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The Application of Atomic-absorption Spectrophotometry to the Analysis of Iron and Steel

A Review*

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Atomic-absorption spectrophotometry is a useful technique for the determination of many of the minor elements commonly present in iron and steel. It is rapid and relatively free from most of the troublesome inter-element effects associated with alternative techniques such as colorimetric and polarographic analysis. This paper reviews published and certain unpublished information dealing specifically with the analysis of iron and steel by atomic-absorption spectrophotometry.

Since 1961 about twenty-five papers have been published concerned with the use of atomic absorption for the analysis of iron and steel. Procedures have been proposed for the determination of twelve elements with the main emphasis on low-level concentrations, but some authors have also suggested possible application to elements present in alloying concentrations. Most of the elements commonly found in iron and steel have been determined. Notable exceptions are carbon, sulphur and phosphorus, the resonance lines of which lie in the vacuum ultraviolet region of the spectrum, and silicon, arsenic, zirconium, niobium, tantalum and tungsten which form refractory compounds in the flame that are not easily dissociated into atomic form. The determination of aluminium is being studied in the author's laboratory, and this will be considered in a separate publication.

In atomic-absorption procedures it is usual for the sample to be dissolved and the solution then sprayed into the flame; hence the outstanding advantage of the method is its simplicity. Most of the published methods have aimed at perpetuating this simple approach; occasionally, suppressing agents are added but the original solution is more often used without any time-consuming separations. The technique can, of course, be used as a means of completing certain determinations, for example, after concentration of the elements sought by the use of selective organic reagents. On many occasions, this approach offers advantages to the analyst but chemical pre-treatment should be avoided when possible.

This review is restricted to papers dealing specifically with iron and steel. In addition, reference is made to unpublished work in the author's laboratory and to information made available by colleagues in industry. Each element is dealt with separately and a table is included in which are listed the instrument, resonance line, flame, gas flow-rate and absorption path length used. Similarly, the composition of the solution sprayed into the flame is given, together with analytical sensitivity in terms of element concentration (in p.p.m.) giving rise to 1 per cent. absorption (0·0044 optical density).

The deficiencies in the use of the term "sensitivity" have been pointed out by Slavin, Sprague and Manning,[1] and Elwell and Gidley.[2] Sensitivity is dependent upon many variables; most authors only provide details of gas flow-rates, but position of the absorption path in the flame, monochromator slit width and rate of solution uptake into the atomiser are equally important. When a stable flame such as air - acetylene is used to determine easily dissociated elements, the actual limit of detection may be several times better than the quoted sensitivity value, but in the determination of elements such as aluminium and titanium with the relatively unstable nitrous oxide - acetylene flame, the signal-to-noise ratio is unfavourable, and the detection limit may be of the same order as the sensitivity. When the noise level is high a chart recorder is an essential accessory in order to permit accurate measurement of absorption signal superimposed on the background noise.

The principles of atomic absorption and the techniques of measurement will not be discussed in this review, as they have been adequately covered by Elwell and Gidley[2] and Robinson.[3] Elwell and Gidley in their monograph also provide a tabulated list of instruments

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

that were commercially available in mid-1966. Since then several new instruments have appeared, notably the Techtron AA4 and the Hilger and Watts Atomspek. Of special interest is the Techtron AR-200, in which the conventional monochromator is replaced by a resonance detector of the type described by Sullivan and Walsh.[4]

Magnesium

Belcher and Bray[5] of B.H.P. Ltd., in Australia, have proposed a simple procedure for the determination of magnesium in iron to replace traditional procedures, most of which are tedious and require separation of matrix elements. Measurements are made by absorption of the 285·2-mμ resonance line in an air - acetylene flame.

The 1-g sample is dissolved in 30 ml of hydrochloric acid (1 + 1) and 5 ml of concentrated nitric acid. After evaporation to dryness the residue is baked at 200° C for 5 minutes, then re-dissolved in 10 ml of concentrated hydrochloric acid. The solution is diluted with 50 ml of water, and silica removed by filtration, washing with dilute hydrochloric acid (5 + 95). After the addition of 5 ml of 18 per cent. w/v strontium chloride solution, the filtrate is diluted to 200 ml and absorption measurements made.

The addition of strontium is made to suppress interference from aluminium present in up to 2 per cent. concentration. No interference is encountered from 0·5 per cent. each of phosphorus, titanium or zirconium, 1 per cent. of zinc, 2 per cent. each of vanadium, manganese or silica, 5 per cent. each of nickel, copper or molybdenum and 10 per cent. of chromium. Variations of ±25 per cent. in the concentration of iron, strontium chloride and hydrochloric acid are without significant effect.

In 1961, the Standards Association of Australia Committee (S.A.A.) CH/4 on Sampling and Analysis of Ferrous Metals tested Belcher and Bray's method by analysing six samples of iron containing 0 to 0·17 per cent. of magnesium.[6] Satisfactory results were obtained by four analysts, and the method was published as Australian Standard Method, AS KI: Part 20: 1964.

The Australian procedure has been tested by Sprague and Slavin,[7] and Clarke (in unpublished work at B.C.I.R.A.). The interference effect of aluminium was confirmed by Clarke, who found that the addition of strontium was effective as a suppressive agent, except for a sample of iron containing 22 per cent. of aluminium. An apparent interference effect caused by a large amount of nickel was also noted by Clarke and Cooke (in unpublished work). Sprague and Slavin, and Clarke, considered the procedure to be satisfactory for the analysis of cast iron. Clarke, who used a rapid method in which removal of silicon by dehydration was omitted, obtained a satisfactory result on a standard sample of nodular cast iron, the time required to complete a determination being less than 7 minutes.

Table I

Instrument conditions and sensitivities for magnesium

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Belcher and Bray[5] Special	Air - acetylene, 285·2 mμ, 10-cm path	0·5 per cent. w/v of sample in dilute HCl (5 + 95) + Sr	Not stated	—
Clarke (unpublished work) Evans Electroselenium Ltd. (E.E.L.)	Air - acetylene, 285·2 mμ	0·5 per cent. w/v of sample in dilute HCl + Sr	Not stated	—
Clarke Southern A1750	Air - acetylene (6 and 1·8 litres per minute), 285·2 mμ, 12-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99) + Sr	0·007	0·0007
Clarke Optica Densatomic	Air - acetylene (15 and 3 cubic feet per hour), 285·2 mμ, 5-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99) + Sr	0·012	0·0012
Clarke and Cooke Unicam Model SP90	Air - acetylene (5 and 1·8 litres per minute), 285·2 mμ, 10-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99) + Sr	0·012	0·0012
Sprague and Slavin[7] Perkin-Elmer Model 303	Air - acetylene, 285·2 mμ	0·1 per cent. w/v of sample in dilute HCl (1 + 99) + Sr	Not stated	—

Calcium

In preliminary, unpublished work in the author's laboratory, it has been shown that calcium can be determined in stainless and maraging steel after a preliminary separation by mercury-cathode electrolysis. Previous work on the development of a method for the determination of lime in steel-making slag has suggested that, in addition to phosphorus, certain other elements, such as vanadium and titanium, which would be present after electrolytic separation, might interfere in absorption measurements. For this reason sufficient strontium solution was added as a releasing agent to give a concentration of 2000 p.p.m. in the final solution.

In the proposed procedure the 1-g sample is dissolved in aqua regia and the solution evaporated to incipient fumes, after the addition of 20 ml of perchloric acid. The solution is then electrolysed and the electrolyte diluted to 100 ml, after the addition of strontium. Rigid precautions must be taken to prevent contamination from the calcium present as a filler in the rubber used in laboratory apparatus.

Calibration graphs, prepared by adding calcium to high-purity iron and electrolysing the solution, were in good agreement with those prepared by adding calcium to dilute solutions of perchloric acid. Further work is required to confirm the non-interference of molybdenum and tungsten present with the calcium after electrolysis.

More recent work has suggested that small amounts of calcium can be determined in alloy steel, without chemical separation, by using a nitrous oxide - acetylene flame. The 1-g sample is dissolved in 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, the solution filtered and diluted to 100 ml. A "standard addition" technique is recommended for calibration purposes.

Table II

Instrument conditions and sensitivities for calcium

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Thulbourne and Scholes Hilger AA2	Air - acetylene, 422·7 mμ, 13-cm path	1 per cent. w/v of sample in dilute $HClO_4$ (1 + 4) + Sr after electrolytic separation	0·2	0·002
Thulbourne and Scholes Hilger AA2	Nitrous oxide - acetylene, 422·7 mμ, 5-cm path	1 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (3 + 1 + 16)	0·15	0·0015

Titanium

Amos and Willis[8] have demonstrated the feasibility of titanium determinations by atomic absorption with a nitrous oxide - acetylene flame. Headridge and Hubbard[9] used this flame to determine titanium in steel, magnet alloy and cast iron without preliminary separation. Hydrofluoric acid was chosen as solvent in order that niobium and tungsten present in alloy steel would be held in solution.

Headridge and Hubbard found that the sensitivity of titanium absorption in the nitrous oxide - acetylene flame was low (6·5 p.p.m.), but a considerable improvement could be achieved by the use of aqueous - ethanolic sample solutions. In a mixture of M hydrofluoric acid and ethanol (1 + 9) the sensitivity was 2 p.p.m.; in the presence of iron, the authors estimated that the actual limit of detection would be about 1 p.p.m. of titanium. With the exception of aluminium, alloying elements commonly present in steel do not affect absorption measurements. Aluminium present at the 10 per cent. level causes a slight enhancement, but this effect can be prevented in the analysis of magnet alloys by omitting the ethanol addition. Analytical results reported by Headridge and Hubbard on four alloy steels, and one cast iron with a slightly different sample solution composition, agreed closely with accepted values by other techniques.

Mostyn and Cunningham[10] determined titanium in nickel and iron alloys with a nitrous oxide - acetylene flame by direct dissolution of the sample in aqua regia, avoiding the use of hydrofluoric acid. Interference from other elements present in alloys was significant, and

it was found that almost complete matching of calibration solutions and test sample was necessary in order to achieve reasonable accuracy. Interference effects could, however, be stabilised by the presence of an alkali metal such as potassium, and an addition of 1000 p.p.m. of this element was adopted in the proposed procedure. Bowman and Willis[11] preferred to use a sulphuric acid sample solution. The presence of iron was found to depress titanium absorption at sulphuric acid concentrations less than N, but to enhance it at higher acid concentrations, maximum absorption being shown at an acid concentration of 4 N. This enhancement effect depends not only on the concentration of iron and acid, but also on the type of flame used and the position of the absorption path in the flame. The method finally adopted was based on matching calibrations with respect to the major constituents present in the test samples. Satisfactory results are given for several standard samples of low alloy and stainless steel.

TABLE III

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR TITANIUM

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Headridge and Hubbard[9] Hilger AA2	Nitrous oxide - acetylene (6·25 and 3·8 litres per minute), 364·3 mμ, 5-cm path	0·5 per cent. w/v of sample in a mixture of 0·1 M HF and ethanol (1 + 1)	3	0·06
Mostyn and Cunningham[10] Perkin-Elmer Model 303	Nitrous oxide - acetylene, 364·3 mμ, 5-cm path	0·1 per cent. w/v of sample in dilute HCl (2 + 98) + 1000 p.p.m. of K	3·5	0·35
Bowman and Willis[11] Techtron AA4	Nitrous oxide - acetylene, 364·3 mμ, 5-cm path	0·8 per cent. w/v of sample in dilute H_2SO_4 (1 + 9)	3	0·04

VANADIUM

There is relatively little published information on the determination of vanadium by atomic absorption. In 1965, Trent and Manning[12] described vanadium determination with a pre-mix, oxy-acetylene burner. In this work clogging of the burner was encountered when aspirating steel-sample solutions. Although the method of iron separation used to avoid this difficulty made the procedure longer than desirable, the vanadium determination could be made on a routine basis, provided that the burner was controlled to prevent flashback. Capacho-Delgado and Manning[13] used a high intensity lamp and made absorption measurements at 318·4 mμ in an acetylene - nitrous oxide flame. With a sample solution containing dilute sulphuric and phosphoric acids satisfactory results are reported for vanadium contents of 0·02 to 0·05 per cent. present in alloy-steel samples. Both sulphuric and phosphoric acids interfere in absorption measurements of vanadium, but this effect is eliminated by calibrating in the presence of both acids.

TABLE IV

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR VANADIUM

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Capacho-Delgado and Manning[13] Perkin-Elmer Model 303	Nitrous oxide - acetylene, 318·4 mμ	0·5 per cent. w/v of sample in a mixture of H_2SO_4, H_3PO_4 and water (3 + 3 + 94)	1·3	0·026

CHROMIUM

Kinson, Hodges and Belcher[14] determined chromium by using the 359·4-mμ resonance line in an air - acetylene flame. Interference from nearby argon lines prevents the use of the more sensitive chromium line at 357·9 mμ, but this line may be used with advantage if lamps are available filled with a gas other than argon.

The effects of different solvent acids were examined; a mixture of sulphuric and phosphoric acids was selected because of its advantage in retaining tungsten and other acid-hydrolysable elements in solution. Belcher used this same solution for the determination of manganese, nickel and copper (see following sections).

In the proposed procedure, the 1-g sample is dissolved in 30 ml of a mixture of sulphuric acid, phosphoric acid and water (3 + 3 + 14), the solution oxidised with nitric acid and then evaporated to fumes. After filtration the solution is diluted to 100 ml for absorption measurements.

Iron causes a major reduction in absorption but this may be maintained at a constant level by using a sample solution containing sulphuric and phosphoric acids. Interference from molybdenum, tungsten and nickel varies with flame type and height of the absorption path above the burner. The most useful flame type is a slightly rich mixture (10·4 litres of air per minute and 2·4 litres of acetylene per minute with the absorption path 8 mm above the burner top. Under these conditions there is no interference from 5 per cent. each of nickel, manganese, copper or tungsten, 2 per cent. each of aluminium or vanadium, and 1 per cent. of molybdenum. Higher percentages of nickel, tungsten and molybdenum cause interference; at the 0·5 per cent. chromium level, 20 per cent. of nickel and 20 per cent. of tungsten give slightly high results, and 5 per cent of molybdenum gives slightly low results.

Giammarise,[15] who used the 357·9-mμ line, investigated the effects of ammonium chloride and strontium chloride for the suppression of iron interference in chromium determination. When iron is present at concentrations of 0·1 g per 100 ml, or less, it is recommended that 20,000 p.p.m. of ammonium chloride should be added to eliminate interference at the 1 to 4 p.p.m. chromium level. Strontium chloride also exhibits a suppressive effect but it is less effective than ammonium chloride. Barnes[16] has also shown that the addition of ammonium chloride doubles the sensitivity for chromium determination in the presence of iron.

Barnes' findings have been confirmed by Clarke and, by using the resonance line at 357·9 mμ and 1 per cent. w/v sample solution in dilute hydrochloric acid (1 + 9), Clarke and Cooke obtained a curved calibration graph over the range 5 to 100 p.p.m. (0·05 to 1 per cent. of chromium). The curvature may be caused by the presence of the nearby argon lines. Results on cast irons and low alloy steels were satisfactory. Further unpublished work by Clarke, with a Southern A1750 instrument and a 0·1 per cent. w/v sample solution, gave an almost linear calibration graph over the range 0·1 to 10 p.p.m. Reid and Goldrich, at Colvilles Ltd.,[17] also noted a pronounced curvature when using the 357·9 mμ line. In the 0 to 0·2 per cent. range these workers found that the 95 per cent. confidence limits of the procedure was similar to that of the British Standard spectrophotometric method (B.S. 1121 : Part 24 : 1952), *i.e.*, $\pm$0·01 per cent., but precision deteriorated at higher chromium levels, possibly because of instrumental difficulties in obtaining a sufficiently fuel-rich flame when using an air - acetylene mixture. These workers also used an air-propane flame in an attempt to improve precision with an addition of ammonium chloride to the sample solution. They found that sensitivity was reduced by a factor of three and that ammonium chloride as a suppressant for iron interference was not effective when using air - propane.

TABLE V

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR CHROMIUM

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Kinson, Hodges and Belcher[14] Special	Air - acetylene (10·4 and 2·4 litres per minute), 10-cm path, 359·4 mμ	1 per cent. w/v of sample in a mixture of H_2SO_4, H_3PO_4 and water (4·5 + 4·5 + 91)	0·5	0·005
Clarke and Cooke Unicam SP90	Air - acetylene (7·6 and 2·0 litres per minute), 10-cm path, 357·9 mμ	1 per cent. w/v of sample in dilute HCl (1 + 9) + 1 per cent. w/v of NH_4Cl	0·5	0·005
Clarke Southern A1750	Air - acetylene (7 and 2·6 litres per minute), 12-cm path, 357·9 mμ	0·1 per cent. w/v of sample in dilute HCl (1 + 99) + 2 per cent. w/v of NH_4Cl	0·2	0·02
Reid and Goldrich[17] Hilger AA2	Air - acetylene (9 and 1·2 litres per minute), 357·9 mμ	1 per cent. w/v of sample in dilute HCl (1 + 9)	0·7	0·007

MANGANESE

A procedure has been described by Belcher and Kinson[18] for the determination of 0·001 to 2 per cent. of manganese in low and high alloy steels with a solution prepared in a similar manner to that described for chromium determination, but with the addition of a little sulphurous acid to reduce any oxidised manganese salts. For best sensitivity the resonance line 279·5 mμ is used, but for higher manganese contents one of the less sensitive lines at 279·8 or 280·1 mμ lines is preferred. Iron interferes with manganese absorption in an air - acetylene flame, but the effect may be largely eliminated by using a stoicheiometric gas mixture (15 litres of air per minute *plus* 2·2 litres of acetylene per minute). Chromium at the 20 per cent. level causes positive interference but this effect may be reduced by confining the absorption path to a small section of the flame and by increasing the slit width of the burner from 0·04 to 0·075 cm. Under these conditions, Belcher and Kinson reported freedom from interference from 30 per cent. each of nickel or chromium, 10 per cent. each of tungsten or cobalt, 5 per cent. each of molybdenum or copper, 3 per cent. of silicon, 2 per cent of vanadium and 0·5 per cent. of aluminium. Results reported on standard steels show excellent precision and accuracy, particularly at low levels of manganese concentration.

Sprague and Slavin[7] used aqua regia to dissolve steel samples by a procedure similar to that described by Belcher and Kinson. A significant interference was experienced due to molybdenum, silicon and tungsten, but on replacing the acetylene cylinder, which was nearly empty, the interference due to molybdenum and tungsten disappeared. Silicon interference was eliminated by modifying the equipment so that only radiation passing through a restricted area of the flame was received by the detector. Results obtained on N.B.S. samples analysed by Sprague and Slavin show poor precision, and in certain cases the agreement with certificate values is unsatisfactory.

Tyou and Catoul[19] studied the effect of monochromator slit width on analytical sensitivity. They used a sulphuric acid sample solution and found slight interference with changes in acid concentration. An enhancement effect due to iron was also noted but this was eliminated by adding iron to the calibration solutions. Excellent results are reported for standard steels, and the coefficient of variation of the procedure is about 1·5 per cent.

Clarke, by using the E.E.L. instrument, obtained low results for cast irons when using a calibration prepared by adding manganese to pure iron. Tests indicated that this might be caused by phosphorus interference and that satisfactory results could be obtained by adding strontium chloride to the samples. This apparent interference was not confirmed by tests made by using the Southern and Unicam instruments. Other elements present in cast irons and low alloy steels did not interfere. On the Southern instrument a markedly curved calibration graph was obtained with the 279·5 mμ line. At 403·1 mμ a linear calibration graph was obtained but sensitivity was considerably reduced. Reid and Goldrich[17] omitted the addition of strontium and obtained satisfactory results on standard samples of mild and low alloy steel.

TABLE VI

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR MANGANESE

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Belcher and Kinson[18] Special	Air - acetylene (15 and 2·2 litres per minute), 279·5 mμ, 10-cm path	1 per cent. w/v of sample in a mixture of H_2SO_4, H_3PO_4 and water (4·5 + 4·5 + 91)	0·08	0·0008
Sprague and Slavin[7] Perkin-Elmer Model 303	Air - acetylene, 279·5 mμ	1 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (12 + 3 + 85)	Not stated	—
Clarke and Cooke Unicam SP90	Air - acetylene (5 and 1·5 litres per minute), 279·5 mμ, 10-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·11	0·011
Clarke Southern A1750	Air - acetylene (7 and 1·8 litres per minute), 279·5 mμ, 12-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·09	0·009
Reid and Goldrich[17] Hilger AA2	Air - acetylene (9 and 1·25 litres per minute), 279·5 mμ	1 per cent. w/v of sample in dilute HCl (1 + 9)	0·11	0·0011

Cobalt

McPherson, Price and Scaife, at J. Lysaghts (Aust.) Ltd.,[20] proposed a method (applicable to all types of steel) for the determination of less than 1 per cent. of cobalt. By using a modified solution procedure the method may also be applied to cobalt contents up to 12 per cent., at which level the tentative "reproducibility" is stated to be $\pm 0{\cdot}2$ per cent. Typical results for the low level cobalt range were reported by McPherson at the 17th Chemists' Conference.[21] Both procedures, which are simple and apparently free from interference, are being considered by the Australian CH/4 Committee as a possible S.A.A. method to replace existing spectrophotometric techniques.

Lockyer[22,23] has also proposed a procedure, with special application to the analysis of small amounts of cobalt in alloy steel. In an attempt to achieve maximum sensitivity, a concentrated sample solution (10 per cent. w/v) was used initially, but results indicated some apparent absorption caused by light scattering by particulate matter in the flame. A less concentrated sample solution (1 per cent. w/v) was preferred with maximum electrical amplification, and with these conditions absorption measurements at 240·7 mμ showed satisfactory agreement with conventional procedures over the range 0·005 to 0·2 per cent. of cobalt. Further successful tests were made in which cobalt was added to the test sample and the percentage recovery determined.

Sprague and Slavin,[7] who determined cobalt with a 1 per cent. sample solution, reported a limited number of satisfactory results on low and high alloy steels.

Preliminary work in the author's laboratory has shown that instrumental sensitivity is not adequate for determination of cobalt at levels below 0·005 per cent.; for this range a preliminary solvent extraction with isobutyl acetate is necessary to remove most of the iron and to permit concentration to give a 10 per cent. w/v sample solution. Large amounts of nickel and chromium remaining in solution after iron removal will enhance cobalt absorption measurements, and it is recommended that calibration solutions should be prepared containing about the same amount of those elements as the test samples. Careful calibration and a sample concentration technique permits results to be produced that are significant to the nearest 0·0001 per cent. of cobalt.

The interference effects of large amounts of nickel and certain other elements have been confirmed by the Australian CH/4 Committee. Interference, which occurs when a fuel-rich air - acetylene flame is used, can be eliminated by using a lean flame.

Table VII

Instrument conditions and sensitivities for cobalt

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
McPherson *et al.*[20] Techtron	Lean air - acetylene, 240·7 mμ, 10-cm path	(*a*) 4 per cent. w/v of sample in dilute HCl (1 + 4)	Not stated	—
		(*b*) 0·5 per cent. w/v of sample in a mixture of H_2SO_4, H_3PO_4 and water (1 + 1 + 23) (for alloy steel)	Not stated	—
Lockyer[22] Hilger AA2	Air - acetylene (10·5 and 1·22 litres per minute), 240·7 mμ	0·4 or 1 per cent. w/v of sample in dilute HCl	Not stated	—
Sprague and Slavin[7] Perkin-Elmer Model 303	Air - acetylene	1 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (12 + 3 + 85)	Not stated	—
Thulbourne and Scholes Hilger AA2	Air - acetylene (10 and 1·25 litres per minute), 240·7 mμ, 13-cm path	10 per cent. w/v of sample in dilute HCl (5 + 95), after solvent extraction	0·25	0·00025

Nickel

With a dilute phosphoric acid solution, Kinson and Belcher[24] determined nickel in steel by absorption of the 232·01-mμ line in a lean air - acetylene flame. Sensitivity is markedly dependent upon slit width because of the difficulty in obtaining resolution from the non-absorbing nickel line at 231·98 mμ; the resultant non-linear calibration graph limits the maximum content of nickel that can be determined to 2 per cent. It seems probable that such difficulties will be minimised by the use of high intensity lamps of the type described by Sullivan and Walsh,[25] or other types of high output lamps.

Kinson and Belcher report no interference from iron, 30 per cent. of chromium, 20 per cent. each of manganese or tungsten, 10 per cent. each of copper or cobalt and 5 per cent. each of vanadium, molybdenum or aluminium.

Clarke and Cooke report that nickel can be determined in cast iron and low alloy steel over the range 0·05 to 0·5 per cent. With a conventional hollow-cathode lamp they recommend use of the line at 341·5 mμ, which gives a nearly linear calibration graph. With a "high spectral output" lamp the line at 232·01 mμ can be used with an appreciable gain in sensitivity. Work by Clarke on other instruments also indicates the advisability of using the 341·5 mμ line. However, on the Optica instrument the calibration graph at 232·01 mμ was appreciably less curved, even although a combined nickel - cobalt - iron lamp was used. Reid and Goldrich,[17] who used standard hollow-cathode lamps and the 232·01-mμ line, reported satisfactory results on standard steels containing up to 1 per cent. of nickel. At higher nickel levels poor precision was noted, possibly because of the curvature of the calibration graph.

Table VIII

Instrument conditions and sensitivities for nickel

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Kinson and Belcher[24] Special	Air - acetylene (10·5 and 1·5 litres per minute), 232·01 mμ, 10-cm path	1 per cent. w/v of sample in a mixture of H_3PO_4, H_2SO_4 and water	0·52	0·0052
Clarke E.E.L.	Air - acetylene, 341·5 mμ	0·5 per cent. w/v of sample in dilute HCl (1 + 9)	0·70	0·014
Clarke and Cooke Unicam SP90	Air - acetylene (5 and 1·20 litres per minute), 232·01 mμ, 10-cm path	1 per cent. w/v of sample in dilute HCl (1 + 9)	0·44	0·0044
	341·5 mμ, 10-cm path	1 per cent. w/v of sample in dilute HCl (1 + 9)	2·6	0·026
Clarke Optica	Air - acetylene (15 and 3 cubic feet per hour), 232·01 mμ, 5-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·28	0·028
	341·5 mμ, 5-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·9	0·09
Reid and Goldrich[17] Hilger AA2	Air - acetylene (9 and 1·25 litres per minute), 232·01 mμ	1 per cent. w/v of sample in in dilute HCl (1 + 9)	0·21	0·0021

Copper

The determination of small amounts of copper in steel by atomic absorption is a relatively simple procedure, first demonstrated by Kinson and Belcher.[26] Absorption measurements at 324·8 mμ in a lean air - acetylene flame are free from interference from 20 per cent. each of nickel, chromium, manganese or tungsten, 10 per cent. each of cobalt or vanadium, 5 per cent. of molybdenum and 1 per cent. of aluminium. Variations in the iron content of the sample solution from 0 to 10,000 p.p.m. cause only a small decrease in copper absorption measurements.

