooxamide titrant solution by dissolving, with gentle heating and continuous stirring, 151.6 mg of dithiooxamide in 700 ml of conductivity water. Then cool the solution, dilute it to 1 litre and store in polythene containers. The reagent appears to be stable for about 4 weeks. (An amount of dithiooxamide between 100 and 200 mg would be appropriate in preparing a stock solution of concentration such that a reasonable number of millilitres would be required for titrating the 100-ml samples containing from 0.700 to 4.000 mg of mercury. Further dilutions of this dithiooxamide solution are required when titrating the more dilute mercury samples containing 0.010 0 to 0.400 0 mg per 100 ml.)

## PROCEDURE—

Measure accurately and deliver the appropriate number of millilitres of the mercury stock solution into 150-ml beakers (1.00 to 40.00 ml of this stock mercury solution, *i.e.*, 0.100 mg to 4.000 mg of mercury, would produce, after dilution to 100 ml, mercury samples ranging from 1.00 p.p.m. to 40.00 p.p.m.; to prepare the 0.1 to 1 p.p.m. mercury samples, the stock mercury solution was first diluted 10-fold). To each beaker add 1 g of analytical-reagent grade potassium hydrogen phthalate to maintain a pH of approximately 4.5, and 0.5 g of analytical-reagent grade sodium fluoride to mask trace amounts of iron(III). Dilute the samples to 100 ml with conductivity water and titrate with the dithiooxamide solution. Allow the potential to reach equilibrium before each reading. In the vicinity of the equivalence-point add the titrant in 0.05-ml increments and wait 3 to 4 minutes for the potential to reach equilibrium. Calculate the end-point by using a graph of millivolts *versus* millilitres of titrant or by other suitable means. This point can usually be estimated to the nearest 0.01 ml.

After each titration, rub the silver electrode with a clean towel or fine sand paper to remove any sulphide film that has formed. Then immerse it in a 0.05 M potassium cyanide solution for 1 minute and rinse with distilled water.

## RESULTS AND DISCUSSION

In this work, synthetic mercury samples and mercury samples with interferences were prepared from known standard solutions and examined for precision, accuracy and interference effects. The procedures involved in preparing natural samples for analysis by wet oxidation with nitric and sulphuric acids, in a suitably designed apparatus to prevent losses of mercury by volatilisation, are described in the literature.<sup>7,9</sup>

TABLE I  
PRECISION OF DETERMINATION FOR 0.100 TO 40.00 p.p.m. OF MERCURY(II)

Mercury, p.p.m.	Dithiooxamide/ ml*	Relative standard deviation, per cent.
0.100†	0.73	1.50
0.200†	1.40	1.43
0.400†	2.88	1.19
0.560†	3.97	0.76
0.700†	5.02	0.72
0.800†	5.69	0.88
1.00†	1.80	1.35
2.00‡	3.70	1.32
4.00‡	7.80	0.26
7.00	1.34	0.78
10.00	1.89	0.49
16.00	3.04	1.09
24.00	4.57	0.71
32.00	6.04	0.67
40.00	7.60	1.33

\* Average of six determinations.

† The stock dithiooxamide solution was diluted 40-fold for these titrations.

‡ The stock dithiooxamide solution was diluted 10-fold for these titrations.

Fifteen standard solutions of mercury(II), ranging in concentration from 0.100 to 40.00 p.p.m. (0.0100 to 4.000 mg of mercury per 100 ml), were prepared by diluting appropriate amounts of the stock standard mercury(II) nitrate solution to 100 ml as already described. Six replicate determinations were made on each of these fifteen solutions to establish the precision of the method; the results (Table I) showed an average deviation of approximately 1 per cent. In order to use a reasonable number of millilitres of dithiooxamide when titrating the samples containing small amounts of mercury (0.100 to 0.800 p.p.m.) the stock dithiooxamide solution was diluted 40-fold. To titrate the mercury solutions ranging from 1.00 to 4.00 p.p.m. the dithiooxamide solution was diluted 10-fold. For the mercury solutions containing from 7.00 to 40.00 p.p.m., the stock dithiooxamide solution was used at the concentration originally prepared.

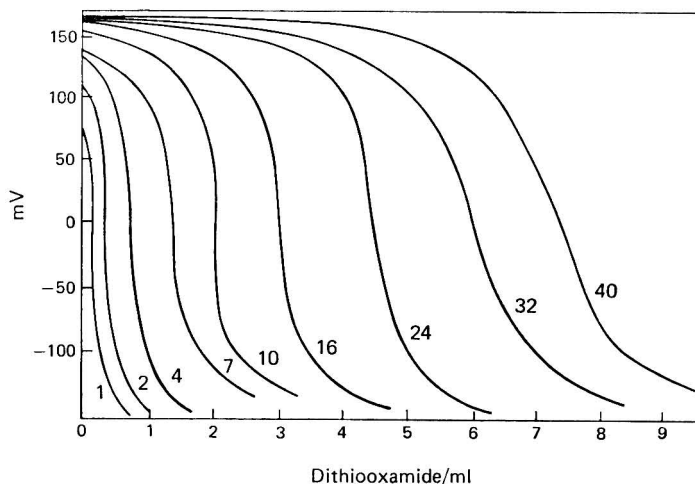


Fig. 1. Representative potentiometric titration curves for 1 to 40 p.p.m. of mercury(II) with 0.00132 M dithiooxamide

Fig. 1 shows representative potentiometric titration curves for the titrations of the 1 to 40 p.p.m. mercury solutions; the breaks are well defined and of the order of 200 mV. By plotting the average volumes of dithiooxamide solution (after correcting for any dilutions of the dithiooxamide) required to react with each concentration level *versus* the mercury concentrations a linear working graph was produced. Extrapolation of this graph to zero p.p.m. of mercury gave a blank value of 0.01 ml of dithiooxamide solution, which probably results from trace amounts of contaminating metals in the water and reagents or from the small amount of dithiooxamide that can exist in the solution at the equivalence-point, or both.

Calculation of the molarity of the dithiooxamide solution based on its weight gave a value of 0.00126. Assuming that all of the mercury(II) ions reacted and were converted into mercury(II) sulphide, one mole of dithiooxamide would react with two moles of mercury. When this 2:1 relationship and the blank correction were used with the results obtained in the titrations of the 1 to 40 p.p.m. mercury solutions, the molarity of the dithiooxamide solution was experimentally calculated to be 0.00132, which is 4.8 per cent. more concentrated than the weight of dithiooxamide taken would indicate. This effect may be caused by absorption of mercury ions by mercury(II) sulphide or may arise as the result of the decomposition of the dithiooxamide before weighing. In any event, the working graphs were linear and reproducible so that no difficulty was encountered in using dithiooxamide as the titrant.

Fig. 2 shows representative potentiometric titration curves for the titrations of the 0.100 to 1.00 p.p.m. mercury solutions; the breaks are slightly smaller, of the order of 100 to 150 mV. A linear relationship was again found when millilitres of dithiooxamide solution were plotted *versus* parts per million of mercury.

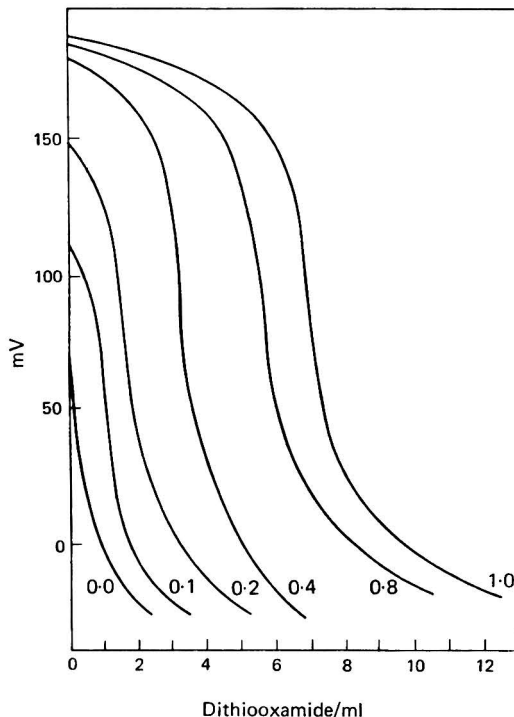


Fig. 2. Representative potentiometric titration curves for 0.1 to 1.0 p.p.m. of mercury(II) with stock dithiooxamide solution diluted 40-fold

It appears that 0.1 p.p.m. (0.01 mg per 100 ml) represents the approximate limit of analysis, because, as the concentrations are made smaller, the curves become more and more ill-defined and the smaller potential breaks reduce the accuracy and precision of the analysis. In addition, when smaller mercury concentrations are determined, as long as 10 minutes may be required in the vicinity of the equivalence-point for equilibrium to be reached before taking potential readings. However, by reducing the volume of the samples (100 ml were used in this work) to 10 ml or below, and by using special small electrodes, the limit of analysis could be extended down to 1  $\mu\text{g}$  (absolute) of mercury and below to submicrogram amounts. As the relative concentration of mercury (0.1 p.p.m.) in these samples of smaller volume and

TABLE II  
ANALYSIS OF SYNTHETIC UNKNOWNNS

Sample	True composition, p.p.m.	Mercury found, p.p.m.	Relative error, per cent.	Sample	True composition, p.p.m.	Mercury found, p.p.m.	Relative error, per cent.
A	Hg 0.100	0.101	+1.00	L	Hg 10.00; Ni 50	10.03	+0.30
B	Hg 1.00	0.99	-1.00	M	Hg 10.00; Fe 500	10.01	+0.10
C	Hg 5.00	5.03	+0.60	N	Hg 10.00; Fe 250	10.04	+0.40
D	Hg 10.00	10.02	+0.20	O	Hg 10.00; Pb 500	10.05	+0.50
E	Hg 20.00	20.00	0.00	P	Hg 10.00; Co 500	10.39	+3.90
F	Hg 40.00	39.90	-0.25	Q	Hg 10.00; Co 250	10.46	+4.60
G	Hg 10.00; Cd 500	10.05	+0.50	R	Hg 10.00; Co 100	9.99	-0.10
H	Hg 10.00; Zn 500	10.05	+0.50	S	Hg 10.00; Co 50	10.03	+0.30
I	Hg 10.00; Zn 250	9.97	-0.30	T	Hg 10.00; Zn 50		
J	Hg 10.00; Ni 500	10.17	+1.70		Cd 50 ; Fe 50	9.99	-0.10
K	Hg 10.00; Ni 250	10.15	+1.50	U	Hg 10.00; Zn 50		
					Cd 50 ; Ni 10	10.00	0.00

the relative concentration of the dithiooxamide solution, which would have to be diluted for such titrations, would be the same as in this previous work, similar potential breaks, as illustrated herein, would be obtained and, therefore, similar accuracy and precision would be expected for these microgram and submicrogram amounts.

#### INTERFERENCES—

Several synthetic mercury solutions of unknown concentration containing mercury alone, ranging from 0.100 to 40.00 p.p.m. (0.0100 to 4.000 mg per 100 ml), and containing mercury with different interferences at various concentrations, were prepared from standard stock solutions. Table II gives their composition and the error encountered in the determination with dithiooxamide of their mercury contents. Zinc, cadmium, iron(III) and lead did not interfere. Cobalt and nickel, in large amounts, showed some interference; however, when present in amounts usually encountered they caused no difficulty. The presence of fluoride and the potassium hydrogen phthalate buffer prevents these and other ions from interfering.

Copper and silver do interfere with the titration of mercury with dithiooxamide solution. When copper is present, two potential breaks are obtained in the titration curve. The second, due to the sum of the mercury and copper, appears at the correct number of millilitres, as calculated by using the experimentally determined molarity of the dithiooxamide solution from actual titrations of samples with known copper and known mercury contents. The first break, which corresponds to the mercury alone, is slightly high, depending on how much copper is present, and so could only be used for a semi-quantitative determination of mercury. Copper can be complexed with EDTA, but this last reagent cannot be used in this titration as it also reacts with mercury. For the exact determination of mercury in the presence of copper the analyst could either subject the sample to a preliminary separation to remove the copper before titrating the mercury with the dithiooxamide solution, or determine the mercury by a potentiometric titration with potassium iodide solution, with which copper causes no interference. (When titrating mercury with potassium iodide solution, the same experimental conditions and the same electrode system were used). Iodide titrations of samples containing 10.0 p.p.m. of mercury and 5 p.p.m. of copper gave results ranging from 9.8 to 10.1 p.p.m. of mercury. With iodide as the titrant, the accuracy at this concentration of mercury is about the same as when dithiooxamide is used as the titrant. However, the potential breaks for the iodide titration of mercury are about 50 mV smaller than the breaks obtained when using dithiooxamide. Therefore, as would be expected, the iodide titration would not, by a factor of about 5, be capable of determining amounts of mercury as small as those determined by dithiooxamide titration. (The dithiooxamide has another advantage over iodide in that it can be applied to the determination of other metals and analysis of mixtures of metals.<sup>13,14,19</sup>)

It is possible to analyse mixtures of mercury and copper for both elements by potentiometric titration with dithiooxamide to give the total mercury and copper, followed by potentiometric titration with potassium iodide on another aliquot to give the mercury alone.

When silver is present only one usable potential break is found (corresponding to the sum of the mercury and silver). Studies indicate that with dithiooxamide titrations it is possible to determine the concentrations of both metals in a mixture by obtaining the sum of silver and mercury on one aliquot of the unknown mixture and, on a second aliquot, after precipitation of the silver with bromide, the amount of mercury alone. When samples containing 10.0 p.p.m. of mercury and 10.0 p.p.m. of silver were analysed by this procedure the results ranged from 10.0 to 10.4 p.p.m. of mercury and from 9.7 to 10.1 p.p.m. of silver. However, the potential breaks for the mercury titration in the presence of excess of bromide ion (added to precipitate the silver) were reduced by a factor of 2 to 3, depending on the amount of bromide present in excess. A 10 to 20 per cent. excess amount over the amount of bromide required to precipitate the silver is recommended.

#### ADVANTAGES OF THE METHOD—

The proposed method is comparable in sensitivity and accuracy with the methods commonly used for the determination of trace amounts of mercury (by using special electrodes, it might be possible to analyse 1-ml samples containing 0.1  $\mu$ g of mercury). It possesses the advantage of using inexpensive equipment normally available in most laboratories. Further, the dithiooxamide reagent is stable for longer periods of time than the reagents commonly

used in colorimetric analysis. Many elements that interfere in the standard colorimetric methods for the determination of mercury, thus requiring lengthy preliminary separations, do not cause interference in this potentiometric titration method. Those which do interfere, such as copper and silver, can be treated as indicated to obtain results for mercury or for both ingredients. The method is also more rapid, requiring only 20 to 30 minutes compared with 3 to 4 hours for most colorimetric methods.

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## Spectrophotometric Determination of Sulphate in Propellents and Nitrocellulose

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An accurate method is proposed for the determination of sulphate in propellents and nitrocellulose that requires only 45 minutes to carry out. The sample is treated with a mixture of nitric acid, perchloric acid and magnesium nitrate, and the solution is evaporated to dryness over a bunsen burner. The salts deposited are heated for 5 minutes with a mixture of hydriodic, hypophosphorous and hydrochloric acids in a simplified distillation apparatus, with nitrogen passing through the system; the hydrogen sulphide that results from the reduction of the sulphate is absorbed into ammonia solution, lead citrate is added, and the brownish yellow lead sulphide colour is measured.

SODIUM sulphate and potassium sulphate are frequently added to propellents in amounts up to 2 per cent. Also, sulphate is found in nitrocellulose as absorbed sulphuric acid or cellulose sulphate ester; unstabilised nitrocellulose contains up to 1 per cent. of sulphate (calculated as  $H_2SO_4$ ) while stabilised (purified) nitrocellulose usually contains less than 0.05 per cent.

Sulphate in propellents has been determined by precipitation as barium sulphate after oxidation of the organic matter by either a mixture of nitric and perchloric acids<sup>1</sup> or a mixture of nitric acid and sodium chlorate.<sup>2</sup> Frequently, the cation of the sulphate salt is determined and calculation made with respect to the sulphate salt.<sup>3</sup>

The above methods for the determination of sulphate in propellents have proved to be troublesome; therefore this laboratory undertook the development of a spectrophotometric method involving the reduction of sulphate to hydrogen sulphide by a mixture of hydriodic and hypophosphorous acids.

St. Lorant<sup>4,5</sup> and St. Lorant and Kopetz<sup>6</sup> showed that sulphate could be determined by reduction to hydrogen sulphide by using a mixture of hydriodic acid and red phosphorus. The hydrogen sulphide was collected in zinc acetate solution and the sulphide determined as methylene blue. Roth<sup>7</sup> modified St. Lorant's method. Johnson and Nishita<sup>8</sup> determined sulphate in plant material by using the hydriodic acid - red phosphorus mixture but finished the determination iodimetrically.

Luke<sup>9,10</sup> proposed the use of a mixture of hydriodic and hypophosphorous acids instead of the hydriodic acid and red phosphorus. He collected the hydrogen sulphide in a solution containing cadmium ions and titrated it with iodate. In applying the method to the determination of sulphate in rubber he conducted a preliminary evaporation to fumes with perchloric acid to destroy organic matter. Luke determined sulphur in metals<sup>11</sup> by dissolving them in hydrochloric and nitric acids, destroying the resulting nitrate with formic acid, adding the hydriodic acid - hypophosphorous acid reagent, collecting the hydrogen sulphide in ammonia solution, adding lead citrate, and finally measuring the brownish yellow colour. However, he used the hydriodic acid - hypophosphorous acid reagent and a titrimetric finish for the determination of sulphur in steels.<sup>12</sup> Bethge,<sup>13</sup> in determining sulphate in organic compounds, evaporated them to fumes with perchloric acid, added the hydriodic acid - hypophosphorous acid reagent, collected the hydrogen sulphide in sodium hydroxide solution and titrated it with iodate. Pepkowitz<sup>14</sup> used a similar method but collected the hydrogen sulphide in ammoniacal cadmium solution.

Pepkowitz and Shirley<sup>15</sup> developed a method for the detection of sulphur by combustion of the sample with copper oxide, treatment of the residue with the hydriodic acid - hypophosphorous acid mixture and reduction of a molybdenum - thiocyanate reagent to produce red molybdenum thiocyanate. Keattch<sup>16</sup> and McKinley and Jones<sup>17</sup> used the hydriodic acid - hypophosphorous acid reagent and an iodimetric titration for the determination of



sulphate in chrome-plating baths, after which Keattch<sup>18</sup> applied the same technique to the determination of sulphate in soils. Steinbergs, Iismaa, Freney and Barrow<sup>19</sup> determined sulphur in soil and plant material by igniting the material with a mixture of sodium hydrogen carbonate and silver oxide for 3 hours, adding a hydriodic acid - hypophosphorous acid - formic acid reagent, and using the methylene blue spectrophotometric method.

Vandael<sup>20</sup> determined sulphate in barium sulphate by refluxing it for 1 hour with the hydriodic acid - hypophosphorous acid reagent. The same investigator considered the chemistry of the reaction and concluded that hydriodic acid and hypophosphorous acid both participate in the reduction of the sulphate. Previously, it had apparently been believed that hydriodic acid was the active reducing agent and that the hypophosphorous acid merely reduced the iodine formed by the reaction between the sulphate and hydriodic acid.

The present investigator used the hydriodic acid - hypophosphorous acid reagent as it is more easily prepared than the hydriodic acid - red phosphorus reagent. The spectrophotometric technique involving the lead sulphide colour was also used.

#### METHOD

##### APPARATUS—

The apparatus (Fig. 1) consists of a 50-ml round-bottomed flask with a 19/38 ground-glass joint, an adaptor, a 100-ml calibrated flask and a 1-litre beaker wrapped in asbestos cloth. Pyrex glassware must be used throughout. The internal diameter of the tubing is 0.6 mm. The 50-ml round-bottomed flask is held by a clamp about 1 foot above the bench and the inlet tube of its adaptor is connected to a tank of nitrogen by Tygon tubing. The nitrogen must be controlled by a needle valve so that if the regulator does not have a satisfactory needle valve, one must be inserted into the system (a Lab-Crest Needle Valve, 1.25 mm, made by Fischer and Porter, Warminster, Pa., was used).

