The
ANALYST

The Journal of the
Society for Analytical Chemistry

A monthly International Publication
dealing with all branches of
Analytical Chemistry

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

Volume 98, No. 1169

August, 1973

Summaries of Papers in this Issue

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E. BISHOP and P. H. HITCHCOCK
Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.

Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part VIII. Single-scan Voltammetry of Vanadium(V) - Vanadium(IV) in the Presence of Chromium, Manganese and Iron, and the Kinetic Parameters of the Vanadium System, at Platinum Electrodes Pre-treated by Five Methods

Continuing the earlier examination of the vanadium system alone, under various conditions and with various electrode pre-treatments, the effect of neighbouring steel-forming d-block elements has been investigated. Chromium(VI) at pH 4·0 suppresses the vanadium(V) reduction wave, and the degree of suppression is quantitatively proportional to the chromium(VI) concentration. Activated electrodes are deactivated by dipping them in a chromium(VI) solution, and remain so even when well washed thereafter, so that chromium(VI) as well as chromium(III) is adsorbed strongly on platinum. In 2·0 M sulphuric acid, chromium(VI) and vanadium(V) are reduced at the same rate. Manganese(VII) in acetate buffer gives a fast, well separated wave, but the separation is not as good in 2·0 M sulphuric acid; slowing the vanadium(V) reduction by using an oxidised electrode effects no improvement: the manganese wave is similarly affected. Addition of chromium(VI) to the manganese - vanadium mixture at pH 4 suppresses the manganese wave only slightly, even when the vanadium wave is completely suppressed. In 2·0 M sulphuric acid, the manganese wave is undistorted and chromium and vanadium are simultaneously reduced. Iron(III) in 2·0 M sulphuric acid does not interfere, but the separation of the vanadium and iron waves is not good. Iron(II) can, however, act as a potentiostatic intermediate. The kinetic parameters of the vanadium system are reproducible in acetate buffer, but only when the electrode is fouled in 2·0 M sulphuric acid. Pattern theory and diffusion-corrected Lewartowicz methods give results that agree. The charge-transfer kinetic parameters are shown to be potential dependent in acidic media. The results are compared with those in earlier reports. The generation current efficiency for vanadium(IV) in acetate buffer was computed.

E. BISHOP and P. H. HITCHCOCK
Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.

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Potentiostatic Coulometric Determination of Vanadium, Vanadium - Manganese and Vanadium - Iron Mixtures and the Influence of Chromium on the Process

Earlier voltammetric work permitted the mass and charge transfer kinetic parameters of the vanadium system to be calculated for diverse media and platinum electrode pre-treatments, and command potentials to be selected for potentiostatic determination of vanadium alone and in certain combinations with other steel-forming elements. A simple coulometric cell and an adaptation of a commercial potentiostat are described. Current integration by strip-chart recorder is too inaccurate and so RC integration is discussed. Philbrick SP456 amplifiers refused capacitive feedback, but very satisfactory results were given by Solartron AA 1023 amplifiers. The design of a very high quality integrating capacitor from S.T.C. polystyrene elements is described; leakage and drift tests were very satisfactory. Pre-treatments of electrolytes and electrodes are discussed. Vanadium(V) is determined at -0.128 V in acetate buffer and at $+0.247$ V in 2.0 M sulphuric acid, in the latter with a relative standard deviation of 0.27 per cent. and a 95 per cent. confidence level result of $(1.008$ to $1.011) \times 10^{-1}$ M compared with 1.012×10^{-1} M for a standard solution. Chromium(VI) suppresses all reduction at pH 4.0, and is reduced simultaneously with vanadium in sulphuric acid. Manganese(VII) is reduced to manganese(III) in the first step at $+0.7$ V at pH 3.5 and manganese(III) and vanadium(V) are simultaneously reduced in the second step at -0.12 V. The separation of iron(III) is possible at $+0.9$ V but impracticable; simultaneous reduction at $+0.25$ V in 2.0 M sulphuric acid followed by re-oxidation of the iron(II) at $+1.0$ V is recommended.

E. BISHOP and P. H. HITCHCOCK
Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.

A Multi-channel Dispenser - Titrator - pH-stat

A multi-channel dispenser - titrator - pH-stat with switch-selection of reagents and reagent volume control and with a directly digital read-out is described. A valve driven by a stepper motor is used to select reagents and as a coarse volume control. A drop generator dispensing - deflection mechanism is used as a fine volume control. The drop generator is also used to reject automatically to waste any reagent contaminated by previously dispensed reagent and, in the titration mode, to add various amounts of reagent to the reaction mixture. The instrument gives outstanding precision (relative standard deviation less than 0.2 per cent. over the range 0.5 to 7.0 ml) and linearity (correlation coefficient $r = 0.999$ over the ranges 0.01 to 1.0 and 0.25 to 7.0 ml).

DOUGLAS G. MITCHELL and KENNETH M. ALDOUS
Division of Laboratories and Research, New York State Department of Health, Albany, New York 12201, U.S.A.

A Modified Field Test for the Determination of Carbon Disulphide Vapour in Air

An improved and more sensitive method is described for the determination of carbon disulphide vapour in air at concentrations up to 40 p.p.m. V/V. Carbon disulphide vapour is absorbed from a 500-ml sample of air into an ethanolic solution containing copper(II) acetate, diethylamine and triethanolamine. The yellow colour produced is compared visually with standard colours or measured spectrophotometrically. For field use, the apparatus is portable and simple to operate, and requires a working time of about 5 minutes per determination.

E. C. HUNT, W. A. McNALLY and A. F. SMITH
Department of Trade and Industry, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, SE1 9NQ.

Determination of the Antioxidant 1,3,5-Trimethyl-2,4,6-tri(3′,5′-di-t-butyl-4′-hydroxybenzyl)benzene in Feeds

1,3,5-Trimethyl-2,4,6-tri(3′,5′-di-t-butyl-4′-hydroxybenzyl)benzene (Ionox 330) is an antioxidant that is used for the preservation of plastic food wrappings. Its use as a fat stabiliser could be extended to animal feeds. By using the method described, 200 p.p.m. of Ionox **330** in a feed can be determined with good reproducibility. The method consists in extracting the Ionox 330 with chloroform, purifying it by using thin-layer chromatography, and measuring at 522 nm the colour developed in the presence of iron(III) chloride and 2,2′-bipyridyl. Possible interference from 2,6-di-t-butyl-p-cresol (butylated hydroxytoluene; BHT) can be avoided by using this chromatographic technique.

G. F. BORIES

Station Centrale de Nutrition, Centre National de Recherches Zootechniques, 78-Jouy-en-Josas, France.

The Determination of Lead in Foods by Atomic-absorption Spectrophotometry

Rapid procedures for the determination of lead in foods by an organic extraction technique and atomic-absorption spectrophotometry are described. The food sample can be dry ashed or digested by using sulphuric acid and hydrogen peroxide. In the latter instance, digestion need not be complete. Lead is extracted from acidic solutions (either the dissolved ashes or the residual solution after acid digestion) into xylene as its diethylammonium diethyldithiocarbamate chelate, and then determined by use of atomic-absorption spectrophotometry. Large amounts of iron and tin do not interfere in the determination. In a 10-g sample, 0·02 p.p.m. of lead can be detected. The standard deviation in the range from 0·2 to 1·0 p.p.m. of lead is about 0·02 p.p.m. Certain products do not require preliminary digestion; in these instances lead is extracted directly from the acidified sample. Liquids, beverages and many canned foods can be monitored very rapidly in this way. The chelate - solvent combination used in this method is more convenient than the ammonium tetramethylenedithiocarbamate - isobutyl methyl ketone system. The method is applicable also to metals other than lead; its use for cadmium has been demonstrated successfully.

R. K. ROSCHNIK

Nestlé Products Technical Assistance Co. Ltd., Control Laboratory, Case Postale 88, Ch-1814, La Tour-de-Peilz, Switzerland.

A Critical Study of Safranine O as a Spectrophotometric Reagent: a Rapid Method for the Determination of Trace Amounts of Antimony in Steel

The behaviour of Safranine O (Basic red 2, C.I. 50240) in aqueous solutions has been investigated and its suitability as a spectrophotometric reagent is evaluated and discussed. A rapid method for the determination of antimony as a hexachloroantimonate(V) ion-association complex with Safranine O is described. This complex is extracted into benzene and is determined spectrophotometrically. The method is as sensitive and reproducible as the Rhodamine B method but it has the advantage that the determination can be carried out directly on solutions of steel without prior separation. Good agreement was found with standardised antimony values for five British Chemical Standards' steels.

C. BURGESS, A. G. FOGG and D. THORBURN BURNS

Department of Chemistry, University of Technology, Loughborough, Leicestershire, LE11 3TU.

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Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part VII.* Conditional Potentials, and Single-scan Voltammetry of Pure Vanadium(V) - Vanadium(IV) Systems in Various Media at Platinum Electrodes Pre-treated by Five Methods†

BY E. BISHOP AND P. H. HITCHCOCK‡

(Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD)

The limited previous work on vanadium is reviewed. Five methods of electrode pre-treatment have been selected and are described. The variation of the conditional potential of the vanadium(V) - vanadium(IV) system with hydrogen-ion concentration is reported. The experimental work is complicated by isopolymerisation reactions, of which at least one is kinetically slow. The voltammetric reduction of vanadium(V) in saturated potassium sulphate - acetate buffer at pH 4·0 is examined: the benefit of shifting solvent reaction potentials to more negative potentials is nullified by the direct reduction of un-ionised acetic acid.

A similar examination is made in a medium of 5×10^{-5} M sulphuric acid and in one of 2·0 M sulphuric acid. Possible adsorption effects are canvassed. The complex behaviour at intermediate hydrogen-ion concentrations is discussed, with illustrations drawn from a sulphuric acid medium of pH 2·0. The anodic oxidation of vanadium(IV) is briefly examined. It is concluded that the electrochemical behaviour of the vanadium system is strongly dependent on hydrogen-ion concentration and on the electrode pre-treatment. The electrode can be chemically oxidised in vanadium(V) solutions. The mechanism is a one-step one-electron process. No evidence could be found for reduction below the +4 oxidation state at platinum. Vanadium(IV) cannot be oxidised without severe loss of current efficiency, nor reduced to vanadium(III) at platinum electrodes.

LINGANE[1] could obtain little information from a polarographic investigation of the vanadium(V) - vanadium(IV) system. The complex structure of the voltammetric waves at carbon electrodes in sulphuric and orthophosphoric acids defied interpretation,[2] although the reproducibility was fairly good. Davis[3,4] examined the reaction chronopotentiometrically and voltammetrically, and concluded that the reduction of vanadium(V) was accelerated by a lightly oxidised platinum surface (the oxygen bridge theory, since rejected[5,6]). Amperostatic determinations of vanadium(V) have been reported for copper(I),[7] iron(II),[8] titanium(III),[9,10] and tin(II)[5] as intermediates. Potentiostatic determination at a mercury cathode has been reported by Israel and Meites,[11] but no report of reduction at platinum has appeared, although Davis[12] remarked that the reaction was slow. A voltammetric study of the system has been made in a variety of media with a view to the determination of the mass and charge transfer kinetic parameters, and the selection of conditions for the potentiostatic determination of vanadium both alone and in mixtures with other steel alloying elements.

EXPERIMENTAL

General apparatus and procedures have been described earlier,[13] and electrode treatments and behaviour have been reviewed.[14] The reagents were of the highest purity available (Aristar, P.V.S. or AnalaR grade) and were further purified if necessary. Sodium perchlorate was made from sodium carbonate and perchloric acid.

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* For particulars of Part VI of this series, see reference list, p. 562; for Part VIII, see p. 563.
† Presented at the Second SAC Conference, Nottingham, 1968.
‡ Present address: Ever Ready Co. (G.B.) Ltd., Central Research Laboratories, St. Ann's Road, London, N15 3TJ.

Water—Throughout this series of papers, the terms water and distilled water refer to sterile, grease-free and surfactant-free water prepared in a special still,[15] and having a total solids content of less than 10^{-12} M, calculated as chloride. It contains dissolved carbon dioxide and oxygen, which are removed by methods described earlier.[16,17]

Primary standard sodium carbonate solution, 0·05 M—This solution was made by direct weighing of P.V.S. sodium carbonate that had been dried at 280 °C for 2 hours.

Primary standard sodium oxalate solution, 0·05 M—This solution was made by direct weighing of anhydrous sodium oxalate that had been dried at 105 °C for 2 hours.

Primary standard potassium dichromate solution, 0·016 67 M—This solution was made by direct weighing of potassium dichromate prepared by twice recrystallising AnalaR potassium dichromate from water, pulverising the crystals and drying them at 160 °C for 3 hours.

Potassium permanganate solution, 0·02 M—Potassium permanganate was dissolved in water, the solution heated to boiling-point, simmered for 1 hour, cooled, filtered through a porosity 4 sinter and transferred into a conditioned amber Winchester bottle. A 25·00-ml aliquot of the 0·05 M sodium oxalate solution was transferred into a 250-ml conical flask containing 8·0 ml of 4·0 M sulphuric acid, the solution heated to between 80 and 90 °C and titrated with the permanganate solution to the first perceptible permanent pink colour. A blank of 8 ml of 4·0 M sulphuric acid in 50 ml of water was titrated in a similar way. In the early stages of the oxalate titration, the permanganate was added very slowly, so that the solution became colourless before the next drop of permanganate was added, until the accumulated manganese(II) rendered the reaction fast. The standardisation was repeated before each period of use of the permanganate solution. A relative standard deviation on this and all other titrations of ±0·04 per cent. was secured.

Vanadium(V) solutions—A solution of ammonium metavanadate was boiled with a small excess of potassium hydroxide until all the ammonia was removed. The solution was cooled and diluted to 0·1 M with water. Standardisation was effected by reducing a large aliquot of the solution with sodium sulphite and sulphuric acid, and the excess of sulphur dioxide was removed by refluxing the solution for 1 hour in a stream of nitrogen. The solution was cooled and diluted to its original volume with water. Aliquots of the vanadium(IV) solution were titrated with the standardised permanganate solution, with sodium diphenylamine-4-sulphonate as the indicator. The 0·1 M potassium vanadate solution was used to prepare solutions of 0·05 M vanadium(V) in 2·0 M sulphuric acid, and 0·05 M vanadium(V) in 4·0 M hydrochloric acid.

Acetate buffer supporting electrolyte, pH 4—A 0·45 M solution of sodium acetate was saturated with potassium sulphate and then acidified with glacial acetic acid to pH 4, as indicated by glass and calomel electrodes and a 39A pH meter.

ELECTRODE ACTIVATION PROCEDURES—

Davis[3,4] oxidised platinum electrodes chemically with a solution of silver(II) oxide in 6·0 M nitric acid, and reduced them either potentiostatically, or by soaking them in iron(II) sulphate solution. He obtained reproducible results if the oxidation immersion time was long enough. Anson[18] suggested that this method of oxidation could leave an adsorbed layer of silver on the electrode, which might have misled Davis to conclude that a thin platinum oxide film could accelerate oxidation - reduction processes. Iron(II) in 1·0 M sulphuric acid was used by Anson[18] for reducing platinum oxide films, and this method was found by Bishop and Riley[17] to be more reliable than electrolytic reduction in preparing platinum for the reduction of silver. Anson[18] found that the oxide was relatively stable to iron(II) in 1·0 M perchloric acid, and Kabanova has confirmed this observation.[19] After many trials with diverse activation procedures, the following methods were selected for extensive testing.

(*a*) *Chemical reduction with iron(II)*—The electrode was immersed in 0·5 M iron(II) sulphate in 1·0 M sulphuric acid for 10 minutes at room temperature, followed by thorough washing with water.

(*b*) *Electrolytic cycling and reduction*—The auxiliary electrode used in all electrolytic treatments was made of platinum. The working electrode in 1·0 M sulphuric acid was anodised at 300 mA cm^{-2} for 30 s, followed by cathodisation at 300 mA cm^{-2} for 30 s; the anodisation and cathodisation were repeated once more, and the electrode was finally washed with distilled water.

(c) *Chemical* plus *electrolytic stripping and cathodisation*—The electrode was immersed in fresh aqua regia at 60 °C for 30 s, washed with distilled water, anodised in 11·6 M hydrochloric acid at 200 mA cm^{-2} for 30 s, and again washed. Finally, the electrode was cathodised at 230 mA cm^{-2} for 10 minutes in 1·0 M sulphuric acid and washed thoroughly.

(d) *Electrolytic reduction*—The electrode was cathodised at 300 mA cm^{-2} for 5 minutes in 1·0 M sulphuric acid and then washed thoroughly.

(e) *Electrolytic cycling and oxidation*—After two cycles of anodisation - cathodisation as in method (b), the electrode was anodised for a third time at 300 mA cm^{-2} for 30 s and thoroughly washed.

Unless otherwise stated, the electrodes were used directly after the last wash; any hydrogen present would be removed chemically on immersion in the electrolyte.

RESULTS AND DISCUSSION

First, in order to make best use of pattern theory,[20] the conditional potential of the vanadium(V) - vanadium(IV) system and its dependence on hydrogen-ion concentration were determined. Then the voltammetric behaviour of vanadium(V) over a range of hydrogen-ion concentrations was examined with respect to the diverse electrode treatments outlined above. In order to abbreviate the presentation, three conditions will be discussed, acetate buffer at pH 4·0, strongly acidic medium, 2·0 M sulphuric acid, and an intermediate state of pH 2·0 in sulphuric acid medium. Unless otherwise stated, electrodes were used for a single scan and then re-activated before further use.

THE CONDITIONAL POTENTIAL OF THE VANADIUM(V) - VANADIUM(IV) SYSTEM—

The zero-current equilibrium potential was found to obey the relationship,

$$E_{eq} = E'_o + \frac{RT}{F} \ln \frac{[V^V]}{[V^{IV}]} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

where E'_o is the conditional potential, which depends on the hydrogen-ion concentration of the medium, as shown in Fig. 1. For solutions 0·1 M or more in sulphuric acid, the acid content was determined by titration against primary standard sodium carbonate solution.
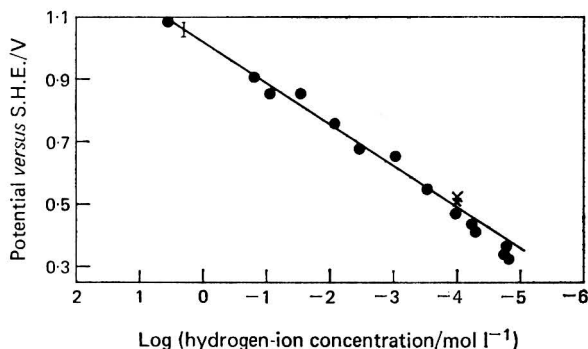
Fig. 1. Variation of the conditional potential of the vanadium (V)- vanadium(IV) system with hydrogen-ion concentration (S.H.E. denotes standard hydrogen electrode). ●, Values measured in sulphuric acid media; ×, values measured in acetate buffer of pH 4·0; and I, range of values reported by Davis[3] for sulphuric acid medium

For less acidic solutions, the pH was measured potentiometrically by using glass and calomel electrodes calibrated with pH standards. The zero-current potential was independent of the method of electrode activation if sufficient time was allowed for the potential to become stabilised. Methods (b) and (c) produced electrodes that became stabilised faster than electrodes treated by other methods; but even for these two methods the stabilisation time varied, from 10 minutes to several hours, indicating very small exchange currents.

VOLTAMMETRY OF VANADIUM(V)—

It was quickly evident that freshly acidified vanadate solutions gave erratic results compared with aged solutions. This behaviour is caused by kinetically slow isopolymerisation, probably[21] the step at pH 7·0 to 6·8:

Reaction				pH	
$2\,[VO_4]^{3-} + 2\,H^+ \rightleftharpoons [V_2O_7]^{4-} + H_2O$	..	..	..	12 to 10·6	(2)
$2\,[V_2O_7]^{4-} + 4\,H^+ \rightleftharpoons H_2[V_4O_{13}]^{4-} + H_2O$	..	..	..	9·0 to 8·9	(3)
$5\,H_2[V_4O_{13}]^{4-} + 8\,H^+ \rightleftharpoons 4\,H_4[V_5O_{16}]^{3-} + H_2O$	..	..	..	7·0 to 6·8	(4)
$2\,H_4[V_5O_{16}]^{3-} + 6\,H^+ \rightleftharpoons 5\,V_2O_5 + 7\,H_2O$	..	..	..	2·2	(5)
$V_2O_5 + 2\,H^+ \rightleftharpoons 2\,[VO_2]^+ + H_2O$	..	..	..	<1·0	(6)
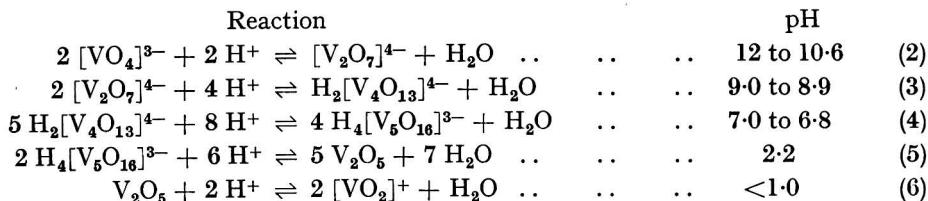
Israel and Meites[11] obtained evidence from ultraviolet spectra that ammonium metavanadate dissolved in sulphuric acid slowly changed form. A recent review[22] indicates that slow steps are involved in the polymerisation reactions, but that the situation is more complicated than equations (2) to (6) suggest, because the degree of polymerisation depends also on the vanadium concentration. To eliminate the external complication of polymerisation equilibria, all voltammetric work was carried out with solutions that had been appropriately acidified and stored for several weeks.

The voltammetric behaviour of vanadium(V) in saturated potassium sulphate solution containing sulphuric acid in the range 10^{-5} to 2·0 M was examined; slight differences in electrode pre-treatment caused significant changes in the voltammograms. Solutions of pH about 2 gave very erratic results. In none of the experiments performed in this study was any evidence found for the reduction of vanadium below the +4 oxidation state. Anson[5] and Davis[3] both found chronopotentiometric evidence for the formation of vanadium(III) at freshly reduced platinum. They also found that the electrode quickly became deactivated towards the second step at +0·25 V. In most of the runs in the present study ramp speeds of ±100 mV min^{-1} were used, and the time required for the electrode to deactivate towards vanadium(III) formation was exceeded before the potential for reduction of vanadium(IV) was reached. The cause of this deactivation is not clear, but adsorption of impurities or polymeric vanadium species on the electrode seems likely.

REDUCTION AT pH 4—

A single reduction wave appeared for reduced electrodes [treatment (*b*) or (*c*)] in both supporting electrolytes, saturated potassium sulphate solution adjusted to pH 4 with sulphuric acid or the saturated potassium sulphate - acetate buffer. In Fig. 2, for the acetate buffer medium, curves 1 and 2 represent the background currents for reduced (*b*) and oxidised (*e*) electrodes, respectively. The oxidised electrode showed a maximum at about 0·7 V corresponding to reduction of the oxide film on the electrode. Addition of vanadate to a concentration of $1·09 \times 10^{-3}$ M gave a wave that is superimposed on curves 1 and 2 to give the composite curves 3 and 4. Chemically reduced electrodes (*a*) gave curves similar to 1 and 3, but the curves were not as reproducible. After curve 2 had been recorded, it was found possible to reproduce it without reactivating the electrode, so a single scan did not deactivate the electrode, and the supporting electrolyte was free from impurities that could be adsorbed. An activated electrode remained stable for 30 minutes or more in the vanadium solution, whether on open circuit or used for scanning, so the whole system could be judged to be free from readily adsorbable impurities.[14]

The shape of the vanadium wave at pH 4·0 is independent of the medium, but the buffer introduced a second wave, which was identified as resulting from the direct reduction of un-ionised acetic acid.

$$2\,CH_3COOH + 2e^- \rightleftharpoons 2\,CH_3COO^- + H_2 \quad .. \quad .. \quad .. \quad (7)$$

The observation of Laitinen and Kolthoff,[23] that in the presence of a large excess of sodium acetate the limiting current of the acetate wave was proportional to the total concentration of acetic acid, was confirmed. The existence of the acetic acid wave nullified the benefit of shifting the background reactions towards more negative potentials by raising the pH. On the other hand, hydrogen ions are consumed in the reduction, and sulphuric

Fig. 2. Reduction of vanadium(V) in acetate buffer saturated with potassium sulphate at pH 4·0: 1, supporting electrolyte alone, electrode treatment (b); 2, supporting electrolyte alone, electrode treatment (e); 3, supporting electrolyte + 1·09 × 10⁻³ M vanadium(V), electrode treatment (b); and 4, supporting electrolyte + 1·09 × 10⁻³ M vanadium(V), electrode treatment (e). Ramp speed −100 mV min⁻¹

acid at pH 4, although adequate for voltammetry, would not provide a sufficient supply unless it was supplemented at intervals during a coulometric determination. The use of a buffer solution in which the salt predominates would ameliorate the situation, but no suitable system could be found. The height of the vanadium(V) reduction wave was proportional to concentration over the range 0·3 to 3·5 × 10⁻³ M. The mass-transfer rate constant was smaller in acetate buffer than in sulphuric acid, because of the higher viscosity of the buffer medium. In both media the limiting current of vanadium reduction decreased with decreasing stirring speed.

Fig. 3. Reduction of vanadium(V) in 2·0 M sulphuric acid: 1, 2·0 M sulphuric acid, electrode treatment (b); 2, 2·0 M sulphuric acid, electrode treatment (e); 3, 2·0 M sulphuric acid + 1·13 × 10⁻³ M vanadium(V), electrode treatment (b); 4, 2·0 M sulphuric acid + 1·13 × 10⁻³ M vanadium(V), electrode treatment (e); 5, constructed by subtracting curve 2 from curve 4, to compensate for oxide reduction; and 6, recorded immediately after curve 3 was recorded, without intervening activation of the electrode. Ramp speed −100 mV min⁻¹

Fig. 2. Reduction of vanadium(V) in acetate buffer saturated with potassium sulphate at pH 4·0: 1, supporting electrolyte alone, electrode treatment (b); 2, supporting electrolyte alone, electrode treatment (e); 3, supporting electrolyte $+ 1·09 \times 10^{-3}$ M vanadium(V), electrode treatment (b); and 4, supporting electrolyte $+ 1·09 \times 10^{-3}$ M vanadium(V), electrode treatment (e). Ramp speed -100 mV min^{-1}

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Fig. 3. Reduction of vanadium(V) in 2·0 M sulphuric acid: 1, 2·0 M sulphuric acid, electrode treatment (b); 2, 2·0 M sulphuric acid, electrode treatment (e); 3, 2·0 M sulphuric acid $+ 1·13 \times 10^{-3}$ M vanadium(V), electrode treatment (b); 4, 2·0 M sulphuric acid $+ 1·13 \times 10^{-3}$ M vanadium(V), electrode treatment (e); 5, constructed by subtracting curve 2 from curve 4, to compensate for oxide reduction; and 6, recorded immediately after curve 3 was recorded, without intervening activation of the electrode. Ramp speed -100 mV min^{-1}

REDUCTION IN 2·0 M SULPHURIC ACID—

Voltammetric curves in this medium (Fig. 3) are more complicated than those at pH 4, but less complex and more reproducible than those at pH 2. The reduction wave showed a limiting current region that varied slightly in height but very greatly in the rising portion of the wave with the method of electrode activation. The chemical treatment, (*a*), gave much less reproducible curves than the electrolytic treatments and was therefore abandoned. Treatments (*b*) and (*c*) gave very similar voltammograms but method (*b*) gave rather more reproducible results, although even then a 5 per cent. difference had to be accepted as being satisfactory. Scan 1 of the background with a reduced [treatment (*b*)] electrode showed that the electrolyte and electrode were clean. Scan 2 is of an oxidised electrode [treatment (*e*)] and shows the oxide reduction peak. When the oxidised electrode is used to reduce vanadium(V), the oxide reduction peak is superimposed on the vanadium wave, as in curve 4. By subtracting curve 2 from curve 4, curve 5 was obtained and showed that the rate of reduction of vanadium(V) remained very slow until some of the oxide on the platinum surface had been reduced, but when about 80 per cent. of the oxide had been reduced, the electrode behaved like a pre-reduced electrode. The observation that the rate of reduction of vanadium(V) decreased at an oxidised platinum surface is in agreement with the findings of Anson and King.[5] It is not, however, easy to explain why the electrode in this experiment behaves as if it were fully reduced, when curve 2 indicates that oxide remains on the electrode. The curves in Figs. 2 and 3 were drawn at the same ramp speed, yet the two oxide reduction curves differ; that in Fig. 3 is less sharp and shows tailing on the cathodic side: the tailing could be diminished by using a slower ramp speed.