Kinson and Belcher's work has been confirmed by other workers. Wollerton and Nall, at the Bragg Laboratory (unpublished work), used a similar procedure to analyse low alloy steels and stainless steel after a fuming treatment with sulphuric acid. Results by Sprague and Slavin,[7] unpublished work at B.C.I.R.A., and Reid and Goldrich,[17] all show satisfactory agreement with results obtained by more conventional procedures.

TABLE IX

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR COPPER

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Kinson and Belcher[26] Special	Air - acetylene (10·5 and 1·5 litres per minute), 324·8 mμ, 10-cm path	1 per cent. w/v of sample in a mixture of H_3PO_4, H_2SO_4 and water (4·5 + 4·5 + 91)	0·10	0·001
Wollerton and Nall Hilger AA1	Air - coal gas, 324·8 mμ	(*a*) 1 per cent. w/v of sample in dilute HNO_3 (5 + 95)	Not stated	—
		(*b*) 2 per cent. w/v of sample in dilute H_2SO_4 (1 + 9)	Not stated	—
Sprague and Slavin[7] Perkin-Elmer Model 303	Air - acetylene	1 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (12 + 3 + 85)	Not stated	—
Clarke E.E.L.	Air - acetylene, 324·8 mμ	0·5 per cent. w/v of sample in dilute HCl	Not stated	—
Clarke and Cooke Unicam SP90	Air - acetylene (5 and 1·5 litres per minute), 324·8 mμ, 10-cm path	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·12	0·012
Clarke Southern A1750	Air - acetylene (7 and 1·5 litres per minute), 324·8 mμ, 12-cm path	As in previous sample	0·09	0·009
	327·4 mμ, 12-cm path	As in previous sample	0·2	0·02
Clarke Optica	Air - acetylene	0·1 per cent. w/v of sample in dilute HCl (1 + 99)	0·15	0·015
Reid and Goldrich[17] Hilger AA2	Air - acetylene (9 and 25 litres per minute), 324·8 mμ	1 per cent. w/v of sample in dilute HCl (1 + 9)	0·17	0·0017

MOLYBDENUM

The original work of David,[27] who examined various factors affecting the determination of molybdenum with the 313·3-mμ resonance line in an air - acetylene flame, has been evaluated by Mostyn and Cunningham.[28] Absorption is extremely sensitive to small changes in solution composition, and it is possible that a complex interfering ion system is formed of the type described by Firman.[29] David added 2000 p.p.m. of aluminium to suppress interference from such elements as manganese and iron, but Mostyn and Cunningham found that the addition of ammonium chloride (2 per cent. w/v) in solution was more efficient.

David, and Mostyn and Cunningham, used fuel-rich luminous flames which tend to give unfavourable signal-to-noise ratios. Mostyn and Cunningham had to use a less sensitive resonance line (379·8 mμ) in order to obtain an acceptable noise level.

Kirkbright, Smith and West[30] also examined molybdenum determination in an air - acetylene flame. Several resonance lines were used but it was found for each that either the noise level was high or the sensitivity was inadequate. They pointed out that the sensitivities reported earlier by David, and Mostyn and Cunningham, benefit from scale expansion and from the use of relatively long absorbance path-lengths.

To overcome the disadvantage of the air - acetylene flame, Kirkbright, Smith and West proposed the use of nitrous oxide - acetylene for special application to the analysis of alloy steel. The noise level is considerably reduced, thus permitting absorption measurements with the most sensitive 313·3-mμ line. Only the matrix element iron interferes, causing severe depression of molybdenum absorption, but, provided that the solution aspirated contains about 1 per cent. w/v of tervalent iron, variation in the ratio of molybdenum to iron is not critical.

In the proposed procedure, the 1-g sample is dissolved in 20 ml of concentrated hydrochloric acid *plus* 2 ml of concentrated nitric acid and diluted to 100 ml without filtration.

For high alloy steel, iron(III) chloride is added before dilution to make the total amount of iron present about 1 g.

The sensitivity of the procedure is comparable to those based on air - acetylene flames, but the main advantage lies in freedom from interference caused by alloying elements present in the sample solution. It has been tested with standard steels containing 0·3 to 5 per cent. of molybdenum with good correlation against certificate values. Samples containing tungsten were included in these tests, but no instructions are given for removal of hydrolysed precipitates in order to prevent atomiser blockage. For the determination of smaller concentrations down to 0·01 per cent., the authors suggest a preliminary concentration stage involving extraction of molybdenum from the iron into an organic solvent, either as an 8-hydroxyquinolinate or thiocyanate complex.

TABLE X

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR MOLYBDENUM

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
David[27] Special	Luminous air - acetylene, 10-cm path, 313·3 mμ	0·25 per cent. w/v of sample + 2000 p.p.m. solution of aluminium	3·3	0·13
Mostyn and Cunningham[28]	Luminous air - acetylene, 10-cm path, 379·8 mμ	Sample in various volumes of dilute HCl + HNO_3 + 2 per cent. w/v NH_4Cl	1·3	—
Kirkbright, Smith and West[30] Unicam SP900A	Nitrous oxide - acetylene, 5-cm path, 313·3 mμ	1 per cent. w/v of sample in 2 M HCl	3·3	0·033

CADMIUM

Wilson[31] has proposed a simple method for the determination of cadmium in alloy steels. Sensitivity is high with an air - coal gas flame; the limit of detection of 0·0003 per cent. can be achieved without chemical separation. The 1-g sample is dissolved in aqua regia and diluted to 100 ml without filtration. If tungsten is present in the sample, 10 ml of phosphoric acid must be added at the dissolution stage.

Absorption measurements are made with the 228·8-mμ resonance line; corrections are made for apparent absorption effects caused by iron by subtracting measurements made at the cadmium line 231·1 mμ, which is known to be non-absorbing.

The presence of iron in the sample solution gives rise to a small positive interference, but 20 per cent. each of manganese, nickel or chromium, 10 per cent. each of cobalt or copper and 5 per cent. each of molybdenum, titanium, vanadium, lead or aluminium have no effect on cadmium absorbance.

TABLE XI

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR CADMIUM

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Wilson[31] Special	Air - coal gas, 228·8 mμ, 10-cm path	1 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (10 + 2 + 88)	0·03	0·0003

LEAD

Progress in the determination of lead was reviewed by Thulbourne and Scholes in 1966,[32] and this section is based on their paper.

Elwell and Gidley[33] determined lead in free-cutting steel and at the 0·005 per cent. level in chromium steel by using a d.c. operated instrument, an air - coal gas flame and the 283·3-mμ

resonance line. While their method appears to be free from direct interference, in the absence of lead a significant background absorption from iron was noted equivalent to 0·05 per cent. of lead. This effect could be allowed for by calibrating with solutions containing high purity iron as well as lead.

Nall and Wollerton based their method on Elwell and Gidley's work, extending its application to the analysis of stainless steel. Analytical sensitivity is increased by the addition of an organic solvent to the sample solution before spraying into the flame: the minimum detection limit is about 2 p.p.m. in the solution, equivalent to 0·005 per cent. of lead.

In Australia a similar procedure based on an air - acetylene flame, is the subject of a S.A.A. procedure.[34] The method is suitable for lead contents between 0·01 and 0·5 per cent.; it is stated to be free from interference from 1 per cent. each of nickel, chromium, molybdenum or silicon, and 2 per cent. of manganese. In more recent collaborative work in Australia, two highly sensitive procedures are being studied for the determination of trace amounts of lead. In the first of these procedures,[35] the 2-g sample is dissolved in a mixture of hydrochloric, nitric and hydrofluoric acids. Thallium is added and lead and thallium precipitated as thiourea complexes. The precipitate is dissolved in acid, hydrogen peroxide added and the solution evaporated. Salts are dissolved in nitric acid and the solution diluted to 10 ml. Absorbance measurements are made at 217·0 mμ with an air - coal gas flame. The method is stated to be satisfactory for all types of irons and steels; the range of application is 0·0001 to 0·1 per cent. of lead. In the second procedure (unpublished), the 1-g sample solution is evaporated to fumes with perchloric acid, hydrogen peroxide added and the lead extracted by solvent extraction with a solution of dibenzyldithiocarbamate in chloroform following the method of Stobart.[36] After wet oxidation of organic material the solution is diluted to 10 ml and sprayed into an air - propane flame. The proposed method is suitable for virtually all types of steel but it is not quite as free from interference as the thallium - thiourea method.

Lockyer's[32,37] procedure was tested at Hilger and Watts Ltd. with a solution preparation similar to that used for cobalt determination.[20,21] For complex alloy steels good agreement with results by a spectrophotometric method was found, except for two samples that gave high results. These anomalous results were explained by what Lockyer has termed "a smoke effect" in the flame caused by the effect of matrix elements.

Following Elwell and Gidley's work,[33] Thulbourne and Scholes[32] examined more closely the application of the original method. By using an a.c. instrument and air - acetylene flame, interference from iron is much less marked when compared with the results reported with air - coal gas and a d.c. instrument. Excellent results were obtained for free-cutting steels, with standard deviations of about ±0·002 in the range 0·1 to 0·3 per cent. of lead. By increasing the sample solution concentration from 0·5 to 2 per cent. w/v the procedure may also be used to analyse mild and low alloy steel containing 0·001 to 0·5 per cent. of lead.

Thulbourne and Scholes also examined the suitability of Lockyer's procedure for the analysis of complex alloy steels. Sensitivity was found to be inadequate for the determination of contents less than 0·005 per cent., and for this purpose a concentration technique was proposed. The major part of the iron in a 2-g sample is removed by a single solvent extraction with isobutyl acetate, and the aqueous extract concentrated to give a 10 per cent. w/v solution. Chromium and nickel, which are present in samples of stainless steel after extraction, interfere in lead-absorption measurements, causing positive errors of up to 0·001 per cent. These effects have also been noted in collaborative Australian work. An attempt by Thulbourne and Scholes to determine the actual degree of interference and to apply an appropriate correction was unsuccessful. The effect of large amounts of nickel and chromium added either separately or together was inconsistent and difficult to interpret. As a practical solution to the problem it is recommended that the effect should be compensated for by calibrating with solutions containing high purity nickel and chromium in similar amounts to those present in the test samples. Alternatively, a "standard addition" technique can be used.

In principle, the influence of matrix elements can be eliminated by extracting lead as lead iodide into isobutyl methyl ketone following preliminary removal of iron by solvent extraction. Several workers[38,39] have proposed procedures based upon this principle, but a double solvent extraction makes the method tedious, thus eliminating the advantage of atomic absorption over other techniques.

Clarke found an air - propane flame more sensitive than air - acetylene when using the E.E.L. instrument. The sensitivity was adequate for lead in leaded steels but was still insufficient for the direct determination of lead in cast iron (at the 0·0001 to 0·001 per cent. level). By using a scale expansion satisfactory results were obtained on steels and cast irons at the 0·002 per cent. level with the Unicam SP90 instrument, but the calibration graph showed a high background absorption, probably caused by iron and equivalent to 0·006 per cent. of lead. Similar results were obtained by Clarke on the Southern A1750 instrument with the resonance line at 217·0 mμ and an air - acetylene flame. In this case the background absorption was equivalent to about 0·0035 per cent. of lead.

TABLE XII

INSTRUMENT CONDITIONS AND SENSITIVITIES FOR LEAD

Author and instrument	Flame conditions	Solution composition	Sensitivity: p.p.m.	Sensitivity: Equivalent content, weight per cent.
Elwell and Gidley[33] Hilger AA1 modified	Air - coal gas, 283·3 mμ	2 per cent. w/v of sample in dilute HCl	Not stated	—
Nall and Wollerton Hilger AA1	Air - coal gas, 283·3 mμ	(*a*) 2 per cent. w/v of sample in a mixture of HNO_3, isopropyl alcohol and water (2 + 5 + 3) (for mild steel)	Not stated	—
		(*b*) 2 per cent. w/v of sample in a mixture of HNO_3, HCl, isopropyl alcohol and water (4 + 16 + 50 + 30) (for stainless steel)	Not stated	
Australian Draft Standard[34]	Lean air - acetylene, 283·3 mμ, 10-cm path	2 per cent. w/v of sample in a mixture of HCl, HNO_3 and water (3 + 1 + 17)	Not stated	—
Australian Draft Standard[35] Techtron AA3	Air - coal gas, 217·0 mμ, 10-cm path	20 per cent. w/v of sample in dilute HNO_3 (5 + 95) after separation	Not stated	—
Australian CH/4 Committee	Air - propane	10 per cent. w/v of sample in dilute $HClO_4$ (1 + 3) after separation	0·2	0·0002
Lockyer[23] Hilger AA2	Air - acetylene (10·5 and 1·2 litres per minute), 283·3 mμ	2 per cent. w/v of sample in dilute HCl	Not stated	—
Thulbourne and Scholes[32] Hilger AA2	Air - acetylene (9 and 1·25 litres per minute), 283·3 mμ, 13-cm path	(*a*) 2 per cent. w/v of sample in dilute HCl either (2 + 98) or (1 + 9)	0·6	0·003
		(*b*) 10 per cent. w/v of sample in dilute HCl (5 + 95) after solvent extraction	0·6	0·0006
Clarke E.E.L.	Air - acetylene, 283·3 mμ, 10-cm path	2 per cent. w/v of sample in dilute HCl (1 + 9)	0·9	0·0045
	Air - propane, 283·3 mμ, 10-cm path	As in previous sample	0·65	0·0033
Clarke Southern A1750	Air - acetylene, 283·3 mμ, 10-cm path	As in previous sample	0·5	0·0025
	217·0 mμ, 10-cm path	As in previous sample	0·2	0·001
Clarke and Cooke Unicam SP90	Air - propane (5 and 0·4 litres per minute), 283·3 mμ, 10-cm path	As in previous sample	0·55	0·0028

CONCLUSIONS

Many of the more common elements present in steel can be determined easily by dissolving the sample in acid, removing insoluble matter by filtration, and diluting to a fixed volume as a preliminary to absorption measurement. There are few problems in the determination

of such elements as magnesium, chromium, manganese, cobalt, nickel, copper and lead when present in small amounts in cast iron, mild and low alloy steel. Molybdenum, vanadium and titanium can also be determined provided that a nitrous oxide - acetylene flame is used instead of air - acetylene.

Difficulties arise in the determination of trace elements below 0·01 or 0·005 per cent., when concentration techniques are often necessary and in the determination of contents exceeding about 2 per cent., mainly because of the unsatisfactory precision of atomic-absorption measurements. Alloying elements, such as nickel and chromium, present in large amounts also cause problems in trace-element determination.

For widest application, it is important to select an instrument that has a high sensitivity, and a measurement precision adequate for the determination of elements in high concentrations. Most manufacturers quote sensitivities based on results obtained with aqueous solutions free from anions and other metals. Of more importance is the performance of the instrument when dealing with solutions containing about 1 g of the steel sample in 100 ml of dilute acid. Measurement precision and calibration drift, which are both largely functions of flame stability, may be readily assessed by making repetitive measurements of the same sample solution over a period of about 1 hour.

Future developments

Atomic-absorption spectrophotometry is an established technique for the determination of elements present in small amounts. It is capable of replacing more traditional colorimetric and titrimetric methods of analysis used in iron and steelworks laboratories. With refinement of instrument precision and careful calibration technique, it should be possible to extend the level of content measured up to about 10 per cent. Success in the determination of trace elements will depend on the development of rapid separation techniques so as to permit the maximum degree of sample concentration. Multi-separations of the type often necessary in colorimetric and polarographic procedures must be avoided, otherwise the inherent advantage of atomic absorption as a simple measuring technique will be lost.

Extension of the range of elements determined will depend on instrumental developments in the case of carbon, sulphur and phosphorus, and the use of hotter flames, such as nitrous oxide - acetylene, for the determination of aluminium, silicon, arsenic, niobium, tin, tantalum and tungsten. In the first group of elements an interesting indirect approach has been suggested by Kirkbright, Smith and West,[40] who complexed phosphorus (and silicon) as molybdates and then measured the molybdenum content of the complexes. Work has been reported on most of the elements in the second group but most sensitivities claimed are rather poor. Brief details of a solution technique suitable for the determination of silicon in cast iron and steel have been reported by McAulife,[41] but no details are given of instrument sensitivity.

This review is concerned with the analysis of iron and steel but there are other applications of atomic absorption in the iron and steel industry. Chief among these is the analysis of slag and, while there has been reference to the analysis of silicate materials in the literature, little attention has been given to the analysis of steel-making slag. In the author's laboratory magnesium[42] is determined on a routine basis after prior removal of silicon, and some success has been achieved in the determination of calcium[43] and magnesium. At Broken Hill Propriety Co. Ltd.[44] and at C.N.R.M. in Belgium[19] procedures are being developed for the determination of calcium and magnesium in sinters, slags, flue dust and a variety of raw materials but no published method details are available. It seems probable that manganese, iron and silicon might also be determined in oxide materials.

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References

1. Slavin, W., Sprague, S., and Manning, D. C., *Atomic Absorption Newsletter*, 1964, No. 18, 1.
2. Elwell, W. T., and Gidley, J. A. F., "Atomic-Absorption Spectrophotometry," Second Edition, Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, and Braunschweig, 1966.

3. Robinson, J. W., "Atomic Absorption Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1966.
4. Sullivan, J. V., and Walsh, A., *Spectrochim. Acta*, **1965**, **21**, 727.
5. Belcher, C. B., and Bray, H. M., *Analytica Chim. Acta*, 1962, **26**, 322.
6. Belcher, C. B., *Proc. R. Aust. Chem. Inst.*, **1963**, **30**, 111.
7. Sprague, S., and Slavin, W., *Atomic Absorption Newsletter*, 1964, No. 23, 8.
8. Amos, M. D., and Willis, J. B., *Spectrochim. Acta*, **1966**, **22**, 1325.
9. Headridge, J. B., and Hubbard, D. P., *Analytica Chim. Acta*, **1967**, **37**, 151.
10. Mostyn, R. A., and Cunningham, A. F., *Atomic Absorption Newsletter*, **1967**, **6**, 86.
11. Bowman, J. A., and Willis, J. B., *Analyt. Chem.*, **1967**, **39**, 1210.
12. Trent, D. J., and Manning, D. C., *in* "Pittsburgh Conference on Analytical Chemistry," **1965**.
13. Capacho-Delgado, L., and Manning, D. C., *Atomic Absorption Newsletter*, **1966**, **5**, 1.
14. Kinson, K., Hodges, R. J., and Belcher, C. B., *Analytica Chim. Acta*, **1963**, **29**, 134.
15. Giammarise, A., *Atomic Absorption Newsletter*, **1966**, **5**, 113.
16. Barnes, L., *Analyt. Chem.*, **1966**, **38**, 1083.
17. Reid, J., and Goldrich, D., *Colville's Research Report*, V 12/2, 1967.
18. Belcher, G., and Kinson, K., *Analytica Chim. Acta*, **1964**, **30**, 483.
19. Tyou, P., and Catoul, P., *La Metallurgie*, **1966**, **98**, 271.
20. McPherson, G. L., Price, J. W., and Scaife, P. H., *Nature*, **1963**, **199**, 371.
21. McPherson, G. L., *in* "Proceedings of the 17th Chemists' Conference, Scarborough, **1964**," British Iron and Steel Research Association, London, **1964**.
22. Lockyer, R. L., *Hilger and Watts Research Report* BR 26, 1966.
23. ——, *BISRA Subcommittee Report* MG/DA/241/65.
24. Kinson, K., and Belcher, C., *Analytica Chim. Acta*, **1964**, **30**, 64.
25. Sullivan, J. V., and Walsh, A., *Spectrochim. Acta*, **1965**, **21**, 721.
26. Kinson, K., and Belcher, C., *Analytica Chim. Acta*, 1964, **31**, 180.
27. David, D. J., *Analyst*, **1961**, **86**, 730.
28. Mostyn, R. A., and Cunningham, A. F., *Analyt. Chem.*, **1966**, **38**, 121.
29. Firman, R. J., *Spectrochim. Acta*, 1965, **21**, 341.
30. Kirkbright, G. F., Smith, A. M., and West, T. S., *Analyst*, **1966**, **91**, 700.
31. Wilson, L., *Analytica Chim. Acta*, **1966**, **35**, 123.
32. Thulbourne, C., and Scholes, P. H., *BISRA Committee Report* MG/D/344/66.
33. Elwell, W. T., and Gidley, J. A. F., *Analytica Chim. Acta*, **1961**, **24**, 71.
34. Draft Australian Standard for the Determination of Lead in Low Alloy and Carbon Steels.
35. Draft Australian Standard for the Determination of Lead in Iron and Steel.
36. Stobart, J. A., *Analyst*, **1965**, **90**, 278.
37. Lockyer, R. L., *Hilger and Watts Research Report* BR 25, 1966.
38. Chakrabarti, C. L., Robinson, J. W., and West, P. W., *Analytica Chim. Acta*, 1966, **34**, 269.
39. Dagnall, R. M., West, T. S., and Young, P., *Analyt. Chem.*, **1966**, **38**, 358.
40. Kirkbright, G. F., Smith, A. M., and West, T. S., *Analyst*, **1967**, **92**, 411.
41. McAulife, J. J., *Atomic Absorption Newsletter*, **1967**, **6**, 69.
42. Thulbourne, C., and Scholes, P. H., *Rept. BISRA*, MG/D/621/1/67.
43. ——, ——, *Ibid.*, MG/D/453/1/68.
44. Clift, B., B.H.P. Technical Bulletin No. 29, **1967**, 31.

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The Spectrographic Determination of Nickel in Molten Steels

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A prerequisite for the direct spectrographic analysis of molten steels in industrial furnaces is the knowledge that good quality spectra can be obtained from molten steel surfaces, and that precise quantitative determinations can be made by using such spectra.

The emission-spectrographic determination of nickel from a molten steel surface at 1600° C under an argon atmosphere has, therefore, been investigated. When a condensed spark between a graphite electrode and the molten steel surface was used, spectra of good quality were produced. The standard deviations in the error for the determination of 0·7 to 1·8 per cent. of nickel in molten and solid steel samples, analysed under similar conditions, were 0·045 and 0·022 per cent., respectively.

THE routine analysis of molten steel is usually made by withdrawing a sample from the furnace, allowing it to solidify and, after suitable machining, subjecting it to emission-spectrographic analysis on a direct-reading instrument. This whole operation takes about 5 to 10 minutes, and, from an economic standpoint, it would be desirable to reduce the time required for an analysis. This could probably be done by carrying out an emission-spectrographic analysis on the molten steel directly, but a search of the chemical literature reveals that only a few studies have been made on the quality and possible analytical application of emission spectra from a molten steel surface, and most of these are of a preliminary nature.

Balandin and Mandel'shtam[1] investigated the possibility of determining the composition of molten steel in an arc furnace without sampling, and state that this method should be practicable. The electric arc of the furnace was used as an excitation source. In experiments on a laboratory scale, Shaevich and Shubina have determined silicon in molten pig-iron[2] and carbon in molten iron - carbon alloys[3] by using emission spectrography with relative standard deviations of about 5 per cent. With a pulsed laser source and a large Littrow spectrograph, Runge, Bonfiglio and Bryan[4] have obtained satisfactory calibration graphs for the determination of 9 to 24 per cent. of nickel and 13 to 25 per cent. of chromium in three samples of molten stainless steels. The preliminary studies on the spectrographic analysis of molten steels made by Hilger and Watts Ltd. and by the British Iron and Steel Research Association are reviewed by Scholes and Williams.[5]

As few results are given in the above papers on the precision of spectrographic methods of analysis of molten steels, the authors have investigated the spectrographic determination of 0·7 to 1·8 per cent. of nickel in five steels at room temperature and in the molten state at 1600° C. These results are now reported.

EXPERIMENTAL

A molten steel surface was produced by the induction melting of a 1·8-lb cylindrical sample of steel in a magnesia crucible. An inert atmosphere was maintained above the molten surface by passing argon into a Vitreosil hood positioned over the crucible. This refractory cover was constructed with three holes in it. Light from the molten surface was directed through one hole to a continuous optical pyrometer, which allowed the temperature to be kept constant at 1600° C. Visual inspection of a spark could be made through the second hole and the third hole permitted light to enter a large quartz spectrograph.

With the electrode gap set at 3·8 mm, 15-kV condensed sparks were struck between the molten surface and two graphite electrodes. Light from one of the sparks, after passing through a quartz lens, was deflected by a surface-aluminised mirror along the optical axis of the spectrograph. Before entering the spectrograph the light beam passed through another quartz lens, which produced a de-focused image of the spark on the slits.

The molten steel surface was half an inch below the top of the crucible and, when the solid samples were analysed at room temperature, a cylinder of steel was placed in the crucible so that its surface was the same distance below the crucible top; otherwise the apparatus was identical.

The spectra from the solid and molten samples were photographed on Kodak B10 plates over the range 2800 to 5000 Å. The exposure time for the solid samples was 3 minutes but, with the molten samples, the intensity of the spark was less and the exposure time was increased to 5 minutes.

The spectra of the five samples, and that from an iron spark in conjunction with a rotating stepped sector, were recorded on the same plate. After developing, fixing, washing and drying in the recommended manner, the optical densities of the nickel line at 3414·77 Å and the iron line at 3417·84 Å were recorded with a Joyce Loebl microdensitometer for each spectrum from the steel samples. The optical densities for each step of the iron line at 3440·61 Å on the spectrum from the iron spark were recorded, and the plate-calibration curve constructed. The log intensity ratios for the line pair nickel 3414·77 - iron 3417·84 Å for the five samples were obtained from the plate-calibration curve and plotted against nickel concentration to obtain a calibration graph. The same procedure was used for both solid and molten samples.

Results

The five steels and their nickel contents are shown below.

Steel	EN 351	EN 352	EN 353	EN 24	EN 354
Nickel content, per cent...	0·77	0·98	1·23	1·40	1·74

Analysed samples of these steels were a gift from the English Steel Corporation Ltd. The calibration graphs for both the solid and molten steel samples are shown in Fig. 1.

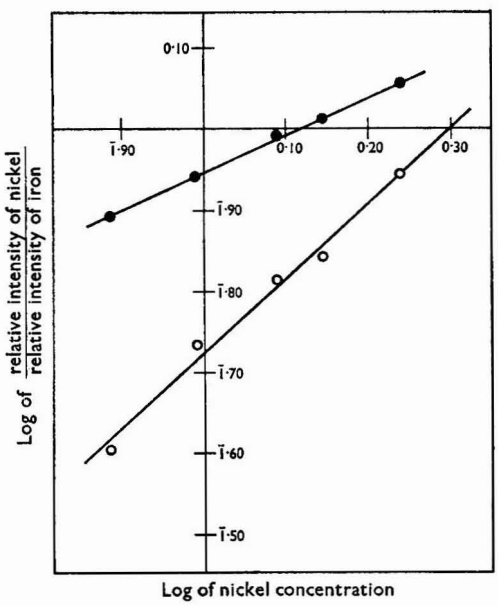

Fig. 1. Calibration graphs of log(relative intensity for nickel/(relative intensity for iron) against log (concentration of nickel): ● solid samples, ○ liquid samples

Discussion

It can be seen from Fig. 1 that the method is more sensitive for molten than for solid steel, as the slope of the calibration graph for the molten steels is the steeper of the two. When the results for the molten steels were re-plotted as intensity ratio against nickel concentration, a straight line passing through the origin was obtained. The standard deviation in the error in nickel concentration was 0·045 per cent., which corresponds to a relative standard deviation of 4·5 per cent. at a nickel concentration of 1 per cent. The standard deviation is based on five results, one for each of the five standards. The error in nickel concentration was expressed by c (observed) - c (calculated), where the values of c (calculated) were points exactly on the straight-line calibration graph of intensity ratio against nickel concentration.