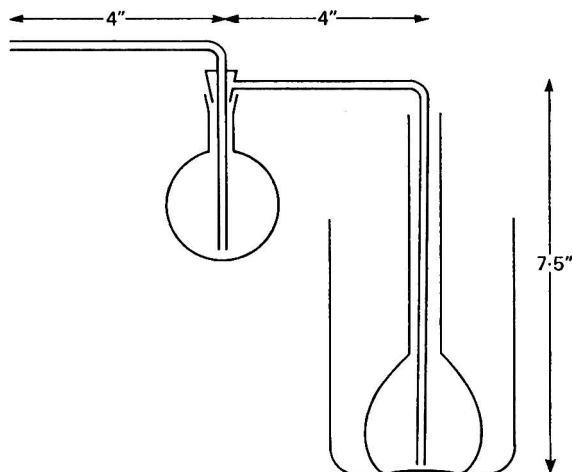


Fig. 1. Distillation apparatus

##### REAGENTS—

*Standard potassium sulphate solution*—Dissolve 0.1088 g of potassium sulphate (previously dried at 120 °C) in water and dilute to 1 litre in a calibrated flask.

1 ml of solution  $\equiv$  0.02 mg of sulphur.

*Hydriodic acid - hypophosphorous acid - hydrochloric acid reagent*—Transfer 200 ml of 57 per cent. hydriodic acid, 50 ml of 50 per cent. hypophosphorous acid and 100 ml of hydrochloric acid (sp.gr. 1.18) to a 500-ml Erlenmeyer flask that has been fitted with a ground-glass neck and stopper. Add several glass beads, boil the mixture for 5 minutes (without a cover) on a hot plate, remove the flask from the hot-plate, insert the stopper, and leave the flask and contents to cool at room temperature.

*Lead citrate reagent*—Dissolve 10 g of lead nitrate in 200 ml of water. Add 40 g of citric acid monohydrate and stir to dissolve. If salts settle out on standing overnight, use the supernatant liquid.

*Nitric acid - perchloric acid - magnesium nitrate reagent*—Mix 300 ml of nitric acid (sp.gr. 1.42), 100 ml of 70 per cent. perchloric acid and 50 ml of water. Add 20 g of magnesium nitrate hexahydrate and stir to dissolve. The small amount of added water is necessary because magnesium nitrate is not very soluble in concentrated acids.

#### PREPARATION OF CALIBRATION GRAPH—

Pipette 0.2, 2, 5, 10 and 12.5-ml amounts of standard potassium sulphate solution (1 ml  $\equiv$  0.02 mg of sulphur) into 50-ml round-bottomed flasks (with 19/38 ground-glass joints) and also carry out a blank. Add 5 drops of approximately 0.1 N sodium hydroxide solution to each flask and evaporate just to dryness. Allow to cool to room temperature.

Attach the adaptor of the apparatus to an empty 50-ml round-bottomed flask and insert the exit tube into a 100-ml calibrated flask containing approximately 90 ml of water. Connect to the nitrogen supply and regulate the flow to 55 to 65 bubbles per 15 s.

Add 30 ml of ammonia solution (sp.gr. 0.90) to each of six 100-ml calibrated flasks and dilute to approximately 90 ml with water in each case. Place the flasks into broken ice contained in a tray. After a few minutes place one of these flasks into the asbestos-jacketed beaker and fill the beaker to the top with broken ice.

With the nitrogen flowing, insert the adaptor into the flask containing the sample and insert the exit tube into the calibrated flask contained in the beaker. Take care that the apparatus fits together properly and that the exit tube reaches to the bottom of the calibrated flask. Raise the adaptor, add 15 ml of the hydriodic acid - hypophosphorous acid - hydrochloric acid reagent, and immediately reconnect the apparatus. Start a timer, heat the round-bottomed flask with a bunsen burner until the solution comes to an incipient boiling, and then move the burner back and forth so as to maintain the solution at or just below an incipient boiling, this requiring an interval of about 2 seconds between each pass. (Incipient boiling is indicated by the presence of bubbles at the interface of the solution and the sides of the flask.) The total heating time is 5 minutes. At the end of this 5-minute period lower the beaker and remove the calibrated flask. Immediately add 5 ml of lead citrate solution, swirl the contents, and dilute to the mark. Within 5 minutes measure the transmittance at 400 nm with a spectrophotometer that has been set to 100 per cent. transmittance with distilled water.

Calculate the actual percentage transmittance as follows—

$$\text{Actual percentage transmittance} = \frac{\text{percentage transmittance of sample versus water}}{\text{percentage transmittance of blank versus water}} \times 100$$

Plot milligrams of sulphur against the actual percentage transmittance.

#### PROCEDURE—

If the material to be analysed is nitrocellulose, dry it by heating at 40 to 45 °C for 2 hours and then at 98 to 102 °C for 2 hours.

Weigh the sample of propellant or nitrocellulose into a 50-ml round-bottomed flask fitted with a 19/38 ground-glass joint. Preferably use a sample containing 0.1 to 0.2 mg of sulphur but in any case do not use a sample with more than 0.4 g. The appropriate size of sample of propellant can usually be ascertained from the specification requirements. Carry out the following oxidation in a fume cupboard with the usual safety precautions. Secure the flask with a clamp attached to a ring stand and add to the sample 7 ml of nitric acid - perchloric acid - magnesium nitrate reagent. Brush the flame of a bunsen burner back and forth across the bottom of the flask in such a manner that the heating is not sufficient to cause the solution to foam out of the flask. When most of the foaming has ceased, place the bunsen burner under the flask, heat until the salts at the bottom of the flask are completely dry, and then heat for approximately 2 more minutes. Allow the flask and its contents to cool and proceed with the addition of the hydriodic acid - hypophosphorous acid - hydrochloric acid reagent and then with the distillation as given under "Preparation of calibration graph." Carry out a blank determination.

Calculate the percentage of sulphur as follows—

$$\text{Sulphur, per cent.} = \frac{\text{milligrams of sulphur as read from curve}}{\text{grams of sample} \times 10}$$

The following factors apply. To obtain the result as sodium sulphate, per cent., multiply the percentage of sulphur by 4.43, as potassium sulphate, by 5.43, as sulphuric acid, by 3.06, or as percentage of sulphate, by 3.00.

**NOTE—**

Rinse the calibrated flasks with nitric acid (1 + 1) before using them for the next determination in order to remove lead salts that adhere to the sides. Rinse the cells with concentrated nitric acid daily.

### DISCUSSION AND RESULTS

#### APPARATUS—

The apparatus used by the present author is similar to that used by Luke,<sup>11</sup> except that a 50-ml round-bottomed flask is used in place of an Erlenmeyer flask to obtain more rapid flushing and better heating control, by allowing the use of a flame. A 100-ml calibrated flask, instead of the 25-ml calibrated flask suggested by Luke, is used as the receiving flask because a larger volume of ammonia solution is used to absorb the larger amount of hydrogen sulphide distilled.

#### MANNER OF HEATING—

The most effective manner of heating the solution during the distillation is to heat it with a bunsen burner to an incipient boiling and then to maintain it at or just below this temperature by brushing the flame of the bunsen burner back and forth across the bottom of the flask. The temperature of the solution remains at approximately 120 °C. Vigorous boiling is unsatisfactory because it drives over too much of the hydriodic and hydrochloric acids, thus causing heating of the ammonia solution by the neutralisation reaction. Luke<sup>11</sup> carried out the distillation by using an electric hot-plate that was regulated so that the temperature of silicone oil placed in a container alongside the distillation flask was  $185 \pm 3$  °C. It is difficult to control heating conditions when using an electric hot-plate.

#### HEATING TIME—

The heating time used in the distillation was only 5 minutes; heating for a longer period did not give a higher result. Luke<sup>11</sup> heated the solution for 5 minutes after the appearance of white fumes in the neck of the calibrated flask. Other investigators, when working with fairly large amounts of sulphate, heated the solution for a total of 30 to 60 minutes. The present author distilled up to 0.25 mg of sulphur (Luke<sup>11</sup> distilled up to 0.05 mg).

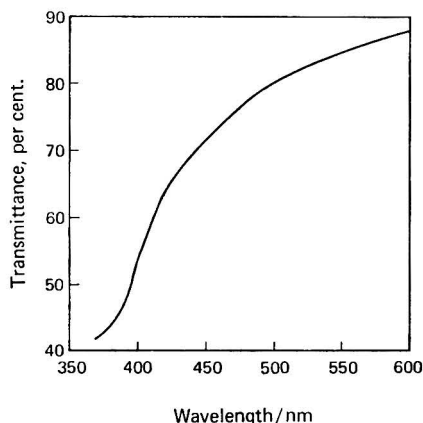


Fig. 2. Spectrophotometric curve for colloidal lead sulphide sol

## FLOW OF INERT GAS—

The optimum flow of inert gas was found to be 55 to 65 bubbles per 15 s as determined by inserting the exit tube of the adaptor into a calibrated flask containing 90 ml of water at room temperature. Luke<sup>11</sup> regulated the flow so that 100 ml of water was displaced from an inverted cylinder in  $30 \pm 1$  s. This manner of controlling the flow-rate is troublesome. The flow-rate as determined in the present method was approximately half that used by Luke.

It is not necessary to flush out the flask before heating with the hydriodic acid - hypophosphorous acid reagent because the small amount of air that remains when the hydrogen sulphide starts to distil does not affect the result (by oxidation). When a flow of air was substituted for the nitrogen, a surprising 80 per cent. recovery of the sulphur was obtained. It is not necessary to purify the nitrogen.

## MEASUREMENT OF THE COLOUR—

The spectrophotometric curve for the colour from 370 to 600 nm is shown in Fig. 2. Maximum absorbance in this range occurs at 370 nm. It is recommended, however, that the colour be measured at 400 nm as better reproducibility was obtained at this wavelength. A study of the stability of the colour showed that the colour developed immediately and was stable for 15 minutes. It then slowly decreased in intensity. It is recommended that the colour be read within 5 minutes.

## BLANK—

As recommended by Luke,<sup>11</sup> the colour is measured against distilled water and a correction made for the blank, which is also measured against distilled water. A blank carried through the entire procedure, including the evaporation to dryness with nitric acid - perchloric acid - magnesium nitrate reagent, and measured against distilled water, gave a transmittance reading of about 95 per cent. and this did not vary significantly throughout the determinations.

The blank value is due to the absorbance of the ammonia - lead citrate solution and trace amounts of sulphur in the reagents. The hydriodic acid - hypophosphorous acid - hydrochloric acid reagent is purified in the course of its preparation. The nitric acid, perchloric acid and magnesium nitrate used in the method were ordinary reagent grade materials. The fact that the blank was low and reproducible indicates that no significant amount of sulphur was picked up from the bunsen burner.

## EFFECT OF WATER—

To test the effect of water on the distillation, various amounts of water were added to evaporated portions of the potassium sulphate solution (containing 0.20 mg of sulphur), and the distillations were carried out with 15 ml of the hydriodic acid - hypophosphorous acid - hydrochloric acid reagent. The results (Table I) show that up to 5 ml of water can be present.

TABLE I  
EFFECT OF WATER ON TRANSMITTANCE

Water/ml	Transmittance, per cent.
0	36
3	36
5	36
7	42
10	67

## PREPARATION OF THE SAMPLE—

It was found that the best means of preparing the sample was to treat it with the reagent containing nitric acid, perchloric acid and magnesium nitrate, evaporate to dryness over a bunsen burner, and then heat for a further 2 minutes. The nitric and perchloric acids destroy the organic matter and fuming to dryness with the perchloric acid eliminates the nitrate. The purpose of the 2-minute heating period after the evaporation to dryness is to drive off the free perchloric acid as it was found that better results were obtained when no free perchloric acid was present. The presence of an excess of the magnesium salt ensures that there is no loss of sulphate during the heating to dryness, and when the addition of the

magnesium nitrate was omitted, low results were obtained. When sodium nitrate was substituted for the magnesium nitrate the results were not satisfactory.

Up to 0.4 g of sample of propellant or nitrocellulose can be handled in the method.

#### SPEED OF THE METHOD—

The method is rapid. A sample can be completely analysed in 45 minutes in contrast with the time-consuming gravimetric method, which requires two filtrations, an overnight standing, and weighing of crucibles.

#### CALIBRATION GRAPHS—

Three calibration graphs were prepared.

The first graph was prepared by treating amounts of standard potassium sulphate solution with 5 drops of approximately 0.1 N sodium hydroxide solution, evaporating the solution to dryness and proceeding with the distillation.

The second graph was prepared by treating amounts of standard potassium sulphate solution with the nitric acid - perchloric acid - magnesium nitrate reagent, evaporating the solution to dryness and proceeding with the distillation.

The third graph was prepared by treating amounts of standard sodium sulphide solution with ammonia solution and lead citrate solution. The difficulty with this method was the preparation of the standard sodium sulphide solution. The usual method of preparing standard sodium sulphide solution is to dissolve hydrated sodium sulphide, which has the approximate formula  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , in water, standardise a portion with iodine and use the remainder of the solution immediately for the required purpose. The author proceeded by first determining sulphide in a sample of fused, flake sodium sulphide (technical, Fisher Scientific Co., containing approximately 60 per cent. of sodium sulphide, the remainder being mainly water). The determination was carried out by dissolving 0.20 to 0.25-g portions in 30 ml of oxygen-free water in glass-stoppered flasks, immediately adding 50.00 ml of 0.1 N iodine solution and 2 ml of hydrochloric acid, and titrating with 0.1 N sodium thiosulphate solution with starch as the indicator. The assay was found to be 24.47 per cent. with respect to sulphide (59.55 per cent. as  $\text{Na}_2\text{S}$ ). A catch weight (0.0487 g) of the material was dissolved in water and the solution diluted to 2 litres in a calibrated flask (the solution now containing 0.005 96 mg ml<sup>-1</sup> of sulphur). Then 10, 20, 30 and 40-ml amounts of this solution were pipetted into 100-ml calibrated flasks and the solutions diluted to approximately 60 ml with water. Thirty millilitres of ammonia solution and 5 ml of lead citrate solution were added, the volume was brought up to 100 ml, and the transmittance was measured.

The three graphs were linear and were identical, a fact that helped to establish the validity of the method. The first method of preparing the graph is recommended because it is the simplest.

#### INTERFERENCES—

No constituent found in ordinary propellents or in nitrocellulose interferes in the method. Cellulose esters in nitrocellulose are readily hydrolysed to inorganic sulphate by nitric acid. As would be expected from the work of Luke,<sup>11</sup> metals such as copper, iron, lead and tin do not interfere. The reason that tin does not interfere, even though it partially distils, is that tin sulphide is soluble in concentrated ammonia solution (see Table III). Ammonium nitrate and ammonium perchlorate, which are found in some propellents, are destroyed during the evaporation and heating.

Barium sulphate does not dissolve readily in the hydriodic acid - hypophosphorous acid - hydrochloric acid reagent and cannot be determined by this method. Fortunately, barium sulphate is not found in propellents or nitrocellulose. Sulphide, sulphite, thiosulphate, elemental sulphur and sulphur-containing organic compounds would interfere but these substances are also not found in nitrocellulose or in ordinary propellents.

#### ABSORPTION OF SULPHIDE IN SODIUM HYDROXIDE SOLUTION INSTEAD OF AMMONIA SOLUTION—

Some experiments were tried with sodium hydroxide solution (25 ml of a 10 per cent. solution diluted to 90 ml with water in the calibrated flask) in place of the ammonia solution. The advantage of sodium hydroxide solution is that it will retain the sulphide quantitatively even when warm, consequently cooling is unnecessary. When sodium hydroxide solution

was used the results were not as reproducible as when ammonia solution was used. Also, the colour was not as stable and did not follow Beer's law. In view of this, the use of ammonia solution is recommended.

The author also investigated the use of the methylene blue method after absorbing the hydrogen sulphide in zinc acetate solution. The results were not as satisfactory as with the lead sulphide spectrophotometric method.

#### RESULTS FOR SULPHATE IN PROPELLENTS AND NITROCELLULOSE—

The results obtained for sulphate in four nitrocellulose-base propellents, one composite propellant and a sample of nitrocellulose by the spectrophotometric method are shown in Table II. Also shown are the results obtained for sulphate in the nitrocellulose-base propellents and the nitrocellulose by the gravimetric nitric acid - perchloric acid method. The

TABLE II  
RESULTS OF DETERMINATION OF SULPHATE IN PROPELLENTS AND NITROCELLULOSE

Sample	Gravimetric procedure		Sample size used for spectrophotometric method/g	Spectrophotometric procedure	
	Sulphate, per cent.	Equivalent sulphur, per cent.		Sulphur, per cent.	Equivalent sulphate, per cent.
140*	0.09 (Na <sub>2</sub> SO <sub>4</sub> )	0.02	0.4	0.027	0.120 (Na <sub>2</sub> SO <sub>4</sub> )
			0.4	0.026	0.115 (Na <sub>2</sub> SO <sub>4</sub> )
			0.4	0.028	0.124 (Na <sub>2</sub> SO <sub>4</sub> )
			Average	0.027	0.120 (Na <sub>2</sub> SO <sub>4</sub> )
297†	0.09 (Na <sub>2</sub> SO <sub>4</sub> )	0.02	0.4	0.020	0.089 (Na <sub>2</sub> SO <sub>4</sub> )
			0.4	0.020	0.089 (Na <sub>2</sub> SO <sub>4</sub> )
			0.4	0.022	0.097 (Na <sub>2</sub> SO <sub>4</sub> )
			Average	0.021	0.092 (Na <sub>2</sub> SO <sub>4</sub> )
487‡	0.43 (K <sub>2</sub> SO <sub>4</sub> )	0.08	0.2	0.084	0.46 (K <sub>2</sub> SO <sub>4</sub> )
			0.2	0.089	0.48 (K <sub>2</sub> SO <sub>4</sub> )
			0.2	0.082	0.45 (K <sub>2</sub> SO <sub>4</sub> )
			0.2	0.084	0.46 (K <sub>2</sub> SO <sub>4</sub> )
			Average	0.085	0.46 (K <sub>2</sub> SO <sub>4</sub> )
446§	0.98 (K <sub>2</sub> SO <sub>4</sub> )	0.18	0.1	0.170	0.92 (K <sub>2</sub> SO <sub>4</sub> )
			0.1	0.184	1.00 (K <sub>2</sub> SO <sub>4</sub> )
			0.1	0.184	1.00 (K <sub>2</sub> SO <sub>4</sub> )
			Average	0.179	0.97 (K <sub>2</sub> SO <sub>4</sub> )
			COM	—	0.00
			0.4	0.000	0.000 (H <sub>2</sub> SO <sub>4</sub> )
			0.4	0.000	0.000 (H <sub>2</sub> SO <sub>4</sub> )
			Average	0.000	0.000 (H <sub>2</sub> SO <sub>4</sub> )
Nitro-cellulose	—	0.00	0.4	0.003	0.009 (H <sub>2</sub> SO <sub>4</sub> )
			0.4	0.004	0.012 (H <sub>2</sub> SO <sub>4</sub> )
			0.4	0.005	0.015 (H <sub>2</sub> SO <sub>4</sub> )
			Average	0.004	0.012 (H <sub>2</sub> SO <sub>4</sub> )

\* Contains, per cent.: nitrocellulose 97.0, nitroglycerin 0.70, dinitrotoluene 0.70, diphenylamine 0.80, calcium carbonate 0.50 and graphite 0.16.

† Contains, per cent.: nitrocellulose 82.4, nitroglycerin 10.07, dinitrotoluene 0.36, diphenylamine 0.92, dibutyl phthalate 5.17, calcium carbonate 0.59 and graphite 0.34.

‡ Special nitrocellulose-base propellant coated with potassium sulphate and containing 0.44 per cent. of potassium nitrate.

§ Contains, per cent.: nitrocellulose 93.0, dinitrotoluene 5.45, diphenylamine 0.68 and graphite 0.14.

|| Contains, per cent.: ammonium perchlorate 70, aluminium 10 and organic binder 20.

results by the proposed spectrophotometric method agree with those for the gravimetric method for the samples of nitrocellulose-base propellents reasonably well, provided that significant amounts of sulphur are present. The gravimetric method gives low and inaccurate results for samples of nitrocellulose or nitrocellulose-base propellents containing less than 0.01 per cent. of sulphur because of incomplete precipitation of the sulphur (this observation was checked by use of synthetic samples).