Curve 3 in Fig. 3 shows that reduction of vanadium(V) at a pre-reduced electrode is not simple: a minimum appears at about 0·6 V. This behaviour occurred whenever the hydrogen-ion concentration of the solution was such that vanadium(V) reduction could be observed at potentials more positive than 0·6 V. Although the conditional potential of the vanadium(V) - vanadium(IV) system could be changed by 0·4 V or more by changing the hydrogen-ion concentration, there was very little change in the potential at which the minimum occurred, which is close to the potential of the platinum oxide reduction maximum, so that it seemed possible that the two might be related. The chemical effect of a 10^{-3} M solution of vanadium(V) in 2·0 M sulphuric acid on a reduced electrode prepared by method (*b*) was investigated by immersing the fresh electrode in this solution for 2 minutes, washing it well with distilled water, transferring it into a pure 2·0 M sulphuric acid solution and making a cathodic scan. The scan showed a small maximum at 0·65 to 0·70 V, thus indicating light oxidation of the electrode surface. Repetition of this procedure with 2·0 M sulphuric acid alone showed that the oxidation occurred chemically in the vanadium(V) solution and not during the washing or transfer. Soaking the electrode for 15 s in the vanadium(V) solution produced a detectable amount of oxide. Although a fully reduced electrode can be immersed in the vanadium(V) solution for scanning, the electrode surface was lightly oxidised before the scan was started. The electrode had to be carefully positioned, as did the Luggin capillary, then connections had to be made to the ramp generator and the circuit tested. This process took 15 to 30 s to complete.

The chemical oxidation of the working electrode, reduction of the oxide at about 0·6 V and the minimum in the vanadium(V) reduction wave at pre-reduced electrodes [methods (*b*) and (*c*)] appear to suggest that light oxidation of the electrode does facilitate the vanadium reduction as compared with a fully reduced electrode. If this be so, then vanadium(V) in 2·0 M sulphuric acid is reducible at three different rates, depending on the amount of oxide on the electrode surface. A heavy oxide film [treatment (*e*)] must, on the evidence of curve 5 in Fig. 3, permit only very slow reduction of vanadium(V). The light oxidation by chemical attack by vanadium(V) permits a relatively fast reduction, while a fully reduced electrode (formed when the potential becomes negative to 0·6 V) must reduce vanadium(V) at an intermediate rate. This effect was, in part, confirmed by lowering the zero-current potential of the vanadium solution by addition of vanadium(IV), so that chemical oxidation did not occur. Curve 1 in Fig. 4 shows no minimum at 0·6 V in the reduction wave, and both *k* and α are obviously decreased. Curve 3 shows the normal behaviour in the initial absence of vanadium(IV) under otherwise the same conditions. Curve 2 is the immediate reverse scan after curve 1 and shows the large hysteresis.
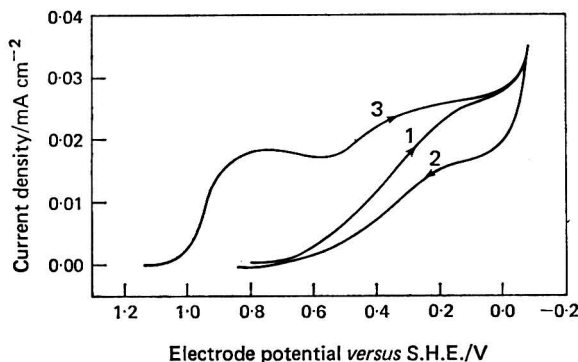
Fig. 4. Reduction of vanadium(V) in 0·1 M sulphuric acid: 1, 0·1 M sulphuric acid + 1·0 × 10⁻⁴ M vanadium(V) + 1·0 × 10⁻² M vanadium(IV), electrode treatment (*b*); 2, reverse scan at + 100 mV min⁻¹ immediately after recording curve 1; and 3, 0·1 M sulphuric acid + 1·0 × 10⁻⁴ M vanadium(V), electrode treatment (*b*). Ramp speed −100 mV min⁻¹

POSSIBLE ADSORPTION EFFECTS IN THE REDUCTION OF VANADIUM(V) IN 2·0 M SULPHURIC ACID—

The hysteresis just mentioned is not confined to solutions containing vanadium(IV). Reverse scans are not shown in Fig. 3 in order to avoid confusion; reverse scans in the context have little significance, but such scans were performed and also showed hysteresis. It appeared possible that a known trace impurity in the sulphuric acid may become adsorbed on the electrode.

Aristar sulphuric acid diluted to 10·0 M was cleaned by electrosorption, as will be described in a later paper, and the solution used to prepare the supporting electrolyte. Background and vanadium(V) reduction scans showed no significant difference from those in Fig. 3, so adsorption of impurities could be eliminated. Nevertheless, it is possible that adsorption of vanadium species could be responsible for hysteresis and for the difference between scan 3 in Fig. 3 with the electrode reduced by method (*b*) and scan 6 performed immediately afterwards with the same electrode and without re-treatment. This conclusion was supported by an experiment in which an electrode used to record a curve similar to scan 3 in Fig. 3 was subjected to treatment (*d*) and then scanned in the same solution. The result was a curve very similar to curve 6 in Fig. 3, and showed that simple cathodisation was not so effective as treatments (*b*) and (*c*) in producing an active electrode. The difference cannot be due to any form of platinum - oxygen structure produced during pre-treatment, because treatment (*c*) does not produce an oxidised surface during the anodic treatment, but merely strips platinum as the soluble hexachloroplatinic(IV) acid. The difference between treatments (*b*) and (*c*) and treatment (*d*) lies in the ability of (*b*) and (*c*) to clean the electrode by anodic stripping. Deactivation of electrodes prepared by methods (*b*) and (*c*) cannot be attributed to reduction products of the electrode reaction, because a freshly activated electrode does become deactivated on standing at zero current in the vanadium(V) solution. It is possible that the chemically produced film may contain vanadium species, perhaps in a mixture of oxidation states. In 2·0 M sulphuric acid a kinetically slower curve than scan 6 in Fig. 3 could not be obtained either by allowing the electrode to stand in the solution or by continually scanning the reduction wave, which showed conclusively that on deactivation the electrode quickly attains a stable and reproducible form.

REDUCTION IN SULPHURIC ACID AT pH 2—

The behaviour of vanadium(V) at the variously treated electrodes in sulphuric acid solutions of 2·0 M down to 0·1 M concentration was found to be similar to that discussed for 2·0 M acid, but with further decrease in acid concentration changes occurred in the voltammograms. In illustration the behaviour at pH 2 will be considered.

Electrodes treated by methods (*b*) and (*c*) again showed a minimum, as in 2·0 M sulphuric acid, but at pH 2 the height of the wave before the minimum was not reproducible, and could

change by 50 per cent. from one experiment to the next, but was always lower than the height of the main wave formed at potentials cathodic to the minimum. The variability of the pre-wave is probably due to small differences in the amount of chemical oxidation suffered by the platinum surface before the scan was recorded. As the hydrogen-ion concentration decreases, the oxidising power of the solution decreases as shown by the conditional potentials in Fig. 1. It has been shown[24,25] that the amount of oxide formed on platinum depends on the time of contact with the oxidising solution and the potential of the solution. The amount of oxide formed at pH 2 seems more time dependent than in 2·0 M sulphuric acid. Attempts to verify this observation by coulometric stripping of electrodes that had been soaked for different periods in vanadium solutions were frustrated by the errors introduced by charging currents.

An electrode activated by method (*b*) gave as its first and second scans curves 1 and 2 in Fig. 5. The deactivation after the first scan was greater than that for a single scan in 2·0 M sulphuric acid. Curve 3 shows the effect of leaving a similar electrode in the vanadium solution for 80 minutes at zero-current potential before starting the scan. In 2·0 M sulphuric acid a single scan gave full deactivation of the electrode; at pH 2·0 the deactivation was greater, and the act of scanning accelerated it. It seems likely from equation (5) that at pH 2·0 colloidal vanadium(V) oxide could form and stick on the electrode, where it could be reduced to an insoluble species such as an oxovanadium(IV) polyvanadate(V), which would interfere with mass transfer.
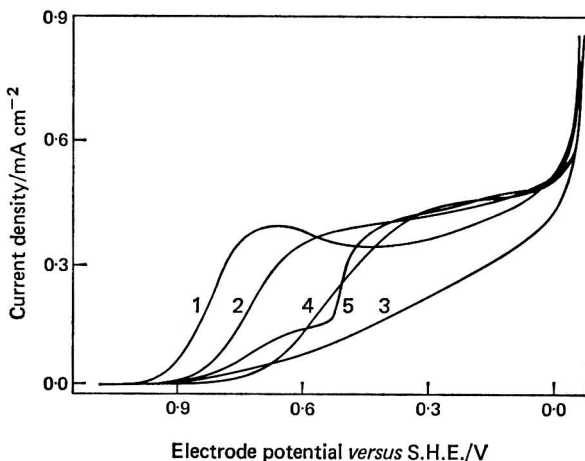
Fig. 5. Reduction of vanadium(V) in sulphuric acid at pH 2·0. All solutions 1·6 × 10⁻³ M vanadium(V) in 5 × 10⁻³ M sulphuric acid adjusted to pH 2·0. Methods used to activate the electrodes: 1, method (*b*); 2, no reactivation after curve 1, used immediately; 3, method (*b*), then left at zero current in the vanadium solution for 80 minutes before being recorded; 4, method (*d*); and 5, method (*e*). Ramp speed −85 mV min⁻¹

The effect of the cathodic activation (*d*) applied to a used electrode is shown in curve 4 in Fig. 5, and is similar to the behaviour in 2·0 M sulphuric acid. Unlike the latter behaviour, however, an electrode having once been activated and used could be reactivated by method (*d*), so that the following scan showed a faster reaction than it would have shown if no additional activation had been applied. Treatment (*e*) produced the same shape of curve as in 2·0 M sulphuric acid, with a potential shift of the leading edge corresponding to the shift in E'_0 with the change in hydrogen-ion concentration. For an activated electrode, the true limiting current at 0·1 V was proportional to the concentration of vanadium(V) in the solution. While the height of the current maximum at 0·75 V increases with increasing vanadium(V) concentration, the relationship is not proportional.

As the pH of the vanadium(V) solution in sulphuric acid increased from 2 to 3 the shape of the voltammograms remained similar to those at pH 2, except for the expected shift to more negative potentials. Furthermore, the electrodes showed less deactivation by the vanadium(V) solutions. When the pH increased to 3·5, the platinum oxide reduction maximum and the vanadium reduction wave no longer coincided and the curves produced resembled those in Fig. 2. At about this hydrogen-ion concentration, the oxidation potential of the vanadium solution dropped below that at which platinum can be extensively oxidised, thus simplifying the voltammograms. The decrease in deactivation of the electrode as the pH increased from 2 to 4 can be explained by the reversal of reaction (5) to produce soluble species such as the tetrahydrogenpentavanadate(V) ion.

VOLTAMMETRY OF VANADIUM(IV) SOLUTIONS—

The high conditional potential and the low charge-transfer speed of the vanadium(V) - vanadium(IV) process forced the oxidation of vanadium(IV) to such a high anodic potential that no limiting current region could be isolated: the wave merged with the solvent oxidation wave. A typical scan in acetate buffer medium is shown in Fig. 6, and as the hydrogen-ion concentration increased in sulphuric acid media the merger of vanadium and solvent waves became more complete until in 2·0 M sulphuric acid the presence of a vanadium wave could scarcely be detected. Davis[26] found that a chronopotentiometric transition time for vanadium(IV) in 1·0 M sulphuric acid could not be measured on account of the simultaneous oxidation of water. Media with pH higher than 4 have not been examined, but it is possible that the change of E_0' with pH would be greater than the shift in solvent oxidation potential and a separate wave might be attainable at pH 6. The curve in Fig. 6 was obtained with cathodised electrodes [treatment (b), (c) or (d)], but the working potential is such that an anodic film must form on the electrode. A heavily oxidised electrode [treatment (e)] was found to give an even slower oxidation, and a rather erratic performance.
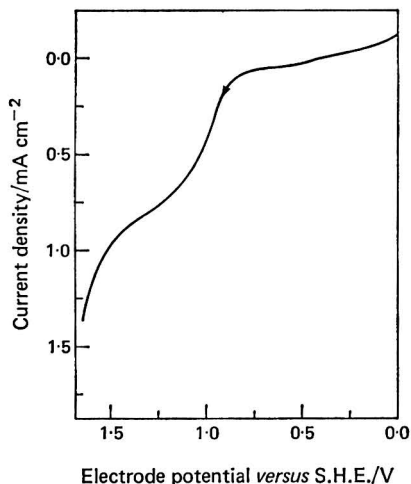
Fig. 6. Anodic oxidation of vanadium(IV). Electrode activated by method (b), acetate buffer saturated with potassium sulphate and adjusted to pH 4·0, 2·78 × 10⁻³ M vanadium(IV) and 0·21 × 10⁻³ M vanadium(V). Ramp speed + 100 mV min⁻¹

CONCLUSIONS

The voltammetric behaviour of the vanadium(V) - vanadium(IV) system at platinum electrodes is highly dependent on the composition of the supporting electrolyte and hydrogen-ion concentration, and on the pre-treatment of the electrodes. It is further complicated by participation of the electrode surface in chemical and electrochemical reactions, and by

direct reduction of the weak acid in buffer media. The values of the mass and charge transfer kinetic parameters will be discussed in a later paper after the behaviour in the presence of other transition-metal compounds has been described. There is no evidence in the voltammetry of pure vanadium(V) and vanadium(IV) solutions that the reaction is other than a single-step one-electron process, although there must at least be a following chemical step, either reaction of VO_2 with hydrogen ion to form VO^{2+} or reaction of VO^{3+} with solvent to give VO_2^+. Isopolymers must be involved at higher pH values, and what appears to be a one electron - one vanadium atom process may be a five electron - one tetrahydrogenpentavanadate(V) ion reaction, certainly by an electron tunnelling process, followed by decomposition or rearrangement of the polymer. A one electron - one tetrahydrogenpentavanadate(V) ion reaction is unlikely in view of the similar mass-transfer rates in 2·0 M sulphuric acid and in acetate buffer. Although the reproducibility cannot be considered excellent, the voltammograms of the reduction of vanadium(V) in 2·0 M sulphuric acid (Fig. 3) and in acetate buffer at pH 4 (Fig. 2) show sufficiently well defined limiting current regions to permit the choice of control potentials for potentiostatic reduction of high efficiency. Vanadium(IV) cannot be oxidised without severe loss of current efficiency, nor reduced to vanadium(III) at platinum electrodes.

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NOTE—References 13, 14 and 20 are to Parts V, VI and III, respectively, of this series.

Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part VIII.* Single-scan Voltammetry of Vanadium(V) - Vanadium(IV) in the Presence of Chromium, Manganese and Iron, and the Kinetic Parameters of the Vanadium System, at Platinum Electrodes Pre-treated by Five Methods†

By E. BISHOP and P. H. HITCHCOCK‡

(*Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD*)

Continuing the earlier examination of the vanadium system alone, under various conditions and with various electrode pre-treatments, the effect of neighbouring steel-forming d-block elements has been investigated. Chromium(VI) at pH 4·0 suppresses the vanadium(V) reduction wave, and the degree of suppression is quantitatively proportional to the chromium(VI) concentration. Activated electrodes are deactivated by dipping them in a chromium(VI) solution, and remain so even when well washed thereafter, so that chromium(VI) as well as chromium(III) is adsorbed strongly on platinum. In 2·0 M sulphuric acid, chromium(VI) and vanadium(V) are reduced at the same rate. Manganese(VII) in acetate buffer gives a fast, well separated wave, but the separation is not as good in 2·0 M sulphuric acid; slowing the vanadium(V) reduction by using an oxidised electrode effects no improvement: the manganese wave is similarly affected. Addition of chromium(VI) to the manganese - vanadium mixture at pH 4 suppresses the manganese wave only slightly, even when the vanadium wave is completely suppressed. In 2·0 M sulphuric acid, the manganese wave is undistorted and chromium and vanadium are simultaneously reduced. Iron(III) in 2·0 M sulphuric acid does not interfere, but the separation of the vanadium and iron waves is not good. Iron(II) can, however, act as a potentiostatic intermediate. The kinetic parameters of the vanadium system are reproducible in acetate buffer, but only when the electrode is fouled in 2·0 M sulphuric acid. Pattern theory and diffusion-corrected Lewartowicz methods give results that agree. The charge-transfer kinetic parameters are shown to be potential dependent in acidic media. The results are compared with those in earlier reports. The generation current efficiency for vanadium(IV) in acetate buffer was computed.

In a previous paper,[1] the influence of hydrogen-ion concentration on the conditional potential of the vanadium(V) - vanadium(IV) system was examined, and the voltammetry of the system in sulphuric acid at concentrations ranging from 5×10^{-5} to 2·0 M, and in potassium sulphate - acetate buffer at pH 4·0, was described. Platinum electrodes treated by five different methods, (*a*) chemically reduced with iron(II) in sulphuric acid, (*b*) cyclically anodised and cathodised and reduced, (*c*) chemically and electrochemically stripped and electrochemically reduced, (*d*) cathodically reduced and (*e*) anodically oxidised, were investigated. Method (*a*) was of little use, while method (*e*) invariably gave the slowest charge transfer. Method (*d*) was moderately effective, but the preferred method was (*b*) because the anodic stripping appeared to remove some adsorbate from the electrode surface. These experiments related to pure solutions of vanadium in pure supporting electrolyte. The objective was to measure the electrode kinetic parameters with a view to selecting control potentials for potentiostatic coulometry, and to determine the current efficiency under various conditions. With the further objective of application to the determination of vanadium in real samples, such as alloy steels, the influence of neighbouring d-block elements was investigated in order to discover whether they offered any interference, and also whether they could be determined

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sequentially in a mixture.   Chromium and manganese gave surprising results, but iron behaved as expected.

EXPERIMENTAL

Apparatus and procedures have been described,[2] the electrode pre-treatments are given in detail and the reagents and supporting electrolytes and their standardisation or treatment are set out in Part VII.[1] Of the latter, the 2·0 M sulphuric acid and the saturated potassium sulphate - acetate buffer adjusted to pH 4·0 have been chosen for this further study, because the behaviour of the system is least complicated when the vanadium is present entirely as the cations, VO^{2+} and VO_2^+, or as the tetrahydrogenpentavanadate ion, $H_4(V_5O_{16})^{3-}$.

RESULTS AND DISCUSSION

EFFECT OF CHROMIUM(VI)—

Hypothetically (because the charge-transfer process is extremely slow and the exchange current is minute) the separation of the conditional potential of the chromium(VI) - chromium(III) system from that of vanadium(V) - vanadium(IV) is adequate to permit the sequential determination of chromium(VI) and vanadium(V).   The vanadium reduction is kinetically slow,[1] and the chromium reduction much slower, so perhaps the sequence vanadium(V) then chromium(VI) could be realised in practice instead.   In the presence of iron(III), the faster reduction of iron(III) would produce iron(II), which would behave as a potentiostatic intermediate and so restore the order to chromium(VI) first and then vanadium(V).
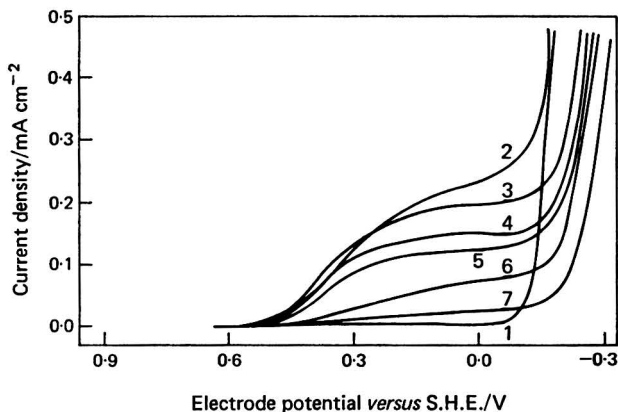
Fig. 1.   Effect of chromium(V) on the reduction of vanadium(V) in saturated potassium sulphate - acetate buffer at pH 4·0.   Before each curve was recorded, the electrode was activated by method (*b*): 1, supporting electrolyte alone; and 2, supporting electrolyte + 1·5 × 10^{-3} M vanadium(V). Portions of a chromium(VI) solution were then added to give the following [V^V] to [Cr^{VI}] ratios: 3, 92; 4, 46; 5, 31; 6, 19; and 7, 14.   Ramp speed −1·0 mV s⁻¹

However, experimentally, in the pH 4 buffer supporting electrolyte the addition of small amounts of chromium(VI) to a vanadium solution caused the vanadium(V) limiting current at freshly activated reduced electrodes [methods (*b*) and (*c*)] to decrease.   This remarkable behaviour is shown in Fig. 1.   Over a limited range of chromium(VI) concentrations, the decrease in the vanadium limiting current is directly proportional to the chromium(VI) content of the solution.   In such solutions, if an electrode was re-used without intervening reactivation the vanadium limiting current progressively decreased until the vanadium(V) wave disappeared entirely.   For the curves in Fig. 1, the vanadium concentration, although small, is much larger than the chromium concentration; when equal concentrations of vanadium(V) and chromium(VI) were present no reduction wave appeared for either species. The reproducibility is such that, for the particular conditions and concentrations used,

chromium(VI) in the concentration range 10^{-5} to 10^{-4} M could be determined to within ± 5 per cent. by the suppressive effect.   The possible development of the method to trace levels is to be pursued.

This behaviour cannot be ascribed to formation of a conventional platinum oxide film, because no maximum was detected at 0·6 V, and all the scans are negative to this potential. Kolthoff and El Din[3] claimed that a solution of chromium(VI) in mineral acids 10^{-3} to 10^{-2} M in hydrogen-ion produced a monolayer of chromium(III) hydroxide on a platinum cathode used in the solution.   The monolayer of, presumably, solvated chromium oxohydroxide had the power of suppressing some electron-transfer reactions, but no report was made on the behaviour of vanadium.   Kolthoff and El Din did not examine the process at pH 4, but the present work indicates that the film thickness or coverage is dependent both on the chromium(VI) concentration and on the number of scans performed with the electrode.

It proved possible to deactivate a freshly activated electrode [method (b), (c) or (d)] simply by dipping it into a $1·67 \times 10^{-4}$ M solution of chromium(VI) in 10^{-2} M sulphuric acid for 5 minutes.   When the electrode was removed, thoroughly washed with water and used to scan a vanadium(V) solution in acetate buffer, the limiting current was 10 per cent. less than that for a similarly activated electrode that was washed but not exposed to the chromium solution.   Chromium(VI) can therefore be directly adsorbed on the surface of an electrode, and when a cathodic current is applied in a weakly acidic medium [in which the chromium(III) hydroxide is presumably insoluble] a layer of chromium(III) hydroxide forms on the electrode surface.   It is not, however, directly proved that the chromium is reduced completely or even reduced at all: formation of chromium(III) chromate(VI), which is sparingly soluble, is not unlikely.

In the 2·0 M sulphuric acid supporting electrolyte both species are reduced at the same rate; the chromium(VI) wave coincides with the vanadium(V) reduction wave, as Davis[4] has found.   Kolthoff and El Din[3] found that, in mineral acids more concentrated than 0·1 M, chromium(VI) did give a reduction wave at platinum cathodes, and identified the product as chromium(III), but do not mention the current efficiency.   They concluded that this finding supported their contention that the film formed on a platinum cathode at lower hydrogen-ion concentrations from chromium(VI) was the hydroxide, but this interpretation is not unequivocal.   Specific adsorption of chromate or polychromate ions on the electrode surface, and physical blockage of the surface, without reduction, does not seem unlikely.

EFFECT OF MANGANESE(VII)—

Scanning a mixture of manganese(VII) and vanadium(V) in the acetate buffer supporting electrolyte at pH 4 gave a manganese wave with a half-wave potential of $+0·962$ V, super-imposed on the usual vanadium(V) wave as shown in Fig. 2.   The manganese wave is sharp and well defined, the reaction being clearly fast, and is well separated from the vanadium wave.   The limiting currents of the individual waves were found to be proportional to the concentrations of manganese(VII) and vanadium(V).

In the 2·0 M sulphuric acid electrolyte, the vanadium(V) and manganese(VII) waves were additive, but the separation, as shown in Fig. 3, was not good.   As the hydrogen-ion concentration increased, both waves moved in the anodic direction, but the vanadium wave moved considerably more than the manganese wave, as would be expected from a knowledge of the homogeneous reaction mechanisms.   Although the vanadium(V) reduction could be slowed down by using an oxidised electrode [treatment (e)] the manganese(VII) reduction was also slowed down, and separation of the waves was not improved.

When separately reduced, the product from manganese(VII) is manganese(II), and scans of mixtures gave no evidence to the contrary.   The mechanism was not fully revealed until the quantitative potentiostatic determinations, to be reported later, were carried out.   In the presence of vanadium(V), manganese(VII) is reduced to manganese(III), and not manganese(II).   Further reduction gives a combined wave representing reduction of manganese(III) and vanadium(V).

COMBINED EFFECT OF CHROMIUM(VI) AND MANGANESE(VII)—

Addition of chromium(VI) to a mixture of vanadium(V) and manganese(VII) in the buffer electrolyte of pH 4·0 suppressed the vanadium wave in exactly the same manner as in Fig. 1, but only slight suppression of the manganese(VII) wave occurred.   Addition of
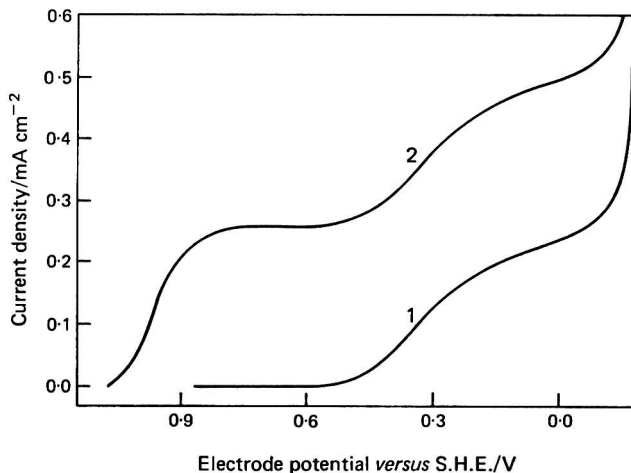
Fig. 2. Reduction of vanadium(V) and manganese(VII) in saturated potassium sulphate - acetate buffer at pH 4·0: 1, $1·1 \times 10^{-3}$ M vanadium(V), electrode treatment (*c*); and 2, $1·1 \times 10^{-3}$ M vanadium(V) + $0·13 \times 10^{-3}$ M manganese(VII), electrode treatment (*c*). Platinum cathode, scan speed -80 mV min^{-1}

sufficient chromium(VI) completely to suppress the vanadium wave decreased the manganese(VII) limiting current by only 8 per cent. Kolthoff and El Din[3] reported that the reduction of manganese(VII) in 10^{-3} M mineral acid was suppressed to the extent of 60 per cent. when a platinum cathode that was completely filmed with chromium(III) hydroxide was used. They did not extend their measurements to pH 4·0, but the difference is rather striking.

In the 2·0 M sulphuric acid supporting electrolyte a mixture of vanadium(V), manganese(VII) and chromium(VI) behaved as can be predicted by the foregoing results. The
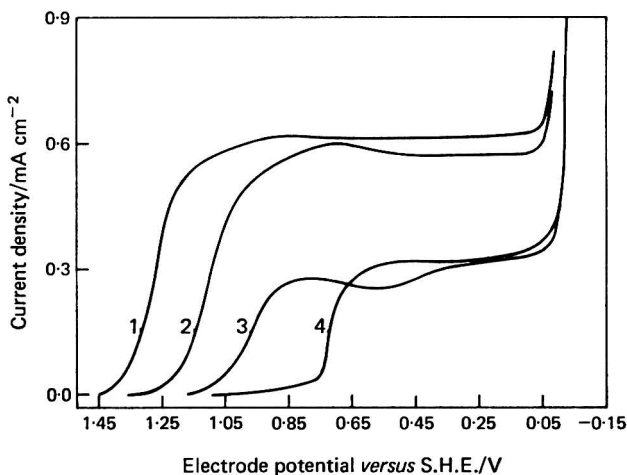

Fig. 3. Reduction of vanadium(V) and manganese(VII) in 2·0 M sulphuric acid: 1, $0·2 \times 10^{-3}$ M manganese(VII), electrode treatment (*b*); 2, $0·2 \times 10^{-3}$ M manganese(VII), electrode treatment (*e*); 3, $1·13 \times 10^{-3}$ M vanadium(V), electrode treatment (*b*); and 4, $1·13 \times 10^{-3}$ M vanadium(V), electrode treatment (*e*). Ramp speed -100 mV min^{-1}

manganese reduction wave was undistorted, and the chromium(VI) and vanadium(V) waves were superimposed one on the other.