A similar type of plot for the solid steels must also pass through the origin and give a curve concave to the nickel-concentration axis. This curvature probably resulted from self-absorption for the nickel line in the spectra from the solid samples. When a similar statistical treatment was made of this curve, the standard deviation in the error in nickel concentration was 0·022 per cent.

This study has shown that the spectrographic determination of nickel in molten steel is feasible and that the precision of the results is acceptable. The precision of the results for the molten steel samples could no doubt be improved if a satisfactory optical system could be devised to allow the exposure time to be appreciably reduced. There is every reason to believe that many other elements with low volatilities at 1600° C could be determined in molten steel by emission spectrography (Note). If this method were to be applied to the spectrographic analysis of molten steel in an industrial furnace, some way would have to be found for isolating a slag-free pool of molten steel under an argon atmosphere on the side of the furnace. This, however, is a problem for the mechanical engineer rather than the analytical chemist.

The authors are now hoping to obtain satisfactory calibration graphs for carbon in molten steels with similar apparatus and a vacuum spectrograph.

Note—The authors started their investigations by trying to obtain a suitable calibration graph for 0·4 to 1·7 per cent. of manganese in molten steel with a medium quartz spectrograph. Although a satisfactory calibration graph was obtained for manganese in five solid steel samples, consistent results for the determination of manganese in the molten samples could not be obtained. It was found that the concentration of manganese in the molten steels was, in fact, decreasing with time, for the vapour pressure of manganese above molten steel at 1600° C is appreciable, and the manganese vapour was being removed from the system by the argon stream.

We are indebted to Mr. Faine of this department and his workshop staff for building the electrode assembly. We gratefully acknowledge the receipt of grants for this work from the Science Research Council, English Steel Corporation Ltd., Firth-Brown Ltd., Guest, Keen and Nettlefold Steel Co. Ltd., Steel Company of Wales Ltd. and United Steel Companies Ltd.

References

1. Balandin, V. N., and Mandel'shtam, S. L., *Zav. Lab.*, **1957**, **23**, 545.
2. Shaevich, A. B., and Shubina, S. B., *Ibid.*, **1962**, **28**, 447.
3. Shaevich, A. B., Mel'nikov, S. I., and Danilevskaya, V. V., *Ibid.*, **1965**, **31**, 169.
4. Runge, E. F., Bonfiglio, S., and Bryan, F. R., *Spectrochim. Acta*, **1966**, **22**, 1678.
5. Scholes, P. H., and Williams, R. V., *British Iron and Steel Research Association Report* MG/D/335/65.

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Spectrophotometric Determination of Small Amounts of Tin in Lead and Antimonial Lead Alloys

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A method is described for the determination of 0·001 to 0·10 per cent. of tin in lead and antimonial lead alloys. The sample (0·25 to 2·5 g) is dissolved in a mixture of nitric and citric acids. After addition of EDTA and ammonium chloride, the pH of the solution is adjusted to 5·5 with ammonia solution before passing it through a column containing silica gel. Tin is adsorbed on the column, while lead, antimony and other metals pass through. After elution with hydrochloric acid solution the tin is determined spectrophotometrically with gallein. The standard deviation on samples containing 0·0051 and 0·038 per cent. of tin is ±0·0005 and ±0·002, respectively. At least eight determinations can be carried out in 1 day.

Some properties of lead, such as resistance to corrosion, fatigue, creep and grain size, are influenced by the presence of small amounts of tin and other metals. An important application of lead is in the manufacture of alloys containing between 1 and 12 per cent. of antimony for accumulator plates, acid pumps, valves and telephone cables. The characteristics of some of these antimonial lead alloys are also dependent on the amount of tin present. It is, therefore, desirable to have a method for determining 0·001 to 0·10 per cent. of tin in lead and antimonial lead alloys suitable for use in a routine laboratory.

In most of the methods reported it is necessary to separate the tin from the lead and other metals before the final determination. For example, the tin has been determined polarographically after distillation of tin(IV) bromide[1] or after removal of lead as lead sulphate.[2] Of the spectrophotometric methods reported, dithiol[3] has been used after co-precipitation of the tin with manganese dioxide, and phenylfluorone[4] after solvent extraction in which cupferron is used. Catechol violet[5] has also been used for the spectrophotometric determination of tin in lead after solvent extraction in which tri-(2-ethylhexyl)phosphine oxide is used. All of these methods are lengthy and tedious and not applicable in the presence of large amounts of antimony found in antimonial lead alloys. It was, therefore, decided to investigate methods of separating tin from lead and antimony.

Ariel and Kirowa[6] reported the anion-exchange separation of tin from lead and antimony and applied the procedure to lead - tin alloy. The method is rather involved, and it is doubtful if it could be applied to the present problem.

Although many paper-chromatographic procedures have been published[7,8,9,10] for the separation of lead from other metals, these have been mainly concerned with the qualitative separation of Groups I and II of the general qualitative scheme. Such separations, although invaluable for qualitative purposes, are not suitable for quantitative analysis.

Šulcek, Dolezal, Michal and Sychra[11] reported a method for the determination of tin in antimony metal, in which column chromatography is used. These workers dissolve the sample in a mixture of hydrochloric acid and bromine, and, after the addition of citric acid, ammonium chloride and EDTA, the pH of the solution is adjusted to 5·5 by the addition of sodium hydroxide solution. When the solution (about 200 ml) is passed through a column

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of silica gel, the tin is held quantitatively and the other metals pass through. The tin is determined polarographically after eluting with hydrochloric acid. In this procedure, a 20-g sample of antimony is recommended when the expected tin content is 0·001 per cent.

The combination of the separation by using silica gel with a spectrophotometric determination does not appear to have been previously used for the determination of tin. It was hoped that by using a sensitive spectrophotometric reagent it would be possible to determine smaller amounts of tin than those determined by Šulcek, Dolezal, Michal and Sychra. Such a procedure would require a smaller sample and a reduction in the volume of solution to be passed through the column.

Wood[12] has compared several different spectrophotometric reagents for tin and concluded that gallein is the most sensitive and simplest to use.

This reagent has been used for all of the investigations described in the present paper, which have resulted in a satisfactory method for the determination of tin (0·001 to 0·1 per cent.) in lead and antimonial lead alloys. A 2·5-g sample is required for an expected tin content of 0·001 per cent., and the volume of solution to be passed through the column is only 50 ml.

Experimental

Investigations of the determination of tin with gallein confirmed the findings of Wood that Beer's law is obeyed up to a concentration of 0·5 μg of tin per ml and that the absorption of the tin - gallein complex at 520 mμ reaches a maximum value after 30 minutes and then remains constant for over 1 hour. It was also verified that the absorption at 520 mμ was constant over the pH range 2 to 3. In all of the subsequent investigations with gallein the conditions were kept as described by Wood, with the pH control achieved by the use of a sodium chloroacetate - chloroacetic acid buffer (pH 2·4 to 2·5). It was also found, as Stanton and McDonald[13] have reported, that the results obtained by the method are independent of the oxidation state of the tin in the original solution. Consequently, it is unnecessary to oxidise or reduce the tin in the hydrochloric acid solution before carrying out the determination of tin with gallein.

The chromatographic columns were prepared as described by Šulcek, Dolezal, Michal and Sychra. Preliminary investigations showed that the mixture of hydrochloric acid and bromine used for dissolution could be replaced with nitric acid when using samples of lead. Also, it was found satisfactory to use concentrated ammonia solution, instead of sodium hydroxide solution, for adjusting the pH of the solution to 5·5. Experiments were also carried out by using the Procedure described below to determine the effect of varying the amounts of citric acid, EDTA and ammonium chloride. It was found that the amount of citric acid could be varied between 5 and 15 g and that of EDTA between 1 and 3 g without influencing the results. Similar results were obtained by varying the volume of 0·1 M ammonium chloride solution between 5 and 15 ml. Other investigations showed that the pH could be varied between 5·4 and 5·6 without affecting the recovery of tin.

Method

Apparatus—

Chromatographic column—This consisted of a glass tube, 1 cm in internal diameter and 50 cm in length, provided at the lower end with 10 cm of rubber tubing with metal clip attached.

A Hilger Uvispek spectrophotometer was used for all of the optical density measurements and a Pye Universal pH meter for pH measurements.

Reagents—

All reagents should be of analytical-reagent grade.

Silica gel, M.F.C.—Special grade for chromatography, obtainable from Hopkin and Williams Ltd. Cover a suitable amount of silica gel with distilled water and leave it to stand for 12 hours (preferably overnight). Wash out the fine fraction by decantation, and then repeatedly wash the residue with dilute hydrochloric acid (50 per cent v/v, aqueous) and distilled water until completely free from iron.

Nitric acid, 20 per cent. v/v, aqueous—Prepare from concentrated nitric acid (sp.gr. 1·42).

Citric acid.

Ammonia solution, concentrated(sp.gr. 0·88).

Ammonium chloride solution, 0·1 M—Dissolve 5·4 g of ammonium chloride in water and dilute to 1 litre.

Ethylenediaminetetra-acetic acid, disodium salt (EDTA).

Sodium citrate solution, 0·5 M—Dissolve 121 g of sodium citrate in water and make up to 1 litre.

Hydrochloric acid, 50 per cent. v/v, aqueous—Prepare from concentrated hydrochloric acid, sp.gr. 1·18.

Hydrochloric acid, 10 per cent. v/v, aqueous—Prepare from 50 per cent. v/v aqueous hydrochloric acid.

Buffer solution—Dissolve 50 g of chloroacetic acid, 50 g of sodium chloroacetate and 25 g of hydroxylammonium chloride in 500 ml of water.

Gallein solution—Warm 5 mg of gallein with 50 ml of ethanol until no more dissolves. Filter through a Whatman No. 540 filter-paper into a 100-ml graduated flask and make up to the mark with ethanol.

Wash solution A—Take 200 ml of sodium citrate solution (0·5 M) and adjust the pH to 5·5 by the addition of citric acid crystals.

Wash solution B—To 200 ml of distilled water add 2 drops of sodium citrate solution (0·5 M). Adjust the pH to 5·5 by adding a few crystals of citric acid.

Pure tin—Obtainable from Associated Lead Manufacturers Ltd.

Standard tin solution A—Dissolve 0·0500 g of pure tin metal in 50 ml of concentrated hydrochloric acid. Add 50 ml of water and then dilute with hydrochloric acid (50 per cent. v/v, aqueous) to 500 ml.

1 ml of solution ≡ 0·0001 g of tin (in 50 per cent. v/v hydrochloric acid).

Standard tin solution B—Transfer 5 ml of standard tin solution A into a 100-ml graduated flask, add 15 ml of 50 per cent. v/v aqueous hydrochloric acid and dilute to the mark with water.

1 ml of solution ≡ 0·000005 g of tin (in 10 per cent. v/v hydrochloric acid).

PREPARATION OF COLUMN—

Prepare a slurry of a suitable amount of silica gel in wash solution A and transfer it to a glass column, after placing a plug of glass-wool at the bottom end. The length of the silica-gel column should be 8 to 10 cm. Pass 10 ml of wash solution A through the column.

PREPARATION OF CALIBRATION GRAPH—

Transfer 1·0, 2·0, 3·0, 4·0 and 5·0 ml of standard tin solution B (which contains 10 per cent. v/v of hydrochloric acid) into 50-ml graduated flasks. Introduce into each flask sufficient 10 per cent. hydrochloric acid solution so that the total volume of 10 per cent. hydrochloric acid is 5·0 ml, *i.e.*, add 4·0, 3·0, 2·0, 1·0 and 0 ml of 10 per cent. hydrochloric acid, respectively, to each flask. Add 20 ml of buffer solution, 5·0 ml of gallein solution and make up to the mark with water. Shake the solution for 30 seconds and, after 45 minutes, measure the optical density in a 4-cm cell at a wavelength of 520 mμ, with water as reference solution.

Carry out a blank determination by adding the above amounts of gallein and buffer solution to 5·0 ml of 10 per cent. v/v hydrochloric acid solution in a 50-ml graduated flask.

Subtract the optical density of the blank from each of the readings and plot the calibration graph.

PROCEDURE—

Transfer a suitable weight of sample (Note 1) into a 100-ml beaker containing 10 g of citric acid. Add 25 ml of 20 per cent. v/v nitric acid solution and heat until dissolution of the sample is complete. Cool the solution, add 12 ml of concentrated ammonia solution and again cool. Add 10 ml of 0·1 M ammonium chloride solution and 2 g of EDTA, and adjust the pH of the solution to 5·5 ± 0·1 with citric acid or ammonia solution (Note 2).

Transfer the solution immediately (Note 3) on to the prepared column (Note 4) by using a small funnel, and adjust the screw-clip so that the rate of flow does not exceed 3 ml per minute. When the solution has passed through the column, wash the column with 100 ml of wash solution A, followed by 50 ml of wash solution B.

When the solution has reached the upper level of the silica-gel column, add 10·0 ml of 50 per cent. v/v hydrochloric acid solution. Allow this acid to remain on top of the column for 5 minutes before eluting into a 50-ml graduated flask. Wash the column with water and collect the washings in the graduated flask.

Transfer, by pipette, 5·0 ml of the solution into another 50-ml graduated flask containing 20 ml of buffer solution. Add 5 ml of gallein reagent, complete the determination and prepare a blank, as described under Preparation of calibration graph.

NOTES—

1. It is recommended that a 2·5-g sample is taken for an expected tin content of 0·001 to 0·01 per cent., and a 0·25-g sample for tin contents between 0·01 and 0·10 per cent.
2. It is sometimes necessary to stir the solution vigorously for about 2 minutes to dissolve the EDTA.
3. If the sample weighs 2·0 g, or more, a precipitate may appear if the solution is allowed to stand for over 20 minutes before transferring the solution on to the column. For such solutions it is recommended that they are transferred on to the column immediately after adjustment of the pH to 5·5. It is essential that no precipitate is in the solution when the latter is transferred on to the column, because this would block the column and reduce the rate of flow.
4. One hundred millilitres of wash solution A is passed through the column at the commencement of each determination.

RESULTS

RECOVERY OF TIN IN THE PRESENCE OF LEAD—

The procedure was studied by using different weights of pure lead samples (0 to 2·5 g), to which was added a known volume of standard tin solution A.

Some typical results are shown in Table I.

TABLE I

RECOVERY OF TIN IN THE PRESENCE OF LEAD

Lead added, g	Tin added, mg	Tin found, mg	Error, per cent.
0	0·20	0·21	+5·0
0·25	0·20	0·20	0·0
0·50	0·20	0·20	0·0
0·75	0·20	0·19	−5·0
1·5	0·20	0·19	−5·0
2·0	0·20	0·20	0·0
2·5	0·20	0·20	0·0

RECOVERY OF TIN IN THE PRESENCE OF ANTIMONY AND LEAD—

According to Wood, antimony gives a colour with gallein similar to that given by tin. Šulcek, Dolezal, Michal and Sychra report that at pH 5·5 ± 0·1 the tin is adsorbed on the silica-gel column, while the antimony passes through. In view of the large amounts of antimony present in some antimonial lead alloys it was necessary to verify that this element was completely separated from the tin and, consequently, did not interfere with the spectrophotometric determination.

Several determinations were carried out, as described under Procedure, by using synthetic samples prepared from pure antimony and lead. Some typical results are shown in Table II.

TABLE II

RECOVERY OF TIN IN THE PRESENCE OF ANTIMONY AND LEAD

Lead added, g	Antimony added, g	Tin added, mg	Tin found, mg	Error, per cent.
Nil	0·025	0·20	0·20	0
0·25	0·025	0·20	0·20	0
2·25	0·25	0·20	0·21	+5·0
2·20	0·30	0·20	0·21	+5·0
2·10	0·40	0·20	0·20	0

DETERMINATION OF TIN IN THE PRESENCE OF OTHER ELEMENTS—

The method was applied to various synthetic samples containing lead and antimony, to which small amounts of other elements that normally occur with lead were added. The results are shown in Table III.

Table III

DETERMINATION OF TIN IN THE PRESENCE OF OTHER ELEMENTS

Lead, per cent.	Antimony, per cent.	Impurity added, per cent.	Form of added impurity	Tin added, per cent.	Tin found, per cent.	Error, per cent.
96	4	Zinc, 0·060	Zinc nitrate	0·0050	0·0047	−6
90	10	Cadmium, 0·035	Cadmium nitrate	0·0060	0·0059	−2
90	10	Copper, 0·050	Copper(II) nitrate	0·040	0·043	+3
88	12	Bismuth, 0·050	Bismuth nitrate	0·040	0·040	0
100	Nil	Arsenic, 0·020	Lead sample containing 0·020 per cent of arsenic	0·0020	0·0020	0
100	Nil	Copper, 0·060	Copper(II) nitrate	0·0040	0·0041	+3
100	Nil	Zinc, 0·035	Zinc nitrate	0·0085	0·0085	0
100	Nil	Nickel, 0·040	Nickel chloride	0·040	0·042	+5
100	Nil	Iron, 0·040	Iron(III) chloride	0·090	0·084	−7

The reproducibility of the method was investigated by determining the tin content of a sample of lead and antimonial lead alloy (Table IV).

Table IV

REPRODUCIBILITY OF THE METHOD WITH A SAMPLE OF LEAD AND ANTIMONIAL LEAD ALLOY

Sample	Composition, per cent.	Tin found, per cent.	Mean	Standard deviation
M91–4	Lead, 91 Antimony, 9	0·037, 0·038 0·040, 0·036 0·037, 0·040	0·038	±0·002
R2	Lead, 99·99	0·0055, 0·0044 0·0056, 0·0050 0·0052, 0·0048	0·0051	±0·0005

Discussion

The proposed procedure is suitable for the determination of 0·001 to 0·10 per cent. of tin in lead and antimonial lead alloys. A single determination takes about 3 hours, but at least eight determinations can be completed by one analyst in a normal working day.

According to Wood, antimony, which itself gives a colour with gallein, is likely to interfere in the spectrophotometric determination of tin by the gallein method. It was found that the chromatographic procedure separated the tin from antimony and so eliminated this interference. No serious interference was observed from other elements investigated (see Table III).

The reproducibility of results by the proposed method is good. For samples containing 0·0051 and 0·038 per cent. of tin the standard deviation was ±0·0005 and ±0·002, respectively.

It is thought that this is the first time that a chromatographic separation, in which silica gel was used, has been combined with a spectrometric determination of tin. It is possible that the method could be applied to the determination of small amounts of tin in other metals and alloys.

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References

1. Kallmann, S., Liu, R., and Oberthin, H., *Analyt. Chem.*, 1958, **30**, 485.
2. Cyrankowska, M., *Chemia. Analit.*, 1960, **5**, 851.
3. "Chemical Determination of Impurities in Lead," *British Non-Ferrous Metals Research Association Report* A985, 1960, p. 53.
4. Gur'ev, S. D., and Saraeva, N. F., *Inst. Tsvet. Met.*, 1961, **18**, 48.
5. Ross, W. J., and White, J. C., *Analyt. Chem.*, 1961, **33**, 424.
6. Ariel, M., and Kirowa, E., *Talanta*, 1961, **8**, 214.
7. Burstall, F. H., Davies, G. R., Linstead, R. P., and Wells, R. A., *J. Chem. Soc.*, 1950, 517.
8. Lederer, M., *Nature*, 1949, **163**, 598.
9. Frierson, W. J., and Ammons, M. J., *J. Chem. Educ.*, 1950, **27**, 37.
10. Tewari, S. N., *Naturwissenschaften*, 1954, **41**, 229.
11. Šulcek, Z., Dolezal, J., Michal, J., and Sychra, V., *Talanta*, 1963, **10**, 3.
12. Wood, G. A., *Tech. Commun. Geochem. Prospect. Res. Cent.*, 1957, No. 11, 6.
13. Stanton, R. E., and McDonald, A. J., *Trans. Instn Min. Metall.*, 1961, **71**, 27.

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The Polarographic Determination of Some Dithiocarbamates and their Heavy Metal Complexes

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Procedures for the determination of monoalkyl- and dialkyldithiocarbamates and some of their metal complexes that are used as pesticides are described. The methods are based on a detailed investigation of the polarographic behaviour of these compounds, and are suitable for the analysis of pesticide preparations and residues.

Dithiocarbamates, **I, II,** have many uses; they are widely used as pesticides, especially as their metal complexes, and are applied in the rubber industry as vulcanisation accelerators and anti-oxidants. This latter property also makes them useful additives for oils and greases. In each instance, accurate determination of the dithiocarbamates is essential.

Most of the analytical methods in general use are based on the Clarke method,[1] in which the dithiocarbamate is destroyed in acidic solution to give carbon disulphide. The latter is absorbed in methanolic potash, and the potassium methyl xanthate so formed is titrated iodimetrically. The conditions for this determination appear to be quite critical, especially for some ethylenebisdithiocarbamate complexes, but standard methods are based on this procedure.[2,3] Dithiocarbamate pesticide residues, however, have been analysed[4,5] by determining the released carbon disulphide spectrophotometrically. Paper chromatography[6] and infrared spectroscopy[7,8] have also been suggested for the determination of dithiocarbamates.

Polarography has proved to be useful in pesticide analysis, both for the analysis of pesticide preparations and for the determination of residues.[9,10,11,12] Furthermore, it has been applied to the determination of the alkali dithiocarbamates[13,14] and to the dithiocarbamate pesticides.[15,16] Nangniot[16,17,18] used the hanging mercury drop to improve the sensitivity of the determination. The polarography of dithiocarbamates has also been used for the determination of carbon disulphide[19] and amino-acids.[20]

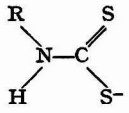
The present study is part of a more general investigation of the polarographic behaviour of dithiocarbamates. This paper describes the polarographic properties of simple monoalkyldithiocarbamates, **I,** dialkyldithiocarbamates, **II,** and ethylenebisdithiocarbamates, **III,** that are relevant to their polarographic determination. A more detailed report of their general polarographic behaviour is given elsewhere.[21] On the basis of these results, methods are devised for the polarographic determination of these compounds and some of the metal complexes that are used as pesticides *viz.*—

NABAM (disodium ethylenebisdithiocarbamate)
ZINEB (zinc ethylenebisdithiocarbamate)
MANEB (manganese ethylenebisdithiocarbamate)

Polarographic studies—

All simple dithiocarbamates give anodic waves. It was originally suggested[22] that these were caused by a reversible couple with the corresponding disulphides, but it was later recognised[23] that they arose from mercury compound formation. Recent papers on the polarographic determination of diethyldithiocarbamate[13,24] reported irregularities in the shape and concentration dependence of the anodic waves, but gave no explanation for this.

* On leave from J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague.



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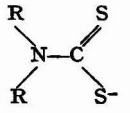
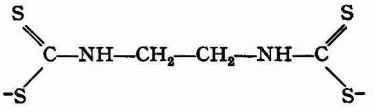
Ic R = C_4H_9



IIa R = C_2H_5
IIb R = $CH_2C_6H_5$



III

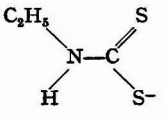
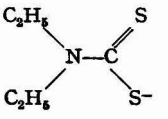
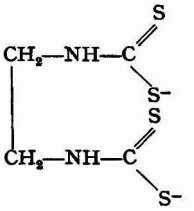
At lower pH values monoalkyldithiocarbamates, **I**, show two waves. They merge in alkaline media. The waves are accompanied by an adsorption pre-wave at the lower pH values. The total wave height over the whole pH range studied (pH 1 to 13), and the height of the single, well developed wave in 0·1 N sodium hydroxide solution are linearly proportional to the concentration of the monoalkyl dithiocarbamates, **I**, and are suitable for analytical applications.

The waves of the dialkyldithiocarbamates, **II**, above pH 6·8 were complicated by an increase in the limiting current caused by adsorption of a film of the mercury compound, and by its desorption accompanied by streaming of the solution.[21] These cause a round-shaped increase in the limiting current and a non-linear dependence of the total wave height on concentration. The height increases with increasing concentration of the dithiocarbamate more than is expected for a linear wave height - concentration relationship. Addition of gelatin or the use of 60 per cent. v/v ethanol - water, 0·1 N in sodium hydroxide, eliminated this complication and a linear wave height - concentration plot was found under such conditions. The anodic wave of diethyldithiocarbamate was accompanied by the usual adsorption pre-wave.

The polarographic behaviour of disodium ethylenebisdithiocarbamate (**III**, NABAM) in aqueous solutions was complicated by adsorption phenomena that caused the wave to be ill-separated and difficult to measure. Well developed waves, suitable for analytical purposes were found in 0·1 N sodium hydroxide solution in 90 per cent. ethanol - water, or 50 per cent. dimethylformamide - water. Even under these conditions the wave was accompanied by an adsorption pre-wave, but the total wave height was proportional to the concentration of NABAM.

TABLE I

COMPOSITION OF DITHIOCARBAMATE COMPLEXES IN 0·1N SODIUM HYDROXIDE

Molar ratio of metal to dithiocarbamate			
Cd^{II}	1:2*	1:2	1:1 and 2:1
Pb^{II}	1:2*	1:2	1:1 and 2:1
Hg^{II}	1:2*	1:2	1:1 and 2:1
Co^{II}, Mn^{II}			No complex
Ni^{II}, Zn^{II}			

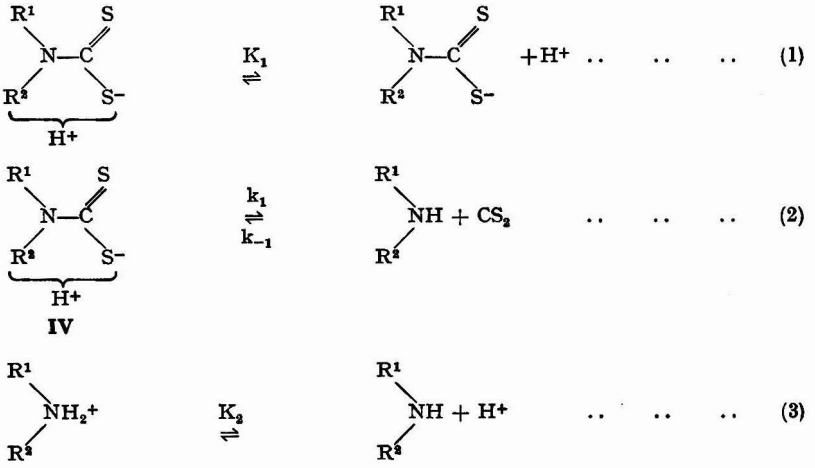
* Formation of 1:1 complex possible; formation of cadmium sulphide observed.