Experiments on recoveries by the spectrophotometric method were carried out by evaporating amounts of potassium sulphate solution to dryness in 50-ml flasks, adding 0.4 g of nitrocellulose or composite propellant, and taking the samples through the procedure. The recoveries were good (Table III).

TABLE III  
RECOVERY OF SULPHATE FROM SYNTHETIC SAMPLES

Sample	Sulphur found/mg	Sulphur recovered/mg
0.4 g of COM* + 0.020 mg of S .. .. .	0.021	0.021
0.4 g of COM + 0.100 mg of S .. .. .	0.105	0.105
0.4 g of COM + 0.200 mg of S .. .. .	0.196	0.196
0.4 g of COM + 0.250 mg of S .. .. .	0.253	0.253
0.4 g of Nitrocellulose† + 0.020 mg of S .. .. .	0.038	0.022
0.4 g of Nitrocellulose + 0.050 mg of S + 10 mg of Sn	0.064	0.048
0.4 g of Nitrocellulose + 0.100 mg of S .. .. .	0.120	0.104
0.4 g of Nitrocellulose + 0.200 mg of S + 10 mg of Sn..	0.212	0.196

\* Contains 0.000 per cent. of S (Table II).

† Contains 0.004 per cent. of S (Table II).

#### APPLICATION OF THE METHOD TO OTHER MATERIALS—

Obviously the method can be used for many materials of interest to Ordnance Departments. This laboratory is investigating the applicability of the method to the determination of sulphate in chrome baths.

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## A Rapid Absorptiometric Method for the Determination of Formates in Corrosion Products Arising from Paints, Lacquers and Woods

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A method has been evolved in which formate ions reduce an excess of silver nitrate to silver under slightly acidic buffered solution conditions. The method is applicable directly to cadmium and zinc corrosion products. Samples of corrosion products from ferrous metals require preliminary separation by distillation from phosphoric acid. The method is also applicable to the study of formic acid vapours evolved from paints, lacquers and woods, the acidic vapour being absorbed in a dilute aqueous solution of an alkali hydroxide. Allowance is made for the presence of residual metallic particles and for chloride interference.

A series of control standards is run concurrently with each batch of samples to compensate for daily changes in sensitivity because of the ageing of the colloid stabiliser. Recovery of formic acid from synthetic mixtures, based on a sample weight of 0.1 g, has been found to be  $\pm 4$  per cent. for aqueous solutions and zinc products and  $\pm 6$  per cent. for cadmium products, with a 95 per cent. confidence limit.

AN extensive range of costly service equipment has to be stored under a wide variety of climatic conditions in close association with paints, polymers, woods, cardboards, etc. Consequently, there is a continuing need to assess all new packaging and protective materials for compatibility with such equipment in order to help the design authority to make the appropriate choice between available materials.

Assessment of materials for freedom from corrosion by emanating vapours is based primarily on whether or not a specimen of pure zinc sheet metal or wire is seen to corrode during the period of test. However, in locating the source of corrosive vapours it is necessary to identify the particular anionic species responsible.

It has long been known that corrosion can result from the exposure of ferrous metals, cadmium and zinc-plated articles to the vapours arising from woods, paints and plastic components. Many investigators have shown the presence of notable amounts of acetic and formic acids in woods as a result of mild hydrolysis conditions, such as elevated temperature and high humidity.<sup>1,2,3,4</sup> Timmel<sup>2</sup> states that the formic acid yield from woods is generally much less than that from acetic acid, and that some of the wood species tested contained few, if any, formal groups. Those that were detected, he concluded, had resulted from hydrolysis of the wood polysaccharides. Arni, Cochrane and Gray<sup>5</sup> have shown that a considerable increase of both acetic and formic acids results from the incubation of certain hard and soft woods at 48 °C and 100 per cent. relative humidity.

The impregnation of woods against infestation and as a protection against fire necessarily results in the increased availability of free acids and is frequently the cause of vapour corrosion of service stores.<sup>6</sup> Similarly, paints, lacquers and polymers all give rise to acidic vapours from either the slow hydrolysis of contained esters, or the natural oxidation of one or another component. Alternatively, incorrect formulation, which results in too high a residual catalytic peroxide content, has been shown to give rise to excessive corrosion.<sup>7,8</sup> Ross has examined a large number of organic peroxides used in the curing of polyesters and has shown notable amounts of formate to be present in the zinc corrosion product.<sup>9</sup>



## EXPERIMENTAL

## PRELIMINARY CONSIDERATIONS—

When this work was started, in 1965, it was not possible to utilise the sensitivity of the gas - liquid chromatographic technique because the flame-ionisation detector then available was not sensitive to formic acid, while the katharometer detector was not sufficiently sensitive to formic acid. It was thus decided to concentrate on a colour-based method. An exhaustive examination of the method involving the condensation of formaldehyde with chromotropic acid, hexamethylenetetramine being used as a standard source of formaldehyde, showed that reproducibility was no better than approximately  $\pm 30$  per cent. of the amount added (D. G. Higgs and A. F. Charles, unpublished work). These findings are not in accord with the work published by Grant,<sup>10</sup> MacFadyen,<sup>11</sup> and Sawicki, Hauser and McPherson.<sup>12</sup> Furthermore, it was considered that the introduction of the reduction stage of formate to formaldehyde, which is necessary for the colour development, would be detrimental to the reproducibility. Consequently, any method based on a reaction with formate ions that could be applied directly to the corrosion product or to an acidic distillate would have a considerable attraction.

Corrosion products arising from research investigations are usually zinc based or, less frequently, cadmium based. The impurities encountered include the higher homologues of the fatty acid series, which usually decrease in concentration with increasing carbon number, and minute particles of base metal. Corrosion products from storage situations might, in addition, contain chlorides, nitrates, sulphates, phosphates, paint residues or volatiles. The first three anions either do not interfere in the method or can readily be counteracted. Phosphates in large excess could be recognised by the immediate formation of a yellow haze or turbidity, but would be removed, like chlorides, by subsequent dissolution in ammonia solution. Paint volatiles in considerable excess have been shown to exert little influence on the reliability of the method.

Consideration of the essential features of any method for processing corrosion products indicated that attention should be paid to various distillation procedures, direct chemical methods, sample form, means of dissolution of solid samples and a study of possible interferences. From general background knowledge it was evident at an early stage that ferritic samples would not be amenable to direct dissolution methods. Experience confirmed that the only effective method of reclaiming formates and other fatty acids from iron-based corrosion products was to subject them to a form of distillation from acidic solution.

Investigations based on corrosion products arising from actual storage life as opposed to research studies are often carried out on a limited weight of sample with unknown corrosion initiations. The analyst is often faced with little sample and a choice must be made as to which anion, or combination of anions, is most likely to be present from a knowledge of probable storage conditions.

In general, sulphates and phosphates can be detected by spot-test reactions and sometimes determined by micro methods on milligram weight samples. All other anions listed above can be determined in the distillate from a vacuum distillation: formic acid by the method proposed herein, other fatty acids by a gas - liquid chromatographic method with Porapak Q as the stationary phase, chloride either nephelometrically or by using an E.E.L. chloride meter and nitrate by an nitrosalicylate colorimetric procedure. Straightforward vacuum distillation (as reported later) yields variably low results (about 50 to 80 per cent. of the theoretical value), but investigations concluded recently, to be published at a later date, have shown that it is possible to obtain a consistently high yield of more than 95 per cent. of the theoretical value for all anions obtained by distillation.

## SEPARATION OF FORMIC ACID—

Altogether some fifty-seven binary mixtures with formic acid are listed by Horsley<sup>13</sup> in addition to numerous tertiary mixtures. Many of the second components referred to also form azeotropes with water. In each instance the aqueous azeotrope has a lower boiling-point and a considerably lower water content than the corresponding acidic azeotrope. These facts do not favour the removal of water, which is necessary to enable the subsequent removal of the acidic azeotrope to be effective. Of these systems, that based on water - toluene - formic acid offered the greatest promise of success. Grant<sup>10</sup> used a similar system to assist in the vacuum separation of formic acid from blood plasma. In practice, a considerable excess of toluene was required to remove all of the water. An additional dis-

advantage was that the distillate emulsified and required a long period of standing to bring about separation of solvent from the aqueous phase. In one experiment only the recovery of added formic acid exceeded 90 per cent.

#### ATMOSPHERIC PRESSURE DISTILLATION—

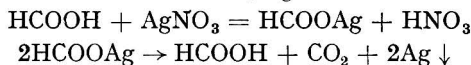
A binary azeotrope of formic acid with water boils at 107.1 °C and contains 77.5 per cent. w/v of formic acid. The amount of acid sought in these experiments is so small that such an azeotropic mixture is unlikely to be formed to any extent. Nevertheless, as there must be a partial pressure of acidic vapour at all times, steam distillation should yield some acid distillate from the onset, as shown experimentally by Reilly and Hickinbottom.<sup>14</sup> Further, McNair<sup>15</sup> has shown that complete collection of formic acid is not possible until the last drop of water has been distilled. Experiments showed that this distillation procedure gave reasonably quantitative yields but that it was subject to strict control because of the possibility of contamination from phosphoric acid spray. It was decided that, in the absence of a more reliable method, this procedure would generally be acceptable for the treatment of solid corrosion products.

#### VACUUM DISTILLATION—

The current procedure evolved in these laboratories for obtaining acetic and higher fatty acids from solid samples involves vacuum distillation from phosphoric acid (D. G. Higgs and V. J. Sanders, unpublished work). Recovery of fatty acids, added as their sodium salts to minimise loss at the evacuation stage, was low and variable. These experiments, repeated at a later date with the method finally accepted in this paper, confirmed the low and variable yields of formic acid obtained by using the current procedure.

#### CHEMICAL METHODS—

A colorimetric method based on the reducing properties of formic acid would offer considerable possibilities as well as avoiding the troublesome reduction to formaldehyde required for a colorimetric condensation procedure. According to Vogel,<sup>16</sup> addition of sodium formate to silver nitrate results in the formation of white silver formate, which is subsequently reduced at room temperature to metallic silver, *e.g.*—



The concentration of formate encountered in the usual amount of corrosion product available for analysis is unlikely to yield weighable amounts of silver. However, the reaction is sensitive enough to give a visible precipitate from 1  $\mu\text{g ml}^{-1}$  of formic acid. Reduction from an ammoniacal medium produced no mirror at the 100  $\mu\text{g ml}^{-1}$  level. Further, experiments showed that reduction of a hot solution of silver nitrate by a known amount of formic acid in the presence of a protective colloid, such as starch, produced a clear brown colour the intensity of which approximated to the Beer - Lambert law. Increasing the starch concentration a hundredfold resulted in linearity up to 110  $\mu\text{g}$  per 25 ml of formic acid and gave sufficient sensitivity to allow a method, based on 0.1-g sample weights, to be developed. Such a method would permit formate contents down to at least 0.01 per cent. to be determined.

The main variables that might be important to the development of a colorimetric method based on colloid stabilisation were expected to include: stabilisation of the colloid; time of boiling for complete reduction; the degree of acidity for optimum reduction; reproducibility of results; and accuracy.

#### CHOICE OF COLLOID—

Substances commonly used for colloid stabilisation include gum acacia, agar-agar, gum tragacanth, starch and gelatin. To test the suitability of these substances, solutions were made up at the 1 per cent. level for starch, gelatine and gum acacia. Fluidity considerations limited tragacanth to 0.2 per cent. and agar-agar to 0.1 per cent. solutions.

A fixed amount of formic acid (105  $\mu\text{g}$ ) was added to water containing 5 ml of stabilising agent, an excess of silver nitrate added and the solution diluted to 25 ml. Each solution was boiled for a fixed 20-minute period, cooled and the resulting colour measured in 10-mm cells by using an absorptiometer with Ilford 601 filters, or any instrument capable of measuring

absorption in the 400 nm region. All solutions were measured in relation to a blank containing the appropriate colloid. The results of two separate series of experiments are given in Table I and indicate the advantages of using starch as a stabiliser.

It is interesting to note that, despite the high blank levels and the difference in colloid colour produced, the differential absorbance due to reduced silver is essentially constant for all systems. The four gums gave rise to excessive frothing during the boiling stage, in contrast to the solution containing starch, which boiled normally. Each of the four gums also decomposed slightly during boiling, with the production of metallic silver.

TABLE I  
COMPARISON OF VARIOUS COLLOIDS FOR STABILISATION OF REDUCED SILVER

Gum	Colour of reduced silver (blank)	Absorption values			Mean absorption difference
		Blank	1st Series	2nd Series	
Starch .. ..	Colourless	0.06	1.00	0.92	0.90
Gelatine .. ..	Reddish brown	0.52	1.40	1.30	0.83
Gum acacia .. ..	Golden brown	0.22	1.21	1.19	0.98
Gum tragacanth .. ..	Pale yellow	0.29	1.21	1.16	0.90
Agar-agar .. ..	Pale yellow	0.30	1.32	1.37	1.05

#### BOILING PROCEDURE—

The reactions given under "Chemical methods" require a definite minimum boiling time and the time *versus* absorbance graph should have a typical asymptotic form. Experimental results showed that boiling for 20 to 25 minutes was sufficient to give maximum colour development for the particular concentration detailed in Fig. 1.

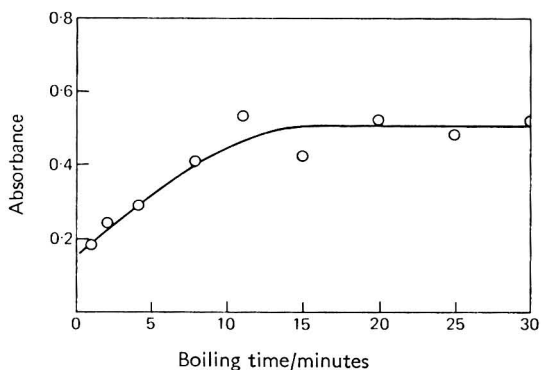


Fig. 1. Determination of minimum boiling time. Conditions: 1 ml of 12.5 per cent. silver nitrate solution; 4 ml of 1 per cent. starch solution; 63  $\mu$ g of formic acid; 10-mm cells with water in the reference cell

#### ACIDITY—

Liberation of free fatty acids from corrosion products results from distillation with strong acids and it was appreciated that possible acid spray might affect the colour sensitivity. In addition to accidental phosphoric acid contamination the most likely acid to be present is acetic acid derived from wood vapours, paints or polymeric materials. Accordingly, two sets of experiments were devised in which various amounts of dilute (0.1 N) acetic and phosphoric acids were added to water containing a fixed amount of formic acid. The solutions were boiled as indicated above. The results of these experiments are given in Table II.

It is evident that the acidity causes marked reduction in sensitivity but that the effect is less marked with acetic acid. In practice, such high acidities are not likely to be encountered. However, consideration must be given to probable levels of formic and acetic acids from corrosion products. The pH of unbuffered solutions resulting from anticipated levels of

TABLE II  
EFFECT OF ACIDITY ON COLOUR SENSITIVITY

Amount of 0.1 N acid added/ml		Absorbance difference
Acetic acid	Phosphoric acid	
—	—	0.50
0.5	—	0.40
1.0	—	0.33
1.5	—	0.25
2.0	—	0.23
—	0.5	0.12
—	1.0	0.09
—	1.5	0.07
—	2.0	0.06

The experimental conditions were as follows: 63  $\mu\text{g}$  of formic acid, 5 ml of 1 per cent. starch solution and 1 ml of 12.5 per cent. silver nitrate were taken; the boiling time was 20 minutes; the final volume was 25 ml; absorption was measured with the solutions in 10-mm cells; and an Ilford 601 filter was used in the absorptiometer.

formic acid was found to range from 4.7, for a solution containing reagents alone, to 3.9, in the presence of 210  $\mu\text{g}$  of formic acid, compared with pH values of 3.8 and 3.5 for 320 and 640  $\mu\text{g}$  of phosphoric acid, respectively.

Further consideration of the reactions indicated that reduction of formic acid was accompanied by the liberation of nitric acid, which has a higher ionic activity. It was therefore expected that the solution under test would become progressively more acidic as reduction proceeded. To obviate the expected change in colour sensitivity consideration was next given to the use of buffered solutions.

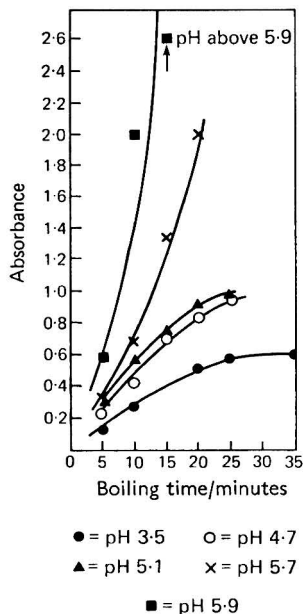


Fig. 2. Dependence of colour intensity of colloidal silver on boiling time and pH. Conditions: 1 ml of 12.5 per cent. silver nitrate solution; 4 ml of 1 per cent. starch solution; 63  $\mu\text{g}$  of formic acid; Ilford 601 filter; 10-mm cells with water in the reference cell

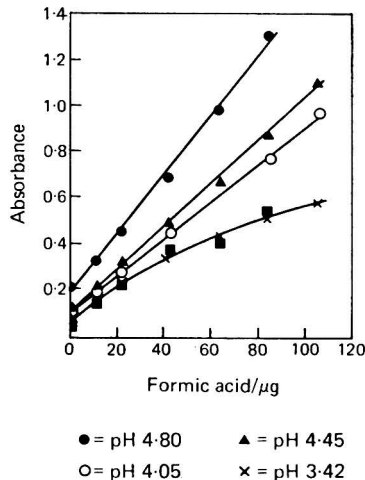


Fig. 3. Dependence of colour intensity of colloidal silver on formate content and pH. Conditions: 1 ml of 12.5 per cent. silver nitrate solution; 5 ml of 1 per cent. starch solution; 30 minutes' boiling time; Ilford 601 filter; 10-mm cells with water in the reference cell. Points  $\blacksquare$  plotted for pH 3.42 show the effect of 360  $\mu\text{g}$  of phosphoric acid on colour intensity

## BUFFERED SOLUTIONS—

A more detailed study of the effect of acidity was undertaken, in which only the hydrogen ion concentration was varied. A series of Walpole buffer solutions,<sup>17</sup> based on 0.2 M solutions of sodium acetate and acetic acid was prepared. By varying the volumes of these two solutions the final acidity was made to vary between the pH limits 3.42 and 5.9, while the acetate ion concentration remained constant at 0.2 M. This particular buffer system was chosen because it contained an anion likely to be present in samples and this, by virtue of its constant concentration, would nullify any possible variations in sensitivity. Also, this system avoided the use of complexing agents (citrate) and silver precipitants (phosphates and phthalates).

A series of solutions was prepared to cover changes in pH, formate content and boiling time. Each solution was contained, as previously, in a 100-ml conical flask, which was covered with a watch-glass to minimise evaporation losses, and boiled for a prescribed time. The solution was cooled, diluted to 25 ml in a standard flask and its absorbance measured. The pH of each solution was measured by using a Cambridge pH meter.

The results of these experiments showed clearly that the colour intensity of colloidal silver is pH-dependent over the range pH 3.5 to 4.8 (Figs. 2 and 3) but that above pH 5 greater reduction than that due to formic acid occurs. The colour intensity increased with increase in pH and the time for maximum colour intensity increased to 30 minutes. The absorbance curves for pH values 5.7 and 5.9 showed a pronounced increase in intensity over that of the solution at pH 5.2 (Fig. 2). The hue of this solution was identical with that for other solutions in the series and signs of turbidity were absent; it is therefore unlikely that the increased intensity was due to a change in particle size. Similarly, this effect was observed in solutions containing only starch, silver nitrate and buffer solution, so that some reaction between these reagents at the higher pH values is indicated.

A pH of 4.45 was finally adopted as standard because it offered high colour sensitivity and also a simple volume ratio between the two components of the buffer solution, *i.e.*, 2 volumes of salt to 3 volumes of acid. It will be shown later that this simple ratio also has other analytical advantages.