EFFECT OF IRON(III)—

The behaviour of iron(III) in acetate buffer was not examined, but in 2·0 M sulphuric acid a well defined reduction wave of half-wave potential 0·647 V was obtained, and the electrode process was clearly moderately fast. Fig. 4 shows the scans of mixtures of iron(III) and vanadium(V) at electrodes treated by methods (b) and (d). The benefit of using the anodic stripping pre-treatment instead of the simple reduction[1] is again apparent, but the separation of the two waves is not good in this medium.
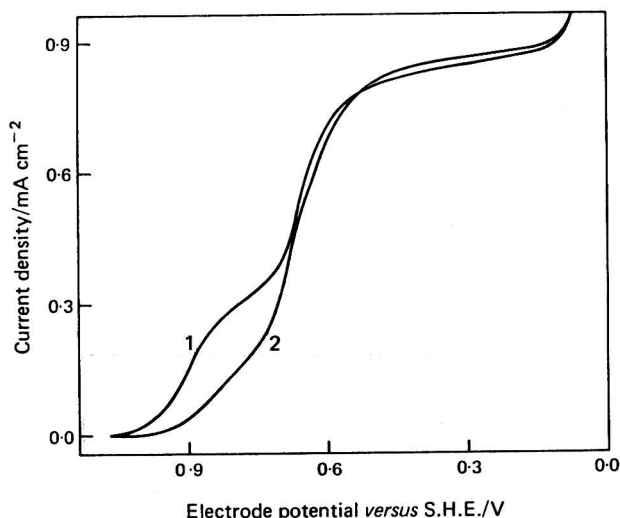
Fig. 4. Reduction of mixtures of vanadium(V) and iron(III) in 2·0 M sulphuric acid [1·13 × 10⁻³ M vanadium(V) +1·03 × 10⁻³ M iron(III)]: 1, electrode activation method (b); and 2, electrode activation method (d). Scan speed −100 mV min⁻¹

KINETIC PARAMETERS OF THE VANADIUM ELECTRODE REACTIONS—

Reduction of vanadium(V)—The work on pure vanadium solutions[1] showed that the most easily reproducible scans were obtained in the potassium sulphate - acetate buffer electrolyte at pH 4·0, and the method of pre-treatment of electrodes for use in this medium is less critical because there is no chemical oxidation of the electrode surface by the vanadium(V). The next most reproducible scans were obtained in sulphuric acid at concentrations of 0·1 to 2·0 M, in which three reproducible conditions of the electrode surface could be defined as follows—

(i) a reduced electrode pre-treated by method (b) or (c);

(ii) an oxidised electrode pre-treated by method (e); and

(iii) a reduced electrode, with adsorption, pre-treated by method (d); this condition is stable and is attained by electrodes treated by other methods after a single scan.

Values for k_{mass}, k and α were readily obtained from the vanadium(V) reduction waves in the acetate medium at pH 4·0, by using pattern theory[5] or Lewartowicz's diffusion-corrected method (but not his dubious second linearisation method).[2] The voltammetric scans in 0·1 to 2·0 M sulphuric acid as the supporting electrolyte (Fig. 3, Part VII[1]) will not yield a single set of charge-transfer parameters, because k and α change considerably with change in working electrode potential or current, which is immediately revealed by using sequential points in the pattern theory equations, and is also shown by the curvature of the Lewartowicz plots. Such behaviour emphasises that not one, but three reactions are in progress: reduction of

vanadium(V), reduction of platinum oxide and a potential-dependent adsorption process. The last two reactions change the nature and activity of the platinum surface and therefore the charge-transfer parameters. Empirical equations, from statistical analysis of the results from pattern theory, can be constructed, but would apply only to a single scan: the experimental reproducibility of the curves for sulphuric acid media is only about 5 per cent., whereas pattern theory has an accuracy of about 0·01 per cent. in the context, so that the empirical equation for one curve would be invalid for the next. Values of the mass and charge transfer parameters for the reduction of vanadium(V) under a variety of conditions are given in Table I. When the parameters are potential dependent the range of variation is given rather than a mean value, which could be misleading.

Also included in Table I are the values reported by Davis.[6] These values are academic and are useless in the real coulometric context. They were obtained in mixtures of vanadium(V) and vanadium(IV) in 1·0 M sulphuric acid at very low currents that did not exceed 1 per cent. of the limiting currents. The relatively small potential range covered would be unlikely to change the electrode surface condition much from its state at zero current, and so Davis was able to obtain "linear" Tafel plots that intersected at the zero-current potential. For the same reasons, Davis' values for α and β summed to $1\cdot00 \pm 0\cdot06$, which is certainly not valid in the wide-ranging potentials of coulometry. Fig. 5 shows three voltammetric curves computed by VOLTAMMETRY 9,[7] by using Davis' values for k and α and assuming no alteration with potential. The difference between these curves and, for example, curve 6 of Fig. 3, Part VII, is very large indeed. Davis' methods of electrode activation were different from those used in the present work, except for the iron(II) treatment (*a*), which in the present work gave a curve very similar to curve 6 of Fig. 3, Part VII. The differences between the
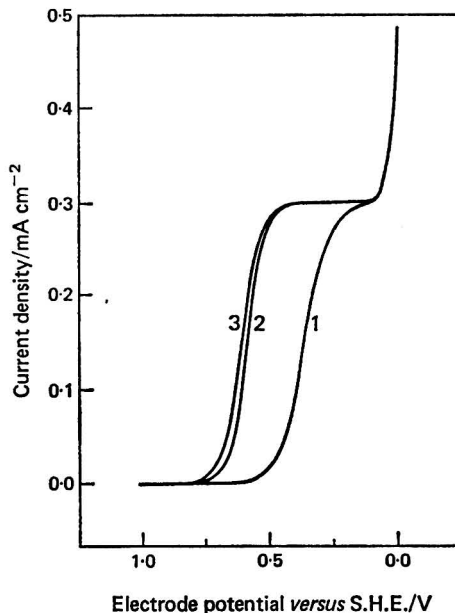
Fig. 5. Voltammograms computed from Davis' kinetic values. Mixed vanadium(V) - vanadium(IV) in 1·0 M sulphuric acid, Davis' values[6] converted to litre units—

	E'_0/V	$k/l\ cm^{-2}\ s^{-1}$	α
1	1·053	$4\cdot06 \times 10^{-12}$	0·52
2	1·057	$3\cdot78 \times 10^{-12}$	0·74
3	1·072	$1\cdot85 \times 10^{-11}$	0·67

Other parameters used were: δx, 10^{-3} cm; k_H, $7\cdot72 \times 10^{-10}$ l cm^{-2} s^{-1}; α_H, 0·5; $[V^V]_B$, 10^{-3} M; $[V^{IV}]_B$, 0; n, 1; $k_{mass\ ox}$, $3\cdot1 \times 10^{-6}$ l cm^{-2} s^{-1}; and $k_{mass\ red}$, $3\cdot1 \times 10^{-6}$ l cm^{-2} s^{-1}.

TABLE I

MASS AND CHARGE TRANSFER RATE PARAMETERS FOR THE VANADIUM(V) - VANADIUM(IV) REACTION AT PLATINUM ELECTRODES AT A VANADIUM CONCENTRATION OF 0.13 TO 1.9×10^{-3} M

Medium	Reaction	Electrode pre-treatment*	$k/1\ cm^{-2}\ s^{-1}$	α	β	$k_{mass\ ox}\dagger/1\ cm^{-2}\ s^{-1}$	$k_{mass\ red}\dagger/1\ cm^{-2}\ s^{-1}$
Acetate buffer, pH 4.0	$V^V + e \rightarrow V^{IV}$	(b), (c), (d), (e) or used electrode	$(7.1 - 9.3) \times 10^{-8}$	0.25 to 0.29	—	$(2.15 - 2.2) \times 10^{-6}$	—
Acetate buffer, pH 4.0	$V^{IV} \rightarrow V^V + e$§	(b), (c) or (e)	2.5×10^{-9}‡ **	—**	0.34**	—**	2.6×10^{-6}†**
2.0 M H₂SO₄	$V^V + e \rightarrow V^{IV}$	(b)	4×10^{-8}††	0.92	—	3.1×10^{-6}	—
		(b)	1.3×10^{-7}‡‡	0.62	—	3.1×10^{-6}	—
		§§	2×10^{-8}††	0.31	—	3.1×10^{-6}	—
		§§	3.5×10^{-8}‡‡	0.22	—	3.1×10^{-6}	—
		(d)	2.1×10^{-8}††	0.27	—	3.1×10^{-6}	—
		(d)	3.3×10^{-8}‡‡	0.22	—	3.1×10^{-6}	—
1.0 M H₂SO₄ (Davis⁶)	$V^V + e \rightarrow V^{IV}$	X	4.06×10^{-12}	0.52	0.41	—	—
		Y	3.78×10^{-12}	0.74	0.30	—	—
		Z	1.85×10^{-11}	0.67	0.29	—	—
2.0 M H₂SO₄	Background cathodic	(b), (c) or (d)	7.72×10^{-10}	0.5	—	9×10^{-4}	—
Acetate buffer, pH 4.0	Background cathodic	(b), (c) or (d)	1.62×10^{-11}	0.5	—	9×10^{-4}	—

* Treatments (b), (c), (d) and (e) are mentioned in the introduction and are described in detail in Part VII.[1]

Davis' activation procedures⁶:

X, Oxidation by silver(II) oxide in 6·0 M nitric acid for a "sufficient" time, then reduction in 1·0 M sulphuric acid at −0·25 V.
Y, Oxidation by silver(II) oxide in 6·0 M nitric acid for a "sufficient" time.
Z, Oxidation by silver(II) oxide in 6·0 M nitric acid for a "sufficient" time, then reduction in iron(II) solution in 1·0 M sulphuric acid.

† $k_{mass\ ox} = Dv^V/\delta x$; $k_{mass\ red} = Dv^V/\delta x$; "apparent" value $\delta x = 1.0 \times 10^{-3}$ cm.
‡ Results approximate on account of distortion by background wave.
§ Positive-going ramp. All other scans negative-going.
** Wave too distorted by background wave to give even approximate values.
†† For the low current portion of the wave, 5 to 20 per cent. of the limiting current.
‡‡ For the high current portion of the wave, 80 to 90 per cent. of the limiting current.
§§ Scan performed immediately after a previous run without reactivating the electrodes. Electrode originally activated by treatment (b).

present and Davis' results cannot be accounted for by differences of electrode treatment, or of the acidity of the medium, and support the finding that the charge-transfer parameters are highly dependent on the potentials at which they are measured.

The oxidation wave of vanadium(IV) was always too close to the wave for the oxidation of water, so that the values of k and α $[= (1 - \beta)]$ cannot be regarded as more than an approximate estimate. Considering the very large difference in potential between the waves for oxidation of vanadium(IV) and reduction of vanadium(V), it is not surprising that considerable changes in the nature of the electrode surface pertain and that the difference in rate constants for the two processes is relatively small in the context.

COMPUTATION OF CURRENT EFFICIENCIES FROM EXPERIMENTALLY DETERMINED PARAMETERS—

Because k and α change with potential and current in sulphuric acid, the simple computation of generation efficiency for the production of vanadium(IV) as an intermediate is not possible without error when using the fully developed VOLTAMMETRY 9 G/P[7] program, without inserting an ecological matrix of parameters. This procedure is now possible with the latest satellite programs to VOLTAMMETRY 9. However, the simple calculation was possible for the acetate buffer medium, because there is no significant change in parameter values with potential in this medium. The background reaction in this instance is not reduction of water, but of un-ionised acetic acid, and parameters had to be faked to simulate this change. This choice of parameters was ratified by matching computer-calculated scans with experimental scans: the fit was excellent, but the parameters listed in Table I have no real significance. The generation efficiency (or, rather, the loss of generation efficiency in parts per million) is plotted against current density in Fig. 6. The sharp decrease essentially marks the diffusion-limited current density.
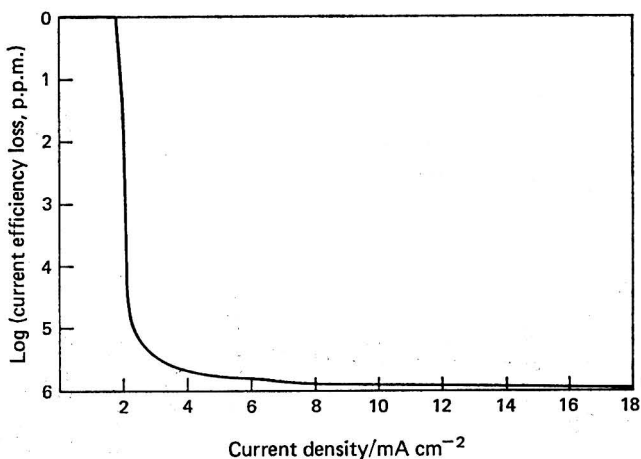
Fig. 6. Computed current efficiency loss in the generation of vanadium(IV) in the acetate buffer medium at pH 4·0: "δx", 10^{-3} cm; "[H+]", 0·051 M; "k_H", $1·61 \times 10^{-11}$ 1 cm^{-2} s^{-1}; "α_H", 0·5; E'_0, 0·525 V; $[V^V]_B$, 10^{-2} M; $[V^{IV}]_B$, 0; n, 1; $k_{mass\ ox}$, $2·2 \times 10^{-6}$ 1 cm^{-2} s^{-1}; $k_{mass\ red}$, $2·2 \times 10^{-6}$ 1 cm^{-2} s^{-1}; k, $8·6 \times 10^{-8}$ 1 cm^{-2} s^{-1}; and α, 0·27.

Parameters in inverted commas are adjusted to give an exact computer fit with the experimental voltammograms

CONCLUSIONS

The voltammetric investigation of the vanadium(V) - vanadium(IV) reaction alone[1] and in combination with manganese(VII), chromium(VI) and iron(III) has permitted kinetic parameters to be evaluated, current efficiencies to be computed and a basis to be laid for the potentiostatic determination of vanadium(V) alone or in certain combinations with other elements. The adsorption of chromium(VI) and chromium(III) on platinum at low hydrogen-ion concentrations has been demonstrated.

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NOTE—References 1, 2, 5 and 7 are to Parts VII, V, III and I, respectively, of this series.

Potentiostatic Coulometric Determination of Vanadium, Vanadium - Manganese and Vanadium - Iron Mixtures and the Influence of Chromium on the Process*

By E. BISHOP AND P. H. HITCHCOCK†

(Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD)

Earlier voltammetric work permitted the mass and charge transfer kinetic parameters of the vanadium system to be calculated for diverse media and platinum electrode pre-treatments, and command potentials to be selected for potentiostatic determination of vanadium alone and in certain combinations with other steel-forming elements. A simple coulometric cell and an adaptation of a commercial potentiostat are described. Current integration by strip-chart recorder is too inaccurate and so RC integration is discussed. Philbrick SP456 amplifiers refused capacitive feedback, but very satisfactory results were given by Solartron AA 1023 amplifiers. The design of a very high quality integrating capacitor from S.T.C. polystyrene elements is described; leakage and drift tests were very satisfactory. Pre-treatments of electrolytes and electrodes are discussed. Vanadium(V) is determined at -0.128 V in acetate buffer and at $+0.247$ V in 2.0 M sulphuric acid, in the latter with a relative standard deviation of 0.27 per cent. and a 95 per cent. confidence level result of $(1.008$ to $1.011) \times 10^{-1}$ M compared with 1.012×10^{-1} M for a standard solution. Chromium(VI) suppresses all reduction at pH 4.0, and is reduced simultaneously with vanadium in sulphuric acid. Manganese(VII) is reduced to manganese(III) in the first step at $+0.7$ V at pH 3.5 and manganese(III) and vanadium(V) are simultaneously reduced in the second step at -0.12 V. The separation of iron(III) is possible at $+0.9$ V but impracticable; simultaneous reduction at $+0.25$ V in 2.0 M sulphuric acid followed by re-oxidation of the iron(II) at $+1.0$ V is recommended.

A VOLTAMMETRIC study of the vanadium(V) - vanadium(IV) system in various media has been made in pure supporting electrolyte[1] and also in mixtures with chromium(VI), manganese(VII), iron(III) and combinations thereof.[2] Examples of current-efficiency calculations for the reduction of vanadium(V) have been reported, and a basis has been laid for the selection of conditions for the potentiostatic determination of vanadium(V) alone or in certain admixtures.[2] Amperostatic coulometric determinations of vanadium have been reported in which such intermediates as copper(I),[3] iron(II),[4] titanium(III)[5,6] and tin(II)[7] were used, and Israel and Meites[8] made a potentiostatic determination at mercury electrodes, but platinum electrodes do not seem to have been used for the potentiostatic determination of vanadium, either alone or in combination with the elements mentioned. Attempts so to do are described in this paper.

EXPERIMENTAL

Reagents and certain of the apparatus have been described elsewhere.[9] Potentials are quoted *versus* the standard hydrogen electrode (S.H.E.).

COULOMETRIC CELL—

The coulometric cell is shown in Fig. 1. The anolyte and catholyte must be separated and diffusion of sample out of, or deleterious species into, the working compartment, in this instance the cathode, must be prevented. With the finest porosity sintered-glass separator, the auxiliary electrolyte was sucked into the working compartment by the stirrer. The junction was therefore immobilised with agar gel in saturated potassium sulphate solution. Tests showed, during a determination, no detectable migration of sample into the auxiliary compartment. As it is a protein, agar could act as a poison or deactivator for the working electrode,[10] but no such action attributable to the agar occurred.
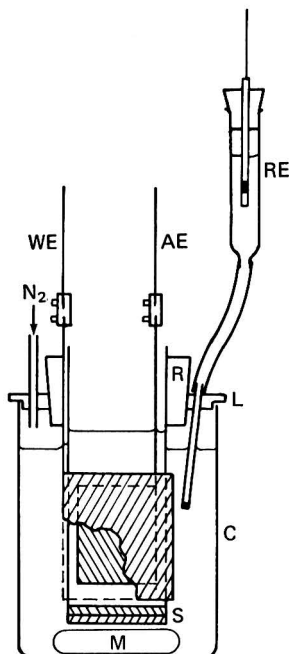
Fig. 1. The coulometric cell and electrodes: C, cell consisting of a 400-ml beaker with top sawn off and ground flat; L, machined Perspex lid appropriately drilled; R, rubber sleeve holding the auxiliary electrode compartment; AE, auxiliary electrode, platinum gauze, JM 72050; RE, reference electrode (S.C.E.) with remote junction; WE, working electrode, platinum gauze, JM 72020; S, porosity 4 sintered-glass junction plugged with agar gel; and M, PTFE-coated magnetic stirrer follower

POTENTIOSTAT—

A Wadsworth (Southern Analytical) electrogravimetric potentiostat was used for high-current work, modified so that the control potential could be set by means of a 39A pH meter; the command potential could be set much more precisely, and the high input impedance prevented polarisation of the reference electrode, which occurred with the unmodified instrument.

CURRENT INTEGRATION—

Initial trials were conducted by recording on a strip-chart recorder the decaying current as a function of the voltage drop across a standard resistor placed between the auxiliary electrode and the potentiostat. The current - time integral was obtained by cutting out the section of chart below the current trace, together with a square portion of paper of known area from above the trace, and weighing the paper on an analytical balance. The results were poor on account of the limitations of the recorder and variations in paper density, and the method was abandoned in favour of electronic RC integration by using chopper-stabilised operational amplifiers.

There are three basic sources of error in RC integration: (1) the leakage resistance of the integrating capacitor, (2) the insulation of the amplifier summing junction, particularly to high voltages, and (3) the noise and drift of the amplifier itself. Morrison[11] has examined some aspects of these errors, particularly (1) and (2). Regarding (2), little could be done; at the time this work was carried out, only Philbrick SP456 and Solartron AA 1023 amplifiers were available. According to their manufacturers, both amplifiers were "capable of high-accuracy integration," but neither manufacturer gave actual figures, particularly about the leakage resistance between the power supply and the summing junction. In the event, the Philbrick SP456 chopper amplifiers refused to operate with capacitance in the feedback loop, although they performed normally with resistive feedback. A second amplifier and different values of the input resistance and feedback capacitance were tried, and different earthing arrangements were tested in order to remove any unsuspected earth-loops, also without success. The standard arrangement of a single earth point, and that on the power supply, was adopted. The Solartron amplifiers performed very satisfactorily as integrators, and advantage was taken of their high-voltage output. As in the ramp generator design,[9] the current-measuring standard resistor was placed in the lead from the working electrode to the potentiostat, in parallel with a Solartron chopper amplifier in the current follower mode. The block diagram is shown in Fig. 2.

Calibration of the integrator was effected by substituting a constant-current source[12] (either the Solartron AS 1411 or the operational amplifier source) for the cell and potentiostat, and integrating known currents for known times, which were measured by a crystal clock.[12] For this purpose, the standard resistor, R_f, was a Cropico RS1 $1\cdot0$-Ω or a Cambridge $0\cdot1$-Ω standard immersed in transformer oil, and the IR drop was measured with a Cropico P3 potentiometer.
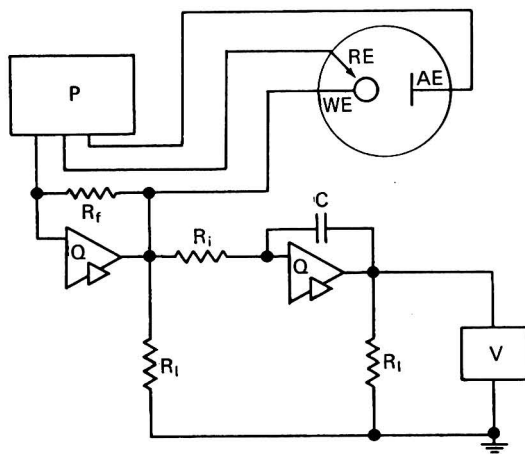
Fig. 2. The coulometric circuit: C, 1-μF poly-styrene integrating capacitor (see Fig. 3); Q, Solartron AA 1023 chopper-stabilised amplifiers driven by Solartron AS 853·3 power supply ($\pm$ 300 V, 100 mA); R_f, standard feedback resistor of current follower ($0\cdot1$ Ω); R_i input resistor to integrator (300 kΩ); R_l, load resistors (8·2 kΩ); P, Wadsworth controlled potential apparatus; V, Venner digital voltmeter; AE, auxiliary electrode; RE, reference electrode; and WE, working electrode

INTEGRATING CAPACITOR—

The integrating capacitor is the most critical component in the circuit; it should be large, at least 1 μF, and have a minimum leakage resistance of 10^{13} Ω, for an error of 0·1 per cent. over a 2-hour integration. A commercial source was long sought in vain, until the Development Department of the Capacitor Division of Standard Telephones and Cables Ltd. (S.T.C.) suggested a trial of high-quality, computer-grade, polystyrene capacitors, which

were then in the experimental stage. These were 0·2 μF $\pm$ 1 per cent. S.T.C. 455/LWA/112 FR capacitors of 500 V d.c. working. They were tested by washing them with ethanol, suspending them in free air in a clean laboratory, charging them to 2 V and connecting them to the input of an E.I.L. 39A pH meter. For all samples, there was no detectable change over 2 hours; thereafter, for five samples the potential began slowly to decrease, at an increasing, although modest, rate as dust and moisture were deposited on them and produced surface leakage, and by the natural ionisation of the air caused by radioactive potassium contained in the materials of construction of the building. Another sample increased its charge slightly with time; this behaviour, although unusual, is not unknown, and came within the experience of the S.T.C. engineers, who could not offer a satisfactory explanation of its cause. The test in free air did not give a measure of leakage resistance but did show that it was satisfactorily low. The final design of the composite capacitor is shown in Fig. 3. Five capacitors, after thorough cleaning in ethanol, were mounted close-packed in parallel so as to give a capacitance of 1 μF. The remainder of the heavy machined material was thoroughly scrubbed with soap and water, washed with water and acetone and baked out before mounting. After assembly, the three-way tap was used for evacuation of the vessel and for leakage testing, and then to admit nitrogen dried over phosphorus(V) oxide. The evacuation and flushing operations were repeated many times, and the vessel was finally filled with dry nitrogen. Nitrogen was chosen as it has a higher excitation energy than argon. The whole assembly was protected from the atmosphere by a polythene bag. The terminals were connected to a Vibron pH meter and the capacitor was charged to 2·0 V. Readings were taken at intervals over a period of 300 hours, and showed that the combined leakage of capacitor, co-axial cable and the meter was 2·8 $\times$ 10^{12} Ω. If the leakage of meter and cable be taken as 10^{13} Ω (which is probably low), then the capacitor leakage resistance is about 3·9 $\times$ 10^{12} Ω.

LIMITS IMPOSED ON INTEGRATION BY LEAKAGE—

Consider the capacitor to be charged to 80 V in a determination. The leakage current at the end of the run is 80/(3·9 $\times$ 10^{12}) = 20 pA. An input current can therefore be summed to within 0·1 per cent. with a feedback capacitor leakage of 3·9 $\times$ 10^{12} Ω. To the question of the loss that could be expected to occur after charging to 80 V and leaving for 1 hour, at such a large leakage resistance a sufficiently accurate answer is given by

$$I_{\text{leak}} = \frac{EC}{t} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where E is the loss in voltage, C is the capacitance and t is the time that remains before reading. Solving for E gives a value of 0·07 V, which represents an error of 0·09 per cent. in 1 hour. In tests of the completed integrator shown in Fig. 2, the drift was about 30 μV s^{-1}, which is less than the manufacturer's specification of 50 μV s^{-1} for a unity gain integrator. Drift invariably increases with increase in the size of the input resistor, which explains the desire for a large capacitance. In the example of integrating for 1 hour to reach a final output of 80 V, the amplifier drift could cause an error as large as 0·108 V, or 0·13 per cent.

GENERAL PROCEDURE FOR A COULOMETRIC DETERMINATION—

The supporting electrolyte and any other necessary reagents were added to the working compartment. The large platinum-gauze electrode was pre-treated as required, and mounted in the cell. The auxiliary electrode and electrolyte were placed in the auxiliary compartment and the tip of the probe of the reference cell salt bridge was positioned near the bottom of the working electrode, as in Fig. 1. This position was found to be the optimum both for reducing the IR drop in the command voltage and for minimising current noise occasioned by the stirring. After de-aeration of the electrolyte, a pre-electrolysis was performed until a constant current (the residual current) was attained. The integrator capacitor was discharged and the residual current integrated for a known time. The electrolysis was stopped, the integrator re-set and the sample added. Electrolysis was then continued until a constant current was again attained, the value of the current and the integrator voltage were noted and electrolysis was stopped. The integral of sample *plus* residual current was corrected for the residual current. The interpretation of the residual current correction is a severe limiting factor in potentiostatic coulometry.[13]

PRE-ELECTROLYSIS OF ELECTROLYTES—

In instances in which the pre-electrolysis described above is known to deactivate the working electrode, or when an impurity can be removed by electrosorption, potentiostatic purification was conducted in a second sealed vessel with a platinum-black working electrode
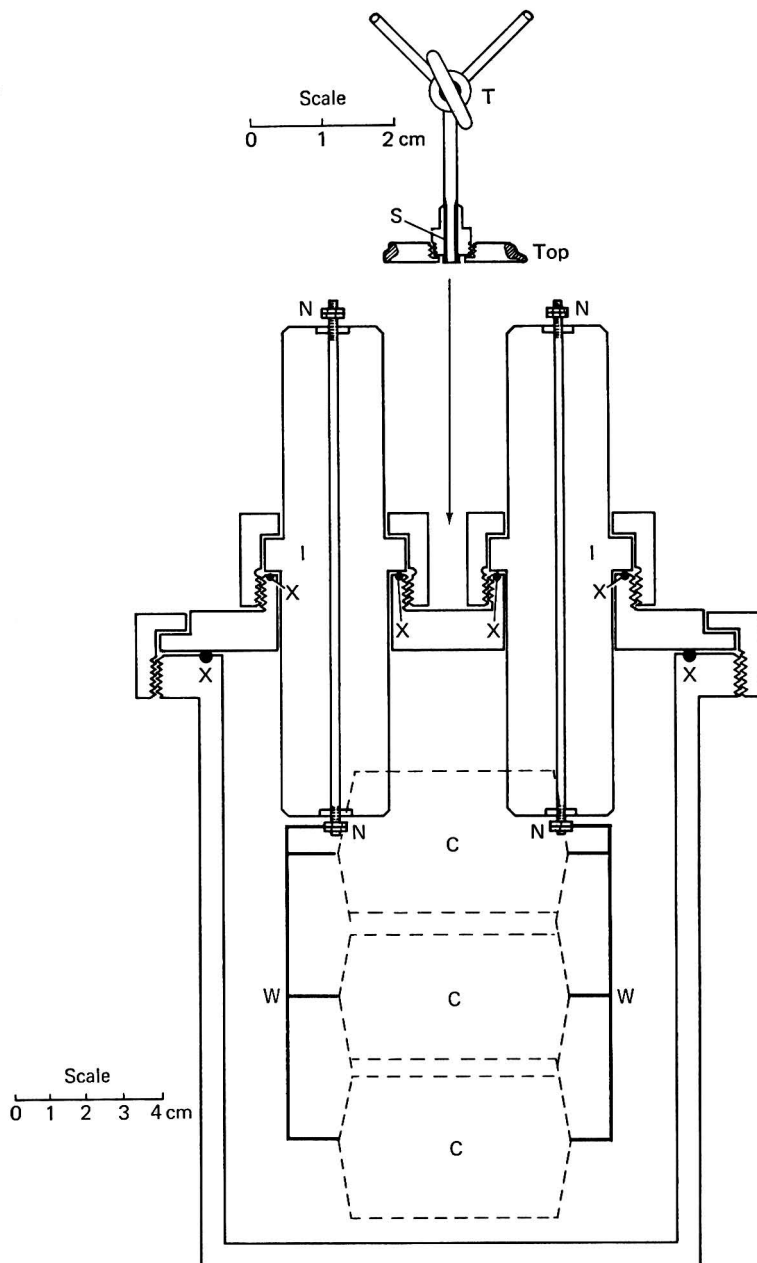

Fig. 3.   Sectional view of integrating capacitor: C, S.T.C. 455/LWA/112 FR polystyrene capacitors (0·2 μF $\pm$ 1 per cent. 500 V d.c. working, five in parallel); N, 2 BA terminal nuts; S, platinum glass to metal seal; T, three-way greased tap; I, machined PTFE insulators; X, neoprene O-rings; and W, copper wire, 22 s.w.g.   All parts are made of brass unless otherwise specified

of geometric area 100 cm². The all-glass cell carried ground-glass joints[9] lubricated with distilled water, and bearing electrodes, a nitrogen bubbler and a glass siphon tube, the other end of which was led to the coulometric cell. After electrolysis to a satisfactorily small residual current, the "cleansed" electrolyte was forced into the voltammetric or coulometric cell by closing the nitrogen outlet so that electrolyte was forced out of the siphon tube. The siphon could be broken by an outlet tap at its highest point. The first few portions of electrolyte transferred were used to rinse out the receiving cell, and were then discarded.