The addition of metal ions to the solutions of dithiocarbamates and recording of the anodic wave of dithiocarbamates and the cathodic waves of the metal ions and soluble metal complex make it possible to determine the stoicheiometric ratio in which metal ions react

with dithiocarbamates, and to elucidate the composition of the compounds formed. These are summarised in Table I for 0·1 N sodium hydroxide solution. The compounds formed by the reaction of mono- and dialkyldithiocarbamates are insoluble, hence in these instances only a decrease of the anodic wave of the dithiocarbamates was observed. However, if the metal ion formed soluble anionic species (*e.g.*, plumbate and zincate) in alkaline media, an excess of the metal ion would give a cathodic reduction wave. In those instances where no reaction was observed (Co^{II}, Mn^{II}, Zn, Ni) the anodic wave was unchanged. The reaction of lead with diethyldithiocarbamate gave the expected PbL_2 complex, but this was partly soluble and gave a cathodic wave at −0·80 volt *versus* S.C.E.

The complexes formed between 1 mole each of NABAM, **III**, and metal ion in dilute sodium hydroxide solutions were soluble. Thus the decrease in the anodic wave of NABAM was accompanied by a rise in the cathodic wave of the complex. However, the metal-$(NABAM)_2$ complexes were hardly soluble, so that this cathodic wave decreased on the addition of more ligand. Manganese and zinc did not complex with NABAM in 0·1 N sodium hydroxide solution. Analytical methods for MANEB and ZINEB were based on these observations. For analytical purposes, 0·1 N sodium hydroxide solution containing 0 to 90 per cent. of ethanol, depending on the compound studied, proved to be the best supporting electrolyte. Under these conditions, the dithiocarbamate anion is liberated and the metal ion is transformed into a soluble complex or an insoluble oxide or hydroxide. Hence an addition of MANEB to the alkaline solution gave an anodic dithiocarbamate wave that was identical in height, shape and half-wave potential with a NABAM wave obtained under identical conditions, and manganese dioxide was precipitated. An analytical method for MANEB based on these observations would not suffer from the uncertain stoicheiometry it shows in the Clarke method. Furthermore, it was established that the sensitivity of the polarographic method was just sufficient to allow the determination of dithiocarbamate residues, particularly MANEB. For greater sensitivity, the hanging drop method could be used.[16]

Finally, polarography can be used in the study of the kinetics of acid decomposition of dithiocarbamates by measuring the height of the anodic dithiocarbamate wave. It was found[25] that the decomposition is that of the conjugate acid form, **IV**, of the dithiocarbamate, and the elimination - addition reaction is accompanied by two acid - base equilibria—



In acidic media equilibrium (1) is shifted to the left and cleavage with rate constant k_1 takes place. Because equilibrium (3) is shifted to the left-hand side, the reaction with rate constant k_{-1} cannot take place. Hence in acidic media at pH 5 ($pK_1 + 1$), irreversible cleavage of dithiocarbamates takes place and condensation does not occur.

In alkaline media, equilibrium (3) is shifted to the right-hand side. Formation of dithiocarbamates from carbon disulphide and amine with constant k_{-1} takes place. Because equilibrium (1) is shifted to the right-hand side, the protonised form, which is the primary product, is transformed into an inactive conjugate base (dithiocarbamate anion). Hence in alkaline media at pH $\geq$ ($pK_2 - 1$), irreversible condensation of amines with carbon disulphide

takes place and the dithiocarbamate anions are stable and do not undergo cleavage. Thus, the determination of carbon disulphide or simple amines based on the formation of dithiocarbamates is best carried out under these conditions.

In this way, it is possible to explain the greater stability of monoalkyldithiocarbamates in acidic solutions when compared with dialkyldithiocarbamates; this is predominantly caused by the fact that the acidity of the protonated form, **IV**, is greater for mono- than for dialkyldithiocarbamates. By a suitable choice of pH of about 3·5 to 5, monoalkyldithiocarbamates can be determined in samples that originally contained dialkyldithiocarbamates because of the rapid decomposition of the latter under these conditions. Conversely, dialkyldithiocarbamates are, unlike the monothiocarbomates, resistant to alkaline decomposition, so that after heating a mixture of these compounds in 2 N sodium hydroxide solution for 2 to 3 hours only the dithiocarbamate remains.

It would be possible to follow the acid cleavage of NABAM in a similar manner. Preliminary experiments indicated two successive reactions. Moreover, the carbon disulphide formed in this reaction can be determined polarographically.

Recommended analytical procedures

1. Determination of a monoalkyldithiocarbamate—

Dissolve the sample in 0·1 N sodium hydroxide solution to obtain a final concentration in the range 5×10^{-5} to 10^{-3} M. Record the polarographic wave, and measure the total anodic wave height. Evaluate the results from a calibration curve.

Note—The solution should not stand for more than 30 minutes before carrying out the polarographic measurements.

2. Determination of a dialkyldithiocarbamate—

Dissolve the sample in 0·1 N sodium hydroxide solution, either 60 per cent. in ethanol or containing 0·02 per cent. of gelatin. The final dithiocarbamate concentration should be in the range 5×10^{-5} M to 8×10^{-4} M. Record the polarographic curve, and measure the total anodic wave height. Evaluate the results from a calibration curve.

3. Determination of a monoalkyldithiocarbamate in the presence of a simple dialkyldithiocarbamate—

Dissolve the sample in a buffer solution of pH 3·5 to 5. Record the anodic waves after this solution has stood for 20 to 30 minutes (in which time the dialkyl derivative will have decomposed completely) and the solution has been purged with oxygen-free nitrogen. Complete the determination as in 1.

4. Determination of a dialkyldithiocarbamate in the presence of a simple monoalkyldithiocarbamate—

Dissolve the sample in 2 N sodium hydroxide solution, and heat the solution for 2 to 3 hours at 70° C (so that the monoalkyl derivative is completely decomposed). Purge the solution with oxygen-free nitrogen. This removes isothiocyanate formed by the decomposition of the monoalkyldithiocarbamate that is capable of forming monoalkylmonothiocarbamate, which gives anodic waves similar to the dithiocarbamates. It also prevents oxidation. Cool the solution, and complete the determination as in 2. A calibration curve should be prepared by taking the standards through the whole procedure.

5. Determination of disodium ethylenebisdithiocarbamate (NABAM)—

Dissolve the sample in 0·1 N sodium hydroxide solution in 90 per cent. ethanol to give a final NABAM concentration of 1×10^{-5} M to 5×10^{-4} M, or in an aqueous 0·1 N sodium hydroxide solution if the final NABAM concentration is to be higher. Record the anodic waves and measure the total wave height. Evaluate by using a calibration curve obtained from experiments in the same medium.

6. Determination of zinc ethylenebisdithiocarbamate (ZINEB)—

Dissolve the sample in aqueous 1·0 N sodium hydroxide solution and record the anodic waves. Measure the total wave height, and evaluate from a calibration curve prepared from NABAM or ZINEB.

For the determination of ZINEB residues (0·3 to 3 p.p.m. of wet weight of vegetable matter), the dithiocarbamate should be extracted from the host material (100 g) by homogenising with 10 ml of N sodium hydroxide solution. A calibration curve should be prepared by adding standard amounts of NABAM or ZINEB to the host material.

7. DETERMINATION OF MANGANESE ETHYLENEBISDITHIOCARBAMATE (MANEB)—

The procedure is the same as that for ZINEB; 3×10^{-6} M to 3×10^{-4} M MANEB can be determined.

All the anodic waves appear in the potential range between −1·0 and −0·2 volt, and were recorded from negative to positive potentials. The reproducibility was that usual for polarographic determinations, *i.e.*, ±2 to 4 per cent. in pure solutions and ±5 to 15 per cent. in the presence of biological material.

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REFERENCES

1. Clarke, D. G., Baum, H., Stanley, E. L., and Hester, W. F., *Analyt. Chem.*, 1951, **23**, 1842.
2. Stevenson, A., *J. Sci. Fd Agric.*, 1964, **15**, 509.
3. Bontogan, W. R., *J. Ass. Off. Agric. Chem.*, 1965, **48**, 562.
4. Cullen, T. E., *Analyt. Chem.*, 1964, **36**, 221.
5. Henermann, R. F., *J. Ass. Off. Agric. Chem.*, 1957, **40**, 264.
6. McKinley, W. P., and Magarvy, S. A., *Ibid.*, 1960, **43**, 717.
7. Fischer, W., and Uhlich, U., *Z. analyt. Chem.*, 1960, **172**, 175.
8. Susi, H., and Rector, H., *Analyt. Chem.*, 1958, **30**, 1933.
9. Brezina, M., and Zuman, P., "Polarography in Medicine, Biochemistry and Pharmacy," Interscience Publishers Inc., New York and London, 1958.
10. Martens, P. H., and Nangniot, R., *in* Gunther, F. A., *Editor*, "Residue Reviews," Springer-Verlag, Berlin, Gottingen and Heidelberg, Volume 2, 1963, p. 26.
11. Gajan, R. J., "Instrumental Detection and Determination of Pesticides and Residues in Foods," Academic Press, New York, 1964, p. 80.
13. Pasciak, J., *Chemia Analit.*, 1963, **8**, 945.
14. ——, *Ibid.*, 1964, **9**, 39.
15. Zawadzka, T., *Roczn. Państ. Zakl. Hig.*, 1966, **17**, 263.
16. Nangniot, P., *Bull. Inst. Agron. Stns. Rech. Gembloux*, 1960, **28**, 365.
17. ——, *Ibid.*, 1960, **28**, 373.
18. ——, *Ibid.*, 1960, **28**, 381.
19. Zuman, P., Zumanová, R., and Souček, B., *Colln Czech. Chem. Commun.*, 1953, **18**, 632.
20. Zahradník, R., *Ibid.*, 1956, **21**, 447.
21. Halls, D. J., Townshend, A., and Zuman, P., *Analytica Chim. Acta*, 1968, **40**, 459; 1968, **41**, 51.
22. Gregg, E. C., and Tyler, W. P., *J. Amer. Chem. Soc.*, 1950, **72**, 4561.
23. Zuman, P., Zumanová, R., and Souček, B., *Chemické Listy*, 1953, **47**, 1522.
24. Stricks, W., and Chakravarti, S. K., *Analyt. Chem.*, 1962, **34**, 508.
25. Zahradník, R., and Zuman, P., *Colln Czech. Chem. Commun.*, 1959, **24**, 1132.

Received *October 12th*, 1967

* 11. Gajan R J., in Gunther, F.A., Editor, Residue Reviews, Springer-Verlag, Berlin, Goltingen and Heidelberg, Vol. 6, 1964, p. 95.

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A Selective Amplification-Titration Procedure for the Determination of Microgram Amounts of Phosphate

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Phosphate is converted into phosphomolybdic acid, which is separated from excess of molybdate by extraction. The phosphomolybdate is back-extracted into aqueous solution, and the twelve molybdate ions accompanying each phosphate ion are reduced on a silver reductor column and titrated with 10^{-3} M cerium(IV) by use of a 50-ml burette. Other heteropoly acid-forming elements, *e.g.*, arsenic, antimony, germanium and silicon do not interfere, and there is no interference from a wide range of other ions. The method is both precise and rapid, and has been applied to the submicro determination of phosphorus in a standard organic compound.

In earlier papers from this Department indirect methods for the sensitive and selective determination of phosphate[1] and phosphate and silicate[2] by molecular-absorption and atomic-absorption spectroscopy, respectively, have been reported. These amplification procedures are based on the determination of the twelve molybdenum atoms associated with each phosphorus or silicon atom after selective solvent extraction of phosphomolybdic or silicomolybdic acid from excess of reagent into isobutyl acetate or butanol. This paper reports a rapid alternative titrimetric procedure of considerably higher precision for the selective determination of microgram amounts of phosphorus that is based on the same amplification procedure.

Phosphomolybdic acid is selectively extracted from excess of molybdate into isobutyl acetate, back-extracted and degraded into alkaline solution, and the molybdenum(VI) reduced to molybdenum(V) by a silver reductor column. The determination is then completed by the direct visual or photometric titration of the molybdenum(V) with standard cerium(IV) sulphate solution, with ferroin indicator and a 50-ml grade A burette.[3]

Experimental

Apparatus—

An E.E.L. photoelectric titrator and galvanometer (Evans Electroselenium Ltd., Halstead, Essex) was used.

Reductor column—Silver for the reductor column was prepared by the method of Kolthoff and Belcher.[4] The column used was a laboratory 10-ml burette of internal diameter 1 cm; a column length of 7 cm was used. This column is smaller than that used by Birnbaum and Walden,[3] so that a smaller total volume of eluate can be obtained. The column was maintained in 2 N hydrochloric acid at all times, and was equilibrated with hot (60° to 80° C) 2 N hydrochloric acid immediately before use.

Reagents—

Standard orthophosphate solution—Dissolve 0·1098 g of analytical-reagent grade potassium dihydrogen orthophosphate in distilled water and dilute to 1 litre.

1 ml of solution ≡ 25 μg of phosphorus.

Molybdate reagent solution—Dissolve 10·69 g of analytical-reagent grade ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in distilled water and dilute to 1 litre.

Cerium(IV) sulphate solution—Prepare by diluting British Drug Houses, Ltd. concentrated volumetric solution. Dilute the stock 0·05 M solution to 10^{-3} M with 2 N sulphuric acid as required.

1 ml of 10^{-3} M cerium(IV) solution ≡ 2·58 μg of phosphorus.

Ferroin indicator solution—Use a 5×10^{-3} M aqueous solution of ferroin, $Fe(C_{12}H_8N_2)_3SO_4$. Two drops of indicator solution were used for each titration.

Hydrochloric acid—Analytical-reagent grade.

Ammonia solution, sp.gr. 0·88—Analytical-reagent grade.

Isobutyl acetate—General-purpose reagent grade.

PROCEDURE—

The optimum conditions for the selective extraction of phosphomolybdic acid from excess of molybdate reagent into isobutyl acetate have already been described,[2,5] and were used here.

Transfer the sample solution (up to 5 ml), containing between 3 and 30 μg of phosphorus, into a 100-ml separating funnel containing 10 ml of molybdate stock solution and 10 ml of water. Add sufficient concentrated hydrochloric acid to make the solution 0·96 M with respect to hydrochloric acid. Allow the solution to stand for 5 minutes, add 10 ml of isobutyl acetate and shake the funnel for 1 minute. Allow the phases to separate, discard the aqueous phase, and wash the organic phase with 10 ml of 2 N hydrochloric acid. Shake the organic phase with 5 ml of 4 M ammonia solution, discard the isobutyl acetate and retain the alkaline solution containing the molybdenum(VI).

REDUCTION AND TITRATION—

Transfer the molybdenum solution from the extraction funnel into a 50-ml beaker, add sufficient 6 N hydrochloric acid to neutralise the ammonia and make the solution 2 N with respect to hydrochloric acid. Transfer the solution quantitatively into the top of the reductor column by using 2 N hydrochloric acid as wash liquid. Reduce the molybdenum(VI) to molybdenum(V) on this column by using the method described by Birnbaum and Walden,[3] eluting the sample three times with 5-ml portions of hot 2 N hydrochloric acid and three times with 5-ml portions of cold 2 N hydrochloric acid. Collect the eluate (35 to 40 ml) in the titration cell, heat rapidly to boiling, cool the solution to near room temperature, and titrate the molybdenum(V) with standard 10^{-3} M cerium(IV) sulphate, with ferroin indicator and E.E.L. filter No. 603. Alternatively, after some experience, the end-point can be detected visually by the disappearance of the last trace of pink colour. We find the visual method to be entirely satisfactory.

RESULTS AND DISCUSSION

Before the determination of phosphate was attempted via the selective solvent-extraction procedure, pure aqueous molybdenum(VI) solutions were reduced and titrated with cerium(IV) sulphate to ensure that quantitative reduction and recovery of molybdenum was obtained on the reductor column. The molybdenum concentrations were chosen in these experiments to correspond to those which would be obtained after the amplification of the initial phosphorus content (3 to 30 μg) of samples. It was found that a significant blank [1·8 ml of 10^{-3} M cerium(IV)] was obtained in the absence of molybdenum in the reduction - titration procedure. At the ferroin indicator concentration used, the indicator blank accounts for about one third of this blank (0·65 ml) when the titration is carried out with 10^{-3} M cerium(IV) sulphate. It is our opinion that the remainder of the blank was caused by the formation of hydrogen peroxide on the silver reductor[4] and can be eliminated by momentarily boiling the eluate before titration. The indicator blank is reproducible and can safely be subtracted from the sample titration volume.

Quantitative recovery and titration of 12 moles of molybdenum is obtained for each mole of phosphorus in the sample. As reported previously, the isobutyl acetate extraction separates phosphomolybdic acid efficiently from the excess of molybdate reagent. The procedure has selectivity equal to those previously reported, and no interference is caused by the presence of large excesses (100-fold by weight) of silicate, arsenate, antimony(V) and germanium(IV). As shown in Table I, phosphorus can be determined in the presence of several milligrams of each of a wide range of cations without interference.

Although we have not established it experimentally, we see no reason why a similar method should not be devised for the titrimetric determination of silicate by modification

of the amplification procedure previously described in earlier papers from this Department. There is no reason to suppose that the presence of silicate ions should interfere in any way with the functioning of the Birnbaum and Walden reductor column.

TABLE I

DETERMINATION OF PHOSPHORUS IN SYNTHETIC MIXTURES TREATED AS UNKNOWNS

Phosphorus taken, μg	Theoretical titre, ml	Titre obtained, ml	Phosphorus found, μg	Foreign ions present, mg	
10·0	3·87	3·87	10·0	Selenium(IV)	1·59
				Tellurium(IV)	1·28
12·5	4·84	4·64	12·0	Barium	6·87
				Manganese	5·5
				Silicon	2·0
20·0	7·74	7·78	20·1	Aluminium	1·0
				Lead	2·07
20·0	7·74	7·88	20·3	Cobalt	2·95
				Nickel	2·95
5·0	1·94	2·05	5·3	Selenium(IV)	1·59
				Tellurium(IV)	1·28
25·0	9·68	9·68	25·0	Arsenic(V)	2·0
				Germanium(IV)	2·0
				Silicon	4·0
				Calcium	2·5
20·0	7·74	7·93	20·5	Iron(III)	3·0
				Zinc	6·5
25·0	9·68	9·94	25·7	Barium	6·87
				Manganese	5·5
				Silicon	2·0
25·0	9·68	10·06	26·0	Zinc	6·5
				Cadmium	5·6
				Copper	6·4

The precision of the reduction - titration procedure was established by repetitive analysis of a pure molybdenum(VI) solution. The standard deviation in the titration value for the determination of 929 μg of molybdenum (equivalent to 25 μg of phosphorus) was 0·05 ml, or 0·55 per cent. The precision of the whole procedure was established by the repetitive determination of 25 μg of phosphorus by the solvent-extraction, reduction and titration procedures. The standard deviation in the titration volume for the determination of 25 μg of phosphorus, repeated seven times, was 0·135 ml, or 1·3 per cent. A measure of the accuracy of the procedure was obtained by determining phosphorus in synthetic solutions containing foreign ions. The results of these analyses are shown in Table I. The results obtained for the determination of phosphorus in microanalytical-reagent grade triphenylphosphine are shown in Table II. Different sample weights (in the range 60 to 200 μg) were digested with a

TABLE II

DETERMINATION OF PHOSPHORUS IN TRIPHENYLPHOSPHINE SAMPLES

Phosphorus in sample taken, μg	Phosphorus found, μg	Error, per cent.	Phosphorus in triphenylphosphine, (theory 11·81 per cent.)
12·11	12·12	+0·1	11·82
11·27	11·25	−0·2	11·79
7·53	7·50	−0·3	11·76
16·77	16·50	−1·6	11·62
9·10	9·00	−1·0	11·68
16·65	16·12	−3·2	11·44
20·20	21·00	+3·9	12·27
21·63	21·25	−1·7	11·76
10·76	10·56	−2·0	11·59
11·72	11·87	+1·3	11·96

sulphuric acid - perchloric acid mixture, and the perchloric acid was removed by evaporation. The residual sulphuric acid smear was then treated directly by the recommended procedure. The determination of 10^{-6}-g amounts of phosphorus, by using an ordinary burette with titration volumes of several millilitres of a 10^{-3} M titrant and visual detection of the end-point, furnishes a good illustration of the analytical value of amplification reactions.

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References

1. Djurkin, V., Kirkbright, G. F., and West, T. S., *Analyst*, 1966, **91**, 89.
2. Kirkbright, G. F., Smith, A. M., and West, T. S., *Ibid.*, 1967, **92**, 411.
3. Birnbaum, N., and Walden, G. H., jun., *J. Amer. Chem. Soc.*, 1938, **60**, 64.
4. Kolthoff, I. M., and Belcher, R., "Volumetric Analysis," Volume III, Interscience Publishers, a division of John Wiley & Sons Inc., New York and London, 1957, p. 15.
5. Paul, J., *Mikrochim. Acta*, 1965, 830.

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The Determination of Actinium-227 in Urine

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A method is described for the determination of actinium-227 in urine. After oxidation of the urine sample with nitric acid, actinium is co-precipitated on barium sulphate. The barium sulphate is converted into carbonate, dissolved in acid and the actinium co-precipitated on iron(III) hydroxide to remove barium and radium. The iron(III) hydroxide precipitate is dissolved in a mixture of nitric and hydrochloric acids and the solution passed through an anion-exchange column upon which iron, thorium and protactinium are absorbed. The column effluent, which contains the actinium, is essentially free from solids. Sources for α-counting may be prepared either by evaporation or by electro-deposition. Actinium recoveries of about 80 per cent. are obtained, with good decontamination from protactinium, thorium, radium, polonium and lead.

ACTINIUM-227 occurs naturally as a member of the actinium ($4n + 3$) series of radioelements, shown in Fig. 1. It decays with a half-life of 22 years, predominantly by β-emission, 98·8 per cent., to thorium-227, and the remaining 1·2 per cent. of the decay is by α-emission to francium-223. Its immediate precursor in the series is protactinium-231, with a half-life of $3{\cdot}4 \times 10^4$ years.

As actinium-227 is a bone-seeking radionuclide giving rise to no less than five α-emitting daughters, its maximum permissible body burden (bone critical) set by the International Commission on Radiological Protection[1] is only 0·03 microcuries, which is one of the most restrictive.

In common with other bone-seeking radionuclides, actinium is only eliminated slowly from the body, and the I.C.R.P. allocate it a biological half-life that is identical with that of plutonium. If the excretion rates of these two elements are similar, then by comparison with Langham's results[2] for plutonium, an investigation level for actinium-227 in urine of 0·3 picocuries per 24 hours can be derived.

There is little information available on the metabolism and excretion pattern of actinium. After intramuscular injection of actinium-227 in rats, Barr[3] found that, after 256 days, 66 per cent. of the injected dose had been excreted in faeces and only 8 per cent. in urine. However, in a recent case[4] of accidental intake of actinium-227 via a puncture wound, the urinary excretion rate was about twice that in faeces.

It is possible to determine actinium-227 by either α- or β-counting. The relative sensitivity of a counting technique is often considered as a function of E^2/B where E is the counting efficiency and B is the background of the counter. The efficiencies of modern α- and β- counters are roughly comparable, but the α-background is generally between one and two orders of magnitude lower than the β-background. Although the initial α-counting rate from separated actinium-227 represents only a small fraction of the disintegration rate, the in-growth of daughters is relatively rapid and after 20 days the α-counting rate will have increased by a factor of greater than 100. High sensitivity is a primary consideration in any bioassay procedure for actinium-227 and it can be seen from the above that this is best achieved by α-counting. If α-counting is to be used it is essential that good decontamination of the actinium-227 from its radioactive daughters is obtained. This is particularly important when analysing samples of excreta, which may contain daughters not only from the actinium-227 therein, but also from this isotope elsewhere in the body.

Following a case of internal contamination with actinium-227, it became necessary to devise a specific method for its determination in samples of urine and faeces. The "gross α" method[5] previously used at Harwell for actinium-227 is not specific for this element. Various methods have been published for the determination of actinium. Petrow and Allen[6] determined actinium in uranium mill effluent by solvent extraction with di-(2-ethylhexyl)phosphoric acid and Hagemann[7] and Hyde[8] used solvent extraction into 1-(2-thenoyl)-3,3,3-trifluoroacetone. However, low yields and poor decontamination factors were obtained when these procedures were applied to the analysis of urine samples.

This paper describes the development of a specific method for actinium-227 in urine, in which recoveries of about 80 per cent. and good decontamination from both parent and daughter radioelements were obtained. A feature of the work is the use of actinium-228 as a γ-tracer for assessing the recovery of actinium. This was prepared by a method similar to that described by Batki and Aldoff.[9]

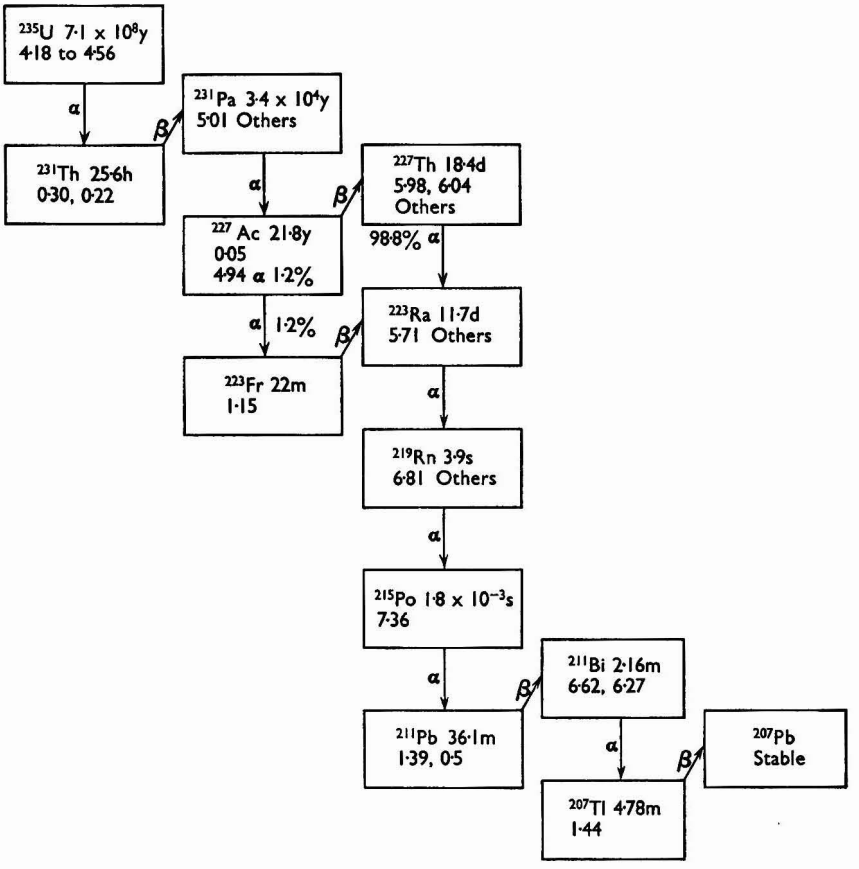

Fig. 1. Decay scheme of the actinium (4n+3) series

Experimental

The determination of actinium-227 in urine may be conveniently considered in three stages: the initial separation of actinium from urine; the purification of the separated actinium; and the preparation of actinium-227 in a form suitable for α-counting.