## REPRODUCIBILITY—

The reliability of reduction in covered flasks, by using the optimum conditions stated above over the concentration range 10 to 105  $\mu\text{g}$  of formic acid, was checked experimentally. Six such calibration tests were run, each being read at at least six concentrations, and the results submitted to a process of least squares fitting. Repeated values for  $c$  (blank) and the slope  $m$  (sensitivity) were thus obtained. In addition, a standard deviation was calculated for the replicate points of each calibration level.

TABLE III  
LEAST SQUARES EVALUATION OF FORMIC ACID CALIBRATION SERIES

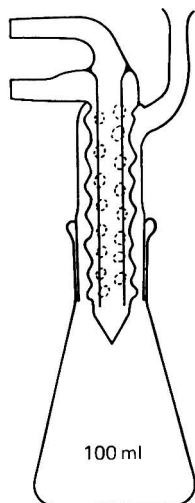
Number of points	$c$	Sensitivity per absorbance of 1.0, m/ $\mu\text{g}$ of formic acid	Standard deviation, $1\sigma/\mu\text{g}$ of formic acid
7	0.12	110	1.9
7	0.15	88	1.6
7	0.22	104	8.4
6	0.17	100	7.8
6	0.13	88	4.7
7	0.11	88	1.5

The results of the above series of calibrations are given in Table III, from which it is evident that a high degree of precision is possible, that sensitivity changes slightly from series to series, that the blank level is fairly constant and that there are some calibrations in which the standard deviation seems excessively high. All experiments were completed within a period of two weeks and the first three sets of results were obtained during a single day, thus indicating variation from both fresh and aged colloid.

The fact that three of the six trials showed a standard deviation ( $1\sigma$ ) less than  $\pm 2 \mu\text{g}$  of formic acid was sufficient justification for further examination. The degree of evaporation during the period of boiling was considered to be the main cause of irregularity.

## REDUCTION UNDER CONSTANT-VOLUME CONDITIONS—

A battery of six reflux condensers, fitted with B24/29 standard sockets, was set up. Each condenser was about 3 inches long and the condensing surface was enlarged by numerous glass spiked baffles. The condensers were mounted in two series of three on either side of a central carrying bar and retained in position with Terry clips. When assembled the battery of flasks was readily transportable and its position could thus be reproduced on the hot-plate. The assembled components of a single complete unit are shown in Fig. 4.



Scale =  $\frac{3}{8}$  full size

Fig. 4. Line diagram of a single reflux reduction unit

In practice it was found that some irregularity was still evident if the water globules retained within the condenser were not mixed with the contents of the flask. Mixing was achieved by removal of each flask in turn from its clip and, with a finger firmly placed over the air vent, inverting the flask twice. Failure to observe this precaution resulted in errors of up to 8 per cent. of the formic acid content.

Experiments carried out under the new conditions involved the pipetting of all reagents into the reduction flask together with sufficient water to make the final volume exactly 25.0 ml. The volumes of solutions comprised 5.0 ml of pH 4.45 buffer solution, 1 ml of 12.5 per cent. silver nitrate solution, 5.0 ml of 1 per cent. starch solution, a measured volume of formic acid solution and water from a burette to make the volume up to 25 ml. The solutions were boiled for a timed period of 30 minutes, cooled in water and mixed as described earlier. The absorbance of each solution was measured in 10-mm glass cells against water with Ilford 601 filters.

The results of calibrations made under the above conditions showed a reproducibility of less than  $\pm 3 \mu\text{g}$  of formic acid, a fairly constant blank level but a somewhat variable sensitivity. However, conditions seemed sufficiently reliable to form the basis of an analytical method provided that it could be suitably adapted to the direct determination of formates in corrosion products and that the procedure allowed for a calibration check on day-to-day sensitivity to be run concurrently with a batch of samples.

## APPLICATIONS

## SAMPLE FORM—

Samples submitted for analysis are in one of two forms, either an aqueous alkaline solution or a solid corrosion product, generally iron, cadmium or zinc-based in origin.

The assessment of the potentially corrosive nature of woods, paints, lacquers, cardboards, etc., depends upon the measurement of the fatty acid vapours emitted by these substances. In practice the specimen under test was enclosed in a glass vessel<sup>6</sup> and suspended above a small volume of dilute sodium hydroxide solution, either at room temperature or under closely controlled conditions of temperature and humidity, for periods of several weeks. During this time the acidic vapours evolved became absorbed in the alkaline solution and were fixed as their sodium salts.

The volume and concentration of the alkaline solution varied according to the circumstances but generally amounts of 0.5 or 1.0 ml of 0.01 N sodium hydroxide were taken. Exceptionally, the alkalinity was increased 10-fold for greater acidic vapour contents. Thus, for laboratory tests, the samples were of known initial volume and alkalinity. Alternatively, samples were in solid form collected from steel components or components plated with either cadmium or zinc. These solid samples arose from standard tests as detailed by Clarke and Longhurst,<sup>6</sup> or from components found to be corroded after long periods of storage.

## TREATMENT OF ALKALINE SOLUTIONS—

The choice of pH buffer permitted rapid and easy attainment of the correct reduction conditions, provided that the original volume and concentration of the alkali used in the vapour absorption tests were known. The addition of a calculated amount of acetic acid, equivalent to 1.5 times the volume of alkali hydroxide originally used as absorbent, automatically brought the pH within buffering range. The addition of 5 ml of 0.2 M buffer solution (which gave approximately twenty times the buffering capacity of the original decinormal solution used) nullified any slight departure from buffering composition resulting from inaccurate volume measurement and strength of the alkali hydroxide originally used as absorbant. When a large amount of formate was present the aqueous solution was diluted to a known volume and an aliquot taken for analysis.

The procedure to be followed for the analysis of solution samples is given in Procedure (a) under "Methods for analysis of test solutions and corrosion samples." Results with solutions of a formic acid content that was unknown to the operator, and contained in a given volume of 0.01 to 0.1 N solutions, are given in Table IV. The formic acid additions were made from an Agla syringe. One millilitre of the standard solution contained 210  $\mu\text{g}$  of formic acid.

TABLE IV  
RECOVERY OF "UNKNOWN" AMOUNTS OF FORMIC ACID FROM  
SODIUM HYDROXIDE SOLUTIONS

Normality of original sodium hydroxide solution	Formic acid added/ $\mu\text{g}$	Formic acid found/ $\mu\text{g}$	Error in determination of formic acid/ $\mu\text{g}$	Error, per cent.
0.01	17	16	-1	-6
0.01	59	61	+2	+3
0.01	13	11	-2	-19
0.01	34	36	+2	+6
0.01	80	80	Nil	Nil
0.01	93	95	+2	+2
0.01	13	14	+1	+7
0.01	50	55	+5	+9
0.01	76	78	+2	+3
0.01	8	10	+2	+20
0.01	25	25	Nil	Nil
0.01	117	110	-7	-6
0.10	6	10	+4	+40
0.10	48	49	+1	+2
0.10	63	59	-4	-7

## DIRECT DETERMINATION ON SOLID SAMPLES—

X-ray diffraction investigations at Fort Halstead during 1962 to 1965 have shown that the wood vapour catalysed corrosion products of zinc and cadmium in moist atmospheres are chiefly zinc oxide and cadmium hydroxide, respectively (G. Todd, unpublished work). When carbon dioxide is present the products may contain variable amounts of basic zinc carbonate ( $4\text{ZnOCO}_2 \cdot 4\text{H}_2\text{O}$ ) and simple cadmium carbonate ( $\text{CdCO}_3$ ).

Previous experience with the silver reduction method suggested that the presence of additional salts would lower the colour sensitivity and it was expected that the presence of both zinc and cadmium would cause a loss of sensitivity. What was not known was the degree of suppression that might result and whether this would be significant for zinc samples, the exact metal content of which was unknown. The metal contents of 0.1 g of zinc oxide and of 0.1 g of basic zinc carbonate are 0.080 and 0.060 g, respectively.

## EFFECT OF METAL IONS—

Experiments based on the colour produced by a constant amount of formic acid with increasing amounts of either zinc or cadmium salts showed that there was a proportional loss in sensitivity with increase in the metal content. The magnitude of sensitivity loss was approximately 36 per cent. for each when 0.1 g of metal was present. An assessment of the error in measured formic acid content consequent upon the difference of 0.02 g of metal resulting from the extremes in composition cited above amounted to 2 to 3  $\mu\text{g}$ . It follows, therefore, that precise compensation for metal content is not justified. It is of interest to note here that the percentage variation of individual calibration sensitivities for the three systems, *i.e.*, aqueous solution, zinc salts and cadmium salts, was found to be 21, 21 and 23 per cent., respectively.

## DISSOLUTION OF SOLID SAMPLES—

A sample weight of 0.1 g was considered adequate for quantitative analysis. This amount permits adequate weighing accuracy and involves a minimum of 10  $\mu\text{g}$  of formic acid from an initial concentration of 0.01 per cent. w/w of formate.

The amount of acetic acid required to dissolve 0.1 g of zinc oxide was calculated to be 0.16 ml of a 4 M solution. However, the resulting solution pH was higher than the required pH (4.45) and a better approximation to the optimum pH value was attained by using 2.0 ml of 1.5 M acetic acid. To ensure adequate control of pH during analysis the amount of buffer solution was increased to 10 ml for all subsequent work. Further, to ensure that formic acid was not lost during the stage of dissolution with heating, all samples and calibration salts were weighed directly into the flasks used for the reduction stage. The reflux condensers were then fitted to the flasks and subsequent additions of reagents made through the air vent tubes.

## INTERFERENCE FROM METALLIC PARTICLES—

The process of corrosion must inevitably result in the inclusion of minute grains of the base metal by its corrosion product. The nitric acid used in the dissolution of cadmium salts is sufficient to ensure complete dissolution of salt and metal. However, acetic acid, as used for zinc, was found not to dissolve particles of zinc metal, and metallic residues could be expected to react with silver nitrate by electrochemical displacement.

To determine the magnitude of the error caused by the possible presence of metallic zinc, synthetic mixtures of zinc oxide and fine metallic dust were subjected to the analytical procedure. Samples containing 10 and 5 per cent. of metal, respectively, gave an immediate blackish brown precipitate, while a sample containing 0.3 per cent. of metal gave rise to a slight haze and a light brown colour of similar intensity to the blank. The smallest metallic concentration tested is not unrealistic for corrosion deposits and any turbidity formed as a result of the metallic content would be masked initially by traces of chloride, if present. The method of dissolution used must, therefore, dissolve the total sample. Nitric acid alone, at the concentration required for correct solution pH, did not attack the zinc oxide. However, if the free acetic acid required to give the correct pH was replaced by nitric acid, both oxide and metal (up to 10 mg) dissolved in a solution containing 14 per cent. of acetic acid and 4 per cent. of nitric acid. The resultant pH was 4.8, which was finally lowered to 4.42 by the addition of the 10 ml of buffer solution.



Percentage recoveries of formic acid were 5 per cent. over the range from 42 to 84  $\mu\text{g}$  of formic acid from samples loaded with up to 10 per cent. of metal.

#### VOLATILE THINNERS FROM PAINTS—

Certain epoxy-based paints were known to contain volatile components as thinners. These compounds, which are the acetate esters of ethyl and methyl glycol ethers, have moderately low boiling-points. The vapours rising from these thinners would be expected to condense on to metallic components and thus contaminate any corrosion product present. Neither compound possesses reducing properties in its normal form, but should hydrolysis or decomposition result in a release of glycol residues, then spurious results might well be obtained.

In order to determine the magnitude of any error in the parent ether, two series of experiments were run in which both compounds were added separately, at the level of 2.6 and 5.2 per cent. by weight, respectively, to 0.1-g amounts of zinc oxide. A corrosion product contaminated to the extent of 1 per cent. with either compound would show an apparent formic acid content of about 0.007 per cent. As a 1 per cent. contamination level of these compounds is extremely unlikely to occur in practice, analytical values obtained may be regarded as arising from the reaction between the formic acid and the corrosion product only.

#### CHLORIDES—

The chloride content, usually resulting from attack by saline atmospheres, was found by experience to vary between 0.01 and 4 per cent. Generally, samples thus attacked are ferritic.

Zinc and cadmium-based samples were treated as already described, the silver chloride formed during the reduction stage being ignored. The colour intensity was finally assessed in an ammoniacal medium in which zinc, cadmium and silver all formed soluble amines.

Calibration with either zinc or cadmium salts, in the presence of up to 1 per cent. of chloride, showed no greater deviation than in its absence. The addition of 1 ml of a solution containing 2 mg of chloride ion was found to be sufficient for most purposes if it was thought desirable to form the colloid under similar ionic conditions.

#### ANALYSIS OF SIMULATED ZINC-BASED AND CADMIUM-BASED SAMPLES—

In order to assess the daily change in sensitivity of colouration and the accuracy to be expected from any single colour series when applied to actual sample analysis, it was decided to run six calibration series for both metals, each consisting of six additions of known amounts of formic acid. Accordingly, the appropriate volume of formic acid was added to flasks containing either 0.10 g of AnalaR zinc oxide or 0.10 g of cadmium carbonate. The flasks were assembled and dissolution was effected as described in Procedure (c) for corrosion products. Each set of experimental values was submitted to a least squares evaluation and a calculation of the standard deviation of the experimental points. The results given in Table V show the slope and intercept for each graph.

TABLE V  
LEAST SQUARES EVALUATION WITH 0.1-g SAMPLES OF ZINC OXIDE  
AND CADMIUM CARBONATE

Calibration number	Zinc oxide		Cadmium carbonate	
	Blank <i>c</i>	Sensitivity <i>m</i>	Blank <i>c</i>	Sensitivity <i>m</i>
1	0.22	194	0.11	191
2	0.21	182	0.14	219
3	0.20	211	0.12	235
4	0.24	220	0.12	196
5	0.22	218	0.12	236
6	0.18	213	0.11	206

The blank, *c*, is expressed in absorbance units and the sensitivity, *m*, represents the number of micrograms equivalent to an absorbance of 1.0.

## DISCUSSION OF CALIBRATION RESULTS—

The statistical assessment of experimental values is based on the measured absorbance. The standard error, derived from the standard deviation of the means for the replicate formic acid additions in the three systems examined, *viz.*, aqueous sodium hydroxide solution, cadmium carbonate and zinc oxide products, is likewise evaluated in terms of absorbance. If the standard error is functionally related to the mean absorbance value for any single replicate series, the percentage error at the 95 per cent. level of confidence can be derived. The mean values for formic acid levels varying from 10.5 to 120  $\mu\text{g}$  for the three systems are calculated as: aqueous sodium hydroxide solution =  $\pm 4.4$  per cent.; cadmium carbonate products =  $\pm 6.3$  per cent.; and zinc oxide products =  $\pm 4.4$  per cent.

The mean sensitivities for all three systems obtained over the last few years, compared with the currently recorded calibration values, are given below in Table VI. A single calibration value for a copper-based corrosion product showed little deviation from individual high values for either zinc or cadmium-based corrosion products.

TABLE VI  
COMPARISON OF MEAN CALIBRATION SENSITIVITIES

Sample system	Calibration values	Working* values
Sodium hydroxide solution .. ..	132	140
Zinc oxide sample .. ..	206	210
Cadmium carbonate sample .. ..	214	200
Copper (acetate) .. ..	—	265

\* These values represent the arithmetical mean of numerous calibration sensitivities found during application of the proposed method to actual samples.

## COMPARISON OF PROPOSED METHOD WITH GAS - LIQUID CHROMATOGRAPHIC PROCEDURES—

Subsequent to the completion of the main investigation it was envisaged that a gas - liquid chromatographic procedure would offer certain advantages over the present method, *e.g.*, all four fatty acids that were of interest could be determined simultaneously by using the Pye 104, Model 44, chromatograph and Porapak Q as the solid phase in the column. Economy of the often already limited amount of sample was the greatest spur to the development of an alternative procedure.

Unfortunately, the prerequisite to any gas - liquid chromatographic method is the need to distil off the fatty acids in order to provide a suitable sample for injection on to the column. In practice it was found that distillation yields, when using the vacuum procedure outlined earlier, were variable and not consistent in relation to the ratio of the fatty acids recovered. Further, a greater disadvantage was the loss of sensitivity incurred through the need to restrict the injection volume to 5  $\mu\text{l}$  out of a total distillate often in excess of 200  $\mu\text{l}$ . The only advantage to be derived from using a gas - liquid chromatographic procedure for acid contents below 0.5 per cent. is that an idea of the relative amounts of all low molecular-weight fatty acids is obtained, when using a katharometer detector.

## METHODS FOR ANALYSIS OF TEST SOLUTIONS AND CORROSION SAMPLES

## APPARATUS—

Any simple form of filter absorptiometer that can take an Ilford 601 filter is suitable.

## REAGENTS—

Unless otherwise stated all reagents are of AnalaR grade and distilled water is used throughout the procedures.

*Acetic acid - nitric acid mixture*—Dilute 14 ml of glacial acetic acid and 4 ml of nitric acid (sp.gr. 1.42) to 100 ml with water.

*Acetic acid, 0.2 M*—Dilute 11.6 ml of glacial acetic acid to 1 litre with water.

*Acetic acid, 0.1 M*—Dilute a given volume of 0.2 M acetic acid with an equal volume of water.

*Acetic acid, 0.01 M*—Dilute a given volume of 0.1 M acetic acid with 9 volumes of water.

*Sodium acetate, 0.2 M*—Dissolve 54.4 g of sodium acetate trihydrate in water and dilute to 2 litres.

*Nitric acid, 3 per cent. v/v*—Dilute 6 ml of nitric acid (sp.gr. 1.42) to 200 ml with distilled water.

*Silver nitrate, 12.5 per cent. w/v solution*—Dissolve 62.5 g of general-purpose reagent grade silver nitrate in distilled water and dilute to 500 ml.

*Buffer solution, pH 4.45*—Mix 2 volumes of 0.2 M sodium acetate with 3 volumes of 0.2 M acetic acid.

*Starch, 1 per cent. solution*—Triturate 5 g of soluble starch with cold water and add the mixture to 500 ml of boiling water. Continue to boil the starch solution for at least 10 minutes, then cool it before use. Preserve this solution with 1 to 2 drops of chloroform.

*Phosphoric acid, 50 per cent. v/v*—Dilute 100 ml of phosphoric acid (sp.gr. 1.75) with 100 ml of water, cool, and dilute to 200 ml with water.

*Ammonia solution, sp.gr. 0.88.*

#### PROCEDURE—

(a) *Sodium hydroxide solutions*—All alkaline solutions to be analysed will be of experimental origin so that their initial volume and concentration will be known. Addition of the appropriate volume of acetic acid of known concentration will ensure attainment of the correct pH conditions. For example, to 2 ml of 0.1 M sodium hydroxide solution would be added 3 ml of 0.1 M acetic acid, and similarly for other strengths of alkali solution. The actual formate content is usually not known with certainty and it will be necessary to dilute the sample to a known volume after pH adjustment, e.g., volumes much less than 10 ml would be diluted to 10 ml in a standard flask. One or more determinations would be necessary according to the formate level indicated by the first determination.

When the sample solution has been diluted to 10 ml, transfer a 1-ml aliquot to a 100-ml reduction flask. Simultaneously, treat not more than two other samples similarly. To the remaining three flasks add appropriate volumes of standard formic acid solution to cover a range of up to 100  $\mu\text{g}$ , e.g., 20, 40 and 80- $\mu\text{g}$  amounts of formic acid. To each flask add successively 1 ml of silver nitrate solution, 10 ml of acetate buffer solution and 5 ml of starch solution. Finally, add sufficient water from a burette to make the total volume of liquid in each flask exactly 25.0 ml. Assemble the six flasks on to the reflux condensers, lower the whole assembly on to the hot-plate, and boil the solutions for 30 minutes. After cooling the assembly in a tank of cold water, withdraw each flask in turn from its retaining clip, place a finger over the air vent and invert the flask twice to ensure complete mixing of the contents. Measure the transmittance of the solutions in relation to water in a 10-mm glass cell with Ilford 601 filters. Convert transmittance values into absorbances for each of the three standard additions and plot these values against formic acid content. The resulting points should lie on a straight line having an intercept at an absorbance of about 0.1 and a slope of slightly more than 45° to the concentration axis.