RESULTS AND DISCUSSION

POTENTIOSTATIC DETERMINATION OF VANADIUM(V)—

Medium—From the voltammetric study,[1] the saturated potassium sulphate - acetate buffer at pH 4·0 and 2·0 M sulphuric acid are both suitable media for the determination. Both show well defined vanadium(V) limiting-current regions of sufficient potential range to permit the choice of a command potential that keeps the desired reaction well separated from background reactions so that a good current efficiency could be expected. Furthermore, in these media the ageing of the working electrode did not seriously affect the limiting-current region of the vanadium(V) wave. At intermediate hydrogen-ion concentrations, the determination is impracticable, if not impossible, because severe deactivation of the electrode would so severely prolong the reduction that background corrections would be much too large to be reliable.

Electrode pre-treatment[1,2]—Method (b)[1,2] was selected and slightly modified on account of the large area of the working electrode; the previously cleaned electrode is immersed in 1·0 M sulphuric acid, anodised for 30 s at 100 mA cm⁻² (*i.e.*, 12·5 A) then cathodised for 30 s at 100 mA cm⁻². The cycle is repeated once more, and the electrode thoroughly washed with water. That this modification made no difference to the electrode behaviour in the two media was confirmed by repeated voltammetric scanning. Selection of method (b) was made on the following grounds. Method (a), reduction with iron(II) in sulphuric acid, had not proved particularly successful, and was suspect in respect of transfer of trace amounts of iron(II) or iron(III), trapped in the gauze meshes, into the test solution.[14] Method (e), oxidation, was deemed unsuitable because the charge-transfer process was slowed down by this treatment, and an error would be introduced by the reduction of the oxide film, although a correction could be applied for the latter. Methods (b), (c) and (d) are very similar, but method (d), simple cathodisation, was considered less suitable because such electrodes appear to be prone to cumulative adsorption of some species in the vanadium sample on repeated use. Such an impurity is known to be removed by anodisation, and so method (b) was chosen, in preference to method (c), stripping and cathodisation, as being simpler and faster. Method (c) remains appropriate for the initial cleaning of dirty electrodes.

Determinations—The results of determinations in the two chosen media with electrodes pre-treated by method (b) are collected in Table I, and show that results obtained in 2·0 M sulphuric acid are substantially better than those for the buffer at pH 4·0. This effect arises from two causes. First, different integration methods were used, and the strip-chart recording - weighing method for group D is not as accurate as the electronic method. The second cause is more fundamental and important. In acetate buffer, the background current, which was substantial, changed during the determination, but the exact manner of the change is not known and therefore cannot be accurately corrected for.[13] There was little alternative but to use a mean value of the pre-titration and post-titration background currents, and the error is magnified by the low charge-transfer rate and the long duration of the determination of 2 to 2·5 hours. In both media, graphs of log current *versus* time were linear. The increased determination time in the buffer of pH 4 is aggravated by the lower mass-transfer rate constant[2] in this medium.

POTENTIOSTATIC DETERMINATION OF VANADIUM(V) IN THE PRESENCE OF OTHER METALS—

Chromium(VI)—In acetate buffer, chromium(VI) is specifically adsorbed on the electrode surface and quantitatively blocks the vanadium reduction.[2] In 2·0 M sulphuric acid, vanadium(V) and chromium(VI) are reduced at virtually identical rates, giving a single wave.[2] In this medium, the total of vanadium *plus* chromium can be determined at a command potential of +0·25 V, but the current efficiency for the reduction of chromium(VI) is unlikely to be high.

TABLE I

RESULTS OF THE POTENTIOSTATIC DETERMINATION OF VANADIUM(V) ALONE

Group	Conditions	Sample taken/mol	Background current Initial/mA	Background current Final/mA	Time/ minutes	Relative error, per cent.
A	Saturated potassium sulphate - acetate buffer at pH 4·0, electronic integration, command potential −0·128 V	2×10^{-3}	0·2	0·1	130	+5·1
		2×10^{-3}	0·15	0·1	140	+1·54
		2×10^{-3}	0·09	0·1	145	+2·04
B	2·0 M sulphuric acid, electronic integration, command potential + 0·247 V	2×10^{-3}	0·15	0·15	84	+0·16
		2×10^{-3}	0·15	0·15	71	−0·51
		2×10^{-3}	0·35	0·24	102	−0·21
		2×10^{-3}	0·15	0·05	99	+0·07
		2×10^{-3}	0·05	0·10	81	−0·45
		2×10^{-3}	0·04	0·05	83	−0·35
		2×10^{-3}	0·05	0·05	150	−0·87
		2×10^{-3}	0·15	0·04	140	−0·10
		2×10^{-3}	0·10	0·10	80	−0·10
		1×10^{-3}	0·10	0·05	76	−0·20
		5×10^{-4}	0·15	0·15	81	−0·28
		1×10^{-4}	0·07	0·08	83	−0·11
C	2·0 M sulphuric acid, strip-chart record integration, command potential + 0·247 V	2×10^{-3}	0·36	0·52	75	−0·93
		2×10^{-3}	0·41	0·50	88	−0·53
D	Saturated potassium sulphate - acetate buffer at pH 4·0, strip-chart record integration, command potential −0·128 V	2×10^{-3}	0·47	0·51	120	−1·5
		2×10^{-3}	0·18	0·37	110	−3·1
		3×10^{-3}	0·34	0·21	130	+3·7
		5×10^{-3}	0·27	0·44	160	+2·1
		5×10^{-4}	0·13	0·37	117	−1·0

The first nine results in section B give a relative standard deviation of 0·27 per cent. For the 95 per cent. confidence level, this value indicated that the stock vanadium(V) solution was (1·008 to 1·011) × 10⁻¹ M. Standardisation by means of sulphur dioxide and permanganate against sodium oxalate[9] gave a value of 1·012 × 10⁻¹ M.

Manganese(VII)—Well separated waves are obtained in the acetate buffer at pH 4·0,[2] and on this basis the sequential determination of manganese(VII) at +0·700 V and vanadium(V) at −0·125 V was attempted. As earlier adumbrated,[2] the quantities of electricity consumed by the two steps showed that they corresponded first to the reduction of manganese(VII) to manganese(III), at +0·7 V, and second to the simultaneous reduction of manganese(III) to manganese(II) and of vanadium(V) to vanadium(IV) at −0·125 V. Replicate experiments showed that the results were inadequately consistent, and also that some manganese(IV) oxide was formed by disproportionation of manganese(III). To depress this latter effect, the pH was decreased to 3·5 by the addition of acetic acid to the medium. Determinations made in this new medium showed that the first stage in the reduction was improved in reproducibility and accuracy, with a relative error of about ±0·3 per cent., as shown in Table II. The second stage in the reduction remained in error by about +2·0 per

TABLE II

RESULTS OF THE SEQUENTIAL POTENTIOSTATIC DETERMINATION OF MANGANESE(VII) AND VANADIUM(V) IN SATURATED POTASSIUM SULPHATE - ACETATE BUFFER AT pH 3·5
Electronic integration was used

Sample taken/mol MnVII	Sample taken/mol VV	Command potential/V MnVII	Command potential/V VV	Relative error, per cent. MnVII	Relative error, per cent. VV
5×10^{-4}	2×10^{-3}	0·697	−0·120	+0·31	+1·1
5×10^{-4}	2×10^{-3}	0·697	−0·120	+0·10	+1·7
5×10^{-4}	2×10^{-3}	0·697	−0·110	+0·11	−1·0
5×10^{-4}	4×10^{-3}	0·697	−0·110	−0·21	+0·8
2×10^{-3}	1×10^{-3}	0·697	−0·110	−0·19	−2·1
2×10^{-3}	1×10^{-3}	0·697	−0·120	+0·09	−1·0
3×10^{-3}	1×10^{-3}	0·697	−0·120	−0·27	+1·6

cent. after correction for the background current. However, the simple determination of vanadium(V) in acetate buffer at pH 4·0 was also in error by this amount, as shown in Table I, so the error in the sequential determination was not unexpected. The two-step reduction of manganese(VII) was not predicted from the voltammetric curves[2] because the mass-transfer rate constant was not independently known for the conditions used.

The voltammograms[2] showed only a single step for manganese(VII) reduction, and although the limiting current could be measured to within 1 per cent., knowledge of one other parameter would be needed in order to calculate the n-value of the wave. A determination on this mixture was not attempted in 2·0 M sulphuric acid, because the voltammograms[2] showed that the wave separation was inadequate for good separation efficiency, although the sum could be determined with good accuracy and efficiency.

Iron(III)—The voltammogram[2] suggests that, by using electrodes activated by methods (b) or (c),[1] it should be possible to reduce vanadium(V) at a command potential of +0·9 V without reducing an appreciable amount of iron(III). Even if some iron(II) were formed, it would act as an intermediate and reduce vanadium(V) chemically. Experimentally, it was found that, in 2·0 M sulphuric acid, the current decayed rapidly to about one third of its initial value during the first 10 minutes and thereafter the decay became much slower. A graph of log current *versus* time for the first part of the reduction was not linear, but convex to the time axis. This result indicated that the electrode surface was being deactivated to the type of surface used to record scan 2 of Fig. 4 in reference 2. Although it remained possible to reduce the vanadium(V) without appreciable reduction of iron(III) by continuing the potentiostatic electrolysis until the current decreased to an acceptable residual value, the time required would be so excessively long that the background correction would be considerable and the determination would be of poor accuracy. Alternatively, it is possible to reduce both vanadium(V) and iron(III) simultaneously and quantitatively in 2·0 M sulphuric acid at +0·25 V, and then to re-oxidise the iron(II) at +1·0 V without any risk of re-oxidising the vanadium(IV) or the solvent, and so obtain the vanadium concentration accurately by difference. Unfortunately, the latter part of this procedure could not be attempted, as the only high-current potentiostat available at the time would operate only in the cathodic mode.

CONCLUSIONS

The potentiostatic determination of vanadium(V) is possible in the two media selected, and the results obtained in 2·0 M sulphuric acid by using electronic integration are both precise and accurate. The sequential potentiostatic determination of manganese(VII) and vanadium(V) in acetate buffer at pH 3·5 is possible, although the mechanism is unexpected in that the first step is reduction to manganese(III), which is then reduced to manganese(II) simultaneously with the reduction of vanadium in the second step. Chromium(VI) can be reduced simultaneously with vanadium(V), but not sequentially. Reduction of vanadium(V) in the presence of iron(III) is possible but not practicable, and it is better to reduce both and then to re-oxidise the iron(II); manganese can be added to this combination.

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A Multi-channel Dispenser - Titrator - pH-stat*

By DOUGLAS G. MITCHELL and KENNETH M. ALDOUS

(*Division of Laboratories and Research, New York State Department of Health, Albany, New York* 12201, *U.S.A.*)

A multi-channel dispenser - titrator - pH-stat with switch-selection of reagents and reagent volume control and with a directly digital read-out is described. A valve driven by a stepper motor is used to select reagents and as a coarse volume control. A drop generator dispensing - deflection mechanism is used as a fine volume control. The drop generator is also used to reject automatically to waste any reagent contaminated by previously dispensed reagent and, in the titration mode, to add various amounts of reagent to the reaction mixture. The instrument gives outstanding precision (relative standard deviation less than 0·2 per cent. over the range 0·5 to 7·0 ml) and linearity (correlation coefficient $r = 0·999$ over the ranges 0·01 to 1·0 and 0·25 to 7·0 ml).

THE dispensing and, to a lesser extent, titration of liquids are basic operations in all wet-chemical analytical procedures. The most common dispensing operations can be conveniently grouped into fixed-volume and variable-volume sample and reagent dispensing. Efficient instrumentation is available for both fixed-volume operations, and some dispenser - diluters can handle variable-volume sample dispensing, but no fully automated instrumentation is available for variable-volume reagent dispensing (Table I). Also, none of the available automatic dispensers are also capable, without modification, of being used in automatic titrations and pH-statting procedures.

TABLE I

INSTRUMENTATION FOR AUTOMATED DISPENSING

Dispensing operation	Available instrumentation
Fixed-volume sample dispensing	Manual: Pipettes, burettes and syringes Automated: Syringe dispensers and diluters
Variable-volume sample dispensing	Manual: Pipettes, burettes and syringes Automated: Some dispenser - diluters
Fixed-volume reagent dispensing	Manual: Pre-set pipettes fitted on to reagent containers, burettes, pipettes and syringes Automated: Probably unnecessary
Variable-volume reagent dispensing	Manual: Burettes and syringes Automated: No fully automated instrumentation available

In this paper, we describe a dispenser - titrator - pH-stat based on the use of a droplet generator, the liquid being dispensed into a stream of uniformly sized and uniformly spaced droplets, as a first step in the dispensing or titrating operation. Droplet generator devices have been previously used to dispense liquids. For example, Schneider and Hendricks[1] and Schneider, Lindblad and Hendricks[2] have used a droplet generator to study the collision and coalescence of liquid aerosols; Sweet[3] has described a high-frequency ink writer; Hieftje and Malmstadt[4] used a droplet generator for sample introduction in flame spectrophotometry; and Hieftje and Manadarano[5] developed a single-channel titrator. A single-channel micro-dispenser (Princeton Fluidics Corporation, Princeton, N.J., Model 390) has also been used.

These instruments are not directly applicable to dispensing and titrating operations in a routine analytical laboratory because of the considerable practical difficulties in changing reagents and because of the lack of a coarse reagent on - off control to prevent wastage. The instrument described herein can dispense or titrate six reagents with dial selection of both reagent and reagent volume. It is also fitted with several devices needed for a routine analytical instrument: a reagent thermostat in order to eliminate variations in volume dispensed because of viscosity changes, a coarse reagent on - off control and a flexible mode of approaching the end-point, this mode being selected by the operator.

PRINCIPLE OF OPERATION—

The basic dispensing system is shown schematically in Fig. 1. Reagents are placed in containers, pressurised at about 11 p.s.i., and connected to the entrance ports of a six-way valve driven by a stepper motor. The appropriate reagent can flow through this valve, through a thermostatically controlled coil, and then through a vibrating needle, from which it emerges as a stream of uniformly sized drops. These drops are either electrostatically charged (by applying +400 V to the cylindrical charging electrode) or left uncharged (electrode at 0 V) and are then passed between two highly charged deflecting electrodes (± 3 kV). Charged drops are electrostatically deflected and allowed to drain to waste, while uncharged drops are allowed to proceed undeflected into the desired container. The flow-rate of the liquid is constant at constant pressure within the reagent vessel and temperature of the liquid; hence the volume dispensed can be controlled by selecting the time during which the liquid is allowed to proceed into the container.
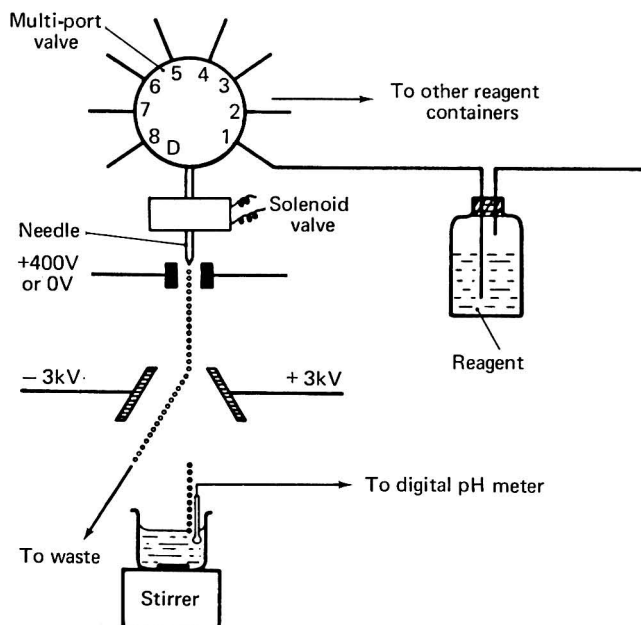

Fig. 1.   Basic dispensing system

A dispensing operation is carried out by setting a switch to select the liquid to be dispensed, setting a digital switch to select the reagent volume and pressing a start button. The following events then occur in sequence:

1. The stepper motor moves the valve from "off" to the pre-selected position, thus allowing the reagent to flow.

2. All liquid flowing during the first few seconds is dispensed to waste (as it is presumed to be contaminated by previously dispensed reagent).

3. Reagent is allowed to proceed undeflected into the desired container for the time required to give the selected volume.

4. The liquid stream is deflected to waste for a few milliseconds so as to avoid switching irregularities.

5. The valve is returned to the "off" position.

Thus the valve acts as a reagent selector and as a coarse on-off control, and the drop generator mechanism acts as a fine volume control and an automatic washing device to prevent cross-contamination.

The same basic mechanism is used for titration and pH-statting procedures, except that a digital pH meter with further control circuitry is used to control the dispensing operation. The pH meter output is fed to comparator circuitry, which senses the difference between the pre-selected pH and the pH of the reaction mixture. Titrant is dispensed at the maximum rate of approximately 8 ml min^{-1} until a pre-selected pH is reached. At this stage, dispensing is stopped for a selected period of between 0 and 20 s so as to allow sufficient time for the chemical reaction to proceed. (This step is necessary, for example, when titrating natural waters with a strongly acidic titrant.) Thereafter, dispensing proceeds at a selected rate of 100, 80, 60, 40, 20 or 10 per cent. of the maximum rate until the pre-selected pH is reached and the valve is turned off. Subsequent changes of pH, as in pH-statting operations, will cause the valve to open, thus allowing further reagent to be dispensed as required in order to maintain the selected pH value.

The circuitry necessary to carry out these operations is shown schematically in Fig. 2.

INSTRUMENT COMPONENTS—

The high-voltage power supplies (400 V, less than 5 per cent. ripple; 3 kV, less than 10 per cent. ripple) and digital timing circuitry were built up from standard electronics components. Suitable components (valve, thermostatically controlled coil, reagent flasks and dispensing heads) for handling liquids were not available commercially and were constructed in our workshop. The thermostatically controlled coil comprises a 5-foot coil of 0·017 inch i.d. polypropylene tubing encased in a metal block and maintained at 30 ± 0·1 °C. A Bellingham, Model 123, air pressure regulator was used to regulate the air pressure in reagent flasks, and a Leedex 170–733–001 stepper motor was used to drive the reagent selector valve.
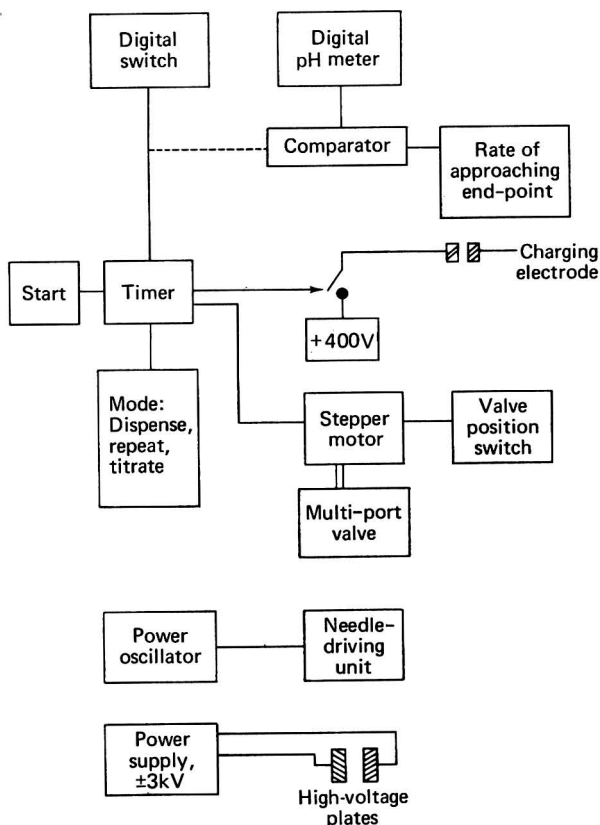

Fig. 2.   Schematic diagram of digital control and counting circuitry for multi-channel dispenser - titrator system

INSTRUMENT OPERATION—

The basic operating procedures are as follows.

Dispense - repeat dispense—(*i*) Select reagent; (*ii*) dial volume; and (*iii*) press "Start."

Titrate - pH-stat—(*i*) Select titrant; (*ii*) fit pH meter and electrode; (*iii*) select pH (mV) at end-point; (*iv*) select pH (mV) at reaction pause; (*v*) select reaction pause time; (*vi*) select rate of approaching end-point; (*vii*) press "Start"; and (*viii*) read titrant volume on display.

RESULTS

DISPENSING MODE—

Precision—The precision was evaluated by dispensing ten successive volumes of distilled water and weighing the dispensed liquid. The results are shown in Table II. Relative standard deviations of less than 0·2 per cent. were obtained over the range 0·5 to 7·0 ml, which is exceptionally good precision, particularly as there is no possibility of "drop at the dispenser tip" error as with conventional syringe dispensers. Most of the variation in dispensed volume is associated with the mechanical switching operation, because if the valve is locked in the "on" position, values for relative standard deviation of better than 0·05 per cent. can be obtained over this dispensing range.

TABLE II

PRECISION RESULTS FOR REPETITIVE DISPENSING

Volume dispensed/ml	Relative standard deviation, per cent.
0·5	0·19
1·0	0·17
3·0	0·19
7·0	0·10

Linearity—Volumes dispensed over the ranges 0·01 to 1·0 and 0·25 to 7·0 ml were measured and plotted against instrument setting (Fig. 3). Correlation coefficients of 0·999 were obtained for both ranges.
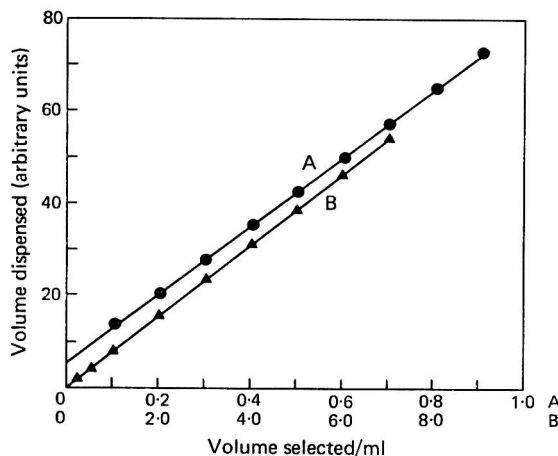
Fig. 3.   Calibration graphs

TITRATION MODE—

Analytical precision in the titration mode was evaluated by connecting the instrument to a digital pH meter (Model NX, Sargent Welch Scientific Co., Skokie, Illinois 60076), by using a glass and platinum electrode as required (Model 117233; Leeds and Northrup, North Waks, Pa. 19545).

Precision results were obtained for strong acid - strong base, strong acid - weak base and redox titrations. These results are shown in Table III.

TABLE III

TITRATION RESULTS: MULTI-CHANNEL DISPENSER - TITRATOR - pH-STAT

Titrant	Sample	Sample volume/ ml	End-point selected	Mean titrant volume/ ml	Relative standard deviation of titrant volume, per cent.	Titration time/s
Sulphuric acid (0·02 N)	Sodium hydroxide solution (approx. 0·02 N)	10·0	pH 8·6	9·23	0·14	150
Sulphuric acid (0·2 N)	Potable water	10·0	pH 4·5	0·47	3·3	50
Ammonium cerium(IV) sulphate solution (0·025 M)	Ammonium iron(II) sulphate solution (0·025 M)	10·0	8·6 mV	10·09	0·74	150

DISCUSSION

The instrument described provides an exceedingly efficient means for carrying out the numerous dispensing and titrating procedures required in most laboratories in which wet-chemical methods are used. It has the major advantage of dial selection of both reagent and reagent volume, with excellent precision, linearity and accuracy, and a directly digital read-out.

The instrument is currently being used in our water analysis laboratory for preparing standard solutions for atomic-absorption spectrophotometry and colorimetry, for neutralising reaction mixtures after acid digestion, for acid - base titrations and for various other dispensing operations.

The instrument maintains calibration for the dilute reagents used in our laboratory but not for concentrated reagents such as 1 M sodium hydroxide solution and organic solvents, which have viscosities that are significantly different from that of distilled water; these reagents require re-calibration. Calibration can be readily checked by dispensing liquid into a 1·0-ml standard flask. As the instrument is completely linear, this check suffices for the whole calibration range.

The directly digital read-out is an additional advantage. We shall shortly interface the dispenser - titrator and digital pH meter directly with a laboratory mini-computer.

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A Modified Field Test for the Determination of Carbon Disulphide Vapour in Air

By E. C. HUNT, W. A. McNALLY and A. F. SMITH

(*Department of Trade and Industry, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, SE1 9NQ*)

An improved and more sensitive method is described for the determination of carbon disulphide vapour in air at concentrations up to 40 p.p.m. V/V. Carbon disulphide vapour is absorbed from a 500-ml sample of air into an ethanolic solution containing copper(II) acetate, diethylamine and triethanolamine. The yellow colour produced is compared visually with standard colours or measured spectrophotometrically. For field use, the apparatus is portable and simple to operate, and requires a working time of about 5 minutes per determination.

THE field test currently in use by H.M. Factory Inspectorate for the determination of carbon disulphide vapour in air[1] is basically the same as that which was first published in 1939 and is derived from a method[2] originally published in 1932. The method is required for assessing the atmosphere within a factory and to give a rapid, approximate determination of concentrations of carbon disulphide in the region of the threshold limit value, currently 20 p.p.m. V/V,[3] in order to judge whether or not a hazard to health exists. (Threshold limit values refer to time-weighted concentrations in air for an 8-hour working day and a 40-hour working week, and represent conditions under which it is believed that nearly all workers may be repeatedly exposed without adverse effect on their health. Detailed conditions and exceptions are given in reference 3.) A re-examination of the method was undertaken for the following three reasons.

(*i*) It was occasionally found that when the component solutions were mixed in the bubbler the absorption solution became turbid and its colour blue instead of remaining a clear, pale green.

(*ii*) The volume of air to be sampled (2·5 litres) was of an inconvenient size; it was excessively large for the use of a rubber-bulb aspirator, which would require twenty aspirations, and too small to warrant the use of an electric pump and flow meter. The rubber-bulb aspirator was preferred because of its portability, and so an increase in sensitivity was sought in order to permit a reduction in the volume of air sampled.

(*iii*) The existing method was devised before threshold limit values for toxic substances in air were first compiled and it does not provide for a standard at the threshold limit value for carbon disulphide.

A survey of published analytical methods disclosed no method that appeared suitable for adaptation as a replacement for the existing method, and modification of the latter seemed to afford the most profitable line of investigation.

EXPERIMENTAL

The current method requires the contaminated atmosphere to be passed through a bubbler containing 10 ml of ethanol, 2 ml of a 2 per cent. V/V solution of diethylamine in benzene and 2 ml of a 0·1 per cent. m/V solution of copper(II) acetate in ethanol; the colour of the copper diethyldithiocarbamate formed is allowed to develop for 20 minutes. For use as a field method, the amount of carbon disulphide collected in the absorption solution is determined by visually comparing the colour formed in this solution with colour standards.