Initial separation of actinium from urine—

As there did not appear to be any information on the chemical form of actinium in urine, samples were completely oxidised by evaporation with nitric acid and ashing the residue

in a muffle furnace. The ash was then dissolved in dilute hydrochloric acid and the actinium co-precipitated with barium sulphate.

From previous work on the determination of radiostrontium in urine[10] it was known that the concentration of inorganic sulphate in urine is about 0·02 N, and that maximum recovery of strontium, as sulphate, is obtained from solutions adjusted to 0·5 N with respect to sulphate. Before addition of barium carrier, therefore, the sulphate concentration was increased to this value. Initially ammonium sulphate was added, but it was found by the use of actinium-228 tracer that improved recoveries were obtained if the additional sulphate was added as sulphuric acid. A 3-ml volume of 3 M sulphuric acid was added to each sample and the recovery of actinium at this stage was increased from 70 to almost 100 per cent. It was also found with this procedure that the total sulphate concentration was not critical, and the volume of the initial urine sample could vary between 500 ml and 2 litres without affecting the actinium recovery. Little calcium sulphate was precipitated under these conditions. Other members of the actinium series, particularly radium and thorium, also co-precipitated with barium sulphate, so that no significant decontamination was obtained at this stage.

PURIFICATION OF THE ACTINIUM-227—

The barium sulphate precipitate was converted by metathesis to the carbonate by digestion with 50 per cent. w/v potassium carbonate solution containing 50 mg of lead. This solution was used instead of the more usual sodium carbonate solution for the following reason.

Many lead salts, including lead sulphate, are soluble in 50 per cent. potassium carbonate solution, so that lead isotopes, co-precipitated with the barium sulphate, dissolve when it is digested in this way. By using lead-212 as a γ-tracer, it was found that 50 mg of lead hold-back carrier were required to obtain a quantitative decontamination of the barium carbonate. As many thorium salts also dissolve in potassium carbonate solution, some thorium is also removed by this method.

The barium carbonate precipitate that carries the actinium, radium and some thorium and protactinium was dissolved in dilute hydrochloric acid and, after the addition of iron carrier, iron(III) hydroxide was precipitated by the addition of ammonia solution. Actinium, thorium and protactinium are co-precipitated on the iron(III) hydroxide but the barium carrier and radium-223 remain in solution. To ensure effective decontamination from radium, the iron(III) hydroxide was dissolved in hydrochloric acid and re-precipitated after the addition of a further quantity of barium hold-back carrier.

Danon[11] showed that thorium, in strong nitric acid solution, is absorbed on anion-exchange resins. In the presence of hydrochloric acid, iron is also taken up. Separation of actinium from the remaining thorium and iron carrier was achieved by dissolving the iron(III) hydroxide precipitate in 7 N nitric - 3 N hydrochloric acid and passing the solution through a column of De-Acidite FF, previously conditioned with the mixed acids. Protactinium is also taken up on the column, as are some other actinides, but actinium is not retained. After washing the column with the mixed acids, the effluent and washings were combined.

PREPARATION OF ACTINIUM FOR α-COUNTING—

The most direct method of source preparation is by evaporation of the acid effluent from the ion-exchange column on a platinum tray. This effluent is almost free from solids and, after flaming, the source obtained is quite thin and suitable for counting in a zinc sulphide screen scintillation counter. This method was used to count actinium-227, isolated from spiked urine samples to determine the recovery. The background of the conventional scintillation counter (type 1093A) used at the U.K. Atomic Energy Research Establishment is about 5 counts per hour. If greater sensitivity is required, low background counters with silicon-junction diode detectors[12] are available. These accept sources of 1-cm diameter and to prepare thin sources of these dimensions, electro-deposition techniques are used.

With actinium-228 as a convenient tracer, experiments were carried out with various electrolytes to find a suitable procedure for the electro-deposition of actinium. Sulphate,[13] nitrate,[14] acetate[15] and fluoride[16] solutions were tried. Recoveries varied between 50 and 70 per cent. and were not really satisfactory. Combinations of nitrate and ethanol, adjusted to pH 2 with ammonia solution, gave recoveries of as high as 95 per cent. on occasions, but consistent results could not be obtained, and no improvement resulted from the addition of microgram amounts of lanthanum carrier.

The best results were obtained by using the acidic ammonium chloride electrolyte described by Mitchell.[17] At pH 2, with a current of 500 mA and a plating time of 1 hour, the mean recovery was 80 $\pm$ 5 per cent. Increasing the plating time to 2 hours did not improve the recovery.

MEASUREMENT OF ACTINIUM-227 BY α-COUNTING—

As mentioned previously, only 1·2 per cent. of the disintegrations of actinium-227 give rise to an α-particle. As there are five α-emitting daughters, all with relatively short half-lives, their in-growth occurs fairly rapidly, and their contribution to the total α-count may be estimated for any given time by the Bateman equation. The theoretical curve, A, showing the ratio of the α-activity of actinium-227 *plus* daughters to that of the actinium-227 alone at various times after its separation is shown in Fig. 2.

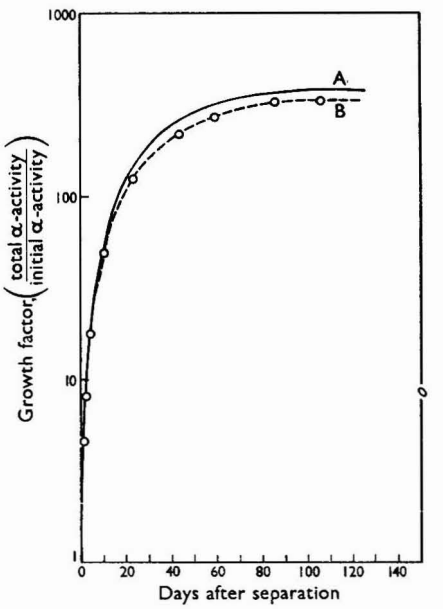

Fig. 2. Growth of α-activity in separated actinium-227 source: A, theoretical curve; B, experimental curve

There are two advantages to be gained by allowing at least two or three weeks to elapse before α-counting the separated actinium-227. Firstly, the count-rate increases almost linearly over this period so that there is a considerable gain in sensitivity and secondly, if decontamination from its α-emitting daughters is incomplete, the actinium-227 activity will be over-estimated in counts made shortly after separation. This source of error will diminish rapidly in significance if counting is not carried out until later, so that a more accurate estimate of the actinium-227 is likely.

In Fig. 3, the α-spectrum obtained from actinium-227 separated from a spiked urine sample is shown. This was measured over a period of 5 hours starting shortly after the anion-exchange separation. The presence of all the radioactive daughters is already evident and their contribution to the total α-count is already approaching that of the actinium-227 alone.

Curve B in Fig. 2 shows a plot of the ratio of the α-counting rate of a separated actinium-227 source, measured at various times, to the initial count made 5 hours after separation and corrected to zero time. Three factors influence the shape of this curve in relation to the theoretical one. Increased counting efficiencies for the actinium daughters caused by their greater α-energies will tend to raise the ratio above the theoretical value. The short half-life of the polonium-215 daughter ($1{\cdot}8 \times 10^{-3}$ seconds) gives rise to many α-particles, which are virtually coincident with those arising from decay of its precursor, radium-219. These are

not recorded as separate counts, and therefore the ratio will be depressed below the theoretical value. Also, any daughters not completely separated in the procedure will tend to reduce the value for this ratio below the theoretical.

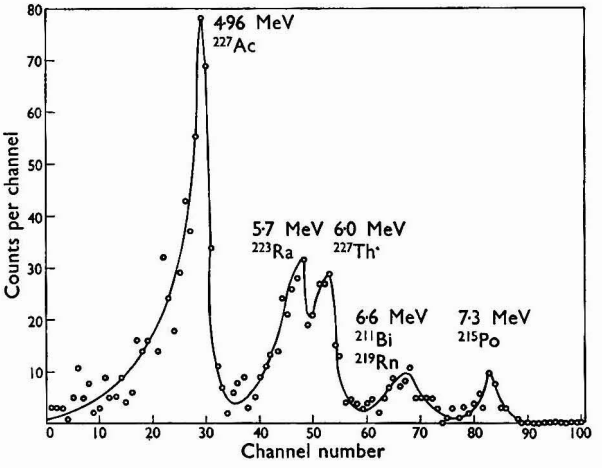

Fig. 3. α-Spectrum of actinium-227 during the first 5 hours after separation from urine

PROCEDURE—

Pour the sample of urine into a 2-litre beaker, add 300 ml of nitric acid (sp. gr. 1·42), 5 ml of octan-1-ol and a few glass beads and evaporate to about 100 ml on a hot-plate. Transfer the solution to a 200-ml silica basin, evaporate to dryness under an infrared lamp, then put it in a muffle furnace at about 500° C for 10 minutes to complete the oxidation.

Dissolve the ash in 70 ml of M hydrochloric acid and transfer with washings to a 100-ml centrifuge tube. Add 3 ml of 3 M sulphuric acid, heat the tube in a water-bath to about 80° C and add 20 mg of barium carrier (2 ml of a solution of 1·78 g of barium chloride dihydrate in 100 ml of water) dropwise, with stirring, then heat for a further 5 minutes. Centrifuge off the barium sulphate precipitate, wash once with 50 ml of water, discard the washing and transfer the precipitate with 20 ml of water to a 150-ml beaker. Add 20 ml of 50 per cent. w/v potassium carbonate solution containing 50 mg of lead carrier (1 ml of a solution of 8·0 g of lead nitrate in 100 ml of water) and boil on a hot-plate for about 10 minutes to reduce the volume to 20 ml. Transfer the slurry to a 40-ml centrifuge tube with potassium carbonate solution and centrifuge off the precipitate, then wash with 10 ml of potassium carbonate solution and 10 ml of water, discarding the washings.

Dissolve the precipitate in 5 ml of 3 M hydrochloric acid and dilute to 20 ml with water. Add 2 mg of iron carrier (1 ml of a solution containing 1·0 g of iron(III) chloride hexahydrate in 100 ml of 0·2 M hydrochloric acid) and ammonia solution (sp. gr. 0·88) dropwise, with stirring, to precipitate iron(III) hydroxide. Centrifuge off the precipitate and wash with 20 ml of 0·05 M ammonia solution, discarding the washing. Dissolve the precipitate in 5 ml of 3 M hydrochloric acid, add 10 mg of barium carrier and re-precipitate the iron(III) hydroxide by the addition of ammonia solution (sp.gr. 0·88). Centrifuge off the precipitate and wash with 20 ml of 0·05 M ammonia solution, discarding the washing.

Fill a 1-cm diameter ion-exchange column to a depth of 5 cm with 200-mesh DeAcidite FF anion-exchange resin. Wash the column with 100 ml of 7 M nitric - 3 M hydrochloric acid solution. Dissolve the iron(III) hydroxide precipitate in 5 ml of 7 M nitric - 3 M hydrochloric acid solution and transfer with a further 5 ml of the acid to the anion exchange column. Allow the solution to pass through and wash the column with 20 ml of the 7 M nitric - 3 M hydrochloric acid solution.

Combine the effluent and washing from the column, and evaporate to about 2 ml in a 100-ml beaker. Pour the solution from the beaker into a platinum tray, wash the beaker several times with water to ensure complete transfer, then evaporate to dryness, and flame

the source. Allow the source to grow as long as possible before counting in a suitable α-counter. Calculate the actinium-227 content by reference to the theoretical growth curve of α-active daughters from actinium-227.

RESULTS

DECONTAMINATION FACTORS—

Decontamination factors were obtained for protactinium, thorium, radium, polonium and lead by using the actinium procedure. In each case six 1·5-litre urine samples were spiked with an appropriate tracer and, after processing the samples, the mean recovery of the tracer was calculated and expressed as a decontamination factor. The results of these measurements are shown in Table I.

TABLE I

DECONTAMINATION FACTORS FOR THE ACTINIUM PROCEDURE

Element	Tracer used	Decontamination factor
Protactinium	Protactinium-233	>100*
Thorium	Thorium-230	250
Radium	Radium-228	>100*
Polonium	Polonium-210	150
Lead	Lead-212	>100*

* These results were obtained by γ-counting. The amount of tracer available and the background of the counter limited the minimum detectable activity to about 1 per cent. of that initially added.

RECOVERIES—

The recovery obtained up to, but not including, the electro-deposition stage was determined by spiking six 1·5-litre urine samples with actinium-228 and analysing them by the previously detailed procedure. The actinium-228, separated in this way, was counted with a γ-ray scintillation spectrometer and the recovery determined by comparing the counting rate in the 0·9-MeV photopeak with that of an aliquot of the spike solution. The recoveries are given in Table II.

TABLE II

RECOVERY OF ACTINIUM-228 FROM 1·5-LITRE URINE SAMPLES

Sample No.	Actinium-228 recovery, per cent.
1	82·2
2	84·9
3	86·1
4	85·6
5	80·7
6	78·6
Mean and standard deviation	83·0 ± 2·7

As a final check, six 1·5-litre urine samples were spiked with actinium-227 in equilibrium with its daughters. These samples were analysed in the usual way and the actinium-227 sources were counted 30 days after separation. From these counts the actinium recovery was determined by reference to the theoretical growth curve shown in Fig. 3. The results are given in Table III and are in excellent agreement with the recoveries obtained with actinium-228.

TABLE III

RECOVERY OF ACTINIUM-227 FROM SPIKED URINE SAMPLES

Sample No.	Actinium-227 recovery, per cent.
1	82·2
2	85·4
3	84·7
4	87·6
5	84·6
6	86·6
Mean and standard deviation	85·2 ± 2·0

With a radiochemical recovery of 85 per cent., a level of 0·3 picocuries of actinium in a 1·5-litre (nominal 24 hour) urine sample can be measured to within ±10 per cent. by counting the source for 8 hours, after it has been allowed to grow in for 30 days.

Conclusions

The work described in this paper shows that by using only three precipitations, and a single ion-exchange step, actinium-227 can be separated from urine samples in good yield and essentially free from its parent and daughter activities. In the development of the method, conventional procedures have been modified to achieve more than one objective in order to reduce the number of chemical steps required. The use of potassium carbonate solution containing lead carrier for metathesis of barium sulphate containing lead isotopes has not been reported before. The use of a mixture of hydrochloric and nitric acids for absorbing both iron and thorium simultaneously on an anion-exchange resin is also novel. Recoveries of actinium have been checked with actinium-228 γ-tracer, as well as with actinium-227, and excellent agreement obtained.

References

1. "Recommendations of the International Commission on Radiological Protection," I.C.R.P. Publication 2. Report of Committee II on Permissible Dose for Internal Radiation, Pergamon Press, Oxford, 1959.
2. Langham, W. H., *Hlth Phys.*, **1959**, **2**, 172.
3. Barr, G., *U.S. Atomic Energy Commission Report*, UCRL–3268, 5, 1955.
4. Newton, D., Rundo, J., and Sandalls, F. J., Paper presented at the "Symposium on Diagnosis and Treatment of Deposited Radionuclides," Richland, U.S.A., May, 1967. Sponsored by the Batelle Memorial Institute, Pacific Northwest Laboratory, Hanford Occupational Health Foundation Inc., and U.S. Atomic Energy Commission.
5. Brooks, R. O. R., *U.K. Atomic Energy Research Establishment Report*, AM60, H.M. Stationery Office, London, 1960.
6. Petrow, H. G., and Allen, R. J., *Analyt. Chem.*, **1963**, **35**, 747.
7. Hagemann, F., *J. Amer. Chem. Soc.*, **1950**, **72**, 768.
8. Hyde, E. K., "Radiochemical separation methods for the actinide elements," *in Int. Conf. Peaceful Uses Atom. Energy, Geneva*, **1955**, **7**, 281.
9. Bhatki, K. S., and Adloff, J. P., *Radiochimica Acta*, **1964**, **3**, 123.
10. Eakins, J. D., and Gomm, P. J., *U.K. Atomic Energy Research Establishment Report*, R4853, H.M. Stationery Office, London, 1964.
11. Danon, J., *J. Amer. Chem. Soc.*, **1956**, **78**, 5953.
12. Sandalls, F. J., and Morgan, A., *U.K. Atomic Energy Research Establishment Report*, R4391, H.M. Stationery Office London, 1964.
13. Dupzyk, I. A., and Biggs, M. W., Paper presented at the 6th Annual Meeting on Bio-assay and Analytical Chemistry, Santa Fe, New Mexico, October 1960; *U.S. Atomic Energy Commission Report* TID–7616, 39, 1960.
14. Iyer, R. H., Jain, H. C., Ramaniah, H. V., and Rao, C. L., *Radiochimica Acta*, **1964**, **3**, 225.
15. Hansen, P. G., Høgh, J., Nielsen, H. L., *Nucl. Instrum. Meth.*, **1964**, **30**, 161.
16. Smith, G., and Barnett, G. A., *U.K. Atomic Energy Authority Report* AEEW–R386, 1964.
17. Mitchell, R. F., *Analyt. Chem.*, **1960**, **32**, 326.

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Loss of Polonium-210 on Dry Ashing Rat Tissues in a Muffle Furnace

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The losses of polonium-210 during dry ashing of rat tissues are reported, and it is shown that losses occur at lower temperatures than generally referred to in the literature.

DURING the dry ashing of biological samples in a furnace some elements are partially or completely lost. In some circumstances losses can be prevented by careful wet ashing of the sample at about 80° C. Radiotracer techniques are convenient when investigating losses of elements during ashing procedures, although those techniques, in which a radioisotope of the element is added to a sample, *in vitro*, are not satisfactory if the radioisotope is not of the same chemical form as the element being assayed. In the work reported here, losses of polonium-210 during the ashing of biological samples were investigated for polonium-210 that was previously incorporated into the animal tissues by injection *in vivo*.

In a previous paper[1] this approach was described for the loss of some selected elements from rat tissues after dry ashing in silica crucibles.

Apart from volatilisation losses, some elements adhere to the internal surfaces of the dishes, as a result either of adsorption or chemical reaction. In the present work these losses were not considered separately from the volatilisation losses.

Male hybrid rats, injected intraperitoneally with 25 microcuries of polonium-210 in 0·25 M hydrochloric acid, were killed after 4 hours. The kidney and femur were removed, and the marrow in the femur extracted by washing with water. Samples were then divided into two, one portion being used for dry ashing and the other as a control from which polonium was extracted after wet ashing. The loss of polonium as a result of wet ashing seems unlikely and has not been reported in the literature.[2,3,4,5,6,7]

TABLE I

LOSS OF POLONIUM-210 ON DRY ASHING RAT KIDNEY AND FEMUR IN A MUFFLE FURNACE

Heating temperature °C	Loss from kidney, per cent.	Loss from femur, per cent.
200	40	~0
300	63	39
400	78	79
500	87	93
600	94	96
700	97	96
900	100	~100

The samples for dry ashing were heated in the furnace for 16 hours at the selected temperatures, and any residue dissolved by the wet-ashing procedure[8] used for the control samples. After both the ashed samples and control specimens had been dissolved to give a clear solution, the chemical yield from subsequent processes was monitored by the addition of polonium-208 as a tracer. The polonium in the sample solutions was separated, by spontaneous deposition, on to clean nickel discs, and the activity from polonium-208 and

polonium-210 determined by α-spectrometry with a gold-plated surface barrier detector under vacuum. The over-all error on plating and counting was ±15 per cent.

The results of our measurements are given in Table I, in which the activity of polonium-210 lost after dry ashing is expressed as a percentage of that found in an equal weight of tissue subjected to the wet-ashing procedures, for which no losses are expected. The results show that while some polonium is lost when dry ashing at temperatures in excess of 100° C, virtually all of the polonium is lost above 800° C. Several references in the literature[2,3,4,5,6] suggest that polonium is lost between 425° and 600° C; this work shows that considerable loss occurs below 425° C. The greater loss of polonium-210 in kidney, compared with femur, at low temperatures is possibly a reflection of differences in chemical binding of the polonium.

References

1. Hamilton, E. I., Minski, M. J., and Cleary, J. J., *Analyst*, 1967, **92**, 257.
2. Holtzman, R. B., *Hlth Phys.*, 1963, **9**, 385.
3. Minto, W. L., *in* Fink, R. M., *Editor*, "Biological Studies with Polonium, Radium and Plutonium," McGraw-Hill Book Co., New York, 1950, p. 15.
4. Holtzman, R. B., and Ilcewicz, F. H., *Science*, 1966, **153**, 1259.
5. Ferri, E. S., and Baratta, E. J., "Radiological Health Data and Reports," U.S. Department of Health, Education and Welfare, Volume 7, No. 9, 1966, p. 485.
6. Blanchard, R. L., *Analyt. Chem.*, 1966, **38**, 189.
7. Figgins, P. E., "The Radiochemistry of Polonium," National Academy of Sciences, Washington, D.C., NAS–NS, No. 3037, 1961.
8. Jeffrey, H., Olubajo, F. O., and Jewell, W. R., *Analyt. Chem.*, 1960, **32**, 306.

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The Determination of Ferrocyanide and Related Compounds in Commercial Sodium Chloride

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Ferrocyanide [hexacyanoferrate(II)] in commercial sodium chloride can be determined spectrophotometrically as its iron complex in the range 0·013 to 50·0 p.p.m. of $[Fe(CN)_6]^{4-}$. The iron complex is concentrated from a large volume of sample solution by filtration on kieselguhr, and a reproducible Prussian blue colour formed in a small volume under controlled conditions. Aquopentacyanoferrate can be determined simultaneously, and the amounts of each complex present are found by a simple calculation. Some interference is caused by carbonylpentacyanoferrate, which only partially reacts under the conditions of the procedure but the amount present can be determined and allowance made. The precise determination of carbonylpentacyanoferrate is carried out by using a similar principle of concentration, but with different reagents to develop the iron complex. No interference is caused by the presence of other stable iron - cyanogen complexes, or by the usual impurities and additives in commercial salts.

For several years alkali-metal ferrocyanides and, to a lesser extent, other complex cyanides, have been in general use as anti-caking agents and crystal-habit modifiers for commercial sodium chloride.[1,2] Although an estimate of the amount of complex present could be found by a determination of total cyanogen, it was considered desirable to have a method for the specific determination of hexacyanoferrates (II) and (III). A preliminary study of the recorded reactions of ferrocyanide indicated that the formation of Prussian blue was the most sensitive procedure for our purpose; ferrocyanide in molasses has been determined with iron(III) chloride.[3]

Experimental

Early experiments showed that when a solution of iron(III) chloride was added to an acidified brine containing 6 p.p.m. of $[Fe(CN)_6]^{4-}$, a trace of blue colour formed only very slowly, whereas iron(II) sulphate gave a relatively intense blue colour almost immediately. Iron(II) ferrocyanide is white when formed, but is quickly oxidised by atmospheric oxygen to a Prussian blue colour. The shade and intensity of the blue colour is influenced by the amount of alkali metal present and the ratio of iron(II) to iron(III) in the molecule. Various means of controlling the reaction were considered, and, finally, an effective procedure was developed, in which the oxidation was controlled by using iron(III) ions to oxidise the initially formed ferrous complex,[4] the whole operation being conveniently carried out with a single reagent solution containing 2·85 per cent. of Fe^{2+} and 0·29 per cent. of Fe^{3+} ions. The colour produced has an absorption that is linear between 0·1 and 5·0 μg of $[Fe(CN)_6]^{4-}$ per ml of final solution. A direct spectrophotometric determination can be carried out on a solution of salt containing 4 to 50 p.p.m. of $[Fe(CN)_6]^{4-}$, provided the solution contains no interfering colour or turbidity. With smaller amounts of ferrocyanide, the iron complex is separated and concentrated by dissolving a large amount of salt in water and vacuum-filtering on to a kieselguhr pad in a crucible. The iron complex, which can be seen as a blue layer on the kieselguhr pad, is then decomposed in a small volume of alkali-metal hydroxide, the solution acidified and the Prussian blue formed under controlled reproducible conditions, the optical density being measured at 700 mμ. This procedure is suitable for the determination of ferrocyanide in amounts as little as 0·10 p.p.m. in salt, which is well below the normal range of concentrations effective for anti-caking purposes.

If required, however, the limit may be extended to 0·013 p.p.m. by using a solution of copper sulphate, in place of the iron(II) - iron(III) reagent, to concentrate the $[Fe(CN)_6]^{4-}$

from a larger volume of solution, then following the described procedure, and finally forming the Prussian blue in a small volume with the iron(II) - iron(III) reagent.

Aquopentacyanoferrate is also quantitatively concentrated and converted into a blue complex by the procedure described, provided the ratio of ferrocyanide to aquopentacyanoferrate is no less than 1:2. It has only rarely been encountered in samples of salt and, on those occasions, an excess of ferrocyanide was present. This is to be expected, because it is unstable in solution, being converted into ferrocyanide. By measuring the optical density at 860 mμ, as well as at 700 mμ, the individual amounts of ferrocyanide and aquopentacyanoferrate present can be determined by means of a simple calculation.

Some interference may be caused by carbonylpentacyanoferrate, but its presence is also unusual, and it has been found only on a few occasions. The iron(III) complex is incompletely formed by the iron(II) - iron(III) reagent, except when large amounts of ferrocyanide are present. Its colour is violet, and even small amounts impart a violet tint to the Prussian blue precipitate on the kieselguhr pad. A correction for its presence can be made by a further calculation after taking an additional optical density measurement at 550 mμ, and at 950 mμ, where the aquopentacyanoferrate reading is not much reduced but the interference by carbonylpentacyanoferrate considerably less. The absorption spectra of the iron complexes of ferrocyanide, aquopentacyanoferrate and carbonylpentacyanoferrate formed by the iron(II) - iron(III) reagent are shown in Fig. 1.