If the initial sample contained less than 100  $\mu\text{g}$  of formic acid, a repeat determination on one half of the diluted solution will be necessary. However, for values within the range 100 to 1 000  $\mu\text{g}$  of formic acid the results from the 1-ml aliquot will be sufficiently accurate.

(b) *Cadmium and zinc samples*—The method of dissolution of these two types of sample is necessarily slightly different, as discussed earlier, but the final treatment is common to both.

The cadmium sample is dissolved under reflux in 3.0 ml of 3 per cent. nitric acid solution. Any deficiency between the sample weight available and 0.100 g is made up with cadmium carbonate of laboratory-reagent grade containing not less than 95 per cent. of cadmium carbonate and not more than 0.1 per cent. of chloride.

The zinc sample is dissolved under reflux in 2.0 ml of the nitric acid - acetic acid mixture. In this instance any deficiency in sample weight is compensated for by using AnalaR grade zinc oxide.

Weigh into each of three clean, dry 100-ml reduction flasks 0.100 g of either three cadmium-based samples or three zinc-based samples and into the remaining three flasks weigh the corresponding salt or oxide. Assemble the flasks into the reflux condensers. Add to each flask, via the condenser vent tube, the correct volume of acid for the type of sample being analysed. Heat the contents of the flask gently, with the condenser water running, until dissolution of the sample is complete. To the three standard flasks add known volumes

of standard formic acid to constitute the calibration range of interest and, finally, to all flasks, the three reagents as detailed under (a) above. Adjust the final volume to exactly 25.0 ml with water from a burette. The remainder of the procedure is as already described.

(c) *Iron*—Transfer a weighed amount of sample to a clean, dry 100-ml spherical distillation flask.\* Add 10 ml of 50 per cent. phosphoric acid, connect the flask to a condenser column and heat gently to boiling. Continue heating in such a manner that the distillate is collected at the rate of a few drops per minute until the theoretical volume of 5.6 ml has been collected. Care must be taken not to overheat the phosphoric acid and cause spitting. Cool the flask, add a further 2 ml of water and repeat the distillation, this time continuing to heat the flask until phosphoric acid vapour condenses gently around the lower part of the neck. Transfer the total distillate to a 10-ml standard flask and continue as for (a) above.

The appearance of a white turbidity on addition of the silver nitrate indicates the presence of either chloride or phosphate contamination from the distillation stage. In either event continue the procedure to the stage immediately before inverting the flask to effect complete mixing and then proceed with the modification detailed for chloride in (d) below.

(d) *Chloride*—The presence of chloride is indicated immediately on addition of the silver solution. If only a slight turbidity is evident the procedure can be continued as already described but modified by the addition of 1.0 ml of ammonia solution. Mixing of the solution in the manner described now results in re-dissolution of the silver chloride, leaving a clear solution for subsequent measurement. Standards must be treated in a similar manner. Calibration sensitivity has been shown experimentally to be affected little by this modification.

When the chloride contamination is sufficiently high to result in the formation of a curdy white precipitate, more accurate results can be obtained if a deliberate addition of chloride is made to samples and standards alike. The addition of 1 ml of a solution containing 2 mg of chloride was found adequate for most purposes.

#### DISCUSSION

An accurate, quick and simple method for the determination of formate has been developed, which is directly applicable to zinc and cadmium corrosion products and, in all probability, to other metals soluble under the conditions described. Allowance has been made for metallic particles and chlorides. The accuracy to be expected at the 95 per cent. confidence level is  $\pm 4$  per cent. for sodium hydroxide solutions used in the assessment of corrosion capability of paints, etc., and  $\pm 6$  per cent. for both metal corrosion products. The method proposed is quicker, more reliable and much more accurate than alternative gas-liquid chromatographic procedures.

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\* The flask is so constructed as to minimise the free volume above the take-off side-arm and thus to improve distillation efficiency. In practice the distillation efficiency was found to be about 90 per cent.

## The Determination of Certain Antioxidants, Ultraviolet Absorbers and Stabilisers in Plastics Formulations by Thin-layer Chromatography

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The use of thin-layer chromatography in the determination of additives in plastics formulations is investigated. Details are given for the detection and determination of antioxidants, organotin compounds and ultraviolet absorbers, and mention is made of other additives likely to be present. Commercially prepared silica gel layers containing a fluorescent additive are used in most cases.

Comparatively small samples of the plastics materials are required, and, by means of the techniques described, it is possible to identify additives in extracts containing several different components. The method can be used to detect additives down to between 10 and 1  $\mu\text{g}$  per sample and both qualitative and more accurate quantitative determinations are made possible.

THE main purpose of the investigation was to evolve a method (or, possibly, several methods) that would be suitable for the simultaneous determination of as many additives in plastics formulations as possible. The method should be easy to apply and should lead to quick results. The methods reported here enable the determinations on the extracted additives to be completed within a maximum time of about 3 hours whereas other methods of determination can take one day or longer.

Most commercial plastics are made in many different formulations. The amounts of the different additives present in any one formulation can vary greatly. For example, a poly(vinyl chloride) formulation could contain, in addition to the polymer, approximately 30 to 40 per cent. of plasticiser (or mixture of plasticisers) and 2 to 5 per cent. of stabiliser (or mixture of stabilisers), together with fractions of 1 per cent. of pigment, optical brightener, antioxidant (often incorporated in the plasticiser or stabiliser), blowing agent, ultraviolet absorber, flame retardant, lubricant or odorant (or any combination of these), as well as filler.

Other types of plastics for which investigations were required included polyethylene and polypropylene (containing small amounts of antioxidant, antistatic agent, lubricant, etc.) and toughened polystyrene (which consists mainly of polystyrene, but also includes rubber containing trace amounts of antioxidant, together with a small amount of a different added antioxidant, traces of catalyst, monomer, dimer, trimer, lubricant, etc.).

The present investigation included the detection and determination of some antioxidants, organotin compounds and ultraviolet absorbers in certain of these polymers.

### ANTIOXIDANTS—

These are of various types and include derivatives of amines, phenol and hydroquinone and esters of phosphorus. They are included in formulations in order to delay oxidation processes in the plastics composition and may be present in amounts varying from about 0.02 to 0.5 per cent., depending on the polymer in question and the purpose for which it is intended.

Several papers have been published on the thin-layer chromatographic separation of antioxidants. Van der Heide and Wouters<sup>1</sup> examined some antioxidants in polyethylene; Slonaker and Sievers<sup>2</sup> and Woggon, Korn and Jehle<sup>3</sup> did similar work and were able to detect

between 300 and 900 p.p.m. of antioxidants in polyethylene. The full range of derivatives given above was not covered, however. Crompton<sup>4</sup> surveyed a variety of techniques based on spectroscopy and chromatography but used 30 g of sample for the tests. It was necessary for us to be able to identify antioxidants present in a sample and determine amounts down to 0.05 per cent.

#### ORGANOTIN COMPOUNDS—

Stabilisers are added to plastics formulations to prevent degradation by heat or light. They may be metal stearates, urea derivatives or organotin compounds. Some stabilisers are added to prevent one and some the other type of degradation, although it is possible to combine the two properties and a wide variety of mixed stabilisers is available for this purpose. Also, some organotin compounds exhibit both heat and light stabilisation characteristics. Amounts of stabiliser present could vary from 0.5 to 5 or even 10 per cent. Only organotin compounds were examined during this investigation. Williams and Price<sup>5,6</sup> separated some of them from a mixture of organotin compounds by using paper chromatography and reversed-phase chromatography. By this means  $25 \times 10^{-6}$  to  $150 \times 10^{-6}$  g were detected but the development times were of the order of 15 hours.

#### ULTRAVIOLET ABSORBERS—

Ultraviolet light tends to degrade plastics compositions and ultraviolet absorbers are incorporated in them in order to delay this effect. These absorbers are usually derivatives of benzophenone, benzotriazole, resorcinol, salicylates, substituted acrylonitriles or organonickel compounds, and may be present in amounts of the order of 0.2 per cent. Wandel and Tengler<sup>7</sup> identified phenyl salicylate and resorcinol in plastics formulations, and Dobies<sup>8</sup> described a method of determining benzophenone derivatives in paraffin wax. We needed to be able to identify and determine amounts of ultraviolet absorbers down to about 0.1 to 0.2 per cent.

### METHOD

#### APPARATUS—

It was found most convenient to use commercially prepared thin-layer plates, of which there are three main types: layers on glass; layers on a flexible backing of polyester or aluminium; and silica gel impregnated glass fibre.

The Merck thin layers on glass were found to be most suitable for our purpose. The layers were robust and were not rubbed off easily, they were not attacked by reagents and were of a thickness (0.25 mm) such as to receive a reasonable sample loading. Another advantage was that the plates were fitted into an Eastman Kodak "Chromagram" sandwich chamber, thus obviating the need for a large developing tank and reducing considerably the time required for solvent saturation of the tank. The plates used for the separation of all three types of additives in question were Merck Kieselgel GF<sub>254</sub> (silica gel containing a fluorescent additive).

#### REAGENTS—

As they were found to be the most suitable for our purpose the following mobile phases were finally used, although other solvent systems based on the elutropic series were examined.

*Benzene - ethyl acetate - acetone* (100 + 5 + 2)—Used for antioxidants.

*Chloroform - hexane* (2 + 1)—Used for ultraviolet absorbers.

*Butanol - glacial acetic acid* (97 + 3)—Used for organotin compounds.

Other reagents required were as follows.

*2,6-Dichloro-p-benzoquinone-4-chloroimine*, 0.2 per cent. w/v solution in absolute ethanol.

*Borax*, 2 per cent. w/v solution—Dissolve 2 g of sodium tetraborate decahydrate in 100 ml of 50 per cent. v/v ethanol.

*Catechol violet*, 0.1 per cent. w/v solution in 95 per cent. ethanol.

*Diethyl ether*.

*Chloroform*.

*Ethanol*.

The last three reagents were of analytical-reagent grade. All other reagents should also be of analytical-reagent grade if possible.

## PROCEDURE

Weigh two 2 to 5-g amounts of plastics material and extract each with diethyl ether for 8 hours in a Soxhlet continuous extraction apparatus. The weight to be taken will vary with the types and amounts of additives expected. If these are not known take the maximum amount, if possible.

Remove the diethyl ether by distillation on a water-bath and add 5 ml of ethanol to each flask. Allow the flasks to stand for 10 minutes. If necessary, at the end of this time, filter the resulting solutions quantitatively to remove any precipitated polymer. Evaporate the contents of one flask to dryness (sample A) and those of the other to very small bulk (sample B).

Dissolve sample A in a small amount of chloroform and transfer the solution quantitatively to a 5-ml calibrated flask. Dilute to volume with chloroform. Then transfer sample B quantitatively to a 5-ml calibrated flask and dilute to volume with ethanol. Use sample A solution for the determination of antioxidant and ultraviolet absorber, and sample B solution for the determination of organotin compounds.

Spot 2  $\mu$ l of solution A on to each of two Merck Kieselgel GF<sub>254</sub> plates and 2  $\mu$ l of solution B on to a third plate. For qualitative work Drummond Microcaps can be used but for quantitative work a microlitre syringe (*e.g.*, Hamilton) should be used. Place each plate into an Eastman Kodak Chromagram sandwich chamber and, by using the appropriate mobile phase, allow the solvent to travel a suitable distance. Locate the spots as described below.

## DETERMINATION OF ANTIOXIDANT—

*Mobile phase*—Benzene - ethyl acetate - acetone (100 + 5 + 2).

*Chromogenesis*—View the plate under ultraviolet light and mark any spots located. Then spray the plate with 2,6-dichloro-*p*-benzoquinone-4-chloroimine solution, heat it with a hand-held drier for a few minutes, and mark any spots coloured by the reagent. Finally, allow the plate to stand in a tank in contact with iodine vapour for 5 minutes.

## DETERMINATION OF ULTRAVIOLET ABSORBERS—

*Mobile phase*—Chloroform - hexane (2 + 1).

*Chromogenesis*—View the plate under ultraviolet light and mark any spots located. Spray the plate with borax solution followed by 2,6-dichloro-*p*-benzoquinone-4-chloroimine solution, heat it with a hand-held drier for a few minutes, and mark any spots coloured by the reagents.

## DETERMINATION OF ORGANOTIN COMPOUNDS—

*Mobile phase*—Butanol - glacial acetic acid (97 + 3).

*Chromogenesis*—Spray the plate with catechol violet solution, then irradiate the plate with ultraviolet light for 10 minutes and re-spray with catechol violet solution.

## RESULTS AND DISCUSSION

Initially, standard solutions containing 1 per cent. w/v of the additive in chloroform or ethanol were prepared and chromatograms were run as described above.

## ANTIOXIDANTS—

Separations of various types of antioxidants were completed: phenols, amines, hydroquinone mixtures, antioxidants of miscellaneous composition and antioxidants of unknown formula. Fig. 1 illustrates, on one plate, the complete series of separations of mixtures of antioxidants. When this diagrammatic representation is considered in conjunction with Table I it will be seen that quite good identification of the various substances is obtained.

It is likely that the number of spots obtained is dependent upon the purity of the material and so it may vary, to a small extent, from batch to batch. It should be possible, however, generally to identify the antioxidants by using the conditions described. It was possible to detect down almost to 1  $\mu$ g per spot applied in certain cases and at least to 10  $\mu$ g per spot applied. More quantitative estimation, by comparison with standards, has been carried out in a number of instances and it is possible to differentiate between 5 and 10  $\mu$ g per spot applied; one such sample is butylated hydroxytoluene (BHT).

TABLE I

## RESULTS OBTAINED IN THE SEPARATION OF ANTIOXIDANTS

Substance	Type of derivative	R <sub>F</sub> value	Locatable by ultraviolet	Locatable by reagent	Locatable by iodine only
Nonox SP	Phenolic	0.61	—	Blue	—
		0.93	—	Purple	—
Nonox TBC	Phenolic	0.98	—	Yellow with red ring	—
Nonox WSP	Phenolic	0.85	—	Yellow	—
Nonox EX	Phenolic	0.56	—	Yellow	—
Nonox WSL	Phenolic	0.82	—	Yellow with red ring	—
BHT	Phenolic	0.98	—	Yellow with red ring	—
2246	Phenolic	0.75	—	Yellow	—
Nonox C1	Amine	0.65	+	—	—
		0.84	—	Red	—
Nonox DPPD	Amine	0.66	+	Yellow	—
Nonox OD	Amine	0.56	+	—	—
Nonox ZA	Amine	0.43	—	Yellow	—
Santoflex 75	Hydroquinone	0.38	+	—	—
		0.15	+	—	—
		0.61	+	Yellow	—
Santoflex AW	Hydroquinone	0.74	—	Blue	—
		0.80	+	—	—
		0.51	+	Blue	—
Santoflex R	Hydroquinone	0.55	+	—	—
		0.26	—	Blue	—
		0.53	+	Blue	—
DLTDP	Miscellaneous	0.61	+	—	+
Nonox NS	Miscellaneous	0.52	(very faint)	Blue	—
		0.64	+	—	—
Superlite	Miscellaneous	0.93	—	Red	—
		0.52	+	—	—
Polygard	Miscellaneous	0.61	+	—	—
			(faint)	—	—
Nonox HO	Unknown formula	0.46	—	Blue	—
		0.64	—	Blue	—
		0.60	—	Blue	—
		0.99	—	Red	—
Nonox WSO	Unknown formula	0.58	+	Yellow	—
Irganox 1076	Unknown formula	0.57	+	—	—
		0.75	+	Red	—

## ULTRAVIOLET ABSORBERS—

Diagrammatic representations of the separations obtained are to be found in Fig. 2, and these should be considered in conjunction with Table II.

TABLE II

## RESULTS OBTAINED IN THE SEPARATION OF ULTRAVIOLET ABSORBERS

Substance	Type of derivative	R <sub>F</sub> value	Colour with reagents
Eastman DOBP ..	Benzophenone	0.39	Very faint green
Uvinul 400 .. ..	Benzophenone	0.08	Yellow - green
Permyl B100 .. ..	Benzophenone	0.08	Blue
Salol .. ..	Salicylate	0.45	Green - blue
Tinuvin HE .. ..	Not available	0.71	Yellow to light brown
Tinuvin P .. ..	Benzotriazole	0.59	Yellow
Eastman OPS .. ..	Salicylate	0.65	No coloration
UV 318 .. ..	Substituted acrylonitrile	0.14	Purple - brown
Cyasorb 1988 .. ..	Salicylate	0.12	Yellow
Cyasorb 1084 .. ..	Organonickel	0.08	No coloration
Uvinul N35 .. ..	Substituted acrylonitrile	0.16	No coloration

All of the spots could be located by means of ultraviolet light but Eastman OPS, Cyasorb 1084 and Uvinul N35 gave no coloration with the spray reagents.



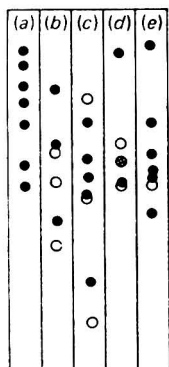


Fig. 1

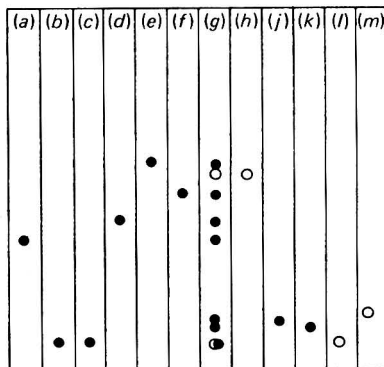


Fig. 2

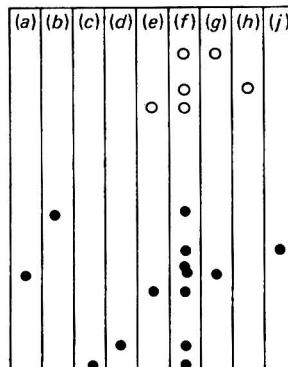


Fig. 3.

Fig. 1. Thin-layer chromatograms of mixtures of antioxidants. Mobile phase: benzene-ethyl acetate-acetone (100 + 5 + 2). Columns are: (a) phenols; (b) amines; (c) hydroquinones; (d) miscellaneous antioxidants; and (e) mixtures of unknown exact formulation

Fig. 2. Thin-layer chromatograms of ultraviolet absorbers. Mobile phase: chloroform-hexane (2 + 1). Columns are: (a) Eastman DOBP; (b) Uvinul 400; (c) Permyl B100; (d) Salol; (e) Tinuvin HE; (f) Tinuvin P; (g) mixture; (h) Eastman OPS; (j) UV318; (k) Cyasorb 1988; (l) Cyasorb 1084; and (m) Uvinul N35

Fig. 3. Thin-layer chromatograms of organotin compounds. Mobile phase: butanol-glacial acetic acid (97 + 3). Columns are: (a) DBTDL; (b) DOTDL; (c) BTTC; (d) DMTDC; (e) DPTDC; (f) mixture; (g) HBDT; (h) TBTL; and (j) DBT bis(2-EHTG). (The names of these organotin compounds appear in full in Table III)

#### ORGANOTIN COMPOUNDS—

Diagrammatic representations of the separations are to be found in Fig. 3, and details of the results obtained in Table III.

TABLE III

#### RESULTS OBTAINED IN THE SEPARATION OF ORGANOTIN COMPOUNDS

Substance	$R_F$ value	Spot located on spraying	Spot located only after ultraviolet irradiation and spraying
Dibutyltin dilaurate (DBTDL)	0.29	+	—
Diocetyl tin dilaurate (DOTDL)	0.46	+	—
Butyltin trichloride (BTTC)	0.0	+	—
Dimethyltin dichloride (DMTDC)	0.04	+	—
Diphenyltin dichloride (DPTDC)	0.21	+	—
	0.76	+	—
Hexabutyltin (HBDT)	0.26	+	—
	0.96	—	+
Tributyltin laurate (TBTL)	0.82	—	+
Dibutyltin bis-(2-ethylhexylthio-glycollate) [DBT bis(2-EHTG)]	0.33	+	—

The most significant feature of the use of catechol violet is that the tin compounds are coloured bright blue on the thin-layer plate. This coloration is not given by any of the completely organic additives, nor by metal stearates—such as lead, barium or cadmium stearate—that are used in stabilising systems. Thus the use of this reagent in this field could be specific for tin compounds.