The first steps taken to improve the sensitivity were to reduce the concentration of copper(II) acetate in the absorption solution from 0·014 to 0·002 per cent. m/V, to eliminate the benzene by preparing the diethylamine solution in ethanol and to reduce the total volume of the absorption solution by adding only 6 ml of ethanol instead of 10 ml. These changes, and the evaluation of the colour by using a longer light path, produced a satisfactory increase n sensitivity, with the added advantage that the reagent blank was colourless instead of

pale green. During the development of the method, colours were measured spectrophoto-metrically[4] at 430 nm after allowing the colour to form for 20 minutes. The optical density was found to reach a maximum at this wavelength after about 2 minutes (Fig. 1) but the colour changed visibly from lemon yellow to amber during the subsequent 18 minutes. The absorption spectrum of the solution, recorded at intervals (Fig. 1), showed initially a single peak with a maximum at 440 nm. Within 5 minutes, the peak had shifted to 457 nm and a shoulder had begun to appear at about 385 nm, which developed into a peak and increased in height for at least 30 minutes. The peak at 457 nm reached a maximum during this time.
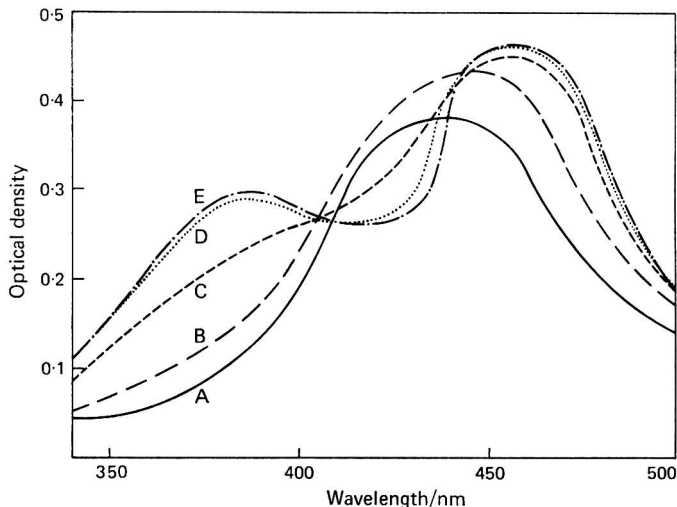

Fig. 1.   Variation of the absorption spectrum with reaction time.
Carbon disulphide (60 μg) added to ethanol containing 0·002 per cent.
m/V of copper(II) acetate and 0·4 per cent. V/V of diethylamine.   Re-action time: A, 1; B, 2; C, 5; D, 15; and E, 30 minutes

EFFECT OF WATER—

It was found, during tests with the current field method for determining carbon di-sulphide, that the addition of a small amount of water to the absorption solution produced turbidity and a change in colour from pale green to pale blue. Application of the test under factory conditions, with possibly perfunctory washing and drying of the apparatus, could lead to retention of moisture, especially as sintered-glass bubblers are used. Similar effects were found with the modified absorption solution described above when water was added. The modified solution was prepared in absolute ethanol (maximum water content 0·5 per cent. V/V) and contained no benzene. Small amounts of water were added to the ethanol used in preparing the reagent solutions in order to study the effect on colour in more detail.

Absorption spectra recorded after the addition of 60 μg of carbon disulphide to the absorption solution, and allowing 30 minutes for reaction time, showed that as the water content increased, the peak at 385 nm was reduced and the main peak at 457 nm shifted to 435 nm. With additions of water to concentrations greater than 5 per cent. V/V, only the peak at 435 nm remained (Table I). At these levels of water concentration, the copper(II) acetate solution deteriorated rapidly, turning dark brown and becoming turbid. Replacement of ethanol with butan-2-ol or 2-methoxyethanol has been recommended[5] in order to eliminate this effect but was found to be unsatisfactory because of the formation of coloured reagent blanks that seriously impaired visual colour comparison. Other workers[6,7] had added tri-ethanolamine to the absorption solution but, when it was added to the solution used in the current field method, the blank solution became blue in colour. However, a stable colour with an absorption maximum at 430 nm was obtained in the presence of carbon disulphide, which was not affected by additions of water in the range 1 to 10 per cent. V/V. With the modified absorption solution, which contained less copper(II) acetate, the reagent blank was

TABLE I

EFFECT OF VARIATION OF WATER CONTENT ON THE COLOUR

Carbon disulphide (60 μg) in 10 ml of ethanol containing 0·002 per cent. m/V of copper(II) acetate and 0·4 per cent. V/V of diethylamine after colour development for 30 minutes

Water content, per cent. V/V	Absorption maximum/nm	Optical density (10-mm cells)
0·5	385	0·300
	457	0·460
1·0	385	0·250
	457	0·455
1·5	385	0·200
	457	0·450
2·0	448	0·450
2·5	442	0·470
3·0	440	0·480
3·5	440	0·495
4·0	440	0·490
4·5	440	0·505
5·0	435	0·500
10·0	435	0·500
20·0	435	0·510

Optical densities at 385 nm remained constant at 0·200 for water contents of 1·5 per cent. or more.

reduced to an acceptable level without unduly affecting the sensitivity of the test. A concentration of 1·0 per cent. V/V of triethanolamine in the absorption solution was chosen because, at this level, small errors in volume measurement, caused by the viscous character of the liquid, would not seriously affect the final colour or the sensitivity of the test (Table II). With the incorporation of triethanolamine, all the reagents could be combined in a single solution that was stable for at least 1 month, and the more widely available industrial methylated spirit (water content about 5 per cent. V/V) could be used instead of absolute ethanol.

TABLE II

EFFECT OF ADDITION OF TRIETHANOLAMINE

Carbon disulphide (60 μg) in 10 ml of 96 per cent. V/V ethanol containing 0·002 per cent. m/V of copper(II) acetate and 0·4 per cent. V/V of diethylamine after colour development for 5 minutes

Triethanolamine content, per cent. V/V	Optical density at 430 nm (10-mm cells)
0	0·492
0·2	0·461
0·4	0·455
0·8	0·455
1·2	0·455
1·6	0·455
2·0	0·450
4·0	0·440

PREPARATION OF A STANDARD ATMOSPHERE—

An atmosphere containing a known concentration of carbon disulphide was required to assess the efficiency of sampling and of the chemical reactions that took place during the application of the field method. The atmosphere was prepared dynamically by an injection - atomisation technique in which carbon disulphide was injected at a known rate into a metered air stream. Part of this atmosphere was diluted with a second metered air stream to give the required concentrations. (The standard atmosphere generator was designed to ensure homogeneity and was checked at several different concentrations by a chemical method other than the described field test and found to give reproducible results.) The generated atmosphere was calibrated by collecting samples at the rate of 125 ml min^{-1} for 8 minutes in three all-glass bubblers in series, each containing 10 ml of ethanolic potassium hydroxide solution (0·2 per cent. m/V). The xanthate formed in each bubbler was determined spectrophotometrically

as its copper salt.[8]   With atmospheres containing up to 40 p.p.m. V/V of carbon disulphide, no colour developed in the last bubbler.

COLLECTION OF CARBON DISULPHIDE—

The efficiency of absorption of carbon disulphide from air with the simple bubbler and absorption solution described in the Procedure was found to be 100, 94 and 89 per cent. at flow-rates of 50, 125 and 200 ml min^{-1}, respectively, for atmospheric concentrations in the range 0 to 40 p.p.m. V/V.   The effect of temperature on absorption efficiency was found to be small and was linear between values of 96 per cent. at 5 °C and 91 per cent. at 35 °C, at the prescribed flow-rate of 125 ml min^{-1}.

RELIABILITY OF REAGENTS—

A comparison was made of reagents used in the test that were obtained from various manufacturers and of different batches from the same manufacturer.   Negligible differences were found.

INTERFERENCES—

Hydrogen sulphide is the substance most likely to be found as an industrial co-contaminant with carbon disulphide and is known to give a positive reaction with the proposed test.   A hydrogen sulphide atmosphere, prepared by an injection technique, was standardised by an iodimetric method.   Samples of this atmosphere at concentrations of 10, 20 and 40 p.p.m. V/V were taken by the proposed field method and were found to give colours equivalent to 3, 5 and 10 p.p.m. of carbon disulphide, respectively.   The current method for determining carbon disulphide in air[1] recommends the use of filter-paper impregnated with lead acetate to remove hydrogen sulphide and this method, together with the use of similarly impregnated cotton-wool, was investigated for use with the revised method. The introduction of a filter into the sampling system considerably reduced the flow-rate and also the effective volume sampled when a rubber-bulb aspirator was used, hence it was essential that the flow-rate of the aspirator be adjusted before use, with both filter and bubbler in circuit.   Once adjusted, no significant change in flow-rate was noted when the filter-paper was changed.   Cotton-wool, however, gave variable flow-rates, depending on its packing density; consequently, its use as a hydrogen sulphide trap was abandoned.   Samples of the standard hydrogen sulphide atmosphere at concentrations of 10, 20 and 40 p.p.m. V/V were taken by the proposed method with a pre-filter of impregnated paper.   Colours equivalent to 1, 2 and 4 p.p.m. of carbon disulphide, respectively, were obtained by using Whatman No.1 filter-paper and 0, less than 0·5 and 1 p.p.m. by using Whatman 3MM paper; the latter was chosen as suitable for use in the test.

By mixing the outputs from the two generators in suitable proportions, a mixed atmosphere was obtained, which was sampled both with and without a pre-filter prepared from Whatman 3MM paper.   The average results obtained are shown in Table III.

TABLE III

INTERFERENCE EFFECT OF HYDROGEN SULPHIDE ON THE FIELD METHOD

Tests with standard atmospheres with and without lead acetate filters

Atmospheric concentration, p.p.m. V/V		Found by field test, p.p.m. V/V of carbon disulphide	
Carbon disulphide	Hydrogen sulphide	With filter	Without filter
22·5	0	22·5	22·5
0	8·7	0	2·3
22·5	8·7	22·5	24·8

PREPARATION OF COLOUR STANDARDS—

Colour standards were prepared by adding aliquot portions of an ethanolic solution of carbon disulphide to the absorption solution, allowance being made for volume changes and the fact that only 94 per cent. of the carbon disulphide present in the atmosphere is collected under the test conditions.   Once prepared, the standards were found to be stable for at least 4 hours, provided that they were kept in well stoppered tubes.   Details of the preparation

of these standards are given later.   Results obtained when carbon disulphide atmospheres of known concentration were sampled by the proposed method are given in Table IV.   The levels were assessed visually by using the colour standards and, more accurately, with a spectrophotometer.   The optical densities of the solutions were measured at 430 nm and the carbon disulphide concentration was determined by reference to a prepared calibration graph.

TABLE IV

EVALUATION OF FIELD METHOD WITH STANDARD ATMOSPHERES

Concentration of carbon disulphide, p.p.m. V/V

	Found by field method	
Present	By visual comparison	Spectrophotometrically
2·5	0 to 5	2·7
4·3	0 to 5	4·5
5·0	5+	4·7
5·3	5+	5·0
5·0	5	4·7
4·3	5	5·0
10·0	10	9·8
10·0	10+	10·3
10·7	10−	10·0
10·7	10+	10·7
16·0	10 to 20	15·3
19·7	20	20·0
20·0	20	20·0
21·0	20+	19·9
29·8	30	30·0
29·7	30	30·0
40·0	40+	39·3
40·3	40	41·3

Plus or *minus* symbols indicate values slightly greater than, or slightly less than, that of the nearest colour standard.

FIELD METHOD FOR THE DETERMINATION OF CARBON DISULPHIDE VAPOUR IN AIR

APPARATUS—

Glass bubbler—As shown in Fig. 2.
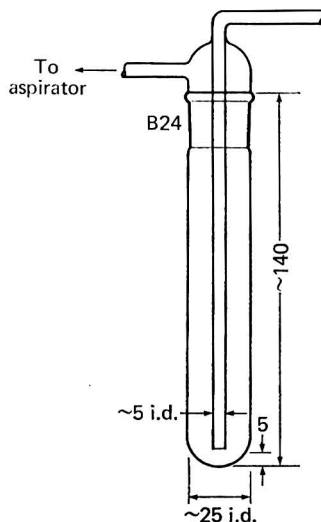

Fig. 2.   Diagram of bubbler.
(All   measurements   are   in millimetres)

Aspirator—A rubber bulb or other device capable of drawing air through the apparatus at the rate of 125 ml min⁻¹.

Colour comparison tubes—Flat-bottomed glass tubes of 10 mm i.d., calibrated with a mark at a height of 50 mm.

Filter-paper holder.

REAGENTS—

Reagents should be of analytical-reagent grade when possible.

Absorption solution—Dissolve 0·01 g of copper(II) acetate monohydrate in a small amount of cold ethanol and transfer the solution into a 500-ml calibrated flask with about 100 ml of ethanol (industrial methylated spirit can be used instead of ethanol if desired). Add, from a measuring cylinder, 5 ml of triethanolamine and wash any residue in the cylinder into the flask with ethanol. Swirl the contents of the flask until the triethanolamine has completely dissolved. Add 2 ml of diethylamine and dilute to 500 ml with ethanol. This solution can be used for 1 month if stored at temperatures below 30 °C in tightly stoppered bottles.

Lead acetate solution—Dissolve 10 g of lead acetate trihydrate in 90 ml of water. Add 5 ml of glacial acetic acid and 10 ml of glycerol to the solution and mix well.

Lead acetate papers—Immerse strips of Whatman 3MM chromatographic paper, 20 mm wide and 100 mm long, vertically for 1 minute in the lead acetate solution contained in a 100-ml measuring cylinder. Remove the papers and allow the excess of liquid to drain. Suspend the papers vertically and allow them to dry at room temperature in an atmosphere free from hydrogen sulphide. When dry, remove and discard portions 25 mm in length from the top and bottom of each strip. Store the prepared papers in stoppered, wide-necked, dark-glass bottles to protect them from light and air. Use within 14 days of preparation.

PREPARATION OF COLOUR STANDARDS—

Carbon disulphide solution—Dilute 1 ml of carbon disulphide to 100 ml with ethanol (or industrial methylated spirit). Dilute 1 ml of this solution to 250 ml with ethanol. This solution can be used for 1 week if stored below 30 °C in a well stoppered bottle.

Prepare four standards representing 0, 10, 20 and 40 p.p.m. V/V of carbon disulphide in air (0, 30, 60 and 120 mg m⁻³) by adding 0, 0·30, 0·60 and 1·20 ml of the carbon disulphide solution to 10 ml of the absorbing solution. Allow the colours to develop for 10 minutes before carrying out colour comparisons. Some approximations are involved in these standards for the visual determination, but allowance is made for volume changes and for the 94 per cent. efficiency of absorption in the bubblers. An additional standard representing 5 p.p.m. V/V (0·15 ml) can be included if required. The colour standards are stable for about 4 hours if kept in well stoppered tubes.

As an alternative, a series of permanent glass standards in a comparator disc, obtainable from Tintometer Ltd., Salisbury (Catalogue No. 6/56), can be used in conjunction with a Lovibond 1000 Comparator with a vertical viewing attachment.

PROCEDURE—

In a carbon disulphide free atmosphere, transfer by means of a pipette 10 ml of the absorption solution into the glass bubbler. Insert the inlet tube and attach the aspirator. Transfer the apparatus to the sampling site and collect 500 ml of the atmosphere. Remove the apparatus to an uncontaminated area and, 10 minutes after collection, transfer the solution into a colour comparison tube, filling the tube up to the calibration mark, and compare its colour with those of the colour standards by viewing downwards through the 50-mm depth of the liquids against a white background in daylight. If the presence of hydrogen sulphide is suspected, connect a suitable paper holder containing a lead acetate paper to the inlet tube of the bubbler. Re-adjust the aspirator, if necessary, so as to sample 125 ml in 1 minute; the resistance of the paper may reduce the volume of air sampled if a rubber-bulb aspirator is used.

DISCUSSION AND RESULTS

Both the turbidity and change of hue found occasionally with the current Factory Inspectorate method,[1] and the change in colour with time observed with the first modifications

to this method, appear to have resulted from the formation of hydrolysed copper species in the solution.   The addition of triethanolamine, which formed a stable ammine-type complex, overcame this effect and imparted a much greater tolerance to the presence of water in the absorption solution.   An added advantage for field use was that this solution could be prepared and transported as a single reagent instead of the two reagent solutions and additional ethanol that were previously required.

The method is capable of giving more accurate results if a spectrophotometer is used and optical densities are measured at 430 nm in 10-mm cells.   A calibration graph can be prepared for use with atmospheres containing 0 to 40 p.p.m. V/V by adding volumes of 0 to 1·20 ml of the carbon disulphide solution to 10-ml calibrated flasks, diluting to the mark with absorption solution and measuring the optical densities after 10 minutes.   Two bubblers in series should be used to ensure complete collection of carbon disulphide.   In calculating the results, an atmospheric concentration of 20 p.p.m. V/V of carbon disulphide can be taken as equivalent to 62·2 μg l^{-1} at 25 °C.

Tests were conducted at a viscose factory where duplicate samples were taken.   One sample of each pair was absorbed in ethanol and returned to the laboratory for spectrophotometric determination of carbon disulphide by the xanthate method.   The results are shown in Table V.   Some of the samples were taken in positions that were not typical of a working environment in order to cover a wide range of atmospheric concentrations and provide a valid test for the method.   None of the areas tested that might be occupied by workers had atmospheric concentrations of carbon disulphide greater than the threshold limit value[3] of 20 p.p.m. V/V.   Two samples (not shown in Table V) were taken in the factory in areas where hydrogen sulphide was known to be present.   The field test[9] for hydrogen sulphide showed the presence of 5 and 8 p.p.m. V/V of this gas, which had little effect upon the colours produced by the carbon disulphide test.   The use of lead acetate paper reduced the intensity of colour produced in each instance but the evaluation of the atmosphere remained the same, both with and without the treated paper, in relation to the nearest visual colour standard because of the low level of interference (approximately one tenth of the threshold limit value) at these concentrations.   It was noted that, although the factory was pervaded by a characteristic "sulphur" odour, neither carbon disulphide nor hydrogen sulphide was detected by its odour, despite the fact that the field tests showed one or both to be present.

TABLE V

TEST OF THE FIELD METHOD AT A FACTORY

Sample	Hydrogen sulphide, p.p.m. V/V	Carbon disulphide concentration, p.p.m. V/V, by	
		xanthate method	field method
1	0	2·6	0+
2	0	25	20 to 40 (25)
3	0	4·6	0 to 5 (5−)
4	<2	6·4	5
5	<2	22·4	20 to 40 (20+)
6	0	160	>80

Figures in parentheses indicate visually estimated values.
Plus or *minus* symbols indicate values slightly greater than, or slightly less than, that of the nearest colour standard.
For sample 6, 250 ml of atmosphere were taken.

The sensitivity of the method was improved by reducing the concentration of copper(II) acetate in the absorption solution, which gave a colourless reagent blank, and by increasing the path length of light used in viewing the colours.   The stability of the absorption solution was improved by the addition of triethanolamine.   The results shown in Tables IV and V show that the modified method is an effective replacement for the earlier method.

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Determination of the Antioxidant 1,3,5-Trimethyl-2,4,6-tri(3',5'-di-t-butyl-4'-hydroxy-benzyl)benzene in Feeds

By G. F. BORIES

(Station Centrale de Nutrition, Centre National de Recherches Zootechniques, 78-Jouy-en-Josas, France)

1,3,5-Trimethyl-2,4,6-tri(3',5'-di-t-butyl-4'-hydroxybenzyl)benzene (Ionox 330) is an antioxidant that is used for the preservation of plastic food wrappings. Its use as a fat stabiliser could be extended to animal feeds. By using the method described, 200 p.p.m. of Ionox 330 in a feed can be determined with good reproducibility. The method consists in extracting the Ionox 330 with chloroform, purifying it by using thin-layer chromatography, and measuring at 522 nm the colour developed in the presence of iron(III) chloride and 2,2'-bipyridyl. Possible interference from 2,6-di-t-butyl-*p*-cresol (butylated hydroxytoluene; BHT) can be avoided by using this chromatographic technique.

THE use of 1,3,5-trimethyl-2,4,6-tri(3',5'-di-t-butyl-4'-hydroxybenzyl)benzene (Ionox 330*) is authorised in France and several other countries as a stabiliser for the plastic wrappings that are used for packing foods. This substance, which has a high relative molecular mass, is not absorbed in the intestine, thus making it attractive as an antioxidant for stabilisation of fat in animal feeds. A method for determining it in lard, which involves the use of gas-liquid chromatography, has been proposed.[1] The high boiling-point of this substance (above 300 °C) presents severe drawbacks, especially the need to heat the chromatographic column to 330 °C. Consequently, the column gives uncertain reproducibility and has a limited life because of fats carried over during the extraction. In order to avoid these difficulties, we tried a colorimetric method of determination that involved the use of Emmerie and Engel's non-specific reaction[2] after purification by thin-layer chromatography.

EXPERIMENTAL

EXTRACTION OF IONOX 330 FROM THE FEED—

Several solvents were tried, but complete extraction could be achieved only by boiling the feed with chloroform under reflux. An aliquot of the extract was concentrated to one tenth of its volume by evaporation in a vacuum before being purified by thin-layer chromatography on silica gel. In order to prevent oxidation of Ionox 330 during the extraction and concentration steps, hydroquinone was added to the feed just before extraction. If this precaution is not taken, as much as 20 per cent. of it may be destroyed in several hours.

PURIFICATION OF THE EXTRACT—

The concentrated extract is purified by thin-layer chromatography under the following conditions: chromatography on silica gel activated for 30 minutes at 105 °C; elution with cyclohexane - toluene mixture (3 + 2); and simultaneous chromatography of some of the same extract so as to produce indicator spots, which are rendered visible by spraying them with potassium permanganate or antimony(V) chloride solution. The corresponding area of unsprayed plate is scraped off and extracted with chloroform.

OUTLINE OF METHOD OF DETERMINATION—

We attempted to find a very sensitive colorimetric method for the determination of Ionox 330 that had been purified by thin-layer chromatography. We adapted Emmerie and Engel's method, which has been used with success for determining several antioxidants[3] and is based on the reduction of iron(III) chloride to iron(II) chloride and reaction of the latter with 2,2'-bipyridyl to give a red-coloured complex that absorbs at 522 nm. The reaction is

carried out in methanolic solution, the colour development taking 30 minutes, after which time the colour is measured. In order to use the chloroform extract of the silica gel adsorbent directly, we carried out the colour development in chloroform - methanol $(1 + 1)$ for 30 minutes. A graph was drawn representing the colour intensity obtained after 30 minutes for a given Ionox 330 concentration in terms of the value of the methanol to chloroform ratio (Fig. 1). It shows that a small variation in the $1:1$ value for this ratio results in large variations in the reading, and the ratio must therefore be rigidly controlled in order to obtain consistent results. The 2,2'-bipyridyl - iron(II) complex has a high specific absorption at 522 nm $(\epsilon = 3 \times 10^4)$. By plotting optical density against concentration of Ionox 330 at concentrations from 5 to 15 μg ml^{-1} a calibration graph was prepared, which passed through the origin. By using this graph, 5 μg ml^{-1} of Ionox 330 can be accurately determined and 0·5 μg ml^{-1} detected.
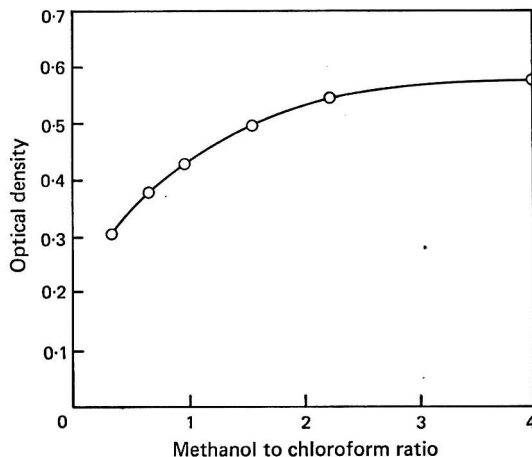
Fig. 1. Effect of the methanol to chloroform ratio on the intensity of the colour developed after 30 minutes with 10 μg ml^{-1} of Ionox 330

METHOD

APPARATUS—

Desaga thin-layer chromatographic apparatus and a Jobin and Yvon spectrophotometer were used.

REAGENTS—

Silica gel—Kieselgel G, Merck.
Antimony(V) chloride solution, 25 per cent. V/V in cyclohexane.
Potassium permanganate solution, 1 per cent.
Methanol—Analytical-reagent grade.
2,2'-Bipyridyl (Eastman Kodak) solution, 2 per cent. m/V in methanol—Keep the solution in a cold and dark place.
Iron(III) chloride solution, 2 per cent. m/V in methanol.

PROCEDURE—

Weigh 10 g of a feed containing 200 p.p.m. of Ionox 330 into a 250-ml round-bottomed flask, add 0·5 g of hydroquinone, then extract the mixture by boiling with 100 ml of chloroform under reflux for 10 minutes. Cool, then filter the mixture on a filter-paper and evaporate 50 ml of the extract contained in a flask down to about 1 ml in a vacuum. Transfer the concentrate with a pipette into a 5-ml vial, rinsing the flask several times with small portions of chloroform, and make the volume up to 5 ml. With a microsyringe, place 0·5 ml on a plate (20 × 20 cm) coated with a 0·5 to 0·75-mm thick layer of silica gel and activated at 105 °C for 30 minutes. Arrange margins on each side of the plate that are wide enough to enable a spot of the same extract to be placed on each margin so as to assist in localising

the site of the Ionox 330 after chromatography. Place the plate in a tank containing the cyclohexane - toluene mixture (3 + 2). After migration of the spots is complete (30 to 80 minutes), dry and render the two spots in the margins visible by spraying with either the antimony(V) chloride or permanganate solution, protecting the centre of the plate by covering it with a glass plate. Outline and scrape the area of the silica gel strip containing the anti-oxidant, and transfer the powder into a small chromatographic column. Elute the column with chloroform and collect the eluate in a 10-ml graduated tube (or vial), ensuring that the volume of eluate does not exceed 5 ml (which is sufficient for complete elution of the Ionox 330), then adjust the volume to exactly 5 ml with chloroform (this constitutes tube X); 5 ml of chloroform in a 10-ml tube (or vial) constitutes the blank solution (tube T).

A 5-ml volume of chloroform containing 50 μg of Ionox 330 and another 5-ml volume containing 100 μg of Ionox 330, placed in two 10-ml tubes, constitute the standard range (tubes A and B, respectively).

In subdued light, add to each of the four tubes A, B, X and T, 1 ml of iron(III) chloride solution and 1 ml of 2,2'-bipyridyl solution; shake the tubes, then complete the volumes to 10 ml with methanol. Allow the colour to develop for 30 minutes, then read the absorption at 522 nm as rapidly as possible, with tube T as a reference.

RESULTS AND DISCUSSION

The method described has been used for the determination of Ionox 330 contained in several types of feeds. The product was incorporated in the proportion of 200 p.p.m. To test the reproducibility of the method, a series of determinations was performed on a control feed to which were added, just before extraction, 200 p.p.m. of Ionox 330 dissolved in a small volume of chloroform. The results shown in Table I were obtained from ten successive determinations on each of the feeds.

TABLE I

RESULTS FOR RECOVERY OF IONOX 330 FROM FEEDS

	Ionox 330 found in feeds stated to contain 200 p.p.m. of this additive, p.p.m.				
Ionox found in control rat feed with 200 p.p.m. added*	Rat feed		Highly pigmented for laying hens (lucerne meal)	Pig feed
	Batch I	Batch II		
192	200	200	192	196
184	216	191	216	192
178	203	189	184	212
184	200	176	182	178
182	210	190	186	184
186	200	186	176	180
194	196	178	194	206
184	190	178	204	200
182	186	178	184	188
182	196	194	180	182
Average .. .. .. 184·8	199·7	186	189·8	192
Average recovery, per cent. 92·5	100	93	95	96
Coefficient of variation .. 2·6	4·4	4·4	6·4	5·6

* Added in solution.

The recovery rate of the additive is satisfactory. It should be noted that the presence of pigments (from lucerne meal) does not affect the percentage recovery. A good separation of Ionox 330 from interfering substances, as well as from 2,6-di-t-butyl-p-cresol (butylated hydroxytoluene; BHT), can be obtained by using the thin-layer chromatographic method described. Finally, by making use of thicker silica gel layers with possibly several elutions with the same solvent system, it should be possible to chromatograph larger amounts of the extract and thus determine 50 p.p.m. of Ionox 330 in a feed with equal precision.

We are grateful to the Compagnie de Produits Chimiques Shell (Paris) for permission to publish this paper, and we thank Mrs. E. Biette for technical assistance.