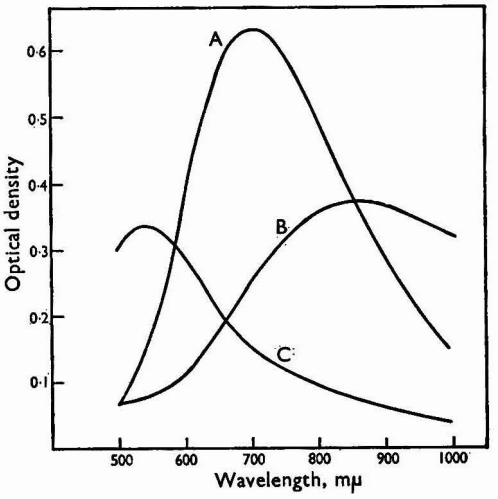

Fig. 1. Absorption spectra of the iron complexes of ferrocyanide, aquopentacyanoferrate and carbonylpentacyanoferrate obtained with the iron(II) - iron(III) reagent: curve A, $[Fe(CN)_6]^{4-}$; curve B, $[Fe(CN)_5H_2O]^{3-}$; curve C, $[Fe(CN)_5CO]^{3-}$

The precise determination of carbonylpentacyanoferrate in the presence of ferrocyanide and aquopentacyanoferrate is best accomplished by using the same general procedure of concentration with copper sulphate, as described for ferrocyanide, and finally forming the iron(III) complex quantitatively with an iron(III) nitrate reagent and measuring the optical density at 530 mμ.

Method for Determination of Ferrocyanide

Reagents—

All reagents should be of analytical-reagent grade.

Dilute sulphuric acid, approximately 0·5 M.

Dilute potassium hydroxide solution, approximately 0·05 M.

Sodium chloride solution, 20 per cent. w/v—Prepare from salt that is free from complex cyanides and filter.

Kieselguhr, white.

Iron(II) - iron(III) solution—Dissolve 200 g of ammonium iron(II) sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, and 25 g of ammonium iron(III) sulphate, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, in distilled water to which 100 ml of dilute sulphuric acid have been added. Make up to 1 litre, filter and store the solution in a dark bottle.

Copper sulphate, $CuSO_4.5H_2O$, solution, 20 per cent. w/v.

Standard ferrocyanide stock solution—Dissolve 0·9964 g of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, in water containing 5 ml of dilute potassium hydroxide and make up to 1 litre with freshly boiled-out distilled water. Store the solution in the dark.

Standard dilute ferrocyanide solution—Dilute 50 ml of standard ferrocyanide stock solution with freshly boiled-out distilled water containing 5 ml of dilute potassium hydroxide and make up to 1 litre.

1 ml of solution ≡ 25 μg of $[Fe(CN)_6]^{4-}$.

PREPARATION OF CALIBRATION GRAPH—

To a series of 100-ml graduated flasks, add standard dilute ferrocyanide solution in volumes covering the range 0 to 500 μg of $[Fe(CN)_6]^{4-}$. Then add, in the following order, mixing after each addition, 50 ml of the 20 per cent. sodium chloride solution, 10 ml of 0·05 M potassium hydroxide, 5 ml of 0·5 M sulphuric acid and, finally, 5 ml of iron(II) - iron(III) reagent. Add water to the mark, mix well and allow to stand for 15 minutes. Determine the optical density of each standard at 700 mμ, with 4-cm cells and distilled water as reference. Correct for the blank and construct the calibration graph.

PROCEDURE FOR RANGE 10 to 500 μg OF $[Fe(CN)_6]^{4-}$ (NOTE 1)—

Dissolve a suitable weight of commercial sodium chloride, usually 100 g, in about 450 ml of distilled water. Add 10 ml of 0·5 M sulphuric acid and 25 ml of iron(II) - iron(III) reagent, shaking after each addition. Allow to stand overnight, but 15 minutes is long enough if the $Fe(CN)_6]^{4-}$ content is greater than 100 μg.

Fit a sintered-glass crucible, No. 1 porosity, 15-ml capacity, on a vacuum-filtration flask and add about 1 g of kieselguhr. Fill the crucible with water, stir, and allow to stand about 15 seconds before applying the vacuum. Press the pad down firmly with a flat-ended glass rod and wash with about 20 ml of 20 per cent. sodium chloride solution. With the vacuum still applied, start the filtration (Note 2).

When the filtration is complete, wash the sample-solution container and crucible twice, each time with about 15 ml of distilled water. Remove the crucible and fit it into a 100-ml filter flask. While under gentle vacuum, add about 10 ml of 0·05 M potassium hydroxide to re-form the soluble alkali-metal ferrocyanide, and wash the crucible with a few millilitres of distilled water. The solution is usually slightly turbid at this stage and should be filtered through a sintered-glass crucible, No. 5 porosity, into a 100-ml graduated flask, and the crucible washed with a few millilitres of distilled water. Remove the flask, add 50 ml of 20 per cent. sodium chloride solution, followed by 5 ml of 0·5 M sulphuric acid, and mix. Finally, add 5 ml of iron(II) - iron(III) reagent, mix, make up to the mark and mix again. Measure the optical density at 700 mμ. Carry out a blank determination (omitting the sample), subtract from the sample reading and calculate the $[Fe(CN)_6]^{4-}$ concentration from the calibration graph.

NOTES—

1. A simple, rapid method of determining the approximate amount of ferrocyanide present is to mix 100 g of sample with 100 ml of distilled water in a 250-ml conical flask, and add to the slurry 10ml of 0·5 M sulphuric acid, 5 ml of the iron(II) - iron(III) reagent and 35 ml of a solution containing 2·5 per cent. of M sulphuric acid *plus* 7 per cent. of potassium dihydrogen orthophosphate, mixing well after each addition. The blue colour of the supernatant liquor is compared visually with similarly treated standards of $[Fe(CN)_6]^{4-}$ in the 100 to 500-μg range. (If any solution is greener than the others, add, dropwise, additional amounts of the potassium dihydrogen orthophosphate solution until the colours are similar.)

2. The tedious manual filtration of large volumes can be avoided by using as a container for the sample solution, a separating funnel, the tap of which has been cut off and replaced by a piece of tubing closed with a screw-clip. By placing the separating funnel so that the open end of the tubing projects about one third into the crucible, inserting the stopper in the funnel and opening the screw-clip, the flow of solution will automatically control the level in the crucible and the filtration will require no further attention.

PROCEDURE FOR RANGE 2·5 TO 20 μg OF $[Fe(CN)_6]^{4-}$—

Dissolve 200 g of sample in about 900 ml of distilled water, add 5 ml of 0·5 M sulphuric acid and 50 ml of 20 per cent. copper sulphate solution. Allow to stand overnight and extract on kieselguhr, as described above, but develop the final colour in a 25-ml graduated flask. For this, the reagents should be reduced to 5 ml of 0·05 M potassium hydroxide, 12 ml of 20 per cent. sodium chloride solution, 1 ml of 0·5 M sulphuric acid and 2 ml of the iron(II) - iron(III) reagent.

METHOD FOR DETERMINATION OF AQUOPENTACYANOFERRATE

PREPARATION OF AQUOPENTACYANOFERRATE FOR CONSTRUCTION OF CALIBRATION GRAPH—

The method of Hofmann,[5] modified by Asperger, Murati and Pavlovic[6] was further modified as follows, giving a product of purity greater than 97 per cent.

All of the solutions are kept at 0° to 1° C during the preparation. Dissolve 20 g of sodium nitroprusside in 60 ml of distilled water and add 300 ml of methanol. Follow with 20 ml of 40 per cent. sodium hydroxide and then 7 g of hydroxylammonium chloride, previously dissolved in 20 ml of distilled water. Allow to stand for 3 days at 0° to 1° C. Filter the precipitate and purify it by dissolving in distilled water and re-precipitating with 300 ml of methanol. Repeat the re-precipitation twice and dry over concentrated sulphuric acid in a vacuum desiccator.

The prepared aquopentacyanoferrate can be assayed by determination of the complex of cyanogen and iron, allowing for any ferrocyanide present by oxidation of a solution of the product with acidified hydrogen peroxide, and determination of ferricyanide after chromatographic separation with an activated alumina column.

Standard aquopentacyanoferrate stock solution—Dissolve 0·334 g of sodium aquopentacyanoferrate, $Na_3Fe(CN)_5H_2O$, in water, add 5 ml of dilute potassium hydroxide solution, and make up to 1 litre.

Standard dilute aquopentacyanoferrate solution—Dilute 100 ml of standard aquopentacyanoferrate stock solution to 1 litre.

$$1 \text{ ml of solution} \equiv 25\ \mu g \text{ of } [Fe(CN)_5H_2O]^{3-}.$$

Solutions should be freshly made before use.

Construct a calibration graph and carry out the determination exactly as described for ferrocyanide, but take a further optical density measurement at 860 mμ.

When ferrocyanide and aquopentacyanoferrate are present together, the corrected optical density (O.D.) for ferrocyanide is calculated as follows.

$$\text{O.D. at 700 m}\mu \text{ of ferrocyanide} = \frac{(\text{total O.D. at 700 m}\mu \times 1{\cdot}5) - \text{total O.D. at 860 m}\mu}{0{\cdot}93}.$$

This is derived from the simultaneous equations—

$$F \text{ at 700 m}\mu + A \text{ at 700 m}\mu = \text{total O.D. at 700 m}\mu$$

and $$(F \text{ at 700 m}\mu \times R_f) + (A \text{ at 700 m}\mu \times R_a) = \text{total O.D. at 860 m}\mu$$

where F is the O.D. of ferrocyanide at 700 mμ,

A is the O.D. of aquopentacyanoferrate at 700 mμ,

R_f is the ratio, $\dfrac{\text{O.D. of ferrocyanide at 860 m}\mu}{\text{O.D. of ferrocyanide at 700 m}\mu}$

and R_a is the ratio, $\dfrac{\text{O.D. of aquopentacyanoferrate at 860 m}\mu}{\text{O.D. of aquopentacyanoferrate at 700 m}\mu}$

(Calculated from calibration graphs at any selected level of concentration).

Similarly, the corrected optical density of aquopentacyanoferrate can be calculated from the relevant considerations—

$$\text{O.D. at 860 m}\mu \text{ of aquopentacyanoferrate} = \frac{(\text{total O.D. at 860 m}\mu \times 1{\cdot}76) - \text{total O.D. at 700 m}\mu}{1{\cdot}08}$$

When carbonylpentacyanoferrate is present, a third term, the optical density at 550 mμ, and relevant ratios at 550, 700 and 950 mμ are introduced to give—

$$\text{O.D. at 700 m}\mu\text{ of ferrocyanide} = \frac{(\text{total O.D. at 700 m}\mu \times 2{\cdot}833) - [(\text{total O.D. at 950 m}\mu \times 1{\cdot}891) + \text{total O.D. at 550 m}\mu]}{1{\cdot}095}$$

and

$$\text{O.D. at 950 m}\mu\text{ of aquopentacyanoferrate} = \frac{[(\text{total O.D. at 950 m}\mu \times 30{\cdot}33) + \text{total O.D. at 550 m}\mu] - (\text{total O.D. at 700 m}\mu \times 10{\cdot}48)}{30{\cdot}86}.$$

Method for determination of carbonylpentacyanoferrate

Purification of carbonylpentacyanoferrate for calibration graph—

To 100 ml of solution containing about 0·25 g of commercial sodium carbonylpentacyanoferrate, $Na_3Fe(CN)_5CO$, add 10 ml of M sodium hydroxide, followed by 3 ml of hydrogen peroxide (100 volume). Boil for 5 minutes and filter. Acidify with acetic acid (glacial), add 5 ml of 8 per cent. w/v lead nitrate solution, stir, and allow to stand for 15 minutes. Filter the solution, then add sufficient sulphuric acid to remove the excess of lead and filter again. Precipitate the sodium carbonylpentacyanoferrate with 5 ml of 6 per cent. w/v iron(III) chloride solution. Leave the mixture to stand, decant off the supernatant liquor, centrifuge and wash the precipitate. Decompose it with 10 ml of M sodium hydroxide, filter and make up to 1 litre. Assay by determining the complex of cyanogen and iron. Store the solution in the dark.

Reagents—

Citric acid, 40 per cent. w/v.
Potassium nitrate solution, 20 per cent. w/v.
Nitric acid, 10 per cent. v/v.
Hydrogen peroxide, 3 per cent. w/v.
Iron(III) nitrate solution—Dissolve 30 g of iron(III) nitrate, $Fe(NO_3)_3.9H_2O$, in 60 ml of distilled water to which has been added 10 ml of concentrated nitric acid. Make up to 100 ml with distilled water and filter.
Standard carbonylpentacyanoferrate solution—Dilute the purified sodium carbonylpentacyanoferrate solution so that 1 ml ≡ 50 μg of $[Fe(CN)_5CO]^{3-}$.

Preparation of calibration graph—

Add to a series of 25-ml graduated flasks, amounts of the standard carbonylpentacyanoferrate solution to cover the range 0 to 500 μg of $[Fe(CN)_5CO]^{3-}$. Make each volume up to about 10 ml with distilled water. Add to each flask, mixing after each addition, 5 ml of 0·05 M potassium hydroxide, 1 ml of 10 per cent. nitric acid, 1 ml of 3 per cent. hydrogen peroxide and 2 ml of 30 per cent. iron(III) nitrate solution. Make up to volume and measure the optical density at 530 mμ, with 4-cm cells and distilled water as reference solution. Subtract the blank from each measurement and construct the calibration graph.

Procedure—

Dissolve 100 g of sample in about 450 ml of distilled water and add, in turn, mixing after each addition, 5 ml of 40 per cent. citric acid and 25 ml of 20 per cent. copper sulphate reagent. Allow to stand for about 15 minutes, then filter through a kieselguhr pad and wash with two 15-ml portions of 20 per cent. potassium nitrate solution. Decompose the iron complex with 5 ml of 0·05 M potassium hydroxide, wash the crucible twice, with 5 ml of distilled water each time, filter, add 1 ml of 3 per cent. hydrogen peroxide, and boil for 3 minutes. Cool and transfer into a 25-ml graduated flask. Add 1 ml of 10 per cent. nitric acid, 1 ml of 3 per cent. hydrogen peroxide and 2 ml of 30 per cent. iron(III) nitrate solution, mixing after each addition. Make up to the mark and determine the amount in micrograms of $[Fe(CN)_5CO]^{3-}$ present from the optical density at 530 mμ, as described in the preparation of the calibration graph.

TABLE I

RECOVERY OF FERROCYANIDE ADDED TO COMMERCIAL SODIUM CHLORIDE

	Ferrocyanide, p.p.m.							
No.	Added	Found	No.	Added	Found	No.	Added	Found
1	4·75	4·70	5	1·42	1·42	9	0·23	0·23
2	2·83	2·76	6	1·13	1·13	10	0·13	0·13
3	2·60	2·60	7	0·85	0·84	11	0·029	0·029
4	1·54	1·58	8	0·29	0·29	12	0·017	0·023

TABLE II

RECOVERY OF FERROCYANIDE AND AQUOPENTACYANOFERRATE ADDED TO COMMERCIAL SODIUM CHLORIDE

	Ferrocyanide, p.p.m.		Aquopentacyanoferrate, p.p.m.	
No.	Added	Found	Added	Found
1	2·79	2·79	0·75	0·74
2	1·53	1·60	1·87	1·76
3	0·36	0·37	1·17	0·92
4	0·31	0·23	0·37	0·35

DISCUSSION

Typical results for ferrocyanide alone are given in Table I. Table II shows results for ferrocyanide and aquopentacyanoferrate, when present together. Table III gives results for ferrocyanide and aquopentacyanoferrate, when in the presence of carbonylpentacyanoferrate. Table IV shows typical results for carbonylpentacyanoferrate, determined by the iron(III) nitrate reagent.

TABLE III

RECOVERY OF FERROCYANIDE AND AQUOPENTACYANOFERRATE IN THE PRESENCE OF CARBONYLPENTACYANOFERRATE ADDED TO COMMERCIAL SODIUM CHLORIDE

	Ferrocyanide, p.p.m.		Aquopentacyanoferrate, p.p.m.		Carbonylpentacyanoferrate, p.p.m.
No.	Added	Found	Added	Found	Added
1	3·60	3·59	1·87	1·95	2·80
2	1·74	1·63	Nil	Nil	3·36
3	1·09	1·03	0·37	0·33	0·56
4	0·54	0·52	0·37	0·23	3·80

TABLE IV

RECOVERY OF CARBONYLPENTACYANOFERRATE ADDED TO COMMERCIAL SODIUM CHLORIDE AND DETERMINATION WITH IRON(III) NITRATE REAGENT

	Carbonylpentacyanoferrate, p.p.m.	
No.	Added	Found
1	4·78	4·88
2	4·15	4·16
3	0·70	0·73
4	0·70	0·76

When the iron(II) - iron(III) reagent is used for concentration of the ferrocyanide, there is no interference from the normal impurities or usual additives in commercial salts, *e.g.*, calcium sulphate, sodium sulphate, magnesium chloride, sodium iodide, sodium bromide, basic magnesium carbonate, silica, silicates or other free-flow additives. There is also no interference from comparable amounts of metals, cyanide, thiocyanate or nitroprusside.

Pentacyanoaminoferrate, $[Fe(CN)_5NH_3]^{3-}$, will interfere, but its presence is unlikely, because it decomposes fairly rapidly in solution to form ferrocyanide (a salt solution with added pentacyanoaminoferrate was tested after 24 hours, and 70 per cent. had become converted into ferrocyanide).

Aquopentacyanoferrate also decomposes to ferrocyanide, but more slowly. The requirement of a ratio of 1:2 of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_5H_2O]^{3-}$ to ensure that the determination of aquopentacyanoferrate is quantitative has not, therefore, presented any problem; there is invariably a relatively large excess of ferrocyanide present. The very occasional appearance of aquopentacyanoferrate may be as an intermediate decomposition product of other complexes, or by formation from ferrocyanide in solution by the action of light.[7]

Any ferricyanide present will be included with the ferrocyanide. When copper sulphate solution is used to concentrate the complexes, any small amounts of cyanide present would interfere with the determination. This could be prevented by pre-treating the sample solution with a dilute solution of hydrogen peroxide before adding the copper sulphate reagent.

The determination of carbonylpentacyanoferrate with the iron(III) nitrate reagent is not affected by the usual impurities in commercial sodium chloride or other cyanogen complexes; the method ensures that pentacyanoferrates are converted into ferrocyanide by boiling with alkaline hydrogen peroxide,[8] the ferrocyanide being then oxidised to ferricyanide by acidifying the solution with nitric acid and adding further peroxide.[9] Iron(III) ferricyanide has a negligible absorption at 530 mμ.

Although designed for samples of salt, the methods have since been used on samples of water and effluents.

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References

1. British Patent 752,582, 1956; British Patent 818,385, 1959.
2. British Patent 667,101, 1952.
3. Marier, J. P., and Clark, D. S., *Analyst*, 1960, **85**, 574.
4. Williams, H. E., "Cyanogen Compounds," Second Edition, Edward Arnold & Co., London, 1948, p. 197.
5. Hofmann, A., *Justus Liebigs Annln Chem.*, 1900, **312**, 18.
6. Asperger, S., Murati, I., and Pavlovic, D., *J. Chem. Soc.*, 1960, 730.
7. Williams, H. E., *op. cit.*, p. 172.
8. ——, *op. cit.*, p. 386.
9. American Cyanamid Co., "The Chemistry of the Ferrocyanides," Volume III, The Beacon Press Inc., New York, N.Y., 1953, p. 34.

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Micro Determination of Carbonate in Dental Enamel

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A method is described for the micro determination of carbonate in 50-μg particles of human dental enamel. The technique is rapid and more sensitive than previous procedures. Amounts of carbonate from 0·5 to 3·0 μg have been determined with an accuracy of 4 to 7 per cent. (standard deviation). Carbon dioxide is liberated by dissolving enamel particles in acid. The gas forms a single bubble, flattened into a 100-μ thick disc between the parallel glass surfaces of a Neubauer haemocytometer. The area of the flattened bubble is measured and the volume of gas calculated. By using this technique in combination with a recently developed sampling procedure, it has proved possible to measure variations in carbonate concentration within thin sections of dental enamel.

Recent investigations into the chemical composition of dental enamel necessitated the determination of micro amounts of carbonate. Previous studies of carbonate distribution[1,2] have been carried out on pooled samples of powdered enamel ground from large numbers of teeth. It was found that human enamel contained between 2 and 3 per cent. of carbonate, expressed as carbon dioxide, and that its concentration increased from the surface to the interior of the enamel. Pooled samples cannot, however, provide information about variations within the single tooth, and the aim of the present investigation was to evolve a method by which this could be done.

A recently developed technique[3] was used to dissect the enamel of sections of teeth just over 100 μ thick, into about one hundred particles, each weighing 20 to 50 μg. A dissected section is shown in Fig. 1. The carbonate content of each particle, expressed as carbon dioxide, would be in the order of 1 μg. No technique was available for determining such a small amount as chemical methods were too insensitive, and most physical procedures could not be adapted easily to the manipulation of the small amounts of carbon dioxide derived from microgram amounts of carbonate. A technique has now been developed, based on a method described by Krogh in 1908[4] and by Lewis and Lippold in 1956.[5] It has proved possible to liberate carbon dioxide as a single, stable bubble from the carbonate present in enamel. The volume of the bubble can be measured and the carbonate concentration of the particle determined. This paper describes the procedure, and presents some results showing the distribution of carbon within a 100-μ thick section of human enamel.

Experimental

Formation of a single, stable carbon dioxide bubble—

Aqueous solutions of strong acids readily dissolve dental enamel, liberating carbon dioxide from the mineral. Initial attempts to measure the carbon dioxide evolved were hampered by two technical problems. Firstly, acid alone produced many separate bubbles (Fig. 2*a*), the total volume of which could not be measured, but this difficulty was surmounted by adding ethanol. With an aqueous solution containing 18 per cent. w/v of perchloric acid and 40 per cent. v/v of ethanol a single measurable bubble was produced (Fig. 2*b*). When, occasionally, two or three bubbles formed, slight manipulation was sufficient to make them coalesce.

The second difficulty arose from the shrinking of the bubbles as the carbon dioxide dissolved in the acid. To avoid this, the acid - ethanol mixture was pre-saturated by bubbling carbon dioxide through it. Under the conditions described below the single bubble of gas remained stable for 1 hour or more.

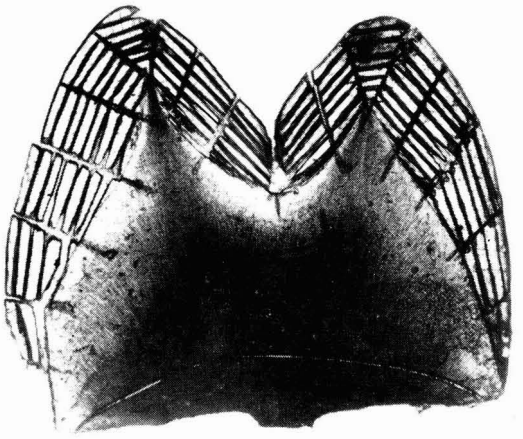
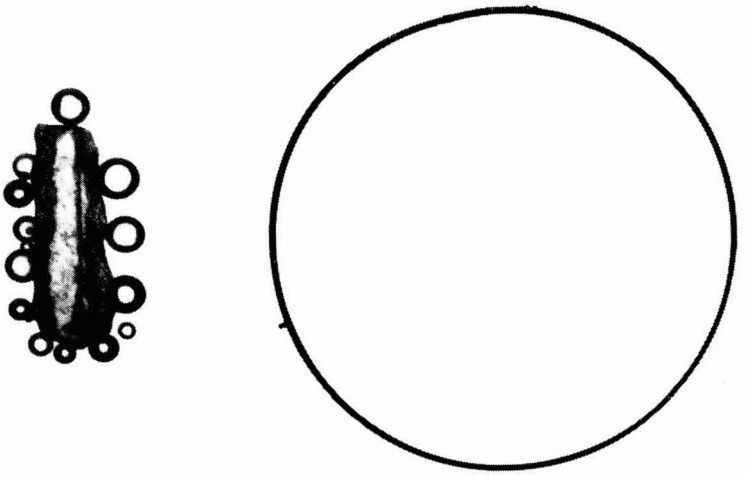


Fig. 1. Dissection of enamel in 100-μ thick tooth section (from Weatherell, Weidmann and Hanim[7])



(*a*) (*b*)

Fig. 2. Formation of gas bubble from enamel particle:

(*a*) separate bubbles forming in aqueous acid ($\times 60$);
(*b*) single bubble produced in acid - ethanol mixture by about 1 μg of carbon dioxide

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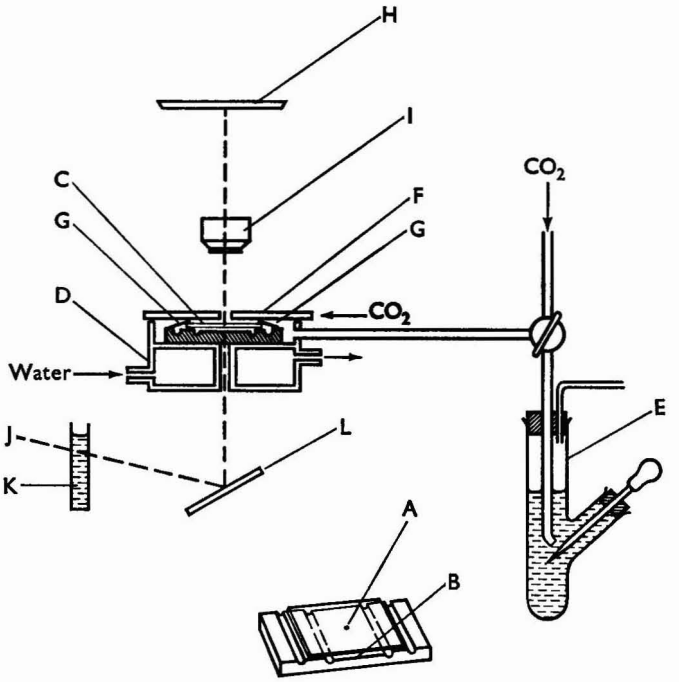

A = Particle of sample under cover-slip
B = Central platform of haemocytometer, showing 100-μ wide gap between platform and cover-slip
C = Optically plane cover-slip
D = Brass chamber
E = Vessel containing acid - ethanol mixture
F = Perspex lid resting on chamber
G = Lead blocks
H = Photographic enlarger screen
I = Enlarger lens
J = Light source
K = Water cell to absorb heat from light source
L = Plane mirror

Fig. 3. Diagram of apparatus and haemocytometer

APPARATUS—

The apparatus is shown in Fig. 3. The particle, A, is placed in the central cell of a Neubauer haemocytometer. This has been illustrated, both apart from the apparatus and also in the position it occupies during a determination. The haemocytometer is a glass slide normally used for blood-cell counts, with a central platform, B, set 100 ± 1 μ lower than the adjacent surfaces. An optically plane cover-slip, C, lies across the platform, forming a 100-μ deep space. When the cover-slip is in close contact with the raised outer faces of the haemocytometer, interference fringes appear between the raised surfaces and the cover-slip. The slide is placed within a brass chamber, D, the base of which is maintained at 22° C by a flow of water. A stream of carbon dioxide can also be passed through this chamber. The acid - ethanol is saturated with carbon dioxide in a vessel, E, from which small amounts of the mixture may be quickly removed. The acid is transferred from this vessel to the haemocytometer by inserting a capillary tube through the hole in the Perspex lid, F, of the brass chamber, and is pulled into the space between slide and cover-slip by capillary action to fill the 100-μ wide cell containing the particle. The front of the acid would sweep out the enamel specimen, but as the particles are dissected from sections slightly more than 100-μ thick, they are held in place by the cover-slip. Because of this, the cover-slip is slightly bowed over the particle of enamel, being weighted at its edges by small lead blocks, G. As the enamel dissolves, the cover-slip flattens out. The entire process of enamel dissolution and bubble formation is observed with the ground-glass screen of a photographic enlarger, H, on to which an image of the particle and bubble is projected with a standard magnification. The area of the bubble is measured and the volume of gas determined, as described below. The determination is extremely rapid, as the time required for the bubble to form is rarely more than 5 minutes.