TABLE IV

RESULTS OBTAINED FOR EACH ADDITIVE IN EACH MOBILE PHASE

Substance	$R_F$ value in butanol - acetic acid	$R_F$ value in benzene - ethyl acetate - acetone	$R_F$ value in chloroform - hexane
<i>Antioxidants—</i>			
Nonox SP .. .. .	SF	0.61, 0.93	0.50
Nonox TBC .. .. .	SF	0.98	0.62
Nonox WSP .. .. .	SF	0.85	0.52
Nonox EX .. .. .	SF	0.56	0.38
Nonox WSL .. .. .	SF	0.82	0.54
BHT .. .. .	SF	0.98	0.91
2246 .. .. .	SF	0.75	0.56
Nonox C1 .. .. .	SF	0.65, 0.84	0.49
Nonox DPPD .. .. .	SF	0.66	0.48
Nonox OD .. .. .	SF	0.56	0.40
Nonox ZA .. .. .	SF	0.43, 0.38	0.38
Santoflex 75 .. .. .	SF	0.15, 0.61, 0.74	0.47, 0.54
Santoflex AW .. .. .	SF	0.80, 0.51, 0.55	0.54, 0.45
Santoflex R .. .. .	SF	0.26, 0.53	0.39
DLTDP .. .. .	SF	0.61	0.41
Nonox NS .. .. .	SF	0.52	0.4
Superlite .. .. .	SF	0.64, 0.93	0.58
Polygard .. .. .	SF	0.52, 0.61	0.53
Nonox HO .. .. .	SF	0.46, 0.64, 0.60, 0.99	0.52
Nonox WSO .. .. .	SF	0.58	0.39
Irganox 1076 .. .. .	SF	0.57, 0.75	0.56
<i>Ultraviolet absorbers—</i>			
Eastman DOBP .. .. .	SF	0.76	0.39
Uvinul 400 .. .. .	SF	0.22	0.08
Permyl B100 .. .. .	SF	0.24	0.08
Salol .. .. .	SF	0.73	0.45
Tinuvin HE .. .. .	SF	SF	0.71
Tinuvin P .. .. .	SF	0.76	0.59
Eastman OPS .. .. .	SF	0.79	0.65
UV 318 .. .. .	SF	0.26	0.14
Cyasorb 1988 .. .. .	SF	0.26	0.12
Cyasorb 1084 .. .. .	SF	0.24	0.08
Uvinul N35 .. .. .	SF	0.28	0.16
<i>Organotin compounds—</i>			
Dibutyltin dilaurate .. .. .	0.29	NL	NL
Diocetyl tin dilaurate .. .. .	0.46	NL	NL
Butyltin trichloride .. .. .	0.0	0.0	0.0
Dimethyltin dichloride .. .. .	0.04	NL	NL
Diphenyltin dichloride .. .. .	0.21, 0.76	NL	NL
Hexabutyltin .. .. .	0.26, 0.96	SF	SF
Tributyltin laurate .. .. .	0.82	NL	NL
Dibutyltin bis-(2-ethylhexylthioglycollate) .. .. .	0.33	NL	NL

SF—Moves with solvent front. NL—Not located with reagents listed.

Table IV illustrates the results obtained for  $R_F$  values of each of the additives investigated in each of the mobile phases used.

Finally, special formulations were prepared for us in order that we could apply the methods to materials the constituents of which were unknown to us at the time of testing. Very favourable results were obtained. The methods discussed have now been in use in these laboratories for a few years. Figs. 4 and 5 give composite representations of results obtained on a toughened polystyrene and a poly(vinyl chloride) formulation, respectively. It is generally necessary to run standards because the  $R_F$  values of the components in the formulations sometimes differ slightly from those of the unformulated components. In Fig. 4 the material shown to have moved with the solvent front is polystyrene of low molecular weight. Fig. 6 illustrates results obtained on a sample of flexible poly(vinyl chloride). It is possible to detect certain plasticisers, non-tin stabilisers and lubricants by thin-layer chromatography and it is hoped to describe this work in a future paper.

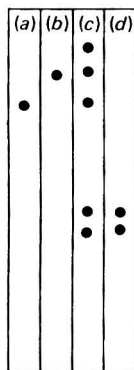


Fig. 4

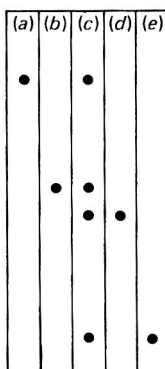


Fig. 5

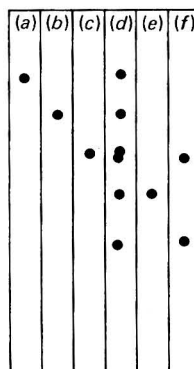


Fig. 6.

Fig. 4. Thin-layer chromatograms of additives detected in toughened polystyrene. Columns are: (a) Nonox WSL; (b) Superlite; (c) extract; and (d) Polygard

Fig. 5. Thin-layer chromatograms of additives detected in poly(vinyl chloride). Columns are: (a) plasticiser; (b) non-tin stabiliser; (c) extract; (d) Tinuvin P; and (e) dibutyltin bis(2-ethylhexylthioglycollate)

Fig. 6. Thin-layer chromatograms of additives detected in poly(vinyl chloride). Columns are: (a) plasticiser one; (b) plasticiser two; (c) non-tin stabiliser; (d) extract; (e) Tinuvin P; and (f) lubricant

If more accurate quantitative results are required on poly(vinyl chloride) formulations, it is necessary to perform an extract additional to the ether extract by using an azeotrope of carbon tetrachloride - methanol (2 + 1) and extracting for a further 4 hours.

We thank Bakelite Xylonite Ltd. for permission to publish this paper.

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# A Rapid Cadmium Reduction Method for the Determination of Nitrate in Bacon and Curing Brines

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A method has been developed for the extraction of nitrate and nitrite from meat by heating at 80 °C for 10 minutes to coagulate the protein and inactivate nitrate and nitrite reductase activity and subsequently treating with alumina cream. The latter treatment alone was used for the clarification of curing brines.

A method for the reduction of nitrate to nitrite by shaking with cadmium has been developed that is quicker, as it takes 5 minutes, than column reduction, which requires 40 to 60 minutes. Quantitative recoveries of nitrate as nitrite were obtained.

Methods of determining nitrate as nitrite involving the use of the diazo compounds formed between sulphanilic acid and each of the four coupling agents 1-naphthylamine, *N*-1-naphthylethylenediamine, 1-naphthylamine-7-sulphonic acid and 1-naphthol were investigated. *N*-1-Naphthylethylenediamine is recommended because of the short time (10 minutes) required for maximum colour development.

NITRATE has been determined by methods based on the nitration of chromotropic acid,<sup>1</sup> phenoldisulphonic acid,<sup>2</sup> 2,6-xylenol<sup>3</sup> and 3,4-xylenol<sup>4</sup> or the oxidation by nitrate of brucine,<sup>5</sup> diphenylamine<sup>6</sup> and strychnine.<sup>7</sup>

Materials that contain water-soluble organic matter with nitrate levels below 1 000  $\mu\text{g g}^{-1}$  produce erratic results with nitration and oxidation methods, as the nitrate can be reduced by the organic material in acidic solutions.<sup>8</sup>

With methods based on the reduction of nitrate to nitrite or ammonia in biological material with the reducing agents copper,<sup>9</sup> hydrazine,<sup>10</sup> aluminium-nickel,<sup>11</sup> zinc<sup>12</sup> or zinc-manganese<sup>13,14</sup> it is difficult to ensure complete reduction or to prevent the reduction of nitrite.

The introduction of cadmium as a reducing agent<sup>15</sup> achieves a reliable quantitative reduction of nitrate to nitrite in an alkaline medium. The cadmium reduction method has been successfully applied by a number of authors<sup>16 to 24</sup> and by G. A. Gardner (private communication) to the determination of nitrate in a wide range of biological material, in which the nitrate concentration (as sodium nitrate) varied between trace amounts and several parts per cent.

Experiments were carried out to determine the efficiency of extraction, reduction and determination of nitrate in meats and curing brines.

## EXPERIMENTAL

### REAGENTS—

*Alumina cream.*

*Buffer, pH 9.6*—A 0.7 M ammonium chloride solution adjusted to the specified pH value with ammonia solution, sp. gr. 0.88.<sup>16</sup>

*Hydrochloric acid, 0.1 N.*

*Acetic acid, glacial.*

*Cadmium, spongy*—Prepare by placing zinc rods in a 20 per cent. solution of cadmium sulphate. The cadmium was treated before and after use with 0.1 N hydrochloric acid, followed by several washes with water, and stored under water.

*Diazotising agent*—A 5 mM sulphanilic acid solution.

*Coupling agents*—These consisted of 5 mM solutions of 1-naphthylamine, *N*-1-naphthylethylenediamine, 1-naphthylamine-7-sulphonic acid and 1-naphthol.

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*Colour reagent*—Prepare, immediately before use, a mixture of 5 mm sulphanic acid, a solution of a coupling agent and glacial acetic acid, (1 + 1 + 3).

*Standard sodium nitrite and nitrate solutions*, 2.5 g l<sup>-1</sup>.

Analytical-reagent grade reagents and de-ionised water were used for the preparation of reagents and test samples.

#### APPARATUS—

The apparatus included an Ultra-Turrax homogeniser,\* a mechanical flask shaker† and an Optica CF4R recording spectrophotometer.‡

### RESULTS

#### METHOD OF EXTRACTION OF NITRITE AND NITRATE—

Curing brines, free of protein, were diluted 100-fold in preparation for reduction. For brines with protein, 1 ml was placed in a 100-ml calibrated flask, 5 ml of alumina cream were added, and the mixture was shaken and diluted to volume with water prior to filtration through a Whatman No. 12 fluted filter-paper. The filtrate was used for the nitrate reduction and the nitrite determination.

For pork and bacon, a 5-g sample was homogenised with 20 ml of water and washed into a 100-ml calibrated flask with not more than 50 ml of water. The flask was immediately placed in a water-bath at 80° C for 10 minutes and 20 ml of alumina cream were added. The flask was shaken vigorously and the contents were diluted to volume with water and filtered prior to analysis.

#### EFFECT OF pH ON EXTRACTION—

Muscle homogenates were prepared with (a) unadjusted pH, range 5.5 to 6.5, (b) pH adjusted to 3.5 with lactic acid, and (c) pH adjusted to 9.5 with ammonia solution. These homogenates with added nitrite and nitrate (500 µg of sodium nitrite plus 500 µg of sodium nitrate) and controls were heated at 80° C for 10 minutes. The mean recovery of total nitrite was 44.2 per cent. from the acidic samples, 92 per cent. from the alkaline samples and 97 per cent. from the homogenates of unaltered pH.

#### EFFECT OF HEATING AT 80° C FOR 10 MINUTES ON EXTRACTION—

Muscle homogenates of pH 5.5 to 6.5 were divided into four aliquots, one being used as a control without addition, and 500 µg each of sodium nitrite and sodium nitrate were added as follows: (i) immediately prior to heating, (ii) after heating, after which the sample was re-heated for a further 10 minutes, and (iii) after heating, with no further heating. The results given in Table I show that heating within this pH range caused no loss of the added nitrite or nitrate.

TABLE I  
RECOVERY OF NITRITE AND NITRATE FROM PORK HEATED AT 80° C FOR 10 MINUTES

Treatment§	Nitrite found/ µg	Recovery, per cent.	Nitrate found/ µg	Recovery, per cent.
Control	20		57	
(i)	525	101	511	91
	550	106	567	102
(ii)	530	102	547	98
	530	102	547	98
(iii)	525	101	567	102
	525	101	511	91
Mean .. ..		102		97.0

§ Control with no added NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>.

500 µg of NO<sub>2</sub><sup>-</sup> and of NO<sub>3</sub><sup>-</sup> were added as follows: (i) immediately prior to heating; (ii) after heating and cooling; and (iii) after heating, then heating repeated.

\* Janke & Kinkel K.G.

† Griffin & George Ltd.

‡ Baird & Tatlock Ltd.

## EFFECT OF THE AMOUNT OF CADMIUM ON NITRATE REDUCTION—

Amounts of sodium nitrate, ranging from 25 to 400  $\mu\text{g}$ , and 5 ml of buffer were placed in 25-ml calibrated flasks containing 0.5, 1.0, 2.5 and 5.0 g of wet cadmium. The stoppered flasks were mechanically shaken, in a vertical position, for 5 minutes at a rate that enabled the cadmium to become dispersed throughout the solution. After the reduction, the contents of the flasks were diluted to volume with water. When more than 1.0 g of wet cadmium was used the test solutions, after shaking, were filtered through a Whatman No. 1 filter-paper into a second 25-ml calibrated flask to avoid the dilution error caused by the volume of cadmium (0.3 per cent. per gram). The 1.0, 2.5 and 5.0-g amounts of wet cadmium gave quantitative conversion of nitrate into nitrite, but the 0.5-g amount produced erratic results.

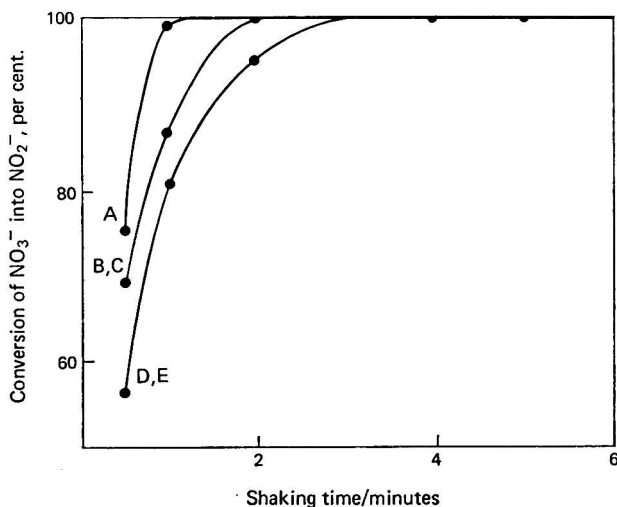


Fig. 1. Effect of shaking time on the reduction of nitrate to nitrite with 1 g of wet cadmium in a 25-ml calibrated flask. Amount of nitrate in flask: A, 25  $\mu\text{g}$ ; B, 50  $\mu\text{g}$ ; C, 100  $\mu\text{g}$ ; D, 200  $\mu\text{g}$ ; and E, 400  $\mu\text{g}$

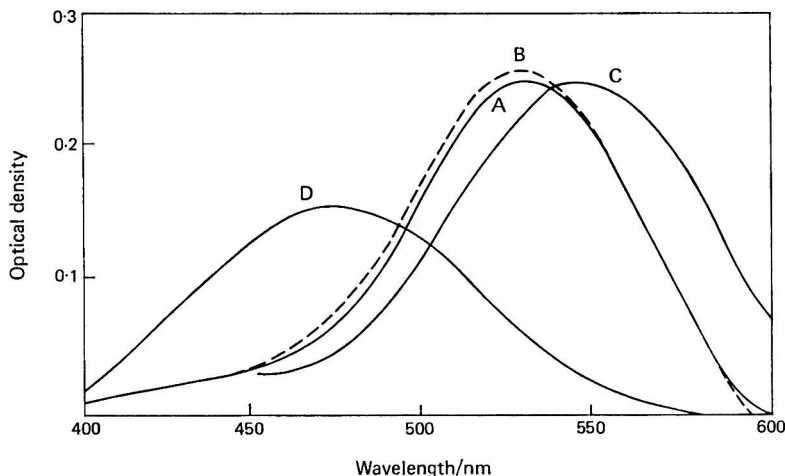


Fig. 2. Absorption spectra of the four diazo pigments, by using 3.5  $\mu\text{g}$  of sodium nitrite. Coupling agent: A, 1-naphthylamine; B, 1-naphthylamine-7-sulphonic acid; C, *N*-1-naphthylethylenediamine; and D, 1-naphthol

## EFFECT OF SHAKING TIME ON NITRATE REDUCTION—

With 1 g of wet cadmium the reduction of solutions containing 25 to 400  $\mu\text{g}$  of sodium nitrate was examined at shaking times of from 30 seconds to 5 minutes. Shaking for 2 minutes quantitatively reduced up to 100  $\mu\text{g}$  of sodium nitrate (Fig. 1) and after 3 minutes 400  $\mu\text{g}$  were reduced.

## METHOD OF COLOUR DEVELOPMENT—

The 5 mm sulphanilic acid solution was used for diazotisation with each of four coupling agents: 1-naphthylamine, *N*-1-naphthylethylenediamine, 1-naphthylamine-7-sulphonic acid and 1-naphthol.

Five millilitres of the colour reagent were added to 5 ml of diluted buffer (1 + 5, with water) containing 3.5  $\mu\text{g}$  of sodium nitrite. The solutions were maintained at  $20 \pm 5^\circ\text{C}$  in dim light prior to measurement in the spectrophotometer. The absorption spectra of the diazo pigments at 400 to 600 nm are shown in Fig. 2.

## TIME REQUIRED FOR MAXIMUM COLOUR DEVELOPMENT—

Optical density readings at the absorption maximum of each pigment were obtained at 2-minute intervals from zero to 30 minutes and at 10-minute intervals from 30 to 120 minutes. The results are shown in Fig. 3. Maximum colour development was obtained in 10 minutes with *N*-1-naphthylethylenediamine, in 13 minutes with 1-naphthylamine, in 25 minutes with 1-naphthylamine-7-sulphonic acid and in 34 minutes with 1-naphthol. The time required for maximum colour development with 1-naphthol was reduced to 20 minutes when ammonia solution was added to the colour reagent.<sup>16</sup>

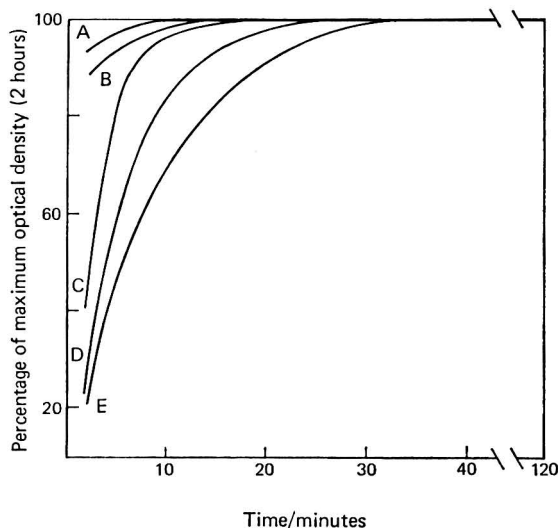


Fig. 3. Effect of time on the increase in optical density at wavelength maxima of the four diazo pigments, by using 10  $\mu\text{g}$  of sodium nitrite. Coupling agent: A, *N*-1-naphthylethylenediamine; B, 1-naphthylamine; C, 1-naphthol, with ammonia solution<sup>16</sup>; D, 1-naphthylamine-7-sulphonic acid; and E, 1-naphthol

The rapidity of colour development with *N*-1-naphthylethylenediamine is an advantage in analysing meat, in which the nitrite-to-nitrate ratio can vary over a wide range. One millilitre of the test solution can be added to the colour reagents and an analyst with experience can assess within 5 minutes whether more test solution or diluted buffer is required to obtain an optical density reading in the range 0.05 to 0.50.

With *N*-1-naphthylethylenediamine 15 to 725  $\mu\text{g}$  of total nitrite per gram of meat can be measured by using 1 to 5 ml of extract. With brines, a concentration range of 0.04 to 1.8 g of total nitrite per 100 ml can be measured.

#### RECOVERY OF NITRATE AND NITRITE FROM MEATS AND CURING BRINES—

Pork *longissimus dorsi* muscle containing additions of 50 to 1 000  $\mu\text{g g}^{-1}$  and cover brines with additions of 0.5 to 1.5 g per 100 ml of sodium nitrite and sodium nitrate were analysed by using the heating - alumina cream method of extraction and shaking with 1 g of cadmium for 5 minutes. The recoveries of nitrite and nitrate are summarised in Table II and are shown to be quantitative.