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The Determination of Lead in Foods by Atomic-absorption Spectrophotometry

By R. K. ROSCHNIK

(*Nestlé Products Technical Assistance Co. Ltd., Control Laboratory, Case Postale* 88, *Ch*-1814 *La Tour-de-Peilz, Switzerland*)

Rapid procedures for the determination of lead in foods by an organic extraction technique and atomic-absorption spectrophotometry are described. The food sample can be dry ashed or digested by using sulphuric acid and hydrogen peroxide. In the latter instance, digestion need not be complete. Lead is extracted from acidic solutions (either the dissolved ashes or the residual solution after acid digestion) into xylene as its diethylammonium diethyldithiocarbamate chelate, and then determined by use of atomic-absorption spectrophotometry. Large amounts of iron and tin do not interfere in the determination. In a 10-g sample, 0·02 p.p.m. of lead can be detected. The standard deviation in the range from 0·2 to 1·0 p.p.m. of lead is about 0·02 p.p.m. Certain products do not require preliminary digestion; in these instances lead is extracted directly from the acidified sample. Liquids, beverages and many canned foods can be monitored very rapidly in this way. The chelate - solvent combination used in this method is more convenient than the ammonium tetramethylenedithiocarbamate - isobutyl methyl ketone system. The method is applicable also to metals other than lead; its use for cadmium has been demonstrated successfully.

LEAD has attracted considerable attention as a public health hazard and legal limits for its occurrence in foods have been set, or proposed, from 0·3 to 8 p.p.m.[1–3] Normal levels found in foods range from 0·1 to 5 p.p.m.[4–7] Contamination during and after processing, notably from containers (cans or glazed earthenware), has been the subject of several studies,[3,8–10] but it is hardly a major hazard today. The most important source of lead contamination of foods would appear to be motor-vehicle exhaust fumes,[4,6] lead being deposited on the leaves of plants. Lead thus enters foods either directly (with fruit and vegetables), or indirectly, through feedstuffs into meat and milk products.[11] Atmospheric industrial fall-out may also be of importance in certain localities. The monitoring of lead in foods is therefore important.

The determination of lead in foods usually requires preliminary destruction or degradation of the organic matter. During dry ashing there is a slight risk of loss of lead by volatilisation of its halides, but this can be eliminated by the addition of sulphuric acid before ashing.[12] The temperature must, however, be kept below 500 °C.[13] Ashing aids such as magnesium nitrate[14] and aluminium and calcium nitrates[13] have been used.

For canned and liquid products wet ashing is usually the more rapid procedure. The use of sulphuric acid is not always advantageous as precipitating alkaline earth sulphates may remove much of the lead sulphate by adsorption. However, this very phenomenon forms the basis of a method for lead determination.[15,16]

The determination of lead by atomic-absorption spectrophotometry is not a very sensitive method, so that special measures usually need to be taken to improve the detection limit in food. Background absorption problems become acute in the presence of large amounts of salts, especially at the more sensitive wavelength of 217·0 nm. The aspiration of aqueous solutions after ashing usually requires some form of background correction, either by use of non-absorbing lines[5] or by using a continuum background.[17] Flameless techniques can result in improved sensitivity but cannot eliminate salt effects so that background correction becomes essential if they are used.

Use of the device of organic extraction avoids most of the background problems in this instance, and also increases the sensitivity. At present only the ammonium tetramethylenedithiocarbamate - isobutyl methyl ketone system appears to have been used for the determination of lead in foods by atomic-absorption spectrophotometry.[4,18–21] The present paper

presents a very useful organic extraction technique that makes use of the diethylammonium diethyldithiocarbamate - xylene system first described by Jordan.[22] Problems of pH adjustment do not arise with this technique, and in favourable instances the determination can be carried out without preliminary ashing of the product.

EXPERIMENTAL

REAGENTS AND APPARATUS—

Normal precautions for trace analysis were taken throughout. Analytical-reagent grade reagents were used, except for the xylene, which was of laboratory reagent grade. No attempt was made to purify the reagents further. Standard lead solutions were prepared from lead nitrate, the working standard containing 10 p.p.m. of lead in 1 per cent. V/V nitric acid. Standard tin(II) solutions were prepared by dissolving tin in concentrated hydrochloric acid (then diluting to 10 per cent. V/V of acid in each instance) and standard tin(IV) solutions by dissolving tin in hot, concentrated sulphuric acid (then diluting to 20 per cent. V/V of acid in each instance). Standard iron(II) solutions were prepared from iron(II) sulphate and preserved in dilute sulphuric acid, while standard solutions of the iron(III) ion were prepared from iron(III) chloride, standardised and preserved in hydrochloric acid.

A Perkin-Elmer 303 atomic-absorption spectrophotometer, fitted with a Hitachi recorder, an ordinary lead hollow-cathode lamp and a three-slot burner head, was used for atomic-absorption measurements. When solutions in xylene were aspirated, the instrument settings were as shown in Table I. A Beckman DB spectrophotometer was used for colorimetric determinations.

TABLE I

OPERATING CONDITIONS FOR PERKIN-ELMER 303 ATOMIC-ABSORPTION SPECTROPHOTOMETER WHEN ASPIRATING XYLENE SOLUTIONS CONTAINING LEAD

Wavelength ..	.. 283·3 nm	Scale expansion	..	×1
Lamp current	.. 30 mA	Damping setting	..	2
Slit setting ..	.. 4	Working range	..	1 to 10 p.p.m.
Air pressure ..	.. 30 p.s.i.; flow setting 8·5	Acetylene pressure	..	8 p.s.i.; flow setting 1·5

Food samples were obtained from local shops. In addition, a number of long-term storage samples of canned and bottled foods from various parts of the world were available to us and included in the study. Some of the older canned products were left in the can for several days after opening in order to increase their lead and tin contents.

STANDARD PROCEDURES

METHOD A (DRY ASHING)—

Add 5 ml of 20 per cent. sulphuric acid to a 5 or 10-g (homogenised) food sample in a silica crucible. (The sulphuric acid can be omitted if it has been confirmed that, after dry ashing, the recovery of added lead is 100 per cent. for the product in question.) Evaporate the contents to dryness and start to ash the residue over a small flame. Then, complete the ashing in a furnace at 500 °C for 3 to 18 hours, according to the product. If an appreciable amount of carbon remains after 18 hours, allow the crucible to cool, then moisten the ash with a few drops of 50 per cent. magnesium nitrate solution. Evaporate to dryness slowly and re-ash at 500 °C for a further hour.

Moisten the cold ash with a small volume of water, then add 5 ml of 6 N hydrochloric acid. Warm the mixture on a boiling water bath to complete dissolution and transfer it quantitatively to a 50-ml calibrated flask. Dilute with water to about 25 ml, cool and add 5 ml of xylene containing 1 per cent. of diethylammonium diethyldithiocarbamate. Stopper the flask and shake it vigorously for 40 to 60 s, allow the phases to separate and add water to bring the organic phase into the neck of the flask. Finally, aspirate the organic phase into the atomic-absorption instrument, under the conditions given in Table I.

A calibration chart is prepared by introducing 0, 10, 20, 30 and 40 μg of lead into a series of 50-ml flasks. To the lead solution add 5 ml of 6 N hydrochloric acid and dilute with water to about 25 ml. Carry out the extraction and aspiration as above. A special blank determination should be carried out so as to check the lead content of each batch of sulphuric acid, and magnesium nitrate, if used.

METHOD B (WET ASHING WITH SULPHURIC ACID AND HYDROGEN PEROXIDE)—

'Introduce 5 or 10 g of homogenised food sample into a 400-ml tall-form beaker. Add about 5 ml of water to powders and other dry products. Add 10 ml of concentrated sulphuric acid, then 1 ml of 30 per cent. hydrogen peroxide. Allow any reaction to subside, then warm the beaker gently, avoiding frothing, and finally bring the contents to the boil. When the reaction subsides or if intense charring takes place add a few more drops of hydrogen peroxide. Continue until no vigorous reaction occurs on the addition of hydrogen peroxide (Note 1).

NOTE 1—
    Degradation need not be complete and the final solution need not be colourless. Products containing appreciable amounts of fat need to be treated for a longer time and heated more vigorously to drive off the more volatile fatty materials.

Cool the beaker and contents, add 50 ml of water, and then transfer the solution quantitatively to a 100-ml calibrated flask by means of 6 N sulphuric acid contained in a wash-bottle. The final volume should be about 70 ml. Cool the solution, add 5 ml of xylene containing 1 per cent. of diethylammonium diethyldithiocarbamate, extract and continue as given under Method A. Calibrate in the same way as before, but use 70 ml of 6 N sulphuric acid instead of 5 ml of 6 N hydrochloric acid.

METHOD C (RAPID PROCEDURE)—

Introduce 2 or 5 g of material into a 50-ml calibrated flask and add 20 ml of 2 N hydrochloric acid. Heat the mixture on a boiling water bath for 15 minutes or until dissolution is complete. Cool the solution and dilute it to about 30 ml with water. Add 5 ml of xylene containing 1 per cent. of diethylammonium diethyldithiocarbamate, extract and continue as described under Method A (but see Note 2). Calibrate in the same way as before, but use 20 ml of 2 N hydrochloric acid instead of 5 ml of 6 N acid.

METHOD D (PROCEDURE FOR FRUIT JUICES AND BEVERAGES)—

Introduce 25 g of material into a 50-ml calibrated flask and add 5 ml of 6 N hydrochloric acid. Heat the mixture on a boiling water bath for 5 minutes. Cool the solution and add 5 ml of xylene containing 1 per cent. of diethylammonium diethyldithiocarbamate; extract and continue as described under Method A (see Note 2).

NOTE 2—
    In methods C and D it is sometimes necessary to centrifuge the mixture briefly so as to obtain a sufficient amount of the organic phase for aspiration.

OTHER METHODS—

When required, determinations were carried out after wet ashing with sulphuric and nitric acids. In this instance the last traces of nitric acid and oxides of nitrogen had to be eliminated before dilution to give a solution that was 6 N in sulphuric acid. From this stage Method B was followed.

Colorimetric lead determinations were carried out on the dissolved ashes by use of the diphenylthiocarbazone (dithizone) method.[23]

DISCUSSION AND RESULTS

ORGANIC EXTRACTION SYSTEM—

In order to test the effect of acidity on the extractability of lead, 5 ml of a 1 per cent. solution of diethylammonium diethyldithiocarbamate in xylene were added to a series of separating funnels containing 0, 10, 20, 30 and 40 μg of lead in 30 ml of the appropriate acid. The funnels were shaken for 1 minute, the organic phases were collected and then aspirated after 10 minutes. For comparative purposes the tests were repeated by using the ammonium tetramethylenedithiocarbamate - xylene and ammonium tetramethylenedithiocarbamate - isobutyl methyl ketone systems. In these instances, 5 ml of the 1 per cent. solution of ammonium tetramethylenedithiocarbamate in water were added first, followed by 5 ml of the solvent. The actual acidity at the time of extraction was therefore lower than that indicated. The upper limits of acidity consistent with satisfactory sensitivity and a linear calibration graph are given in Table II for the three systems.

TABLE II

MAXIMUM ACIDITIES FOR THE SATISFACTORY EXTRACTION OF LEAD WHEN USING
VARIOUS CHELATE - SOLVENT SYSTEMS

Acid	With diethylammonium diethyldithiocarbamate - xylene/N	With ammonium tetramethylene-dithiocarbamate - xylene/N	With ammonium tetramethylene-dithiocarbamate - isobutyl methyl ketone/N
H_2SO_4	12	12	12
HCl	4	2	2
HNO_3	4	2	0·5

The results for 12 N sulphuric acid (about 30 per cent. V/V) indicate that lead extraction can take place at high hydrogen-ion concentrations. With nitric acid, the reagents are presumably oxidised at high acidities.

When hydrochloric acid is used, formation of $PbCl_4{}^{2-}$ begins to occur in preference to complexation with the organic reagent as the acidity is increased. This behaviour was confirmed for the diethylammonium diethyldithiocarbamate - xylene system by extracting 20 μg of lead from 30 ml of 2 N hydrochloric acid containing various amounts of sodium chloride and sodium sulphate. Recoveries were as follows:

Salt	Concentration/N	Recovery, per cent.
No salt added	—	100
NaCl	2	37
NaCl	4	0
Na_2SO_4	2	100
Na_2SO_4	4	100

With diethylammonium diethyldithiocarbamate - xylene, the extractability from 6 N sulphuric acid was unaffected when 1 ml of 30 per cent. hydrogen peroxide was added to the separating funnels. However, no lead was extracted when 1 ml of 65 per cent. nitric acid was added (i.e., no extraction took place from a mixture that was about 6 N in sulphuric acid and 0·5 N in nitric acid). At the other end of the pH scale, lead is extracted up to pH 12.[24]

In practice, final acidities of 1 to 2 N for hydrochloric acid and of about 6 N for sulphuric acid were used after dry and wet ashing, respectively. At these acidities the sensitivity did not alter in response to slight changes in acidity, so that exact matching of the acidity of the standard and sample solutions is not required.

The calibration graphs of the four methods described are linear up to at least 40 μg of lead. For all products studied the calibration graphs obtained by the method of additions are also linear and have the same slope as those given by the external standards. This similarity indicates that the extraction of lead into the organic phase is complete and that there are no matrix interferences in the organic phase. The results obtained with the two methods of calibration are the same.

The effect on recovery of filling the calibrated flasks with water prior to aspiration was investigated. The recovery of 10 μg of lead in this way compared with that for extraction in a separating funnel (in which the organic phase does not come into further contact with water after phase separation) was 98 per cent. The loss is negligible in relation to the standard deviation of the methods. When the extract was shaken vigorously with 25 ml of water in a separating funnel, 98 per cent. of the lead remained in the organic phase, while 96 per cent. remained after two such extractions. It is considered that the addition of water down the side of the flask does not invalidate the results. Similar conclusions have been reached for lead with the ammonium tetramethylenedithiocarbamate - isobutyl methyl ketone system by other authors.[18,25]

The diethylammonium diethyldithiocarbamate - lead chelate is relatively stable with respect to time. Recoveries of lead from the organic phase, left in contact with about 50 ml of aqueous solution in the calibrated flasks for various times at room temperature, were as follows:

Time/hours	Recovery, per cent.
0	100
2	98
24	70
72	0

Provided that aspiration takes place within 2 hours of the extraction, results will be valid even if extraction of the standards and the sample solution are not performed simultaneously.

The presence of iron and tin does not affect the extractability of 20 μg of lead by 5 ml of a 1 per cent. solution of diethylammonium diethyldithiocarbamate in xylene in amounts up to 10 mg of iron(II) or iron(III), or 10 mg of tin(II) or tin(IV). In the presence of 20 mg of iron(III) no lead is extracted. As 5 ml of 1 per cent. diethylammonium diethyldithio-carbamate solution corresponds to 50 mg of the solid it can be assumed that lead extraction is suppressed because all of the chelating agent has been used preferentially by the iron(III). Such amounts of iron are not likely to be found in a food sample of 5 to 10 g (10 mg in 5 g corresponds to 2000 p.p.m.) and, in any event, the effect can be suppressed by the addition of ascorbic acid.

The presence of 20 mg of tin(IV) did not affect the extractability of lead; with 20 mg of tin(II), however, only 77 per cent. of 20 μg of lead was extracted. Again, such levels of tin are most unlikely to occur in a 5 to 10-g food sample. After ashing or acid digestion most of the tin would be in the form of tin(IV).

The diethylammonium diethyldithiocarbamate - xylene extraction system used here possesses the following advantages over the more widely used ammonium tetramethylene-dithiocarbamate - isobutyl methyl ketone system.

1. Xylene is superior to isobutyl methyl ketone for reasons of solubility as virtually no xylene is dissolved in the aqueous phase (0·02 g per 100 ml of water). As a result of this lack of solubility the volume of the aqueous phase need not be kept rigidly constant throughout one series of determinations, nor is it necessary to saturate the xylene with water before use.

2. Diethylammonium diethyldithiocarbamate is soluble in xylene. The two can there-fore be added in one operation. However, ammonium tetramethylenedithiocarbamate must be added in aqueous solution separately from the organic solvent.

3. Use of diethylammonium diethyldithiocarbamate allows the use of solutions that contain more hydrochloric and nitric acids. With ammonium tetramethylenedithiocarba-mate neutralisation or pH adjustment is usually carried out in practice.[4,18–20]

4. Diethylammonium diethyldithiocarbamate is less sensitive to oxidising agents than is ammonium tetramethylenedithiocarbamate; it is more stable to nitric acid, for example.

PRE-TREATMENT—

Much has been written on the relative merits of dry and wet ashing for lead determina-tions.[15,16,26] We generally prefer dry ashing, because it normally requires less supervision and lends itself more readily to dealing with large numbers of samples, and because the risks of contamination are reduced. Some products, however, require sulphuric acid to be present in order to prevent volatilisation of lead, and a maximum temperature of 500 °C must not be exceeded in this instance. Calcination may therefore take a long time and certain products cannot be ashed satisfactorily without the addition of nitrates.

Wet ashing is the more rapid method for single samples. The risk of the occurrence of losses by volatilisation is eliminated, but contamination from large amounts of reagents is more likely. As has been stated by several authors, samples high in calcium may give low results if sulphuric acid is used. In Method B, hydrogen peroxide is used rather than nitric acid for three main reasons. First, trace amounts of nitric acid must be removed before the addition of diethylammonium diethyldithiocarbamate if lead extraction is to be complete. Trace amounts of hydrogen peroxide do not affect the extractability of lead from 6 N sulphuric acid. Also with hydrogen peroxide, degradation need not be complete and the final solution can be dark in colour without invalidating the results. Therefore, the method involving the use of hydrogen peroxide requires much less time. Secondly, lead losses by co-precipitation with calcium sulphate occurred very much less often when hydrogen peroxide was used than when nitric acid was used in the presence of sulphuric acid. The mixture remains more dilute because with nitric acid the removal of the last traces of nitric acid by boiling results in dehydrating conditions that favour the precipitation of calcium sulphate. Thirdly, wet ashing with sulphuric and nitric acids gives results that are too low for products with tin contents above about 150 p.p.m., *i.e.*, for certain canned foods. The effect is due to the nitric acid in combination with the tin, as it was not noticed when wet ashing was performed with sulphuric acid and hydrogen peroxide (Tables III and IV). Because tin does not affect the extractability of lead at these concentrations the phenomenon was un-doubtedly caused by the precipitation of hydrated tin oxides, which absorbed lead.

TABLE III

RECOVERY OF 20 μg OF LEAD FROM REAGENT BLANK SOLUTIONS
CONTAINING VARIOUS AMOUNTS OF TIN

	Recovery of lead, per cent., by wet-ashing with	
Tin added/μg	$H_2SO_4 - H_2O_2$	$H_2SO_4 - HNO_3$
0	100	100
500	100	95
1000	100	24
2500	100	0

A similar effect was observed after dry ashing. In the absence of tin, dissolution of the ashes in hydrochloric or nitric acid gave the same results for lead. In the presence of tin, however, the recovery of lead was incomplete when nitric acid was used. This observation is in accordance with the known solubilities of tin(IV) oxide in hydrochloric and nitric acids.

TABLE IV

LEAD FOUND IN A VARIETY OF FOODS AFTER VARIOUS METHODS OF ASHING

Food	Tin, p.p.m.	Recovery, p.p.m., following dry ashing: solution in		Recovery, p.p.m., following wet ashing with	
		HCl	HNO_3	$H_2SO_4 - H_2O_2$	$H_2SO_4 - HNO_3$
Tomato purée	520	6·92	2·52	7·16	0
Curry sauce	510	0·30	0·11	0·30	0
Puszta soup	82	0·22	0·22	0·21	0·22

RESULTS OF ANALYSES—

The results obtained by atomic-absorption spectrophotometry after various methods of ashing are presented in Table IV. The results for a crude seasoning, obtained by use of Methods A and B, as well as with dry ashing followed by colorimetric lead determination, are listed in Table V. The seasoning comprised about 50 per cent. m/m of dry matter *plus* about 16 per cent. m/m of sodium chloride, and may be considered to be a "difficult" substance, with respect to both ashing and atomic-absorption spectrophotometry.

TABLE V

LEAD FOUND IN A CRUDE SEASONING BY VARIOUS METHODS
Five-gram sample used

	Lead found by use of Method A: dry ashing, followed by atomic-absorption spectrophotometry, p.p.m.	Lead found by use of Method B: wet ashing, followed by atomic-absorption spectrophotometry, p.p.m.	Lead found by use of dry ashing, followed by colorimetry, p.p.m.
	1·38	1·14	1·00
	0·94	1·18	1·04
	1·14	—	1·03
	1·18	—	1·26
	1·27	—	1·09
	1·15	—	1·16
	1·21	—	—
	1·20	—	—
	1·17	—	—
Mean	1·18	1·16	1·10
Standard deviation	0·12	—	—
Degrees of freedom ..	8	—	—

The results show good agreement and indicate that the atomic-absorption and colorimetric methods give comparable results and also that there is no loss of lead during ashing. The standard deviation for Method A is rather high for this product. Values found for three

more "normal" products, a goulash soup, a "Russian salad" (mixed vegetables) and a baby food (chicken dinner), are given in Table VI.

TABLE VI

LEAD FOUND IN VARIOUS FOODS BY USING METHODS A AND B

| | Lead content, p.p.m. | | | | | |
| | Goulash soup | | Mixed vegetables | | Chicken dinner | |
Method	A	B	A	B	A	B
	0·18	0·22	0·23	0·18	0·07	0·11
	0·18	0·16	0·23	0·20	0·10	0·11
	0·16	—	0·23	0·22	0·08	—
	0·18	—	—	0·20	0·17	—
	0·18	—	—	0·20	0·08	—
	0·17	—	—	0·22	0·14	—
	0·14	—	—	0·20	0·11	—
	0·14	—	—	0·20	0·13	—
	0·20	—	—	0·20	0·11	—
	0·21	—	—	0·22	0·08	—
Mean	0·174	—	—	0·204	0·107	—
Standard deviation	0·023	—	—	0·013	0·032	—
Degrees of freedom ..	9	—	—	9	9	—

DETECTION LIMIT AND SENSITIVITY—

The 283·3-nm wavelength line on the atomic-absorption instrument was chosen in preference to the 217·0-nm line because it is less noisy (the sensitivity when using the 217·0-nm line is about twice that for the 283·3-nm line, but it is difficult to translate this extra sensitivity into an improvement of the detection limit or of the precision because the 217·0-nm line is much noisier) and, more important, because the calibration is linear over a longer range.

The detection limit in foods, found by using 10-g samples, is about 0·02 p.p.m. under the conditions of Methods A and B. A further improvement should be obtained with integrating facilities or a high-intensity lamp, or both. At present, this limit precludes the methods from giving exact values for uncontaminated milk,[27–29] for which a 50-ml sample is required.

RAPID PROCEDURES—

The ashing step is not required for certain products that give a uniform suspension or a solution in water. Dissolution or suspension in 2 N hydrochloric acid, usually with heating, is satisfactory. In this instance the whole determination is carried out in a single calibrated flask and can be completed in 30 to 40 minutes (Method C).

The results obtained by use of this method are given in Table VII for tomato and apple purées. As all the lead in these products is extracted into the organic phase by diethyl-ammonium diethyldithiocarbamate, it is presumably present in the ionic form or else so loosely bound to the proteins that it is separated by acidification and warming.

The recovery of added lead was found to be 100 per cent. for saccharose on a 5-g sample. The rapid method, however, fails for lactose, full and skimmed milk powders because too much emulsion is formed on shaking. These last products must be ashed. Liquid milk also creates too much emulsion and must be ashed.

Recoveries of added lead were equally satisfactory for fruit juices and beverages, but normal levels of lead in these products, when uncontaminated, are too low to enable accurate results to be obtained.[21,30–32] For these, Method D, which entails the use of a larger sample size (25 g), gives a slight improvement and is preferred. The recovery of lead remains at 100 per cent. and the detection limit is less than 0·01 p.p.m. Method D is equally applicable to carbonated beverages, although it may be necessary to decarbonate them before analysis so as to avoid excessive formation of froth and emulsion on shaking. It is also successful for beer; no wines or spirits were included in the study.

No fruit juice or beverage was found that contained sufficient lead to facilitate the determination of a significant value for the standard deviation with Method D. The results for an artificially contaminated fruit juice are included in Table VII.

We have also used Method C to monitor the lead content of miscellaneous food additives, such as spice extracts, iron salts and lactic acid.   With iron salts, such as the saccharate and other products containing more than about 0·2 per cent. of iron, ascorbic acid (5 ml of a 10 per cent. solution) is added to reduce the iron to its bivalent state.   For lactic acid, the method of additions must be used for calibration because the partial solubility of lactic acid in xylene changes its viscosity, and thus its sensitivity (slope of the graph given by the sample relative to that given by the external standards).   Some results for iron saccharate are given in Table VII.

TABLE VII

LEAD DETERMINATION IN VARIOUS MATERIALS BY THE RAPID METHODS

Lead content, p.p.m.

	Apple purée, Method C* (10-g sample)	Tomato purée, Method C (5-g sample)	Orange juice, Method D*	Iron saccharate, Method C (2-g sample)
	0·13	1·90	0·67	2·0
	0·15	1·76	0·65	2·2
	0·13	1·84	0·62	2·4
	0·16	1·84	0·60	1·8
	0·13	1·76	0·60	1·9
	0·13	1·82	0·62	1·9
	0·14	1·88	0·62	2·1
	0·15	1·88	0·62	1·9
	0·15	1·82	0·60	1·9
	—	1·76	0·60	2·1
Mean	♦ 0·14	1·83	0·62	2·02
Standard deviation ..	0·012	0·053	0·024	0·181
Degrees of freedom ..	8	9	9	9

Lead content, p.p.m., by—

	Method B	Method B	dry ashing, followed by colorimetry
	0·15	1·80	1·95
	0·14	1·77	1·90

* With centrifugation.

EXTRACTION OF OTHER ELEMENTS—

According to the literature,[24,33] several elements in addition to lead can be extracted into carbon tetrachloride or chloroform with diethylammonium diethyldithiocarbamate.   Of these, silver, arsenic, bismuth, cadmium, copper, iron(III), mercury, molybdenum, selenium and zinc are probably of most interest in foods.   Provided that a suitable method of pre-treatment is available, there seems to be no reason why the diethylammonium diethyldithiocarbamate - xylene extraction system should not give equally reliable results for more than one of these elements, determined in the final extract from a single sample.   We have used it successfully for the simultaneous determination of lead and copper in lactic acid.

It was also confirmed that after wet ashing of a goulash soup according to Method B, cadmium and lead could be determined together in the final extract and that the recovery of added cadmium was 100 per cent.

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A Critical Study of Safranine O as a Spectrophotometric Reagent: a Rapid Method for the Determination of Trace Amounts of Antimony in Steel

By C. BURGESS,* A. G. FOGG and D. THORBURN BURNS

(Department of Chemistry, University of Technology, Loughborough, Leicestershire, LE11 3TU)

The behaviour of Safranine O (Basic red 2, C.I. 50240) in aqueous solutions has been investigated and its suitability as a spectrophotometric reagent is evaluated and discussed. A rapid method for the determination of antimony as a hexachloroantimonate(V) ion-association complex with Safranine O is described. This complex is extracted into benzene and is determined spectrophotometrically. The method is as sensitive and reproducible as the Rhodamine B method but it has the advantage that the determination can be carried out directly on solutions of steel without prior separation. Good agreement was found with standardised antimony values for five British Chemical Standards' steels.

A REVIEW of the literature[1–3] has shown that many workers have recently found basic dyes to be useful in determining large anions, and particularly P-block elements, as ion-association complexes. From the point of view of solution chemistry, however, the most important disadvantage of basic dyes is their behaviour in aqueous acidic solutions, *i.e.*, the slow protonation of the one or more basic amino groups present, and hence the lack of equilibrium in the aqueous phase during the extraction process. Xanthene dyes usually protonate very rapidly in aqueous solution but those in common use have two drawbacks: the ion pairs produced do not form true solutions, but can give rise to unstable colloidal suspensions[4]; and xanthene dyes can lactonise and be extracted in this colourless form. The extracted lactone can revert to the highly coloured quinonoid form under certain conditions.[5,6]

Various other dye groups have been investigated in these studies and Safranine O (Basic red 2, C.I. 50240), an azine dye, was found to show promise as a potential reagent for antimony.

EXPERIMENTAL

Safranine O protonates in acidic solution to yield the three forms shown in Fig. 1. The singly protonated blue form predominates in a solution of 5 to 7 M hydrochloric acid, but at higher acidities its concentration decreases. The analytically useful R^+ dye cation is virtually non-existent at a hydrochloric acid concentration higher than 6 M. The above conclusions were reached after considering the spectra of 0·0035 per cent. m/V solutions of Safranine O in solutions of various concentrations of hydrochloric acid, obtained in 10-mm glass cells with water as the reference solution (Fig. 2). It was found that at hydrochloric acid concentrations of 5 M and above, the absorbance at 520 nm was due almost entirely to the band overlap of the blue form ($\lambda_{max.} = 593$ nm).

Ideally, a dye cation that is not protonated in highly acidic solutions would be useful for the complexation of anions such as the hexachloroantimonate(V) ion, which are formed only under acidic conditions. This is true of Safranine O in 2 M hydrochloric acid, the optimum acidity for the formation and extraction of the complex formed with hexachloroantimonate(V), for which the R^+ form predominates.