PROCEDURE—

Before carrying out a series of determinations, saturated the acid - ethanol mixture with carbon dioxide by bubbling the gas through it at a rate of about 500 ml per minute for about 1 hour.

Place the specimen in the centre of the Neubauer haemocytometer, position the cover-slip over it and across the 100-μ deep cell. Lay the slide on the thermostatically controlled base of the brass chamber and place the two lead blocks carefully on the edges of the cover-slip. Put the Perspex lid on the brass chamber and position the specimen beneath the photographic enlarger. By turning the 3-way tap, flush the chamber with a stream of carbon dioxide for about 90 seconds. The gas flow, at a rate of about 500 ml per minute, must be maintained until the determination is complete. Remove about 20 μl of acid - ethanol by glass capillary or micropipette from the saturation vessel and introduce it under the Neubauer cover-slip. Attention should meanwhile be concentrated on the magnified image of the specimen, which is focused on the ground-glass screen of the photographic enlarger, watching carefully to ensure that none of the gas evolved from the specimen is swept by the acid from below the cover-slip. Observe the formation of the bubble, or bubbles of gas until the enamel particle is completely dissolved. The time of dissolution varies from about 40 seconds to 5 minutes, depending on the size of the particle and the solubility of the enamel. If more than one bubble has formed, a slight pressure on the Perspex lid, which just rests on the two lead blocks, is usually sufficient to cause the bubbles to coalesce. To ensure satisfactory bubble formation it is essential to maintain a high standard of cleanliness. The haemocytometer and cover-slip should be kept in chromic acid between determinations. Provided this is done, interference fringes will have formed between the cover-slip and the raised portions of the slide when the determination is complete. Under these conditions the depth of the Neubauer well is 100 ± 1 μ.

The area contained within the outer edges of the meniscus of the bubble is measured by tracing round its magnified image and determining the area of the tracing. The total volume of the bubble is determined as described below.

CALCULATION

ASSESSMENT OF BUBBLE VOLUME—

In calculating the volume of the bubble from the area enclosed by the outer edge of the meniscus, a correction must be made for the error caused by the curve of the meniscus itself. Lewis and Lippold[5] made an approximate correction by assuming the meniscus to be semi-circular in cross-section. In the present experiments the apparatus was calibrated directly. The shape of the bubble was assumed to be similar to that of a flattened drop of mercury. Small weighed drops of mercury, the volume of which could be calculated from their known weight, were placed beneath the cover-slip of the haemocytometer. The haemocytometer was placed in the brass chamber and the areas of the flattened drops measured by drawing round their projected images. This correlation between area and volume gave results similar to those derived from calculation, but provided at the same time a convenient means of making direct comparisons between one haemocytometer and another, and of checking the effect of any alteration in the geometry of the apparatus on the estimated volume of the bubble.

CORRECTIONS FOR TEMPERATURE AND PRESSURE—

The brass chamber in which the haemocytometer slide was placed was maintained at 22° C by water circulating through its hollow base. The bubble was assumed to be formed at atmospheric pressure. Any small effect the surface tension of the narrow gas - liquid interfaces might have on the internal pressure of the bubble was ignored. This was justified by the calibration results shown in Table I. The weight of carbon dioxide was calculated after correction of the carbon dioxide volume to standard conditions of temperature and pressure.

CALIBRATION—

It proved extremely difficult to find a suitable calibration substance. The material had to be soluble in the acid - ethanol mixture, possess a carbonate content similar to that of enamel, be chemically homogeneous and sufficiently stable, especially with regard to carbon dioxide and water, to permit its use as a weighable standard substance.

These criteria were not fulfilled by any of the numerous inorganic or mineral carbonates considered, or by many artificially prepared fused materials. The most suitable calibration substance was an amorphous calcium - phosphate - carbonate precipitate prepared according to the precipitation diagram of Bacchra, Trautz and Simon.[6] The material was compressed into a thin disc and its carbonate content determined both by micro diffusion with Conway cells and also by using the bubble technique. For the less sensitive micro-diffusion procedure it was necessary to use about fifty times the weight of sample used in the bubble technique. The small particles of compressed precipitate tended to effervesce vigorously. Thus to prevent a loss of carbon dioxide, the particles were moistened with a tiny spot of glycerol, which appreciably slowed their rate of dissolution. The results are shown in Table I; the accuracy of the present method appears to be between 4 and 7 per cent. (standard deviation). As some of this error undoubtedly arose from slight differences between the particles of compressed precipitate, the determination itself may well be more accurate than this.

TABLE I

COMPARISON OF CARBON DIOXIDE CONTENT OF THE CALIBRATION MATERIAL, AS DETERMINED BY THE CONWAY MICRO-DIFFUSION METHOD AND BY THE BUBBLE TECHNIQUE

	Conway micro-diffusion method		Bubble technique	
Precipitate used	Number of determinations	Mean result	Number of determinations	Mean result
A	6	4·49 ± 0·10 Standard deviation = 2·2 per cent.	6	4·48 ± 0·17 Standard deviation = 3·8 per cent.
B	6	3·16 ± 0·11 Standard deviation = 3·5 per cent.	5	2·86 ± 0·12 Standard deviation = 4·2 per cent.
C	6	2·69 ± 0·09 Standard deviation = 3·3 per cent.	12	2·75 ± 0·19 Standard deviation = 6·9 per cent.

RESULTS

Some results obtained by the analysis of single enamel particles, each weighing between 20 and 50 μg, are shown in Fig. 4. Three of the curves shown (open circles) were obtained by determining the carbonate content of three columns of contiguous particles dissected from a single section. The carbonate distribution is essentially similar to the curve obtained by Little and Brudevold[1] (closed circles) by determining the carbonate in pooled samples of enamel ground in layers from large numbers of teeth.

DISCUSSION

The technique described is considerably more sensitive than previous methods of carbonate determination, enabling amounts of carbon dioxide of the order of 1 μg to be determined. The procedure is straightforward, the apparatus simple, and analyses can be carried out rapidly. It has made possible a study of carbonate distribution in thin sections of dental enamel. The results presented in Fig. 4 show that the carbonate concentration was lower in surface regions of the tooth section than in the enamel interior. This distribution is essentially similar to that described by Little and Brudevold[1] and by Nikiforuk and Grainger[2] from the analysis of pooled enamel. The absolute values obtained by these workers for the carbonate content of the surface regions agree well with those of the present study, although their results for samples taken from the tissue interior were lower. The difference may be partly attributable to biological variation, or could be ascribed to the ability of the sampling technique used in the present work to assess more accurately the area of sampling without danger of dentinal contamination.

The method was specifically designed for studying dental enamel and cannot be applied directly to the analysis of other mineralised tissues. In enamel, the small amount of organic material present, usually less than 0·5 per cent., dissolves or disintegrates and so does not interfere with the determination. The 20 per cent. of collagenous matrix present in bone or dentine, however, hinders dissolution of the mineral and mechanically prevents the

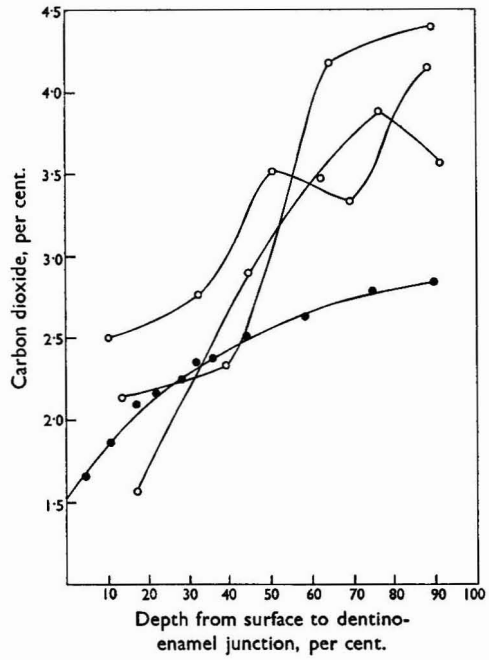

Fig. 4. Distribution of carbonate from surface to dentino-enamel junction in human dental enamel: ○, results from three series of particles from one 100-μ thick section of enamel; and ●, results obtained by analysis of pooled enamel powder (from Little and Brudevold[1])

formation of a measurable bubble. Preliminary tests suggest that this difficulty can be overcome by removing the organic material before the determination of carbonate. Small particles of bone or dentine were refluxed overnight in a 3 per cent. solution of potassium hydroxide in ethylene glycol. The specimens were thoroughly washed with methanol to remove all traces of the alkaline reagent. Carbonate was then determined in the de-proteinised material that remained. The results obtained were similar to previous estimates of the carbonate concentration in bone and dentine.

Certain questions remain. If the gas bubble is absorbed in 0·1 N sodium hydroxide, a small amount of gas, constituting about 1 per cent. of the original bubble volume, invariably remains, the nature and origin of which is unknown. There is also uncertainty about the true internal pressure of the bubble. In the light of the calibration results, however, these factors do not appear to be significant.

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References

1. Little, Marguerite F., and Brudevold, F., *J. Dent. Res.*, 1958, **37**, 991.
2. Nikiforuk, G., and Grainger, R. M., *in* Stack, M. V., and Fearnhead, R. W., *Editors*, "Tooth Enamel," A report of the Proceedings of an International Symposium on the Composition and Fundamental Structure of Tooth Enamel, London Hospital Medical College, 1964, John Wright and Sons Ltd., Bristol, 1965, p. 26.
3. Weatherell, J. A., Weidmann, S. M., and Hamm, Stella M., *Archs Oral Biol.*, 1966, **11**, 107.
4. Krogh, A., *Scand. Arch. Physiol.*, 1908, **20**, 279.
5. Lewis, H. E., and Lippold, O. C. J., *J. Scient. Instrum.*, 1956, **33**, 254.
6. Bachra, B. N., Trautz, O. R., and Simon, S. L., *Adv. Fluorine Res. Dental Caries Prevention*, 1965, **3**, 101.
7. Weatherell, J. A., Weidmann, S. M., and Hamm, Stella M., *Caries Res.*, 1967, **1**, 42.

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The Titrimetric Determination of Molybdenum in Ammonium Molybdate, Molybdic Acid and Molybdenum Trioxide with Sodium Hydroxide

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Titrimetric methods have been developed for the determination of molybdenum in ammonium molybdate, molybdic acid and molybdenum trioxide, based on their reactions with sodium hydroxide.

ANALYTICAL-GRADE ammonium molybdate, molybdic acid and molybdenum trioxide are usually assayed oxidimetrically[1] after prior reduction with a Jones reductor, or gravimetrically.[2] The Jones method has recently been critically examined,[3] a variety of reductants and oxidants being used.

Previous studies of the effect of sodium hydroxide on ammonium molybdate,[4] molybdenum trioxide[5] and molybdic acid[6] were concerned with physical and chemical aspects of the state of aggregation in polymolybdates.

The present paper describes investigations of the attempts to develop methods of assaying molybdates based on their reactions with sodium hydroxide solution.

Experimental

Samples—

Ammonium molybdate, AnalaR—Samples from two separate batches were used.
Molybdic acid, AnalaR—Samples from four separate batches were used.
Molybdenum trioxide, AnalaR—Samples from two separate batches were used.

Reagents—

Standard sodium hydroxide solution, 1·000 N.
Standard hydrochloric acid solution, 1·000 N.
Standard potassium permanganate solution, 0·1000 N.
Phenol red indicator solution—A mixture of 0·1 g of phenol red and 2·8 ml of 0·1 N sodium hydroxide was made up to 100 ml with water.

Apparatus—

A Pye Dynacap pH meter and Ingold combined electrode were used.

Procedure—

All of the samples were analysed first by permanganate titration, after reduction with a zinc Jones reductor by using the standard method,[1,7] then by using sodium hydroxide in the following manner.

Ammonium molybdate—Portions of 6 g were accurately weighed and dissolved in 150 ml of water, with heating. The solutions were cooled and titrated with N sodium hydroxide. The pH was recorded after each addition of 0·5 ml in the region of the end-point, which was located by calculating the first and second derivatives of the titration curve.

Molybdic acid—As molybdic acid is almost insoluble in water, it is necessary to dissolve it in sodium hydroxide solution and back-titrate the excess.

Portions of 3 g were accurately weighed, dissolved in 50 ml of N sodium hydroxide and boiled until all of the ammonia had been removed. The solution was cooled, diluted to 150 ml with water and back-titrated with N hydrochloric acid. A potentiometric titration curve showed that phenol red was a satisfactory indicator, and it was used in these experiments.

Molybdenum trioxide—As molybdenum trioxide, like molybdic acid, is almost insoluble in water, it is also necessary to dissolve it in sodium hydroxide solution and back-titrate the excess.

Portions of 3 g were accurately weighed and dissolved in 50 ml of N sodium hydroxide solution and 50 ml of water. The solution was heated to 80° C to aid dissolution, cooled, and back-titrated with N hydrochloric acid. A potentiometric titration curve again showed that phenol red was a satisfactory indicator, and it was used in the experiments.

Results

The results given in Table I, which are the means of five determinations, have been calculated for the sodium hydroxide reactions by using the equations given under Discussion. For each sample, the maximum difference from the mean was not greater than ±0·2 per cent.

Table I

Comparison of results for molybdenum determination

Compound	Sample No.	Molybdenum, per cent.	
		Jones method	Sodium hydroxide method
Ammonium molybdate ..	1	54·5	54·5
	2	54·5	54·5
Molybdic acid	1	61·2	61·2
	2	60·8	61·1
	3	60·7	60·6
Molybdenum trioxide ..	1	66·9	66·7
	2	66·9	66·7

As a further check, an additional sample of molybdic acid was assayed gravimetrically, as the 8-hydroxyquinolinate,[7] and by the sodium hydroxide method.

The mean results by each method of 59·4 per cent. of molybdenum were in agreement.

Discussion

The titration curve of ammonium molybdate shows two inflections; one between pH 5 and 7, corresponding to the conversion of the paramolybdate into the orthomolybdate, and the other between pH 9 and 10, corresponding to the displacement of ammonia.

The first stage of the reaction may be given by—

$$Mo_7O_{24}^{6-} + 8\,OH^- \longrightarrow 7MoO_4^{2-} + 4H_2O.$$

A well defined end-point is obtained at a point corresponding to the above equation. This end-point has to be determined potentiometrically, as the rate of change of pH with addition of titrant is not fast enough to give a sharp change with a pH indicator.

Molybdic acid, which is prepared commercially by the careful addition of nitric acid to a concentrated solution of ammonium molybdate, is a complex mixture of paramolybdates and contains between 4 and 7 per cent. of ammonia. The empirical formula may be written $[(NH_4)_2MoO_4]_x[MoO_4]_y.(H_2O)_z$. Its reaction with sodium hydroxide can be given by—

$$[(NH_4)_2MoO_4]_x(MoO_3)_y.(H_2O)_z + 2\,(x+y)\,NaOH \longrightarrow (x+y)\,Na_2MoO_4 + (2x+y+z)\,H_2O + 2xNH_3.$$

Thus, provided that all of the ammonia is boiled off, the amount of sodium hydroxide consumed allows the molybdenum content to be calculated, irrespective of the ratio of $(NH_4)_2MoO_4$ to MoO_3 in the sample.

The reaction between sodium hydroxide and molybdenum trioxide is a special instance of the previous reaction and may be given by—

$$MoO_3 + 2NaOH \longrightarrow Na_2MoO_4 + H_2O.$$

The procedures based on the reactions of the compounds with sodium hydroxide possess the advantages of speed and simplicity over the oxidimetric and gravimetric methods.

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References

1. AnalaR Standards for Laboratory Chemicals, Sixth Edition, 1957, AnalaR Standards Limited, London, 1967, pp. 64, 325 and 327.
2. Rosin, J., "Reagent Chemicals and Standards," Fifth Edition, D. Van Nostrand Company Inc., New York, 1967, p. 311.
3. Becker, J., and Coetzee, C. J., *Analyst*, 1967, **92**, 166.
4. Ghosh, J. C., and Biswas, A. B., *J. Indian Chem. Soc.*, 1945, **22**, 287.
5. Cannon, P., *J. Inorg. Nucl. Chem.*, 1959, **9**, 252.
6. Chani, K. V. R., Jain, D. V. S., and Mitra, R. P., *J. Scient. Ind. Res.*, 1961, **20B**, 294.
7. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis, including Elementary Instrumental Analysis," Third Edition, Longmans Green & Co., London, 1961, p. 333.

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Fumigant Residues in Wheat and Flour: Solvent Extraction and Gas-chromatographic Determination of Free Methyl Bromide and Ethylene Oxide

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Methods are described for the cold solvent extraction and analysis of traces of the fumigants methyl bromide and ethylene oxide present in flour and wheat after treatment, and for determining the efficiency of extraction, in which a combination of gas-chromatographic and chemical techniques is used.

Results are given showing the loss of fumigant caused by reaction with cereal constituents before recovery, and a method for correcting this is described. Recoveries generally of 95 per cent., or more, were obtained with a lower detection limit of about 0·3 p.p.m. The application of the method to other volatile compounds is indicated.

There is a growing awareness of the need for methods to monitor all types of pesticide residues in foods.[1,2] Most attention has naturally been given to the problem of the highly persistent insecticides, but when a substantial proportion of the national consumption of a commodity may be treated with a less persistent pesticide, for example, methyl bromide, as a fumigant for imported grain, it is important that the most minute amount of such a toxic agent should be detectable and its significance assessed.[3]

Ethylene oxide, which is sometimes used for flour fumigation, and methyl bromide are alkylating agents. Winteringham, Harrison, Bridges and Bridges[4] studied the methylation of wheat constituents, such as protein amino-acids, by methyl bromide. Ethylene oxide has been shown to produce hydroxy-ethylated derivatives of similar substances and also of celluloses and sugars in dried fruit.[5] In addition, ethylene oxide has been shown to react with inorganic chloride in foods to form ethylene chlorohydrin.[6] The reaction products of methyl bromide were considered by Winteringham[7] not to constitute a hazard in normal dietary requirements. The extent of ethylene chlorohydrin formation by ethylene oxide in flour under normal fumigation conditions is at present being studied.

These reactions and the volatility of the fumigants indicate that most of any residual methyl bromide or ethylene oxide will quickly disappear after treatment and during subsequent processing. To show whether this disappearance reaches completion, more efficient and more sensitive methods are required than have hitherto been available.[3] Classical methods have included grinding and dry aeration to remove volatile fumigant,[8] steam-distillation or aeration of solvent extracts,[8] and indirect determination from the difference in total bromide before and after solvent extraction.[9] Recoveries of added fumigant have generally been low, partly because of incomplete removal from the substrate, as in dry aeration, and partly because of reaction of the added fumigant with grain constituents, either in the dry state or during recovery, for example, during steam-distillation.[10]

The authors obtained almost 100 per cent. recovery of ethylene chlorohydrin and ethylene dibromide from flour and wheat[10] by cold extraction with a mixture of acetone and water (5 + 1 v/v), followed by direct injection of 2 to 10-μl aliquots of the supernatant liquor into a gas chromatograph. During the chromatography of such extracts from wheat flour, in which ethylene chlorohydrin had been produced *in situ* by reaction of naturally occurring inorganic chloride with ethylene oxide, the presence of ethylene oxide in the solvent was detected by flame ionisation as an early peak emerging from the column before acetone and water. It appeared that if precautions were taken to prevent losses by premature volatilisation from the extracts, substances more labile than ethylene dibromide and ethylene chlorohydrin should also be recovered with high efficiency.

Experimental

Determination of percentage recovery of known amounts of fumigant—

To determine the rate of recovery by a candidate-extraction method by establishing a precisely known content of a volatile and reactive substance, such as ethylene oxide or methyl bromide, in cereals, in the form in which it would be present in practice, presents problems caused by reaction losses of the added fumigant and the difficulty of complete removal by aeration of the fraction more firmly held by sorption.

Field samples received for analysis will have received some aeration in the course of normal handling. It is, therefore, necessary in experiments involving laboratory application to remove the loosely held vapour by preliminary aeration, as this might be extracted with high efficiency, whereas the more firmly held residue, which is of concern, might tend to give a lower recovery by the method under investigation. During the necessary exposure period for the application of the vapour phase and the preliminary aeration, some of the initially applied fumigant will have been lost by reaction, and with ethylene oxide, because of the complexity of the reaction products, the starting amount can no longer be fully accounted for.

If now, however, a second aeration of the material is carried out, and the vapour is collected in bubblers and chemically analysed, the amount of vapour removed *plus* that which has reacted with the material during this aeration period will represent the change in content of the free fumigant.

Let the amount in milligrams of fumigant collected in bubblers per gram of material aerated be a; the amount of fumigant, in milligrams per gram, reacted with unit weight of material during aeration be r; the amount of fumigant, in milligrams per gram, recovered by the method under test, calculated from representative samples taken before and after aeration, be g_1 and g_2, respectively; and the percentage recovery of fumigant by the method under test be x.

Then

$$a + r = \frac{100}{x}(g_1 - g_2) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

and hence

$$x = \frac{100\,(g_1 - g_2)}{a + r} \quad .. \quad .. \quad .. \quad .. \quad (2),$$

and the percentage recovery by the candidate method can be calculated if r is known.

While the measures outlined are necessary in evaluating a proposed analytical procedure, only g_1 is required to be found when determining residual unchanged fumigant subsequently when the percentage recovery is known.

Analytical procedure

Extraction and determination of free fumigant (*e.g.*, g_1 and g_2)—

About 10 g of wheat or 5 g of flour are quickly weighed and transferred into a stoppered flask containing 30 ml of a mixture of analytical-reagent grade acetone and water (5 + 1 v/v), and allowed to stand for at least 1 hour at 20° C, with occasional shaking. At suitable intervals (see Fig. 1), 2-μl aliquots of the clear supernatant liquor are quickly withdrawn with a 10-μl Hamilton syringe and injected into a vaporising U-tube, as described by Heuser and Scudamore,[10] for introduction into the carrier-gas stream of a gas - liquid chromatograph (Perkin-Elmer 452). Alternatively, the injection may be made directly into the injection block if it is fitted with a removable glass liner, *e.g.*, a Perkin-Elmer F11.

With these highly volatile components in solution it is advisable, before injection, to withdraw the liquid from the needle into the barrel of the syringe after filling it to the required volume. Reproducibility of peak heights from duplicate injections is generally ± 1 per cent.

With a 2 metre × 4·6-mm i.d. stainless-steel column containing 15 per cent. w/w poly(propylene glycol) ("Ucon" oil LB–550–X) on 60 to 80-mesh Chromosorb W, dry helium carrier at 80 ml per minute, flame-ionisation detector, injection U-tube or block at 125° C and column oven at 85° C, ethylene oxide is eluted at 42 seconds and methyl bromide at 45 seconds. (In the unlikely event that the two fumigants are required to be determined simultaneously, a lower column temperature would be preferable.) They are eluted as sharp peaks before the solvent peaks, giving a highly stable base-line. High amplification can thus be used, and ultimate sensitivity is about 2×10^{-10} g for ethylene oxide and 5×10^{-10} g

for methyl bromide. About 12 minutes must be allowed to elapse for complete removal of water from the column before another sample is injected, as traces of water temporarily lower the sensitivity of the detector.

Standard solutions of methyl bromide and ethylene oxide were prepared for calibration purposes by adding drops of chilled liquid fumigant to a previously weighed volume of chilled acetone - water (5 + 1 v/v) in a calibrated flask, re-weighing and making up to volume at 20° C. By using the flame detector, a linear relationship between peak height and weight was obtained in the range 10^{-9} g to 10^{-6} g, with a standard injected volume (2 or 10 μl).

Dry flour added to solutions of ethylene oxide or methyl bromide of known strength in acetone - water (5 + 1 v/v), and held in sealed flasks, did not lower the amount of fumigant determined by gas chromatography in the supernatant liquor, after allowing it to stand for periods up to 4 hours at 20° C. This shows that no adsorption of fumigant from the solvent takes place; that there is no measurable loss of volatile fumigant from the solutions into the head space; and that no reaction with cereal constituents takes place under these conditions, and hence that reaction of sorbed vapour on treated flour is halted by solvent extraction.

PREPARATION OF SAMPLES FOR DETERMINATION OF g_1 AND g_2—

Known weights of ethylene oxide or methyl bromide were introduced as vapour into 250-ml cylindrical separating funnels, fitted with 2-mm bore stopcocks at each end and containing 10 to 100 g of wheat or flour, by using the method with a gas pipette, as described by Heuser.[11]

After allowing them to stand for a set period (Tables I and II), a preliminary aeration of 15 minutes' to 2 hours' duration at 100 ml per minute was carried out to remove loosely held fumigant. A small proportion of the flour or wheat was then quickly weighed out for solvent extraction of fumigant and determination of g_1, as described above, and the aeration then continued for several hours, during which the fumigant removed was collected in two sintered-glass bubblers in train. For ethylene oxide, the absorbent reagent used was a 50 per cent. w/v solution of anhydrous magnesium bromide in 0·1 N sulphuric acid, and for methyl bromide a mixture of monoethanolamine and dioxan (1 + 1 v/v). Determination of the weight of ethylene oxide absorbed in the bubblers was carried out as described by Lubatti,[12] and that of methyl bromide as described by Winteringham, Bridges and Harrison.[13]

After the second aeration, further portions of flour or wheat were similarly analysed for their free fumigant content to evaluate g_2.

EVALUATION OF r—

An estimate of the value of r in equation (2) for the second aeration period can be obtained by measuring the disappearance of free fumigant in wheat or flour, under sealed conditions. This is related to the initial fumigant content of the material under test, and it can be shown that after several hours' exposure, the rate of reaction thus measured (milligrams per hour per gram of material) does not differ greatly from that in material that has been partially aerated after the initial exposure. This suggests that it is the more firmly adsorbed fumigant that reacts and not that which is easily removable by aeration.

As the amount of reaction is small compared with the total amount of fumigant removed by aeration, little error is introduced by assuming that r is the same under both sets of conditions if the temperature remains the same for the period being considered.