TABLE II  
PERCENTAGE RECOVERY OF NITRITE AND NITRATE ADDED TO PORK, BACON  
AND CURING BRINES

Material (mean of 20 samples)	Nitrite, per cent.	Nitrate, per cent.
Pork* and bacon† . . . . .	99.9 $\pm$ 1.4 (standard deviation $\pm$ 1.8)	98.3 $\pm$ 5.3 (standard deviation $\pm$ 5.8)
Cover brines (containing protein)‡ . .	100.2 $\pm$ 0.9 (standard deviation $\pm$ 0.7)	98.0 $\pm$ 3.0 (standard deviation $\pm$ 3.5)

\* Added: 50, 100, 200 and 1 000  $\mu\text{g}$  of  $\text{NaNO}_2$  and of  $\text{NaNO}_3$  per gram of pork.

† Added: 200 and 1 000  $\mu\text{g}$  of  $\text{NaNO}_2$  and of  $\text{NaNO}_3$  per gram of pork.

‡ Added: 500, 1 000 and 1 500 mg of  $\text{NaNO}_2$  and of  $\text{NaNO}_3$  per 100 ml of curing brine.

#### DISCUSSION

##### EXTRACTION OF NITRITE AND NITRATE FROM MEAT—

For the reduction of nitrate and the colorimetric determination of total nitrite a clear colourless solution is required. Like Grau and Mirna,<sup>15</sup> we found that trichloroacetic acid, lead acetate, tungstic acid and colloidal iron caused a loss of nitrite and nitrate or interference in their determination. These authors used a hot alkaline borax - zinc sulphate reagent to obtain an extract suitable for analysis. Follett and Ratcliff<sup>16</sup> replaced this reagent with hot potassium aluminium sulphate solution, because of the colloidal precipitate of zinc hydroxide that may occur with the former procedure. The potassium aluminium sulphate is added from a burette to prevent the pH of the hot extract falling below 5.0, when loss of nitrite would occur.

The heating process, in addition to coagulating the protein, appears to us to inactivate nitritase and nitratase activity of muscle and bacterial origin. This is an important consideration, as after homogenisation the bacteria that are normally restricted to the surface area of the sample are freely mixed in the homogenate with the nitrite and nitrate. With heating at 80 °C for 10 minutes, clear colourless meat extracts were obtained in most instances, provided the ratio of meat to water was low. Heating occasionally produced a colloidal solution, but with the addition of alumina cream a clear colourless extract is obtained without loss of nitrite and nitrate. Meat homogenates and brines that have a pH below 5.0 should be treated with alkali before heating to prevent the loss of nitrite and nitrate.

##### REDUCTION OF NITRATE TO NITRITE BY CADMIUM—

The production of cadmium *in situ*<sup>25</sup> by adding cadmium acetate and zinc dust to the test solution proved unreliable when applied to meat and curing brines, probably because of the presence of the zinc.<sup>24</sup>

The Grau and Mirna<sup>15</sup> separating funnel system has, in general, been replaced by Follett and Ratcliff<sup>16</sup> columns, which prevent the cadmium from drying out and losing reduction activity. The flow-rate of these columns decreases with use as the cadmium forms a dense mass. The decrease in the flow-rate can be prevented by converting the columns to an ascending flow pattern with the inlet at the bottom of the columns.

The shaking procedure is simple and rapid, and the reduction is achieved in 5 minutes while column reduction, with the preparation and reduction, takes 40 to 60 minutes. A further advantage is that special glassware is not needed. The globular shape of the 25-ml



calibrated flask permits efficient mixing of the cadmium with the test solution. Flasks by three manufacturers (Pyrex, E. Mil and Volac) made to British Standards Institution Specification 1792 showed no measurable differences when used as reduction vessels. After dilution to volume, 1 to 5-ml aliquots are easily removed by pipette for colorimetric analysis.

#### COLORIMETRIC DETERMINATION—

Three of the four couplers examined, 1-naphthylamine, *N*-1-naphthylethylenediamine and 1-naphthylamine-7-sulphonic acid, are similar in sensitivity. 1-Naphthylamine is considered dangerous for laboratory use.<sup>26</sup> Of the other two couplers, *N*-1-naphthylethylenediamine is preferred owing to the rapidity of colour development, which is an advantage for meat analysis, when the nitrite and nitrate concentration can vary over a wide range.

The efficiency of the cadmium reduction shaking method, as shown by the recovery values, indicates that under the conditions described the technique is a reliable and sensitive method for determining nitrite and nitrate in meat and curing brines. The recovery values compare favourably with those obtained with descending cadmium columns.<sup>15,16,18,19,21</sup> With suitable dilution the method may be applicable to water and sewage. The procedure should be capable of being applied to a wide range of foods, and further studies are being undertaken.

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## A Simple Field Test for the Determination of Cyclohexanone and Methylcyclohexanone Vapours in Air

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A field method is described for determining either cyclohexanone or methylcyclohexanone vapour in air at concentrations up to 400 and 920  $\text{mg m}^{-3}$ , respectively. The vapour of the ketone is collected in water and then coupled with the diazonium salt of H-acid. The two ketones form similar colours and the concentration of each can be determined by comparing the intensity of the colour produced with a series of permanent colour standards common to both. The procedure is simple and the time required for a complete analysis is about 25 minutes.

CYCLOHEXANONE and methylcyclohexanone find use in industry mainly as solvents for lacquers and resins. In addition, the former is an intermediate in the production of adipic acid, which is used in the manufacture of certain grades of nylon. Although not normally considered unduly toxic, the vapours of these ketones have a strong irritant and narcotic effect on persons exposed to them. The current threshold limit value for cyclohexanone in air<sup>1</sup> is 200  $\text{mg m}^{-3}$ . Of the isomeric methylcyclohexanones, only 2-methylcyclohexanone has been assigned a threshold limit value, which is currently 460  $\text{mg m}^{-3}$ . However, it seems reasonable to assume a similar threshold limit value for commercial methylcyclohexanone. Consequently, and as part of a programme to develop tests<sup>2,3</sup> for determining vapours of ketones found in industrial atmospheres, a simple field method was required to enable cyclohexanone and methylcyclohexanone to be determined at concentrations of the order of those given above. Preferably, the test would be specific for these alicyclic ketones in the presence of the aliphatic ketones with which they might co-exist in atmospheres, and also sufficiently sensitive to be carried out with small sample volumes.

Maslennikov<sup>4</sup> described a colorimetric procedure for the determination of cyclohexanone in the presence of other ketones. The chemical reaction used does not involve the carbonyl group, therefore apparently ensuring specificity in the presence of aliphatic ketones. Cyclohexanone is coupled with the diazonium salt of H-acid (4-amino-5-hydroxynaphthalene-2,7-disulphonic acid) in the presence of sodium sulphite and sodium hydroxide to give a red azo dye. This test was later applied by the same worker to the determination of cyclohexanone vapour in air.<sup>5</sup> More recently Adamiak,<sup>6</sup> who has been engaged in the development of a test for the determination of cyclohexanone vapour in air in the presence of acetone, has conducted a critical examination of various parameters of the original work<sup>4,5</sup> and effected certain improvements. These consisted in better absorption of the cyclohexanone vapour and improved stability of the coloured complex formed.

In this present study, preliminary experiments with aqueous solutions of cyclohexanone substantiated the work of Adamiak.<sup>6</sup> By using aqueous solutions of 3-methylcyclohexanone, one of the major constituents of commercial methylcyclohexanone, it was shown that this ketone also formed a coloured complex with the diazonium salt of H-acid. The respective colours formed by the two ketones appeared to be visually indistinguishable and they gave identical visible spectra when these were plotted by using a spectrophotometer. Therefore it appeared possible that by manipulating the sampling conditions for each ketone, a field test involving one set of colour standards could be devised for these two ketones. This approach depended on the proviso that when sampling an atmosphere the nature of the contaminant, which is either cyclohexanone or methylcyclohexanone in this instance, is known; this is usual in any industrial process in which solvents are used.

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## EXPERIMENTAL

## PREPARATION AND CALIBRATION OF STANDARD ATMOSPHERES OF CYCLOHEXANONE AND 3-METHYLCYCLOHEXANONE—

Standard atmospheres of each ketone were required so as to assess the efficiency of the sampling technique and to use in the development of the field test. These were prepared by using the permeation technique devised in this laboratory.<sup>7</sup> The appropriate ketone was allowed to permeate the walls of a sealed bag made from 0.0635-mm thick polythene, which was suspended in a glass tower through which passed a metered air stream. The concentration of cyclohexanone or 3-methylcyclohexanone in an atmosphere was determined from the rate of loss of weight of the polythene bags and the flow-rate of the diluting air stream. The atmospheric concentration thus obtained was checked by quantitatively absorbing the ketone vapour in two all-glass impingers in series, each containing 10 ml of water, at a sampling rate of 100 ml minute<sup>-1</sup>. The ketone was then determined colorimetrically as its 2,4-dinitrophenylhydrazone.<sup>2</sup>

## DEVELOPMENT OF FIELD TEST—

The colour development procedure of Adamiak<sup>6</sup> was adopted with minor modifications, and H-acid was replaced by its more readily available monosodium salt. As the manipulation of volumes of less than 1 ml is inconvenient for field-test purposes, the 0.2-ml amount of a 5 per cent. w/v sodium nitrite solution originally used<sup>6</sup> in the diazotisation step was replaced by 1 ml of a 1 per cent. w/v solution.

The test was to be developed on the basis of the use of one set of four colour standards representing concentrations of each ketone equal to 0, 0.5, 1.0 and 2.0 times the current threshold limit values. Therefore, a sample of an atmosphere of cyclohexanone containing 100 mg m<sup>-3</sup> would be required to give a colour identical with that of a sample of an atmosphere of methylcyclohexanone containing 230 mg m<sup>-3</sup> under the conditions of the test. To achieve this, it was decided that different sample volumes and different volumes of absorbing solution (water) would be required for each ketone. Linear spectrophotometric calibration graphs (up to 200  $\mu$ g for cyclohexanone and 230  $\mu$ g for 3-methylcyclohexanone) were prepared by using the proposed colorimetric procedure as follows.

To 2 ml of aqueous ketone solution were added 2 ml of a 0.5 per cent. w/v solution of the monosodium salt of H-acid in 0.1 N sulphuric acid, 1 ml of a 1 per cent. w/v sodium nitrite solution and 1 ml of a 10 per cent. w/v solution of anhydrous sodium sulphite in 5 per cent. w/v sodium hydroxide solution, making a total volume of 6 ml of reaction mixture. At room temperature (23 °C) the colour development was complete after 20 minutes but, in view of the intensity of the colours formed, dilution was necessary. Consequently, 1 ml of each of the reaction mixtures was diluted to 10 ml with water and the optical densities were measured in 10-mm cells at 550 nm against the reagent blank. Under these conditions 200  $\mu$ g of cyclohexanone (equivalent to a 500-ml sample of an atmosphere of twice the threshold limit value) gave an optical density that was greater by a factor of 1.10 than that for 230  $\mu$ g of 3-methylcyclohexanone (equivalent to a 250-ml sample of an atmosphere of twice the assumed threshold limit value). When, as with cyclohexanone alone, a 3-ml volume of aqueous solution was used instead of 2 ml, giving a total reaction mixture volume of 7 ml instead of 6 ml, the ratio was reduced to 0.92.

At this stage in the development of a test for the two ketones, it appeared that an atmosphere containing  $x$  times the threshold limit value of cyclohexanone would produce a colour that was similar to and approximately as intense as an atmosphere containing  $x$  times the assumed threshold limit value of 3-methylcyclohexanone. This would be so when a 500-ml sample of a cyclohexanone atmosphere was collected in 3 ml of water and a 250-ml sample of 3-methylcyclohexanone atmosphere was collected in 2 ml of water, assuming that both ketones were collected with 100 per cent. efficiency. Tests were next carried out to assess the trapping efficiencies for the two ketones, over a temperature range of 7 to 31 °C, by using all-glass absorbers.<sup>2</sup> For 3-methylcyclohexanone atmospheres over the range 0 to 2.5 times the assumed threshold limit value when sampling 250 ml at the rate of 125 ml minute<sup>-1</sup>, the trapping efficiency in 2 ml of water was 85.4 per cent. The trapping efficiencies in 3 ml of water for 500 ml of cyclohexanone vapour sampled at the same rate were 100 per cent. from

a half threshold limit value atmosphere ( $100 \text{ mg m}^{-3}$ ) and 94.5 and 87.1 per cent. from the threshold limit value atmosphere and for twice this value, respectively. Taking these various trapping efficiencies into account the optical density measured at 550 nm on sampling 500 ml of a threshold limit value atmosphere of cyclohexanone would, by calculation, have been expected to be greater by a factor of 1.02 than that measured on a 250-ml sample of an assumed threshold limit value atmosphere of 3-methylcyclohexanone. The corresponding calculated ratios for half and twice the threshold limit value concentrations were 1.08 and 0.97, respectively. The results of sampling atmospheres of the two ketones (shown in Table I) substantiated these ratios. This was considered acceptable for field-test purposes as it involved a maximum error of only 5 per cent. (at the half threshold limit value) if, as was intended, the colour of each standard could be designed to be matched between the cyclohexanone colour and that obtained with 3-methylcyclohexanone.

TABLE I

COMPARISON OF THE OPTICAL DENSITIES OBTAINED ON SAMPLING ATMOSPHERES OF CYCLOHEXANONE AND 3-METHYLCYCLOHEXANONE OVER THE CONCENTRATION RANGE ZERO TO TWICE THE THRESHOLD LIMIT VALUES BY THE PROPOSED FIELD-TEST PROCEDURE

Level of ketone atmosphere (threshold limit value)†	Cyclohexanone		3-Methylcyclohexanone		a/b
	*Mean optical density (a)	No. of runs	*Mean optical density (b)	No. of runs	
0.5	0.205 ± 0.009‡	10	0.185 ± 0.006	8	1.11
1.0	0.366 ± 0.009	15	0.374 ± 0.014	12	0.98
2.0	0.729 ± 0.007	5	0.754 ± 0.021	5	0.97

\* Read at 550 nm in 10-mm cell against reagent blank.

† Threshold limit value of 3-methylcyclohexanone assumed to be  $460 \text{ mg m}^{-3}$ .

‡ Standard deviation of mean optical density.

The colours obtained by using the proposed test for a concentration range of zero to twice the assumed threshold limit value atmospheres of 3-methylcyclohexanone were slightly more yellow than those obtained with cyclohexanone at the same levels. This was because of the greater dilution, 7 ml instead of 6 ml, of the blank colour in the latter instance. Again the effect was negligible and due allowance for this was made in the preparation of colour standards. Also, the variation of the responses of the ketones and blanks with temperature was acceptable provided that the temperature of colour development was between 15 and 30 °C.

Attempts to eliminate the dilution stage by reducing the sensitivity of the test were unsuccessful. Reduction in the concentrations of H-acid, sulphuric acid and sodium nitrite lengthened the time for diazotisation while reduction in the concentrations of sodium hydroxide and sodium sulphite reduced the ketone response compared with that of the blank. Reduction in the volumes of the ketone atmospheres sampled reduced the discrimination between the levels of 0, 0.5, 1.0 and 2.0 times the threshold limit value. No differences in response were noted when using samples of the monosodium salt of H-acid from different suppliers.

#### COLOUR STANDARDS—

With the co-operation of Tintometer Ltd., a standard disc was prepared representing the intensity of colours produced by sampling either 500 ml of cyclohexanone or 250 ml of methylcyclohexanone vapour atmosphere at levels of 0, 0.5, 1.0 and 2.0 times their respective threshold limit values. The standard colours were prepared as nearly as possible midway between the appropriate colours produced by the two ketones.

#### INTERFERENCES—

Possible interferences with the test by other organic solvents were examined. Stock solutions of these solvents were prepared in water, methanol and ethanol or their combinations. An aliquot of 1 ml of each solution was treated by the proposed field-test procedure and compared with a blank test on 1 ml of water. The substances listed, up to the levels indicated in column 4 of Table II, did not interfere in the test. (These were the respective levels at which a red colour was first discernible). The figures in column 5 are the equivalent atmospheric concentrations had the various weights of interfering solvents been quantitatively collected from 500-ml samples of atmosphere. Of the samples studied, only cyclohexanol appeared likely to interfere to any extent in the proposed test. Further tests showed

TABLE II  
 MAXIMUM LEVELS OF VARIOUS SOLVENTS SHOWING NO INTERFERENCE IN  
 THE PROPOSED FIELD TEST

Class	Compound	Threshold limit value/ mg m <sup>-3</sup>	Appearance of first discernible red colour		Appearance of yellow - brown colour of intensity > blank, Weight/mg
			Weight/mg	Equivalent atmosphere concentration*/ mg m <sup>-3</sup>	
Ketones	Isophorone	140	0.28	5.6 × 10 <sup>3</sup>	0.14†
	Diacetone alcohol	240	> 2.40	> 4.8 × 10 <sup>3</sup>	0.06
	Acetone	2400	> 24.00	> 4.8 × 10 <sup>4</sup>	2.40†
	4-Methylpentan-2-one	410	> 4.10	> 8.2 × 10 <sup>3</sup>	0.21
	Butan-2-one	590	> 5.90	> 1.18 × 10 <sup>4</sup>	0.59†
	5-Methylheptan-3-one	130	> 1.30	> 2.6 × 10 <sup>3</sup>	0.032†
	Mesityl oxide	100	> 1.00	> 2.0 × 10 <sup>3</sup>	0.10
	Cycloheptanone	NL	> 40.00	> 8.0 × 10 <sup>4</sup>	8.00
Aldehydes	Acetaldehyde	360	> 3.60	> 7.2 × 10 <sup>3</sup>	0.36
	Benzaldehyde	NL	> 80.00	> 1.6 × 10 <sup>5</sup>	80.00
	Salicylaldehyde	NL	> 80.00	> 1.6 × 10 <sup>5</sup>	80.00
Alcohols	Methanol	260	26.00	5.2 × 10 <sup>4</sup>	2.60
	Ethanol	1900	> 570.00	> 1.14 × 10 <sup>6</sup>	570.00
	Cyclohexanol	200	0.05	1.0 × 10 <sup>3</sup>	0.025
Halogenated hydrocarbons	Methylcyclohexanol	470	> 4.70	> 9.4 × 10 <sup>3</sup>	4.70
	1,1,2,2-Tetrachloroethane	35	> 0.35	> 7.0 × 10 <sup>2</sup>	0.35
	Chlorobenzene	350	> 3.50	> 7.0 × 10 <sup>3</sup>	0.35
Hydrocarbons	Toluene	750	> 7.50	> 1.5 × 10 <sup>4</sup>	0.75†
	α-Methylstyrene	480	> 4.80	> 9.6 × 10 <sup>3</sup>	0.48†
	White spirit	NL	> 15.00	> 3.0 × 10 <sup>4</sup>	15.00
Ethers	Dioxan	360	> 3.60	> 7.2 × 10 <sup>3</sup>	0.36
	2-Methoxyethanol	80	> 0.80	> 8.0 × 10 <sup>2</sup>	0.08†
Esters	Ethyl acetate	1400	> 14.00	> 2.8 × 10 <sup>4</sup>	14.00

\* In a 500-ml sample, assuming 100 per cent. efficiency of trapping of the vapour.

† Enhanced optical brilliance of the test solution.

NL denotes no threshold limit value listed.

that the interference was minimal; with 65 μg the ratio of its colour intensity to that of the same weight of cyclohexanone was only 0.16. However, it was also noted that the intensity of the colour obtained by applying the test to a solution containing 65 μg each of cyclohexanone and cyclohexanol was 12 per cent. greater than the sum of the colour intensities obtained from the individual determinations with similar weights of each compound. No explanation can be offered for this effect, but it was not considered serious enough to invalidate the proposed method for field-test purposes and at worst could involve only a small error, which would lie on the side of safety.

The interfering effect of cyclohexanol on a test for cyclohexanone when using H-acid reagent has been noted previously by Maslennikov,<sup>5</sup> who sought to obviate the problem by adding hexamine and acetic anhydride to the absorbing solutions and so inactivate the alcohol prior to the determination of the ketone. We confirmed the efficiency of this modification but, on finding that the response of cyclohexanone to the test became variable and was reduced by about 60 per cent., this approach was not pursued further.