It was noted that the molar absorptivities of Safranine O complexes were solvent dependent, in direct contrast with Brilliant green systems previously studied.[2,3] In order to examine this effect, a pure Safranine O salt that was soluble in a range of solvents was required; the tetrachloroaurate(III) salt was chosen because of its ease of preparation and its stability. Safranine O tetrachloroaurate(III) was prepared by precipitating the dye from an acidic, alcoholic solution with sodium tetrachloroaurate(III). The precipitate was filtered off, washed well with water and dried at 110 °C. Analysis of the salt, by ignition

* Present address: Department of Chemistry, The University, Southampton, SO9 5NH.
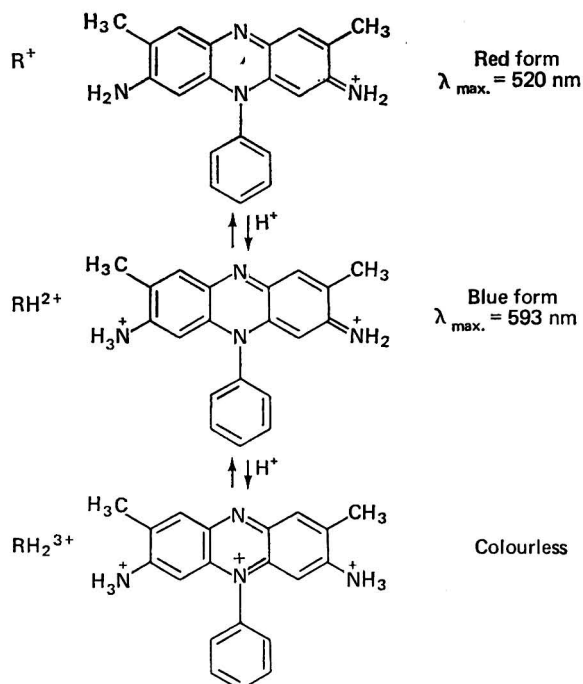
Fig. 1.   Equilibria of Safranine O in acidic solutions

at 600 °C to constant mass, showed the mean content of gold to be 29·3 per cent. (calculated for $C_{20}H_{19}N_4AuCl_4$: 30·1 per cent.).

A solution of this standard in $9 + 1$ V/V dioxan - acetone, diluted with various other solvents, enabled molar absorptivities to be calculated. As dilution ratios of 100:1 were used it was assumed that any original solvent effects would be swamped by the diluent. The results are shown in Fig. 3. The wavelength of maximum absorption varied from 522 to 538 nm.
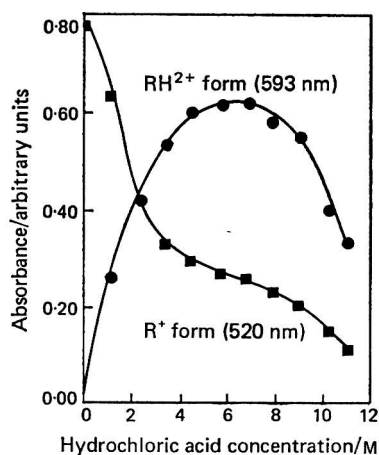
Fig. 2.   Variation of the forms of Safranine O with hydrochloric acid concentration

The reason for the variation of molar absorptivity with dielectric constant and the anomalous behaviour of alcohols is not clearly understood. It does explain, however, why some Russian workers needed to "stabilise" their extracts with ethanol or acetone when using non-triphenylmethane dyes.[7]
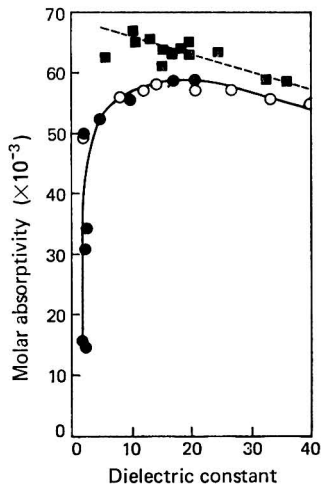
Fig. 3. Molar absorptivity of Safranine O tetrachloroaurate(III) in various solvents: ■, alcohols; ●, solvents other than alcohols; and ○, dioxan-water mixtures

In a preliminary study of the suitability of Safranine O as a reagent for antimony, the extractability of the hexachloroantimonate(V) anion into various solvents was examined. By using values obtained from Fig. 3 it was possible to calculate the percentage recovery of the antimony, assuming that the molar absorptivities of the tetrachloroaurate(III) and hexachloroantimonate(V) salts were identical in the same solvent. This assumption is reasonable as the chromophore in each instance is the dye cation. The results in Table I show that the higher apparent molar absorptivity obtained when isobutyl acetate rather than benzene is used as the extractant arises partly from the higher absolute molar absorptivity of the dye in isobutyl acetate and partly from a higher recovery of antimony. Subsequent work, however, showed that, of the solvents examined, only benzene could be used without interference from other ions present. The use of toluene in place of benzene was tried but, although free from interferences, it gave extracts that were not stable with time and much lower apparent molar absorptivities were obtained (see Table I). While this work was in progress, it was noted that Pilipenko and Shinh[8] had tentatively proposed a very similar method for the determination of antimony in steel. Their method, however, had not been applied to analysed steels and the extraction conditions were not optimised.

TABLE I

EXTRACTION RECOVERIES OF ANTIMONY UNDER EXPERIMENTAL CONDITIONS

Solvent			Apparent molar absorptivity*/ $l\,mol^{-1}\,cm^{-1} \times 10^{-4}$	Calculated apparent molar absorptivity†/ $l\,mol^{-1}\,cm^{-1} \times 10^{-4}$	Recovery, per cent.
Benzene	..	..	27·0	34·4	78·5
Toluene	..	..	16·2	31·2	51·9
Isobutyl acetate	..	..	48·3	53·5	90·3
o-Dichlorobenzene	..	..	36·3	55·5	65·5

* Obtained from extraction studies.
† Based on values shown in Fig. 3.

As the purpose of this work was to develop a method for the determination of antimony in steel, the following procedure was adopted with benzene as the extractant, in spite of its inherent toxicity.

CAUTION—

Benzene is a carcinogen and a cumulative poison and care should be taken with its use.

REAGENTS—

Standard antimony solution, 1000 μg ml⁻¹—An amount (1·3343 g) of antimony potassium tartrate was dissolved in 50 per cent. V/V hydrochloric acid and the solution made up to 500 ml in a calibrated flask. Working solutions containing 10 μg ml⁻¹ of antimony were made up by dilution of this standard with 50 per cent. V/V hydrochloric acid, and were prepared freshly when required.

Pure iron sponge—Johnson Matthey, Specpure grade.

Sodium nitrite solution—A 10 per cent. m/V aqueous solution was prepared.

Urea solution—A saturated aqueous solution was used.

Potassium chloride solution—A 40 per cent. m/V aqueous solution was prepared.

Tin(II) chloride solution—A 10 per cent. m/V solution was made up in 50 per cent. V/V hydrochloric acid.

Safranine O solution—A 0·1 per cent. m/V solution of the dyestuff in 0·1 M hydrochloric acid was made up. Hopkin and Williams RevectoR grade is suitable for use without further purification.

PROCEDURE—

Dissolve 1·00 g of steel in 10 ml of a 9 + 1 V/V mixture of concentrated hydrochloric and nitric acids and boil the solution so as to remove oxides of nitrogen. Cool, and dilute to volume with concentrated hydrochloric acid in a 25-ml calibrated flask.

Place 2-ml volumes of this solution and 8-ml volumes of 50 per cent. V/V hydrochloric acid in 100-ml separating funnels and cool them in a refrigerator to less than 5 °C. Add tin(II) chloride solution dropwise until all the yellow iron(III) colour is discharged and then add 1 ml of sodium nitrite solution. Shake the funnels for 1 minute, then to each add 2 ml of saturated urea solution and 40 ml of potassium chloride solution, and shake for 1½ to 2 minutes until all effervescence has ceased (carefully releasing the pressure from time to time).

Add 5 ml of Safranine O solution to each mixture and extract twice with 10-ml portions of benzene. Filter the benzene extracts through a Whatman No. 31 filter-paper, combine the two extracts in a 25-ml calibrated flask and make up to volume with pure benzene, after washing the filter-paper well. Measure the absorbance of the well mixed extract in 40-mm glass cells at a wavelength of 527 nm.

Prepare a calibration graph by using pure iron sponge and additions of standard antimony solution.

RESULTS

The calibration graph obtained was linear over the range 0 to 25 μg of antimony, with a small blank reading. The standard deviation at the 20 μg of antimony level was less than 2 per cent. The results obtained when using British Chemical Standards' steels are given in Table II.

TABLE II

DETERMINATION OF ANTIMONY IN BRITISH CHEMICAL STANDARDS' STEELS

B.C.S. number	Antimony content, per cent. *m/m* (standard value)	Antimony found, per cent. *m/m**	Coefficient of variation, per cent.
325	0·002	0·0014	2·8
326	0·005	0·0055	4·0
327	0·033	0·034	<1
328	0·026	0·028	3·1
330	0·018	0·019	2·5

* Mean of six determinations.

DISCUSSION

The results obtained with the British Chemical Standards' steel samples agree well, in most instances, with the standard values. The certificates of analysis of the standard steels indicated that the Rhodamine B method was used in obtaining the antimony value. The method generally adopted was that proposed by Kidman and Waite.[9]

In addition to the general disadvantages of xanthene dyes discussed earlier, the quantitative oxidation of antimony to antimony(V) was assumed to occur in the presence of nitric acid. Morello[10] has since shown that the oxidation with nitric acid may be incomplete.

In the recommended procedure, all of the antimony is reduced to the tervalent state prior to oxidation with sodium nitrite. The proposed method eliminates the necessity for evaporation to fumes and prior separation of the antimony required with the Rhodamine B method. Although the extraction of antimony is not complete, the extractability remains constant over the range studied. The procedure is rapid, the time for a single determination being largely dependent on the rate of dissolution of the steel sample. If dissolution is rapid, then the time taken for a complete determination is less than half an hour. Recently, Rhodamine S has been proposed as a reagent for antimony,[11] but we experienced difficulties with this method owing to the large, variable blank values obtained.

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An Emanation Method for Determining Radium Using Liquid Scintillation Counting

By K. G. DARRALL, P. J. RICHARDSON and J. F. C. TYLER

(*Department of Trade and Industry, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, SE1 9NQ*)

A very simple emanation method for determining radium is described. Radon is adsorbed on silica gel at the temperature of liquid nitrogen and the silica gel is transferred at 0 °C to a toluene-based liquid scintillator for counting in an automatic liquid scintillation spectrometer. The lowest limit of detection is 0·1 pCi of radon.

MOST of the methods that have been developed for the determination of radium by the emanation method involve the use of complex de-emanation systems and a special detector, the scintillation chamber. Lucas[1] achieved an efficiency of detection of 5·4 counts min^{-1} pCi^{-1} of radon at a background level of 0·06 counts min^{-1} and this probably represents the peak of development. In the emanation method of the "Standard Methods for the Examination of Water and Wastewater"[2] a Lucas cell is used. Other less complex systems have lower efficiency (E) and higher background (B) values; for example, E is 3·6 counts min^{-1} pCi^{-1} and B 1 count min^{-1} according to Conlan, Henderson and Walton,[3] and E is 2·5 counts min^{-1} pCi^{-1} and B 0·33 count min^{-1} according to Collinson and Hague.[4]

Our need was for a simple system for occasional use for the determination of radium in effluents and waters, and for unsupported radon in waters, *i.e.*, radon in excess of the equilibrium amount of radium parent, with a lower limit of detection of less than 1 pCi. It would be advantageous to use readily available counting equipment, and the automatic liquid scintillation spectrometer was attractive because of its high reliability and automatic facility for sample changing. It was expected that the high efficiency of alpha counting by liquid scintillation (100 per cent.) might offset the disadvantage of high background.

Noguchi[5] had attempted to use liquid scintillation counting for the determination of radon. After trapping the radon at the temperature of liquid nitrogen, without an adsorbent, he evaporated and collected it in a liquid scintillator but the results were not quantitative. Bonev and Akrabova[6] also attempted to determine radium by direct dissolution of radon in a liquid scintillator.

In the present investigation we have developed a system in which the main stages of ingrowth, de-emanation, trapping and counting can be carried out easily and simply with readily available apparatus. The radon is trapped on silica gel at the temperature of liquid nitrogen and transferred at 0 °C into the liquid scintillator, in which it is desorbed and counted. The losses of radon are small and reproducible.

METHOD

REAGENTS—

Nitric acid, sp. gr. 1·42—Analytical-reagent grade.

Potassium hydroxide pellets—Analytical-reagent grade.

Silica gel—"Purified" grade. Grind to a mesh size of 14 to 30 per inch and dry at 105 °C for 2 days.

Liquid nitrogen.

Toluene-based liquid scintillator, NE 233, *or equivalent.*

Alkaline EDTA solution—Dissolve 10 g of the disodium salt of ethylenediaminetetraacetic acid *plus* 10 g of sodium carbonate in water and dilute to 1 litre.

APPARATUS—

The apparatus as shown in Fig. 1, with a selection of de-emanation heads (B) to fit flasks of various sizes.

Liquid scintillation spectrometer—We used a Packard, Model 3320, Tri-carb and the temperature of the counting compartment was adjusted to 6 °C.

PROCEDURE—

The de-emanation apparatus is shown in Fig. 1. Add sufficient nitric acid to the de-emanation flask (A) to make the acidity 0·3 N when the flask is full. Fill the flask with a measured volume of sample, fit the de-emanation head (B) and bubble nitrogen through the solution until a volume equal to ten times that of the sample has been passed. Stopper the flask, making sure that no air bubbles are present. If necessary top up the contents of the flask with distilled water.
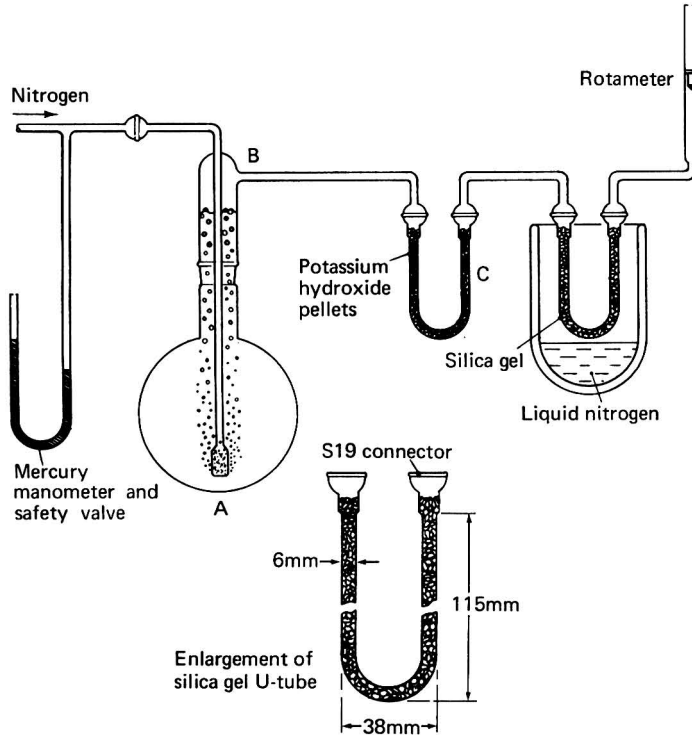
Fig. 1. Apparatus for de-emanation and trapping of radon
(lettered parts are described in the text)

Allow the solution to stand for the requisite ingrowth period and then remove the stopper and, without delay, connect the flask to B, which is already connected to the apparatus shown in Fig. 1. (During ingrowth the flask A is stoppered and is completely filled with solution. When the stopper is removed and replaced with B, there is a small displacement of solution equal to the volume of the glass frit and tube and then a large displacement is produced by bubbles when the nitrogen is turned on.) Pass ten volumes of nitrogen through the solution. Stop the flow, remove the flask containing liquid nitrogen and replace it with an ice-bath for 5 minutes. Remove the ice-bath, wipe the silica gel tube dry, disconnect it and pour the silica gel into 17 ml of liquid scintillator contained in a counting vial. Cap the vial, set it aside at room temperature for 3 hours, and then count. Carry out a blank and standard at the same time.

From the standard derive E, the number of counts per minute per picocurie of radon. Then

$$\text{Radium activity} = \frac{c}{Ef} \text{ pCi}$$

where c is the number of counts per minute (less background) for the sample and f the ingrowth factor $= 1 - e^{-\lambda t}$ where t is the ingrowth period and λ the disintegration constant for radon.

DISCUSSION

INGROWTH—

The vessel used for ingrowth and de-emanation can be of any size or shape but there may be restrictions on the material of construction. In this investigation only glass vessels with glass stoppers have been used. The vessel opening must, of course, be compatible with the de-emanation head. During the ingrowth period the vessel must be full. If a head-space remains, then radon will be lost when the stopper is removed. The solubility coefficient for radon in water is 0·25 at 20 °C, so the ratio of the concentration of radon in the gaseous phase to that in the aqueous phase is 4:1. Thus, for a 1-litre flask with a 2-ml head-space, 0·8 per cent. of the radon is in the head-space, whereas with a 150-ml flask, the smallest used here, 5 per cent. of the radon is in the 2-ml head-space. The ingrowth period should be at least 4 days (50 per cent. ingrowth) and there is little advantage in extending it beyond 84 per cent. ingrowth at 10 days.

DE-EMANATION—

The de-emanation head is sufficiently long to provide space for bubbling and can be made bulbous if necessary. The end of the inner tube is fitted with a sintered-glass diffuser, which should reach nearly to the bottom of the de-emanation vessel; this arrangement is essential for efficient de-emanation.[7] The sinter can become contaminated with radium, and the radon from this radium can appear in the first sample of a batch that is de-emanated. The sinter should therefore be stored in alkaline EDTA solution. Jacobi[7] recommended a total flow of nitrogen of volume equal to ten times that of the sample and it appears from the present results [Fig. 2(*a*)] that this is a satisfactory rule.
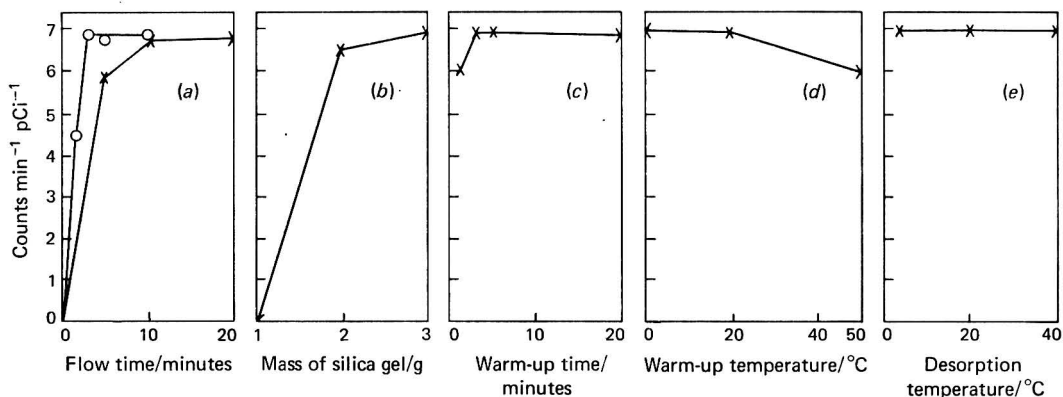
Fig. 2. The effect on the efficiency (counts min⁻¹ pCi⁻¹) of varying one at a time the parameters (*a*) flow time, (*b*) mass of silica gel, (*c*) warm-up time, (*d*) warm-up temperature and (*e*) desorption temperature. The constant parameters were: flow time, 10 minutes; mass of silica gel, 3 g; warm-up time, 5 minutes; warm-up temperature, 0 °C; flask volume: o, 150 ml and x, 1 litre; flow-rate of nitrogen, 0·6 l min⁻¹. The gain and discriminator controls of the liquid scintillation spectrometer were set to detect the maximum number of particles

DRYING—

The nitrogen stream from the de-emanation vessel is dried over pellets of potassium hydroxide in the U-tube (C), which is re-charged for each de-emanation with 20 g of the pellets.

ADSORPTION ON SILICA GEL—

The particle size of the silica gel is small enough to permit 100 per cent. adsorption of radon but large enough to give a stable bed at high nitrogen flow-rates and to have suitable pouring characteristics. The tube is charged with 3 g of silica gel and the diameter of the tube is such that the level of the bed is several centimetres above the top of the flask containing liquid nitrogen so as to minimise the condensation of radon on the walls of the tube. The variation in response with the mass of silica gel is shown in Fig. 2(*b*). The tube must not dip

into the liquid nitrogen, but only into the vapour above it, otherwise nitrogen will condense in the tube and when the temperature is subsequently raised the boiling nitrogen will remove some of the radon from the silica gel.   Even so, some nitrogen is adsorbed on the silica gel and for this reason the temperature is raised to 0 °C before adding the silica gel to the scintillator in order to prevent the release of this gas in the liquid scintillator.

TRANSFER OF RADON TO SCINTILLATOR—

When de-emanation is complete the nitrogen flow is stopped, the flask containing liquid nitrogen is replaced with an ice-bath and the tube warmed for 5 minutes.   It is wiped dry, unclipped, the silica gel is poured through a funnel into a 20-ml counting vial containing 17 ml of scintillator, and the cap is replaced immediately.   The volume of liquid scintillator is that which will give a small head-space, although the need for this precaution is not so great as with aqueous solutions, the solubility coefficient in toluene being 13·2 at 18 °C.   The effects of warm-up time and temperature on the count-rate are shown in Fig. 2 (c) and (d).

COUNTING—

The decay scheme for radon-222, with half-lives and particles emitted as indicated, is as follows—

^{222}Rn
(3·825 days)

$\downarrow \alpha$

^{218}Po ^{214}Po
(3·05 minutes)   (1·6 × 10^{-4}s)

$\downarrow \alpha$ ^{214}Bi ——— β α
                        (19·7 minutes)

^{214}Pb ——— β ^{210}Pb
(26·8 minutes)   (22 years)
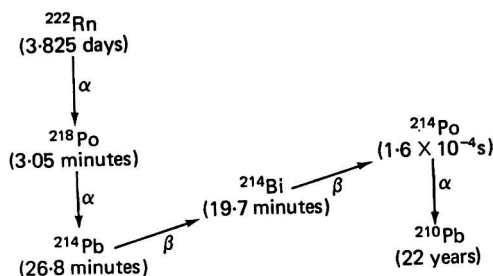
Radioactive equilibrium is reached after about 3 hours and the vials are left for this period before counting.   The growth of activity as radioactive equilibrium is attained and the subsequent decay as measured on the liquid scintillation spectrometer are shown in Fig. 3. During the 3-hour period the radon and its daughters equilibrate between the silica gel and the scintillator.   Most of the activity has been found to be present in the liquid scintillator and only a small proportion of the daughters remains adsorbed on the silica gel.   Horrocks
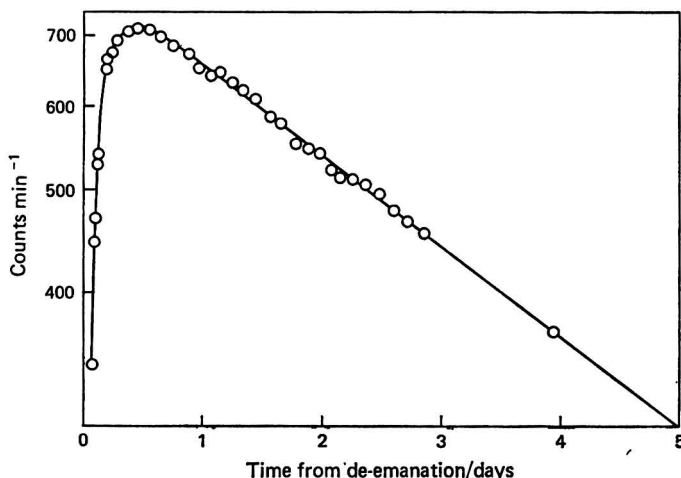
Fig. 3.   Growth and decay of radon and its daughters in a liquid scintillator

and Studier[8] showed that there was some adsorption of the daughters on small glass vials of 0·025-ml volume.

The final count-rate is independent of the temperature during the desorption period [Fig. 2(e)]. If the three alpha-particles and the two beta-particles were counted with 100 per cent. efficiency, 10·9 counts min⁻¹ pCi⁻¹ would be the maximum attainable over-all efficiency. In fact, only the alpha-particles are counted with an efficiency approaching 100 per cent., so that, in practice, when the gain and discriminator controls of the liquid scintillation spectrometer are set to detect the maximum number of particles, the highest efficiency observed is 7·0 counts min⁻¹ pCi⁻¹ of radon. Under these conditions the background is high at 60 counts min⁻¹. The best conditions for counting, *i.e.*, when the function (efficiency)²/(background) is at a maximum, are with the discriminators set as shown in the liquid scintillation spectrum recorded after the 3-hour equilibrium period in Fig. 4. At these optimum discriminator settings the over-all efficiency is 3·7 counts min⁻¹ pCi⁻¹ of radon and the background 6 counts min⁻¹. The lower limit of detection at the 95 per cent. confidence level for a 100-minute count is then 0·1 pCi of radon, which, for example, is equivalent to 0·2 pCi of radium after 50 per cent. ingrowth. Normally, five samples and a blank are run and these are counted for 20-minute periods in five cycles, which takes 10 hours. There is about 7 per cent. decay during this time, but it need not be taken into account if the standard is counted in the same cycle pattern.
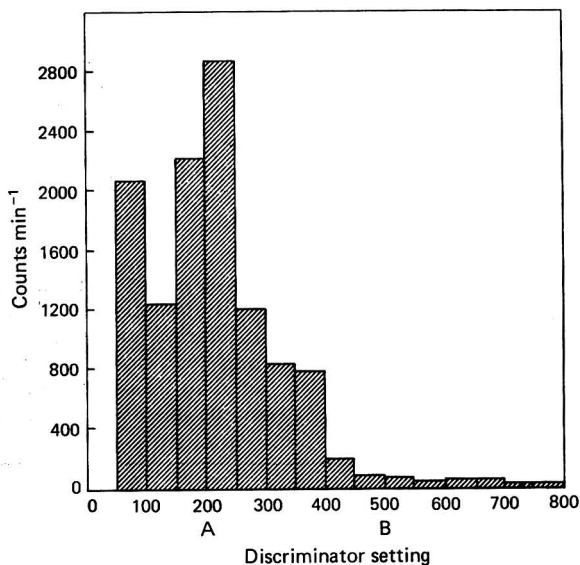
Fig. 4. The liquid scintillation spectrum of radon and its daughters at equilibrium. A to B is the counting region, *i.e.*, A is the lower discriminator setting and B is the upper discriminator setting

TOTAL RADON—

For total radon, the sample is taken directly in the de-emanation flask and care is taken to ensure that it is not aerated and that no head-space remains. The radon obtained from the first de-emanation is the total radon, and that from the second de-emanation, after a period of ingrowth, is the radon in equilibrium with radium. Some natural waters have a total radon activity several thousand times greater than the radium activity, *e.g.*, 20 000 pCi l⁻¹ of radon and 10 pCi l⁻¹ of radium. In this event, it is necessary to ensure that the remnants of the unsupported radon have been removed by additional periods of de-emanation before the start of the ingrowth period.

RESULTS

The recovery of radon was measured in two series of experiments by adding various

amounts of a radium standard obtained from The Radiochemical Centre to de-ionised water contained in the de-emanation flask (see Table I).

TABLE I

RECOVERY OF RADIUM-226 FROM 1 LITRE OF WATER

	Radium added/pCi	Radium found/pCi
	0·95	1·04 ± 0·33
	1·90	1·71 ± 0·34
Series I	4·73	4·52 ± 0·38
Ingrowth factor 0·498	9·47	9·75 ± 0·45
	18·93	19·29 ± 0·55
	47·34	47·13 ± 0·77
	118·2	117·7 ± 1·2
	0·95	0·65 ± 0·28
	1·90	1·88 ± 0·30
Series II	2·85	3·19 ± 0·32
Ingrowth factor 0·585	3·80	3·69 ± 0·33
	4·75	5·08 ± 0·35
	5·70	5·05 ± 0·35

The radium in a series of effluents was determined by the emanation method and by a barium sulphate co-precipitation method[9] (see Table II).

The limits of detection and the statistical limits shown in Tables I and II are based on counting only and are for 1·64 times the standard deviation.

TABLE II

RESULTS FOR THE DETERMINATION OF RADIUM-226 IN EFFLUENTS

	Radium-226, pCi l⁻¹, by		Total activity, pCi l⁻¹	
Effluent	Present method	Chemical method	Alpha-activity	Beta-activity
A	60·1 ± 0·9	64·1	310	18 000
B	99·4 ± 1·1	106·0	440	14 000
C	<0·14	0·10 ± 0·02	80	88 000
D	<0·14	0·21 ± 0·02	70	44 000
E	<0·14	0·36 ± 0·02	170	47 000
F	23·9 ± 0·8	25·2	433	7000
G	78·5 ± 1·2	64·9	320	32 000
H	41·0 ± 0·9	48·9	460	34 000
I	203·3 ± 2·0	210·0	1000	108 000

It is difficult to assess the accuracy of the chemical method, for radium-224 was present in the effluents in amounts up to one third of the radium-226 activity. Therefore, the total radium activity had to be resolved into its component activities by following the change in activity over a period of a few weeks,[10] except that with effluents C, D and E, in which the radium activity was very low, any radium-224 activity was allowed to decay away for 1 month before the source was counted. It is doubtful whether the activity recorded by the chemical method for effluents C, D and E was from radium for it was about one five-hundredth of the total alpha-activity of the effluent, and in a barium co-precipitation method the decontamination might not be more efficient than is indicated by this result.

We thank the Government Chemist for permission to publish this paper.

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Analytical Methods Committee

REPORT PREPARED BY THE ESSENTIAL OILS SUB-COMMITTEE

Application of Gas - Liquid Chromatography to the Analysis of Essential Oils

Part II.* Determination of 1,8-Cineole in Oils of Cardamom, Rosemary, Sage and Spike Lavender

THE Analytical Methods Committee has received the following report from its Essential Oils Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The constitution of the Essential Oils Sub-Committee responsible for the preparation of this report was: Mr. A. M. Humphrey (Chairman), Mr. J. H. Greaves, Mr. B. E. Kent, Mr. W. S. Matthews, Mr. R. G. Perry, Mr. J. Ridlington, Mr. R. A. Stocks and Mr. G. Watson, with Mr. P. W. Shallis as Secretary.

INTRODUCTION

The oxide 1,8-cineole, $C_{10}H_{18}O$, is a constituent of many essential oils, including cardamom, eucalyptus, lavender, rosemary, sage and spike lavender. The determination of cineole in essential oils has interested analysts for many years and several different methods have been proposed, none of which is entirely satisfactory. The application of gas chromatography to the determination of cineole was therefore studied by the Essential Oils Sub-Committee of the Analytical Methods Committee of the Society for Analytical Chemistry.

HISTORICAL REVIEW

Among the early analytical methods were those based on freezing-point determinations,[1,2] but such methods were generally restricted to oils of high cineole content. Cocking[3] recommended the formation of a cineole - o-cresol complex from which the original concentration of cineole could be assessed, but it has been shown to be unsatisfactory for certain oils of eucalyptus that contain only small amounts of cineole, and Cross, Gunn and Stevens[4] demonstrated the shortcomings of the method by means of infrared spectrophotometry when applied to a range of oils of spike lavender. Other methods involving complex formation were based on the use of 1-naphthol,[5] resorcinol[6] and phosphoric acid,[7] but such techniques necessitated a high initial level of cineole in the oils. A spectrophotometric method of utilising the development of a colour with an acidic solution of p-dimethylaminobenzaldehyde[8] was proposed, but has subsequently been criticised by Montes.[9] Infrared spectra of many essential oils containing cineole have been presented by Naves,[10] Presnell[11] and Maennchen,[12] but the work described by Cross, Gunn and Stevens[4] appears to be the first quantitative approach to the determination of cineole by this technique. The Essential Oils Sub-Committee, in its report issued in 1931,[13] included a detailed study of the o-cresol method of analysis, which has been included in the Society's book of standardised and recommended methods[14] and as a B.S.I. recommendation.[15]

The Sub-Committee responsible for the work at that time made the following statement: "The presence of alcohols, esters, aldehydes and ketones in quantity in cineole-containing oils has been shown to raise the freezing-point of the o-cresol compound. The method, therefore, indicates a higher result than the actual content. No means has been found for carrying out accurate determinations under these conditions, but the Sub-Committee is of the opinion that the 'apparent' cineole content shown by the o-cresol method has a considerable value. Fractions of eucalyptus oil are frequently used as adulterants in rosemary oil, and the apparent cineole content is a useful figure in the examination of such oils. The Sub-Committee recommends that the term 'Apparent Cineole Content by o-Cresol' should be used in connection with the oils of rosemary, spike and sage."

* For particulars of Part I of this series, see reference list, p. 623.

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The preliminary studies by gas chromatography of the determination of cineole included experiments on the resolution and recovery of mixtures of cineole, limonene, camphor and linalol. This work indicated that the flame-ionisation detector was particularly suitable for use in quantitative determinations, together with poly(ethylene glycol) (PEG) 400 as a stationary phase, but there could be problems with the satisfactory resolution of cineole.

The collaborating laboratories then applied their usual gas-chromatographic procedures to the determination of cineole in a selection of essential oils of commercial quality. Three oils were investigated and the cineole contents reported ranged from 12·7 to 15·3 per cent. for oil of rosemary, from 27·2 to 32·5 per cent. for oil of spike lavender and from 3·2 to 7·7 per cent. for oil of lavender, 40/42. It was agreed that there was some difficulty in obtaining satisfactory resolution of the cineole peak in the oil of lavender. Accordingly, a further study was made of (i) a natural oil of French lavender, (ii) a natural oil of spike lavender, and two additional samples, prepared by adding a known amount of cineole (5 per cent.) to each of these oils. It was decided that certain operating conditions and the method of measurement should be specified in order to achieve some degree of standardisation. The following conditions were agreed for the tests: stationary phase, PEG 400; column temperature, 75 to 85 °C; a flow-rate to ensure adequate resolution; flame-ionisation detector; and cyclohexyl acetate as the internal standard. The results and the method for the calculation of the peak areas are shown in Table I.

TABLE I

DETERMINATION OF CINEOLE (PER CENT. m/m) IN OILS OF FRENCH AND
SPIKE LAVENDER AND THE OILS WITH ADDED CINEOLE

Laboratory	French lavender	French lavender + cineole	Spike lavender	Spike lavender + cineole	Measurement*
A	2·31, 2·03 2·13, 2·04	6·1, 5·8, 5·7	24·2, 25·8, 27·5	32·1, 35·3, 31·8	(b)
B	3·6, 3·2, 3·3 2·2, 2·2, 2·2	6·5, 6·1 5·6, 5·7, 5·4	26·9, 28·4, 25·0 28·6, 29·1, 29·3	31·4, 33·6, 32·2 33·5, 34·5, 36·0	(b) (c)
C	2·84, 2·88, 2·93	6·3, 6·4, 6·2	29·4, 29·8, 29·4	33·0, 33·3, 33·2	(a)
D	2·69, 2·67, 2·72 2·92, 2·96, 2·90 2·75, 2·65, 2·72	5·6, 5·7, 5·7 5·7, 6·0, 5·8 5·8, 5·7, 5·6	25·6, 27·0, 25·9, 27·0 26·2, 26·8, 25·5, 26·5 28·2, 27·8, 27·9, 28·4	30·8, 30·5, 29·9, 29·3 27·6, 29·7, 29·1, 28·7 31·4, 31·8, 31·9, 31·8	(a) (b) (c)
E	1·97, 1·90, 1·93	5·0, 5·2, 5·1	27·4, 28·5, 27·4	32·7, 33·6, 32·9	(b)
F	1·76, 1·60 1·54, 1·46 1·53, 1·46	5·2, 5·3 4·6, 4·6 4·6, 4·6	24·0, 24·8 23·3, 24·6 23·1, 24·3	30·3, 28·5 27·0, 27·3 26·6, 27·3	(b) (c) (d)

*Method of calculating peak "area"—

(a) Integration.
(b) Peak height × width at half-height.
(c) Peak height × retention distance.
(d) Peak height only.

The results indicated that with the oil of spike lavender, it is possible to recover the cineole with an accuracy of 100 ± 10 per cent. Under similar operating conditions, the laboratories were unable to obtain adequate resolution of the cineole peak in oils of lavender so as to enable a satisfactory quantitative measurement to be made.

The Sub-Committee agreed that further studies would be necessary in order to develop a gas-chromatographic method for use with oils of low cineole content that would be acceptable to the analysts. It was further agreed that the o-cresol method was satisfactory for determining cineole contents of oils of over 40 per cent. In view of the findings from the experiments on oil of spike lavender, it was decided to concentrate on a procedure that could be applied to the examination of essential oils with cineole contents in the range 10 to 40 per cent.

For this investigation, a collaborative exercise was arranged on samples of oils of cardamom, rosemary, sage and spike lavender. It was decided that certain operating conditions should be similar for all laboratories, as follows: the column packing was to be supplied

from one source and to consist of 10 per cent. PEG 400 as stationary phase on Chromosorb W of 85 to 100 mesh, acid washed and silanised; cyclohexyl acetate as internal standard; column temperature 75 to 85 °C; and a flame-ionisation detector.   The assessment of peak areas was carried out by the peak height × retention distance method and the mean was determined from triplicate results. This procedure was discussed by the Sub-Committee in a previous report.[16] The results of these tests are shown in Table II, from which it can be seen that good agreement between laboratories was obtained; typical tracings for the different oils are shown in Figs. 1 to 5.

TABLE II

DETERMINATION OF CINEOLE IN OILS OF CARDAMOM, ROSEMARY, SAGE
AND SPIKE LAVENDER

| Oil | Laboratory | Cineole found, per cent. m/m | | | |
		1	2	3	Mean
Sage	A	11·91	11·43	—	11·7
	B	11·98	12·10	12·03	12·0
	C	12·19	12·02	11·98	12·1
	D	10·80	11·00	11·20	11·0
	F	10·8	10·7	10·8	10·8
	G	11·67	11·83	11·95	11·8
	H	—	—	—	11·7
	J	11·73	11·29	11·86	11·6
Spike lavender	A	25·19	25·65	—	25·4
	B	25·13	25·54	25·09	25·3
	C	25·40	25·08	25·02	25·2
	D	24·60	24·90	24·70	24·7
	F	25·5	25·8	24·8	25·4
	G	25·22	25·04	24·99	25·1
	H	—	—	—	24·4
	J	24·61	24·47	24·85	24·6
Cardamom	A	29·10	29·48	—	29·3
	B	28·88	29·72	30·07	29·6
	C	29·37	29·02	29·01	29·1
	D	28·85	28·40	28·50	28·6
	F	27·1	27·8	27·4	27·4
	G	28·80	29·08	28·99	29·0
	H	—	—	—	28·8
	J	29·05	29·92	29·29	29·4
Rosemary	A	42·91	42·35	—	42·6
	B	41·74	41·80	42·05	41·9
	C	40·87	40·50	40·80	40·7
	D	40·95	41·10	41·35	41·1
	F	42·0	42·2	42·5	42·2
	G	40·68	41·06	40·91	40·9
	H	—	—	—	41·1
	J	42·03	41·91	41·51	41·8

The Sub-Committee considered that the high cineole content of the oil of rosemary shown in Table II indicated that it was not a typical sample. Further tests under similar operating conditions were carried out on authentic samples of oils of Spanish and Tunisian rosemary, and the results are shown in Table III.

VARIATION IN LABORATORY WORKING CONDITIONS—

The operating conditions used by the collaborating laboratories are outlined in Table IV. PEG 400 was selected by the laboratories for use as the stationary phase as it was found to give satisfactory resolution and reproducible results. No apparent difference was observed in the results obtained by the use of either glass or stainless-steel columns.

No difficulty was experienced by collaborating laboratories when using "on column" injection, but it was felt that unduly high "flash injection" temperatures, as used by some members, could have adverse effects on the stationary phase. It was determined by experiment that a minimum flash temperature of 110 °C was required in order to vaporise the sample without affecting the peak shapes and their resolutions. An injection temperature of 120 °C

was considered preferable and a further experiment showed that this temperature did not make any noticeable difference to the performance of the column when operated under this condition for several days.

TABLE III

DETERMINATION OF CINEOLE IN OILS OF ROSEMARY

| Oil | | | Laboratory | Cineole found, per cent. m/m | | | |
				1	2	3	Mean
Spanish	..	..	B	23·4	22·9	23·3	23·2
			D	22·3	22·2	22·7	22·4
			F	23·0	22·9	23·1	23·0
			H	23·4	22·9	23·0	23·1
			J	23·1	23·3	23·2	23·2
Tunisian	..	..	B	26·8	26·7	26·6	26·7
			D	25·6	25·7	25·5	25·6
			F	27·0	27·3	27·4	27·2
			H	26·8	27·3	26·7	26·9
			J	26·8	26·5	26·9	26·7

CONCLUSIONS

Gas chromatography can be used for the quantitative determination of cineole. The results obtained from the series of oils of cardamom, rosemary, sage and spike lavender, containing cineole in the range of about 10 to 40 per cent., have enabled the Sub-Committee to recommend the procedure described in the Appendix, which should give results of acceptable precision, both within and between laboratories. The recommended method affords a means of determining the cineole contents of the stated oils without interference from other components, which gives a determination of hitherto unattainable accuracy.
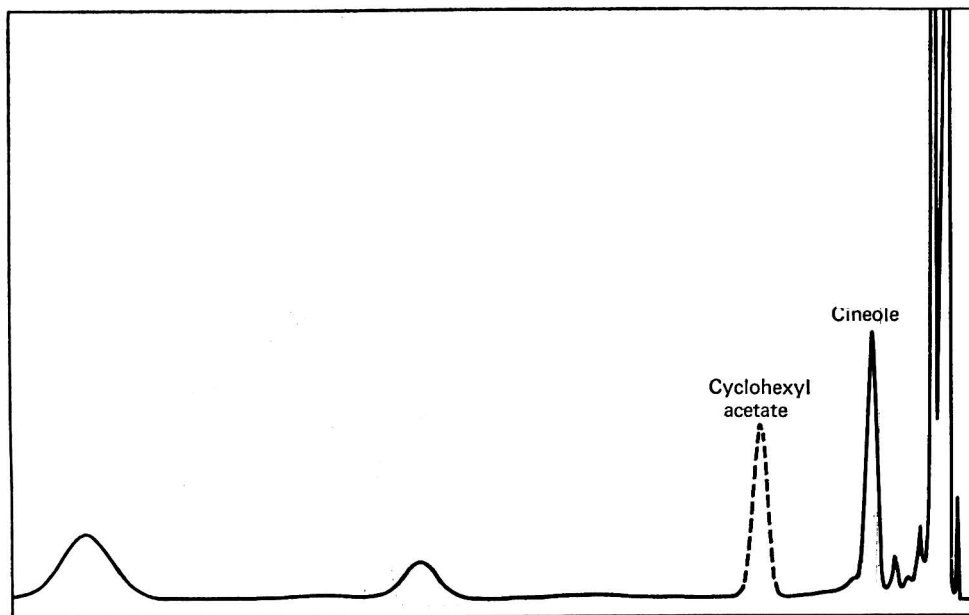
Fig. 1. Typical chromatogram of oil of spike lavender, with cyclohexyl acetate as internal standard.   Analysis time 1½ hours
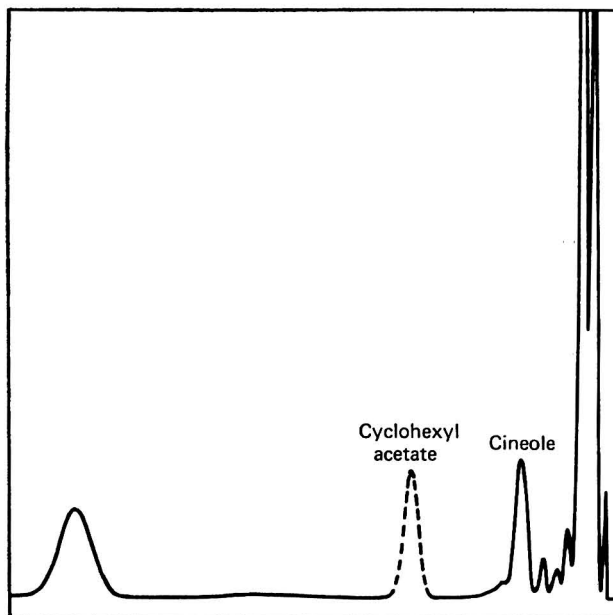
Fig. 2. Typical chromatogram of oil of sage, with cyclo-
hexyl acetate as internal standard.   Analysis time 1 hour
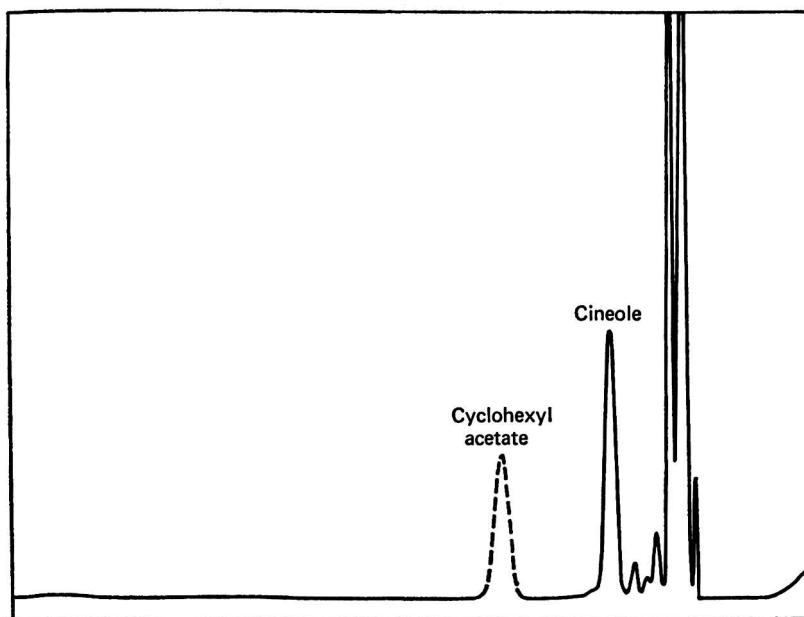
Fig. 3. Typical chromatogram of oil of cardamom, with cyclohexyl acetate
as internal standard.   Analysis time 2 hours
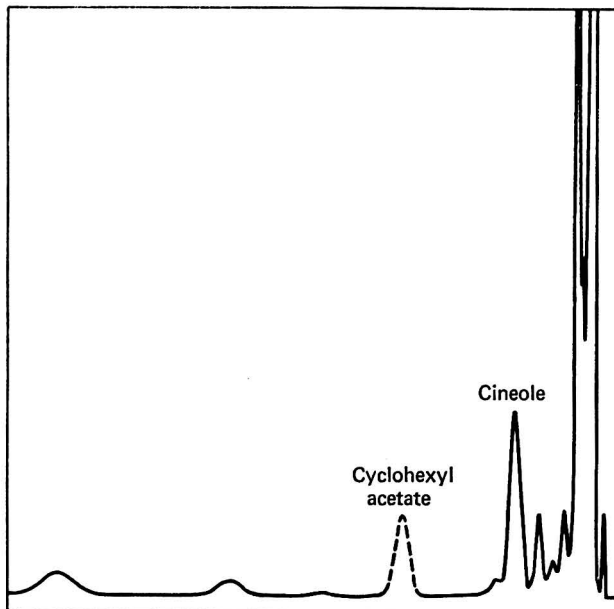
Fig. 4.   Typical chromatogram of oil of Tunisian rosemary, with cyclohexyl acetate as internal standard.   Analysis time 1 hour
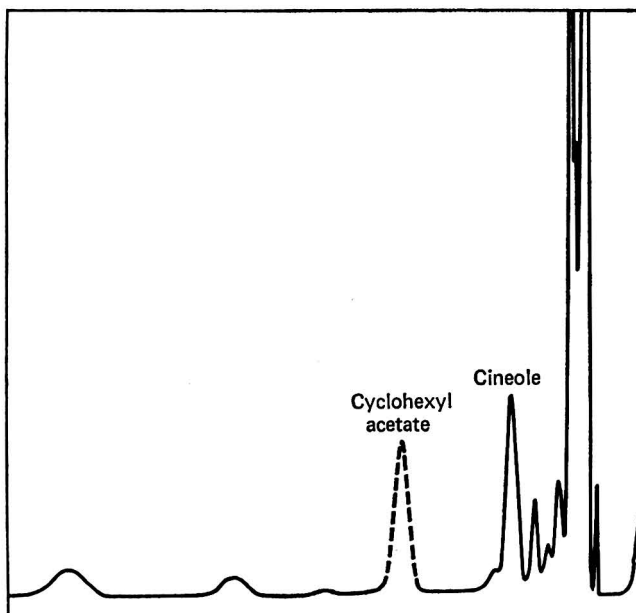
Fig. 5.   Typical chromatogram of oil of Spanish rosemary, with cyclohexyl acetate as internal standard.   Analysis time 1 hour

TABLE IV

GAS-CHROMATOGRAPHIC OPERATING CONDITIONS USED BY THE
DIFFERENT LABORATORIES

	A	B	C	D	F	G	H	J
Instrument	Pye 104	F & M 700	P.-E. F11	Pye 104	Pye 104	P.-E. F11	P.-E. 800	Pye 104
Detector	Dual flame	Dual flame	Dual flame	Dual flame	Dual flame	Dual flame	Flame	Dual flame
Internal standard				Cyclohexyl acetate				
Stationary phase				10 per cent. PEG 400				
Support				Chromosorb W, 85 to 100 mesh				
Column—								
Length	5 ft	6 ft	2 m	6 ft	6 ft	6 ft	6 ft	5 ft
Diameter	$\frac{1}{4}$ in	$\frac{1}{8}$ in	2·2 mm	$\frac{1}{4}$ in	$\frac{1}{4}$ in	$\frac{1}{8}$ in	$\frac{1}{8}$ in	$\frac{1}{8}$ in
Material	Glass	Stainless steel	Stainless steel	Glass	Glass	Stainless steel	Stainless steel	Stainless steel
Temperature/°C	90	90	85	85	90	90	90	90
Injector temperature/°C	On column	250	200	On column	On column	200	110	160
Flow-rate of carrier gas (nitrogen)	60 ml min⁻¹	40 ml min⁻¹	20 p.s.i.	40 ml min⁻¹ (argon)	9 p.s.i.	20 p.s.i.	40 ml min⁻¹	37 ml min⁻¹
Chart speed/ in h⁻¹	15	30	18	24	24	24	24	30
Sample size/μl	1·5	1	0·2	1	1	0·3	1	0·6

Appendix

RECOMMENDED METHOD FOR THE DETERMINATION OF 1,8-CINEOLE IN OILS OF
CARDAMOM, ROSEMARY, SAGE AND SPIKE LAVENDER (RANGE 10 TO 40 PER CENT.)
BY GAS CHROMATOGRAPHY

OPERATING CONDITIONS—

It is essential that throughout a determination the operating conditions are maintained as constant as is practicable. It is also essential to use the detector - amplifier system within its linear range.[17]

Detector	Flame ionisation.
Stationary phase	Poly(ethylene glycol) (PEG) 400.
Support	Chromosorb W, acid washed, silanised, 85 to 100 mesh.
Stationary phase loading ..	About 10 per cent. *m/m*.
Column	Length 6 feet; diameter $\frac{1}{8}$ to $\frac{1}{4}$ inch; glass or stainless steel.
Column temperature	Isothermal, 90 °C maximum.
Injection	On column, or if a pre-heater is used, maximum temperature 120 °C.
Gas flow-rates	To give satisfactory instrument performance.
Chart speed	15 inches per hour (minimum).
Peak heights (internal standard and cineole)	Within 40 to 75 per cent. of full-scale deflection.
Internal standard	Cyclohexyl acetate (purity by gas chromatography not less than 99·0 per cent.).
Cineole	Purity by gas chromatography not less than 99·0 per cent.
Solvent	Ethyl acetate.
Sample size	Such that the internal standard and cineole peaks fall within the linear range.

DETERMINATION OF THE FACTOR, *f*, FOR THE INTERNAL STANDARD (CINEOLE = 1)—

Make all weighings to an accuracy of 0·2 mg.

Weigh about 0·25 g of cineole and 0·5 g of cyclohexyl acetate (or such other mass as will give about equal heights for the two peaks), and dilute them with 10 ml of solvent. Inject

1·0 μl, or such other volume as will ensure response within the linear range, and calculate to three decimal places the factor, f, from the equation—

$$f = \frac{h \times d}{h_c \times d_c} \times \frac{m_c}{m}$$

where h_c is the height of the cineole peak; d_c the retention distance of the cineole peak; h the height of the cyclohexyl acetate peak; d the retention distance of the cyclohexyl acetate peak; m the mass of cyclohexyl acetate; and m_c the mass of cineole.

Repeat twice on the same solution, and use the average of the three values of f in the calculation of the cineole content of the sample.

DETERMINATION OF THE CINEOLE CONTENT OF THE SAMPLE—

Weigh an adequate amount of the sample (0·5 to 2·5 g, according to whether more or less cineole is present) and about 0·5 g of cyclohexyl acetate that will give about equal heights for the two peaks, and dilute with 10 ml of solvent.   Inject about 1·0 μl, or such other volume as will ensure response within the linear range of the instrument, and calculate the cineole content of the sample to two decimal places from the equation—

$$\text{Cineole, per cent.} = f \times \frac{H_c \times D_c}{H \times D} \times \frac{M}{M_s} \times 100$$

where f is the factor determined as described above; H_c is the height of the cineole peak; D_c the retention distance of the cineole peak; H the height of the cyclohexyl acetate peak; D the retention distance of the cyclohexyl acetate peak; M the mass of cyclohexyl acetate; and M_s the mass of sample.

Repeat twice with the same solution and report the average of the three results to one decimal place.

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NOTE—Reference 16 is to Part I of this series.

Book Reviews

ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGION. Edited by L. LÁNG. Volume XVII. Pp. 400 (loose-leaf). Budapest: Akadémiai Kiadó. 1972. Price £7.

This volume takes the series to 3212 compounds. It contains spectra of a considerable range of substances but on this occasion the main emphasis is on heterocyclic compounds. There is a long series of pyrimidinone derivatives and among the other groups considered are pyrazines, pyridazines, quinoline and quinolone derivatives together with quinoxalines and quinolizines. Included also are some imidazole, thymine, uracil and tryptophan derivatives. In most instances, spectra in two solvents are recorded and, when appropriate, in acidic and alkaline media.

The high standard of the series is maintained.   R. A. MORTON

ENVIRONMENTAL MERCURY CONTAMINATION. Edited by ROLF HARTUNG and BERTRAM D. DINMAN. Pp. x + 349. Ann Arbor, Michigan: Ann Arbor Science Publishers Inc. 1972. Price £9·40.

Any information concerning the distribution of a heavy metal in the environment is very welcome, especially when that metal is as toxic or as topical as mercury. This book is admirable in that it states the problems involved and gives many examples of work undertaken and makes it clear that a great deal of work still has to be done, and also that better analytical techniques need to be achieved, particularly for very low levels of mercury.

The book can be divided into four parts. In the first part, the occurrence of mercury in the environment and man is described, together with the various ways in which mercury is released into the environment. Special attention is given to results of work in areas where the release of mercury is or was high, such as the Great Lakes in America and Minimata in Japan. The analyses are mainly of water, fish, birds and humans. The second part describes the methods of analysis that have been suggested or used, the first half of which contains a very comprehensive review with thirty-two pages of references. The second half gives a series of short accounts of promising analytical methods applied to real samples, including the use of neutron-activation analysis for determining total mercury. This section underlines the usefulness of round-robin sample surveys and the need for more standard reference materials. In the third part, the environmental dynamics of mercury are discussed. The questions asked are—When the various forms of mercury are released, where do they finish up? What chemical transformations are there? Thus topics such as methylation of mercury, interaction with food chains and adsorption - release from soils are given in some detail. In the fourth part, the biological effects of mercury compounds are presented. This very important section contains a detailed account of the effect and distribution of methylmercury in humans and other animals during the terrible Minimata incident. It also contains a survey on people subjected to chronic exposure to inorganic mercury from an industrial plant. Work on attempts to correlate dose - response relationships and to arrive at toxicity limits are included, with interesting comments on the possibility of detecting sub-clinical effects of mercury ingestion.

Frankly, this is a good book that can be recommended in spite of its very high cost. The only criticism that may be levelled is that the data are based on a conference held in 1970 while we are now in 1973.   G. NICKLESS

METALLURGICAL STEREOGRAPHIC PROJECTIONS. By J. S. SMAILL. Pp. viii + 262. London: Adam Hilger Ltd. 1972. Price £7.

This book is based on a computer program developed to aid structure identification by electron diffraction with the electron microscope. Stereographic projections (162 in all) are given in Chapter 5 for the structures of the common metals and metal oxides, carbides, nitrides and sulphides.

It is claimed that the program is not restricted to metallurgical structures but is completely general in application and could be applied to mineralogical structures. The program is capable of generating stereographic structure about any given pole direction or pole plane.

The book would be of some interest to specialists in X-ray analysis and those who use the A.S.T.M. powder diffraction file.   V. J. JENNINGS

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Part II.   Determination of 1,8-Cineole in Oils of Cardamom, Rosemary, Sage and Spike Lavender

Report prepared by the Essential Oils Sub-Committee.

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