In the course of carrying out the interference tests it was noted that each compound exhibited a threshold concentration (see Table II, column 6) beyond which the yellow - brown colour of the test solution became more intense than that of the blank; in addition, the presence of certain compounds also enhanced the optical brilliance of the blank colour. However, none of these colour effects interfered in any way with an observer's ability to differentiate between the zero and half threshold limit value colour standards.

FIELD TEST FOR THE DETERMINATION OF CYCLOHEXANONE AND  
METHYLCYCLOHEXANONE VAPOURS IN AIR

## APPARATUS—

*All-glass absorbers*—These were of the type previously described.<sup>2</sup>

*Aspirator*—A rubber-bulb hand aspirator adjusted to sample at the rate of 125 ml minute<sup>-1</sup>.\*

*Colour comparison tubes*—Optically matched glass tubes of 13.5 mm i.d., wall thickness 0.5 mm and calibrated with a mark at 10 ml.†

*Colour standards*—A comparator disc† containing coloured glass standards for this test and to be used with a Lovibond "1000" Comparator is available. Four standards are provided, O, A, B and C, representing either 0, 100, 200 and 400 mg m<sup>-3</sup> of cyclohexanone vapour in air or 0, 230, 460 and 920 mg m<sup>-3</sup> of methylcyclohexanone vapour in air when atmospheres containing the respective ketones are sampled and determined as described under Procedure below.

## REAGENTS—

All reagents should be of analytical-reagent quality whenever possible and all solutions prepared with de-mineralised or de-ionised water.

*H-acid solution*—Dissolve 1.25 g of the monosodium salt of H-acid in 250 ml of 0.1 N sulphuric acid. The reagent is stable for up to 2 months.

*Sodium nitrite solution, 1 per cent. w/v*—This solution is stable for at least 2 months.

*Sodium sulphite - sodium hydroxide solution*—Dissolve 10 g of anhydrous sodium sulphite and 5 g of sodium hydroxide in water and dilute to 100 ml. The reagent is stable for up to 1 month.

NOTE—The above solutions should be kept tightly stoppered when not in use and stored below 25 °C in dark glass bottles in an uncontaminated atmosphere.

In the interest of safety, pipette fillers should be used for dispensing reagents used in this test.

## PROCEDURE—

*Atmosphere sampling*—For cyclohexanone atmospheres, pipette, in an uncontaminated atmosphere well away from the suspected source of cyclohexanone vapour, 3 ml of water into the receiver, insert the inlet tube and connect the aspirator to the side-arm. At the sampling site, collect a 500-ml sample (*i.e.*, four aspirations) of the atmosphere.

For methylcyclohexanone atmospheres, carry out the sampling as for cyclohexanone, but collect a 250-ml sample (*i.e.*, two aspirations) of the atmosphere in 2 ml of water.

*Colour development*—Remove the apparatus from the suspected source of contamination, disconnect the aspirator, remove the inlet tube and to the receiver add successively, from pipettes, 2 ml of H-acid solution, 1 ml of sodium nitrite solution and 1 ml of sodium sulphite - sodium hydroxide solution. Stopper the receiver and mix the contents well by inverting several times, ensuring that no liquid is lost through the side-arm. Allow the solution to stand for 20 minutes. Should the ambient temperature be below or above the range 15 to 30 °C, immerse the receiver in a water-bath the temperature of which is within these limits.

Transfer 1 ml of the resulting solution to a comparator tube, dilute with water to the graduation mark and mix well. Fill a similar tube to the same depth with water and insert both tubes into the comparator. By using the colour standards and viewing through the solutions, obtain the nearest colour match between standards and sample.

## DISCUSSION AND APPLICATION OF METHOD

All of the development work on the test for methylcyclohexanone was carried out with the 3-isomer, which is the major constituent of the commercial material (Sextone B). Later, two samples of Sextone B of different manufacture were examined by the proposed test. The use of gas - liquid chromatography showed that each sample contained about 45 per cent. of the 3-isomer, about 35 per cent. of the 4-isomer and about 10 per cent. of the 2-isomer,

\* Obtainable from Siebe Gorman and Co. Ltd., Davis Road, Chessington, Surrey.

† Obtainable from Tintometer Ltd., Salisbury, Wiltshire.

the balance being mainly cyclohexanone (about 10 per cent.). The response of the Sextone B to the proposed test was about 90 per cent. of that of the pure 3-methyl isomer. 2-Methylcyclohexanone was found to give a negligible response to the test and, as it was known that cyclohexanone gave a response that was greater by a factor of 1.27 than that of the 3-isomer (on a w/w basis), it was inferred that the response of the 4-isomer was very close to that of the 3-isomer. The resultant reduced response of the Sextone B was well within acceptable field-test limits, and no modification of the colour standards was necessary.

The lack of response of the 2-isomer to the test is consistent with the reaction proposed by Maslennikov,<sup>4,5</sup> in which coupling of cyclohexanone with the diazonium salt of H-acid takes place in the ortho positions of the ketone. In 2-methylcyclohexanone one of these positions is already filled; hence the likelihood of any coupling of that nature taking place is probably remote.

The proposed method was checked at industrial premises where methylcyclohexanone was being used in a screen-printing process. At various sites parallel samples were taken from a single sampling point by the proposed field test and by collection in water for subsequent laboratory analysis by a method<sup>2</sup> involving the use of 2,4-dinitrophenylhydrazine reagent. Unfortunately, isophorone vapour was also present at some sampling sites and this vitiated to some extent the value of the exercise, because with the 2,4-dinitrophenylhydrazine check method the total ketone content of the atmosphere was determined. In view of this a further series of similar check tests was carried out in the laboratory with static atmospheres of each of cyclohexanone and methylcyclohexanone (Sextone B) within a PVC container of nearly 600-litre capacity. The results obtained (shown in Table III) indicate the validity of the field test for the determination of the vapour of either of these ketones in atmospheres at concentrations up to twice their respective threshold limit values. No provision can be made in this test for the separate determination of either ketone when both are present in an atmosphere. In such an event, sampling and the determination should be carried out on the assumption that all of the ketone present is cyclohexanone, which has the lower threshold limit value.

TABLE III

COMPARISON OF THE RESULTS OF ANALYSIS OF CYCLOHEXANONE AND METHYLCYCLOHEXANONE ATMOSPHERES BY THE PROPOSED FIELD TEST AND 2,4-DINITROPHENYLHYDRAZINE METHOD

Sample	Ketone* concentration found/mg m <sup>-3</sup>	
	By 2,4-dinitrophenylhydrazine method	By field test†
1	59	100—
2	73	100
3	140	100+
4	217	200
5	341	~300
6	391	400—
7	~800	≥400
8	26	0+
9	104	~115
10	187	230
11	217	230+
12	312	~345
13	376	~345
14	744	~690
15	935	920
16	996	920+

\* Samples 1 to 7 are of cyclohexanone atmospheres and 8 to 16 are of Sextone B atmospheres.

† A (+) symbol indicates a value slightly greater, and a (—) symbol slightly less, than the nearest colour standard.

Although this method was specifically developed for field use with visual standards, it has been found in the laboratory that, by using a spectrophotometer and standard solutions, calibration curves for the two ketones can be prepared, and from measured optical densities of samples more precise determinations of the cyclohexanone or methylcyclohexanone content of an atmosphere can be made. The only modification necessary to the Procedure described

above would be the use of two all-glass absorbers in series, each containing 2 ml of water to ensure the 100 per cent. collection of the vapour of either ketone. Spectrophotometric readings should be made at 550 nm in 10-mm cells against a reagent blank.

This work was carried out on behalf of the Department of Employment Committee on Tests for Toxic Substances in Air. We thank the Government Chemist for permission to publish this paper, H.M. Factory Inspectorate for arranging facilities for the field tests, and Mr. J. S. Poynter for his technical assistance.

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## Book Reviews

THE CURRENT STATUS OF LIQUID SCINTILLATION COUNTING. Edited by EDWIN D. BRANSOME, jun. Pp. xxi + 394. New York and London: Grune & Stratton, Inc. 1970. Price \$19.75; £8.90.

This book is the result of a symposium held at Massachusetts Institute of Technology, U.S.A., in April, 1969. In the preface the editor refers to the first book on liquid scintillation counting, edited by Bell and Hayes, from a symposium in 1957, and suggests that the field is now well established and a further work of reference is now required. The present report of proceedings is therefore "intended to answer the needs of the neophyte as well as the user of liquid scintillation counters." This is always a difficult task, particularly with the large authorship that is drawn from a symposium. The main user will be the established analyst but the newcomer will find some assistance at points throughout the review. The book is divided (somewhat arbitrarily) into six main sections on Basic Mechanisms, Uses, The Labelled Sample, Quenching, Chemiluminescence and Data Handling, and I will consider each section separately.

Section I (three chapters) on Basic Mechanisms starts at a fundamental level and the novice could well ignore this section until he has established a rapport with the subject. Birks (U.K.) presents a well argued paper on the physics of the interactions and transfer processes. It contains an unusual definition of resolution (p. 4), *viz.*,  $R = N^{-1}$  where  $N$  is the number of electrons. A more normal definition is the peak width at half height divided by peak position (for a Gaussian distribution  $R = 2.35 N^{-1}$ ). Thus a "resolution" of 20 per cent. at 10 keV becomes 47 per cent. This is still optimistic at 10 keV. Laustriat, Voltz and Klein (France) suggest that there has been little improvement in solvents whilst Horrocks (U.S.A.) gives a well written account of solutes at the right technical level for this review.

Nine papers on the main uses of the scintillation counter for counting liquids and counting in liquid scintillators constitute section II. Kobayashi and Maudsley (U.S.A.) give an informative analysis of double isotope counting, while a study on limits of detection for about twelve isotopes by Moghissi (U.S.A.) provides much useful data. Two papers by Parker and Elrick (U.K.) and Ross (U.S.A.) give the necessary details for Cerenkov counting: the second paper demonstrates that carbon-14 can be counted with an efficiency of 12 per cent. owing to a region of anomalous refractive dispersion in some solvents. The chapter by Wyld (U.S.A.) on statistics is somewhat out of place in this section. It is, however, clear and well written and should have been extended to include later chapters on the statistics of two-channel counting and automatic external standardisation.

The Labelled Sample (section III) ranges over many techniques requiring the liquid scintillator as the final counting method. Three problems of sample preparation are discussed in chapters on chemical stability, isotope effects and loss by adsorption. The remaining twelve chapters present various authors' solutions to the counting of soluble and insoluble materials. This is the part for the chemist and biochemist with problems.

By sections IV and V we have reached quenching and chemiluminescence, the basic problems with the method; perhaps a little late for the unwary. These chapters are the most readable and relevant in the whole review. Two chapters by Neary and Budd (U.S.A.) and Peng (U.S.A.) represent a very thorough assessment of quenching problems and they point up the distinct difference between colour and chemical quench. Similarly Bransome (U.S.A.) presents the second *bête noire*, *i.e.*, chemiluminescence. Indications of these effects are often noted by accident and the chosen method of correction (two-channel or automatic external standardisation) is used without thought when use of both together could often indicate that colour quenching or chemiluminescence was present. This is not mentioned explicitly here nor is it suggested in the next section on data handling.

Section IV (Data Handling) is the weakest part of the book, partly because it is divorced from the statistics section but mainly because the field is still wide open and every laboratory has its own technique (and computer?). Some guide lines for both on-line and off-line computers and desk top calculators will be found in these final three chapters.

This is basically a very readable book in spite of changes in style between chapters. It can replace "Bell and Hayes" as a reference book, particularly since it offers advantages over the much shorter journal review articles. The main advantage is that the essence of each reference

is distilled in a few sentences and the reader need not embark on a wide search of irrelevant references that are common in such articles. The book is well produced with two columns per page, which is very readable but can cause havoc with equations. The index and cross-referencing have been well prepared and the very few printing errors are not likely to cause problems. The newcomer will find the words of experts difficult at first but I am sure that this book will be a convenient source of reference over the next few years.

J. A. B. GIBSON

ELECTROANALYTICAL CHEMISTRY. A SERIES OF ADVANCES. VOLUME 4. Edited by ALLEN J. BARD. Pp. xiv + 327. New York: Marcel Dekker Inc. 1970. Price £8.90; \$18.75.

This is the fourth volume in this series of advanced electrochemical review articles. It continues the high standard set by the previous three and is likely to be equally well received. Volume 4 contains just three articles: (1) Sine Wave Methods in the Study of Electrode Processes, by Margaretha Sluyters-Rehbach and Jan H. Sluyters; (2) The Theory and Practice of Electrochemistry with Thin Layer Cells, by A. T. Hubbard and F. C. Anson; (3) Application of Controlled Potential Coulometry to the Study of Electrode Reaction, by Allen J. Bard and K. S. V. Santhanam. Each chapter is by acknowledged experts in their field and the first article is particularly to be welcomed as a summary of the present views of the Utrecht school. The series is well edited, clearly presented and strongly to be recommended.

G. J. HILLS

MOLECULAR PHOTOELECTRON SPECTROSCOPY. A HANDBOOK OF HE 584 Å SPECTRA. By D. W. TURNER, C. BAKER, A. D. BAKER and C. R. BRUNDLE. Pp. x + 386. London, New York, Sydney and Toronto: Wiley-Interscience, a division of John Wiley & Sons Ltd. 1970. Price £7.

The authors of this volume have been pioneers in the development of molecular photoelectron spectroscopy as a method for the study of the molecular electronic structures of substances in the vapour state. The techniques developed prove to be singularly powerful for these purposes and they complement other spectroscopic techniques used for structural investigation. As its subtitle suggests, this volume is effectively an atlas of spectra obtained, largely by the authors, by using the radiation from a helium discharge as source. The authors state in their preface that the motive for the production of this volume is the feeling that their good fortune in acquiring a large mass of previously inaccessible data leaves them with an obligation to collect them into one place for ease of access even before a complete account of their interpretation is possible.

The book gives a brief general account of the underlying physical nature of the processes involved and the experimental techniques developed. The following twelve chapters are devoted to various types of molecules ranging from simple diatomic molecules to complex organic and inorganic systems. Within each chapter the photoelectron spectra are presented for the compounds considered and brief interpretative comment is made for each.

This book will be bought by those wishing to gain access to the data collected by the authors in one readily assimilable form. It will be read by those who wish to be informed of the power, scope and potential of the technique. It is not a textbook and does not treat the underlying theory and the practice of the technique in great depth. It should fulfil its aim of stimulating those research workers in the field of chemistry and chemical physics who may be interested in applying the technique in their particular area.

G. F. KIRKBRIGHT

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### **The Determination of Certain Antioxidants, Ultraviolet Absorbers and Stabilisers in Plastics Formulations by Thin-layer Chromatography**

The use of thin-layer chromatography in the determination of additives in plastics formulations is investigated. Details are given for the detection and determination of antioxidants, organotin compounds and ultraviolet absorbers, and mention is made of other additives likely to be present. Commercially prepared silica gel layers containing a fluorescent additive are used in most cases.

Comparatively small samples of the plastics materials are required and, by means of the techniques described, it is possible to identify additives in extracts containing several different components. The method can be used to detect additives down to between 10 and 1  $\mu\text{g}$  per sample and both qualitative and more accurate quantitative determinations are made possible.

#### **DIANA SIMPSON**

Bakelite Xylonite Ltd., Research and Development, Lawford Place, Manningtree, Essex.

#### **and B. R. CURRELL**

Department of Chemistry, Northern Polytechnic, Holloway, London, N.7.

*Analyst*, 1971, **96**, 515-521.

### **A Rapid Cadmium Reduction Method for the Determination of Nitrate in Bacon and Curing Brines**

A method has been developed for the extraction of nitrate and nitrite from meat by heating at 80 °C for 10 minutes to coagulate the protein and inactivate nitrate and nitrite reductase activity and subsequently treating with alumina cream. The latter treatment alone was used for the clarification of curing brines.

A method for the reduction of nitrate to nitrite by shaking with cadmium has been developed that is quicker, as it takes 5 minutes, than column reduction, which requires 40 to 60 minutes. Quantitative recoveries of nitrate as nitrite were obtained.

Methods of determining nitrate as nitrite involving the use of the diazo compounds formed between sulphanilic acid and each of the four coupling agents 1-naphthylamine, *N*-1-naphthylethylenediamine, 1-naphthylamine-7-sulphonic acid and 1-naphthol were investigated. *N*-1-Naphthylethylenediamine is recommended because of the short time (10 minutes) required for maximum colour development.

#### **R. J. ELLIOTT and A. G. PORTER**

Technical Division, Ulster Curers' Association, 2 Greenwood Avenue, Belfast, BT4 3JL, N. Ireland.

*Analyst*, 1971, **96**, 522-527.

### **A Simple Field Test for the Determination of Cyclohexanone and Methylcyclohexanone Vapours in Air**

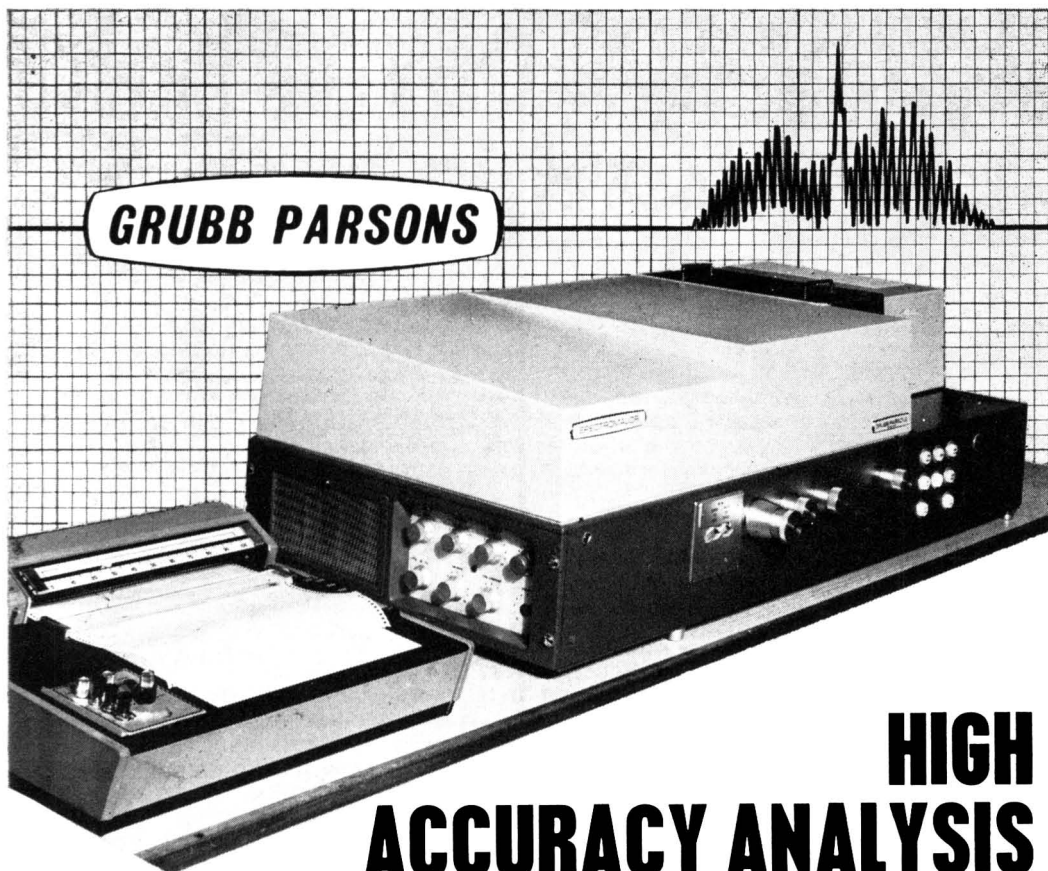
A field method is described for determining either cyclohexanone or methylcyclohexanone vapour in air at concentrations up to 400 and 920  $\text{mg m}^{-3}$ , respectively. The vapour of the ketone is collected in water and then coupled with the diazonium salt of H-acid. The two ketones form similar colours and the concentration of each can be determined by comparing the intensity of the colour produced with a series of permanent colour standards common to both. The procedure is simple and the time required for a complete analysis is about 25 minutes.

#### **P. ANDREW, A. F. SMITH and R. WOOD**

Department of Trade and Industry, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

*Analyst*, 1971, **96**, 528-534.





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