The amount of reaction taking place in a portion of the partially aerated material, held in a sealed flask, was, therefore, determined by extraction of total free fumigant from 5 g of flour or 10 g of grain with 30 ml of acetone - water (5 + 1 v/v), before and after allowing it to stand at constant temperature for a period equivalent to the second aeration period. The solvent was introduced into the flask through a stopcock, after rapidly cooling to reduce internal pressure to avoid loss of free vapour. The fumigant content of the extracts was determined by gas chromatography, as already described.

Let the total amounts of fumigant determined per unit weight of material before and after standing be g_3 and g_4, respectively, and the percentage recovery of fumigant by the method under test be x.

Therefore

$$r = \frac{100}{x}(g_3 - g_4) \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3).$$

TABLE I

RECOVERY OF FREE ETHYLENE OXIDE AND METHYL BROMIDE FROM PARTIALLY AERATED FLOUR

Experiment number	Fumigant	Initial exposure, hours	Preliminary aeration, hours	Main aeration, hours	W, g	Initial dose, mg	Recovered in bubblers from W g ($=aW$), mg	g_1W, mg	g_2W, mg	g_3, mg per g	g_4, mg per g	rW, mg	x, per cent.
1	C_2H_4O	1	¼	3	6·9	22·6	2·87	4·67	1·86	0·683	0·675	≯0·09	95·0
2		1	¼	3	6·9	62·3	7·97	11·87	4·02	1·714	1·697	≯0·24	95·6
3		16	2	4	14·5	57·0	5·05	13·00	7·85	0·889	0·868	0·32	95·8
4	CH_3Br	16	2	2	10·4	86·6	2·16	9·60	7·38	0·922	0·908	≯0·18	94·9
5		19	2	4	10·3	85·2	3·26	8·48	4·90	0·821	0·783	0·40	97·5
6		66	¼	2	6·2	88·3	5·00	12·60	7·50	2·025	1·985	0·25	97·0

TABLE II

RECOVERY OF FREE METHYL BROMIDE FROM PARTIALLY AERATED WHEAT GRAINS

Experiment number	Initial exposure, hours	Preliminary aeration, hours	Main aeration, hours	W, g	Initial dose, mg	Recovered in bubblers from W g, mg	g_1W 24-hour (extraction*), mg	g_2W 24-hour (extraction*), mg	g_3, mg per g	g_4, mg per g	rW, mg	x, per cent.
7	18	2	4	60·6	135·5	3·89	7·89	3·28	0·128	0·118	0·60	103·0
8	17½	2	4	70·3	141·1	3·86	11·53	6·89	0·167	0·156	0·76	100·5
9	19	2	4	15·1	83·1	1·35	3·75	2·29	0·244	0·235	0·14	97·8

* See Fig. 1.

CALCULATION OF THE VALUE OF x—

By incorporating this value for r in the result from an aeration experiment on an aliquot weight of the same material, from equation (1)—

$$a = \frac{100}{x}\left[(g_1 - g_2) - (g_3 - g_4)\right] \quad .. \quad .. \quad .. \quad (4),$$

hence

$$x = \frac{100}{a}\left[(g_1 - g_2) - (g_3 - g_4)\right] \quad .. \quad .. \quad .. \quad (5).$$

RESULTS

The amounts of each fumigant recovered from W grams of white flour by aeration and by extraction, with the calculated value for r to obtain x, the percentage recovery for the extraction method, are shown in Table I. In experiments 1, 2 and 4 the differences in value between g_3 and g_4 are within the limits of experimental error for the reproducibility of chromatogram peak heights (± 1 per cent.). Here r has been calculated as not greater than 2 per cent. of g_3, and hence the percentage recoveries for these experiments given in the last column of Table I are minimum values.

The percentage recovery of methyl bromide from wheat grains, without grinding, by extraction for 24 hours, is shown in Table II. With this result as a final estimate, the amounts of methyl bromide extracted into the supernatant liquor in shorter periods were calculated as a percentage of the maximum and plotted in Fig. 1 to show the rate of extraction of methyl bromide from the wheat grains. The greater part of the residual free fumigant appears in the supernatant liquor within 6 hours.

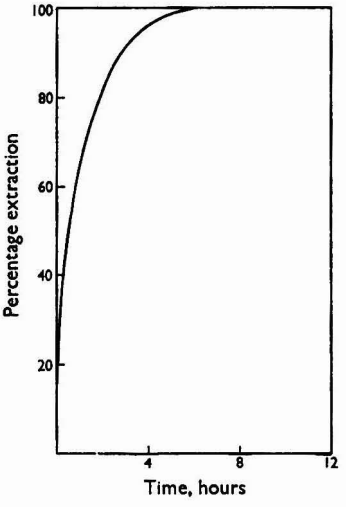

Fig. 1. Rate of extraction of methyl bromide from wheat grains by acetone - water (5+1 v/v)

With flour, extraction of about 95 per cent. of the methyl bromide or ethylene oxide is obtained in a few minutes.

DISCUSSION

It could be argued that the percentage recovery by extraction might still be lower after the second aeration than before it and that equation (1) should be re-written thus—

$$a + r = \frac{100}{x_1}g_1 - \frac{100}{x_2}g_2 \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where x_1 and x_2 are the percentage extraction efficiencies before and after aeration and x_1 is greater than x_2.

If equation (6) is multiplied through by x_1 and re-arranged thus—

$$x_1 = \frac{100\,g_1}{a+r} - \left(\frac{x_1}{x_2}\right)\frac{100}{a+r}g_2 \quad .. \quad .. \quad .. \quad (7),$$

each set of experimental results shown in Table I can be incorporated in equation (7), and a straight line drawn for calculated values of x_1 plotted against $\frac{x_1}{x_2}$, the ratio of the extraction efficiencies, for values of, say, 1·3 to 0·9 (Fig. 2).

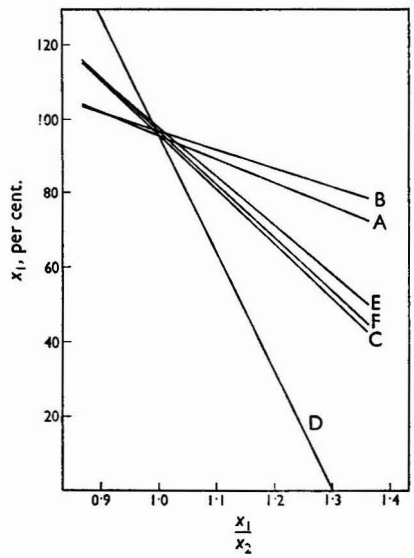

Fig. 2. Values of x_1 plotted as a function of x_1/x_2 in equation (7) by using results from experiments 1 to 6 (Table I): graph A, experiment 1; graph B, experiment 2; graph C, experiment 3; graph D, experiment 4; graph E, experiment 5; graph F, experiment 6

The convergence of these lines when x_1 is about 1·0 indicates clearly that the results from the various experiments can be correlated to give a working value for x_1 when x_1 is equal to x_2, and not otherwise, hence equation (1) is shown to be valid.

In experiments 1 to 6, different periods of exposure were chosen to vary the proportion of reacted fumigant, and different aeration periods were used so that the remaining free fumigant was more or less firmly held by adsorption or solution, or both. Despite these variations the recovery of free fumigant appeared to be consistent.

Because each percentage recovery calculation is based upon five separate analyses the variability is greater than in the single extraction subsequently required to determine the free fumigant content of a sample. Reproducibility of results from separate extractions and gas - liquid chromatographic analyses of the same material was ± 2 per cent. for flour and ± 3 per cent. for wheat grains.

These results are similar to those obtained in the recovery of the more stable ethylene chlorohydrin and ethylene dibromide[10] by the same method and suggest that the actual extraction of fumigant into the supernatant liquor is remarkably constant and complete.

The uniformly high rate of recovery of these volatile aliphatic compounds with boiling-points ranging from 3·6° to 131·6° C, and other widely differing physical characteristics, indicates that a range of similar compounds with intermediate boiling-points should be recoverable in the same way.

The technique of controlled partial aeration described, and the accompanying calculations, may be generally applicable to the determination of the percentage recovery, by alternative methods, of other volatile substances, for which complete aeration is either tedious or impracticable.

References

1. Meeting Report of the Food and Agriculture Organisation No. PL/1965/10/1 and World Health Organisation Food Additives/27, Rome, 1965.
2. Moore, N. W., *J. Appl. Ecol.* (*Suppl.*), **1966**, **3**, 261.
3. Meeting Report of the Food and Agriculture Organisation No. PL/1965/10/2 and World Health Organisation Food Additives/28, Rome, 1965.
4. Winteringham, F. P. W., Harrison, A., Bridges, R. G., and Bridges, P. M., *J. Sci. Fd Agric.*, **1955**, **6**, 251.
5. Gordon, H. T., Thornberg, W. W., and Werum, L. N., *J. Agric. Fd Chem.*, **1959**, **7**, 196.
6. Wesley, F., Rourke, B., and Darbishire, O., *Fd Res.*, **1965**, **30**, 1037.
7. Winteringham, F. P. W., *J. Sci. Fd Agric.*, **1955**, **6**, 268.
8. Lubatti, O. F., *J. Soc. Chem. Ind., Lond.*, **1944**, **63**, 133.
9. Shrader, S. A., Beshgetoor, A. W., and Stenger, V. H., *Ind. Engng Chem. Analyt. Edn*, 1942, **14**, 1.
10. Heuser, S. G., and Scudamore, K. A., *Chem. & Ind.*, **1967**, 1557.
11. Heuser, S. G., *J. Sci. Fd Agric.*, **1959**, **10**, 90.
12. Lubatti, O. F., *J. Soc. Chem. Ind., Lond.*, **1935**, **54**, 424T.
13. Winteringham, F. P. W., Bridges, R. G., and Harrison, A., *J. Sci. Fd Agric.*, **1950**, **1**, 185.

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The Determination of Quebracho in Mixtures with Some Other Tannin Extracts and Related Materials

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A spectrophotometric method is described for the determination of quebracho in mixtures with other tannin extracts and related materials. The accuracy of the method is to within a range of ±10 per cent. A method is also described for the identification of quebracho.

IN recent years attention has been given to problems dealing with the elucidation of composition and structure of the many complex components present in vegetable tannin materials. Much of this work has been reviewed by Haslam.[1] In the present paper emphasis is given to the identification and determination of a particular vegetable tannin extract in the presence of other tannin extracts and related materials. This work was undertaken in connection with a proposed extension of a drawback scheme at present in operation for the payment of drawback on soluble quebracho made from the insoluble and duty paid imported variety. Under the proposed provisions of the scheme it is necessary to be able to identify and determine the amount of quebracho in admixture with other tannin materials of vegetable origin, *e.g.*, mimosa, myrobalan and mangrove, with other tanning agents, sulphite cellulose and sulphite lye, and with other added materials, such as lignite and Vandyke brown.

Vegetable tannins can be divided into two categories, namely the "condensed" or "catechol" type and the "hydrolysable" or "pyrogallol" type. Sohn[2,3] has shown that these two general classes of vegetable tannin extracts can be distinguished by their ultraviolet absorption spectra. White[4] has shown that an ultraviolet-absorption technique can be adapted to permit the determination of any one vegetable tannin extract in a limited range of binary blends of the materials, provided that certain conditions are observed. One condition is that the identities of the components of a blend are known and another is that at a specified wavelength sufficient difference exists between the absorption of solutions of the separate components when prepared under identical conditions. White[4,5] established the identity of the components by a paper-chromatographic technique. Maranville and Goldschmidt[6] used a differential ultraviolet-absorption technique for the determination of the phenolic hydroxyl content of lignin preparations in which the absorption of solutions of equal concentration in acidic and alkaline media are compared.

We have found that by a combination of the methods of these workers it has been possible to determine the quebracho content of a range of binary and tertiary blends of the specified materials. For the determination of the quebracho content of any blend, it is essential that samples of the blend and of its components are available. A thin-layer chromatographic method is used to establish the identity of the quebracho by comparing the characteristic distribution of fluoresence of the blend with that of the quebracho ingredient. Under the conditions specified, the other vegetable tannin extracts and related materials have relatively little or no fluorescence. For the quantitative determination of quebracho extract, it has been found that by using the differential ultraviolet-absorption technique to be described, the catechol and pyrogallol-type tannin extracts have absorption maxima at about 290 and 320 mμ, respectively. In Table I, optical densities are shown for 0·008 per cent. w/v aqueous solutions of the vegetable tannin extracts and related materials, recorded at the peak maximum of about 290 mμ, and it can be seen that White's condition relating to differences in optical density is satisfied.

For quebracho - myrobalan mixtures measurements can also be made of the absorption maximum at about 320 mμ. Measurement at this wavelength is more accurate when the quebracho content falls below 37·5 per cent. The optical densities recorded for 0·008 per cent. w/v aqueous solutions of quebracho and myrobalan at 320 mμ are about 0·090 and 1·40, respectively.

TABLE I

OPTICAL DENSITIES OF 0·008 PER CENT. W/V AQUEOUS SOLUTIONS OF VARIOUS TANNIN MATERIALS AT 290 mμ

Extract	Optical density
Quebracho	0·780 to 0·860
Mimosa	0·410 to 0·440
Mangrove	0·530 to 0·550
Myrobalan	0·320 to 0·360
Sulphite cellulose	0 to 0·070
Sulphite lye	0 to 0·060
Lignite	0 to 0·010
Vandyke brown	0·200 to 0·250

METHOD

APPARATUS—

Recording spectrophotometer.

Chromatographic tank, and plates, 20 × 20 *cm.*

Camag adjustable spreader.

REAGENTS—

Hydrochloric acid, 0·001 N.

Borate buffer, pH 10—Dissolve 6·184 g of boric acid, 7·45 g of potassium chloride and 87·8 ml of N sodium hydroxide in 2 litres of carbon dioxide free water.

Kieselgel G.

Ethyl methyl ketone.

PROCEDURE—

Prepare separately 0·1 per cent. w/v aqueous solutions of the blend and of the two components (A and B) of the blend (*i.e.*, solutions A and B). Centrifuge portions of the solutions, if necessary, and transfer, by pipette, aliquots of 0, 1, 2, 3 and 4 ml of solution A and 4, 3, 2, 1 and 0 ml of solution B into 50-ml graduated flasks, so that for each the total concentration of the solution, when diluted to volume with 0·001 N hydrochloric acid, is 0·008 per cent. w/v. Prepare another series of solutions of the same strengths but dilute to volume with borate buffer. Transfer by pipette 4 ml of the 0·1 per cent. w/v solution of the blend into each of two separate graduated flasks and make one up to volume with 0·001 N hydrochloric acid and the other with buffer. Record the ultraviolet absorption of the alkaline series of 0·008 per cent. w/v solutions over the wavelength range 260 to 330 mμ, in 1-cm quartz cells, with the corresponding acidic solution for each reference. Plot a calibration graph relating optical density, measured at the wavelength corresponding to the absorption maximum of the solution containing only quebracho extract, to concentration of quebracho. Read off from the calibration graph the composition of the blend. In order to avoid possible hydrolysis of the tannin materials, it is advisable to record the spectra of the solutions as soon as possible after preparation.

RESULTS

The quebracho contents found for a series of binary blends are given in Table II.

It can be seen that the quebracho content found is within a tolerance of ±10 per cent., which is acceptable in this type of analysis. The use of the method can be extended to cover the analysis of ternary blends containing quebracho extract and two other vegetable tannin extracts. In this method it is necessary in preparing the calibration graph to fix the concentration of one of the components in the solutions while varying the concentration of the other two components. The quebracho content of a blend incorporating quebracho - mimosa - myrobalan (1 + 1 + 1) was found to be 36 per cent. In this particular experiment the concentration of the myrobalan in the reference solutions was fixed at 33⅓ per cent., and the measurements were recorded at 290 mμ.

TABLE II

RESULTS OF QUEBRACHO DETERMINATIONS IN BINARY BLENDS

Composition of blend as given by supplier			Quebracho found, per cent.
47% soluble quebracho	+	53% mimosa	48
64% soluble quebracho	+	35·5% myrobalan	69
17·5% insoluble quebracho	+	82·5% mimosa	15
75% soluble quebracho	+	25% mangrove	78
50% soluble quebracho	+	50% sulphite cellulose	53
60% soluble quebracho	+	40% sulphite cellulose	62
75% soluble quebracho	+	25% sulphite cellulose	74
85·8% soluble quebracho	+	14·2% sulphite lye	85
60% soluble quebracho	+	40% lignite	61
60% soluble quebracho	+	40% Vandyke brown	56

Identification of quebracho—Prepare 10 per cent. w/v aqueous solutions of the blend and of the quebracho extract used for preparation of the blend. Prepare the carrier plates in the usual way with Kieselgel G (150 μ thick) as substrate. Divide the plate into two parts and transfer a portion of the blend solution (100 μl), spotwise, on to one half of the plate along an origin line 1·5 cm from one edge of the plate and parallel to it. Apply the quebracho solution (equivalent to the amount of quebracho present in the blend) in a similar manner to the other half of the plate. Develop the plate by ascending chromatography in a suitable tank, with ethyl methyl ketone, until the solvent front has travelled about 15 cm. Remove the plate from the tank, allow the solvent to evaporate, and examine the plate under ultraviolet light. The presence on both parts of the plate of a pattern of fluorescent compounds of similar distribution and intensity may be taken as positive identification of the quebracho present in the blend.

A method for the identification and determination of quebracho present in blends has been described. The accuracy of the method is to within a range of ± 10 per cent.

We thank the British Leather Manufacturers Research Association for their advice and assistance in checking the method, and the British Tannin Extract Manufacturing Association for their interest and for supplying the samples. We also thank the Government Chemist for permission to publish this paper.

REFERENCES

1. Haslam, E., "Chemistry of Vegetable Tannins," Academic Press, London, 1966.
2. Sohn, A. W., *Angew. Chem.*, 1950, **539**.
3. ——, *Leder*, 1951, **2**, 4.
4. King, H. G. C., and White, T., "Symposium on Chemistry of Vegetable Tannins," Society of Leather Trades' Chemists, Croydon, 1956, p. 31.
5. White, T., Kirby, K. S., and Knowles, E., *J. Soc. Leath. Trades Chem.*, 1952, **36**, 148.
6. Maranville, L. F., and Goldschmidt, O., *Analyt. Chem.*, 1954, **26**, 1423.

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A Simple Device for Delivering an Approximately Metered Amount of a Powdered Catalyst Mixture into a Sample Boat

BY M. ELLISON

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A device for delivering a metered amount of a powdered catalyst mixture into a sample boat is described. The design of the dispenser ensures that the hygroscopic mixture is stored and dispensed under clean conditions.

DURING the preparation of a sample for combustion in an F. & M. 185 CHN Analyzer it is necessary to introduce an oxidising catalyst mixture into a sample boat.

This catalyst mixture (in fine powder form) is normally heated to about 500° C before use, to ensure a low carbon, nitrogen and water content. After a sample boat, containing catalyst, is placed in the cool portion of the Analyser combustion tube, a waiting period of 4 to 5 minutes is necessary before the combustion procedure is carried out.

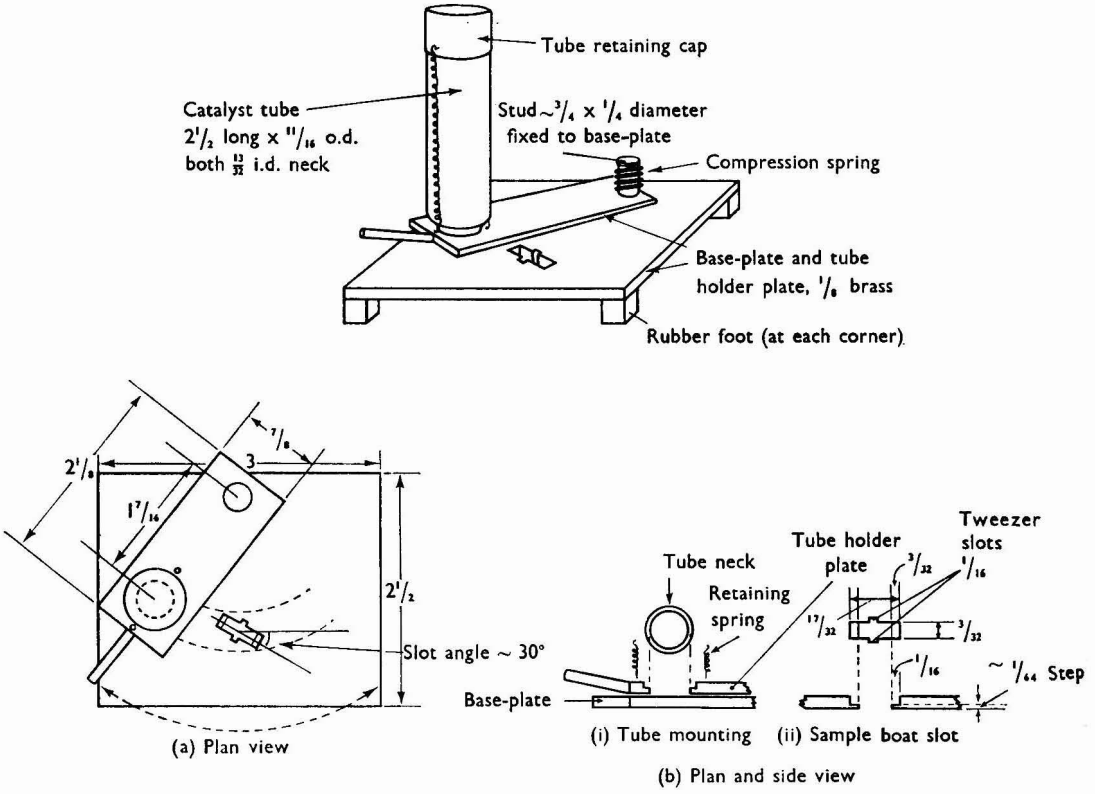

Fig. 1. Details of the catalyst dispenser: (a) plan view; (b) plan and side view; all measurements are in inches

During this time, moist helium carrier gas is passed through the apparatus and over the sample boat, and, because of the hygroscopic nature of the catalyst, a small but significant amount of water is retained. During combustion this entrained water is driven off and appears as a blank on the resulting chromatogram.

Two factors influence the reproducibility of this blank, the time the catalyst is exposed to moist carrier gas, and the amount of catalyst mixture in the sample boat. The former can readily be standardised but the latter would require weighing the mixture before each determination.

To overcome this problem a dispenser was constructed, the details of which are shown in Fig. 1.

Experimental

Method of operation—

With the aid of forceps place a sample boat in the boat slot in the base-plate. Make sure that the boat is sunk flush with the top surface of the base-plate, *i.e.*, the boat is sitting on the countersunk steps [see Fig. 1, detail (*b ii*)]. Then move the arm controlling the catalyst-tube holder from side to side over the sample boat. Two or three passes are usually sufficient to fill the boat. Insert the forcep points in the slots provided and carefully transfer the boat to a prepared sample-rod holder.

Conclusions

The use of a dispenser for the catalyst eliminates the need for a spatula, and also reduces the possibility of contamination, both to the sample and catalyst. The dispenser provides a convenient and virtually sealed store for the catalyst; one tube filling will last for 2 or 3 days. It also ensures that a constant weight of catalyst is added to the sample boat, within ± 3 per cent.; this total weight depends on particle size and constituents of the catalyst but is normally between 0·1 and 0·2 g.

The whole of the pre-combustion procedure is simplified by using the dispenser for the catalyst mixture.

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Accurate Dispensing of Small Volumes of Volatile Liquids with a Micro Syringe and Aluminium Capillary Tubes

By M. ELLISON

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A device for delivering and sealing accurate volumes of volatile liquids into aluminium capillary tubes is described.

The need for dispensing liquids within fairly close limits of weight arises from the more recent use of automatic analysers, with which elements in organic compounds are determined on small sample weights, *viz.*, less than 1 mg.

More specifically, with an F. & M. 185 CHN Analyzer it is important that during operation sample weights must be kept within certain limits. The design of this instrument also requires that a sample container must not be greater than 1·5 cm in length, thus making a scaled-down version of the well known semi-micro sealed-tube technique difficult, if not impracticable, to carry out.

Open-ended glass capillaries holding about 1 μl can be used for liquid samples, but this simple technique of filling by capillarity can be tedious if a weight within 50 μg is required, and even more difficult with a volatile compound.

Experimental

Apparatus—

Fig. 1 shows a sealed-tube liquid dispensing device for overcoming this particular problem. Essentially, a 1-μl Hamilton micro syringe is mounted through two sliding supports; the rear or right-hand support carries a screw clamp so that the syringe may be held rigidly when required. The front or left-hand support consists of a length of glass tubing with a capillary just large enough to allow movement of the syringe needle. This glass tube is rigidly supported at both ends, and radial movement of the needle for aligning purposes is carried out with three radially mounted worm screws on the left-hand support.

A tube-crimping device is shown in Fig. 2. It consists of a grooved platform to hold aluminium capillaries (o.d. 0·025 inch, i.d. 0·020 inch).

A short length of rod is mounted vertically through a hole over this recess and, during operation, a capillary is crimped by pressure on this rod.

The sample holder shown in the diagram is L-shaped and has five holes in one face, into which melting-point tubes containing samples can be inserted.

Alignment of the micro syringe—

As individual syringes differ slightly in dimensions it is necessary to carry out the following adjustments before use.

Put the needle-guide tube into position longitudinally so that the syringe needle protrudes out of this tube by about half an inch when the syringe is moved fully to the left.

Place an aluminium capillary in the crimper groove and slide the crimper into load position.

Check the radial position of the needle, as described earlier, so that free capillary entry can be carried out.

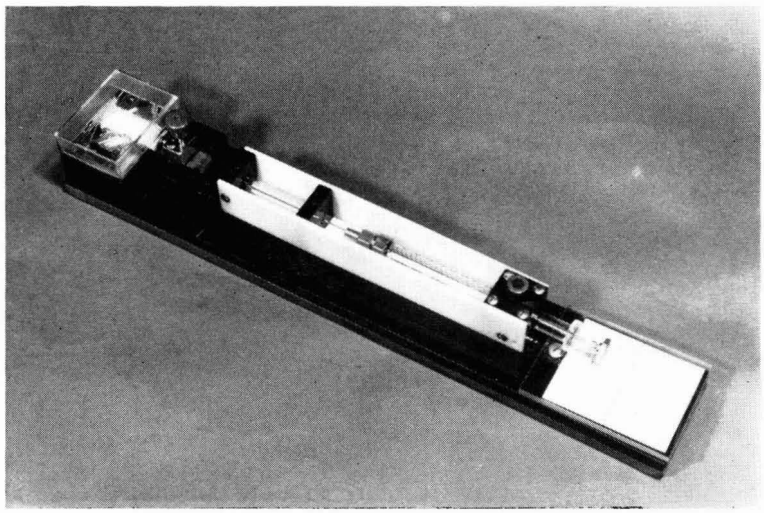

Fig. 1. Sealed-tube liquid dispensing device

[To face page 264

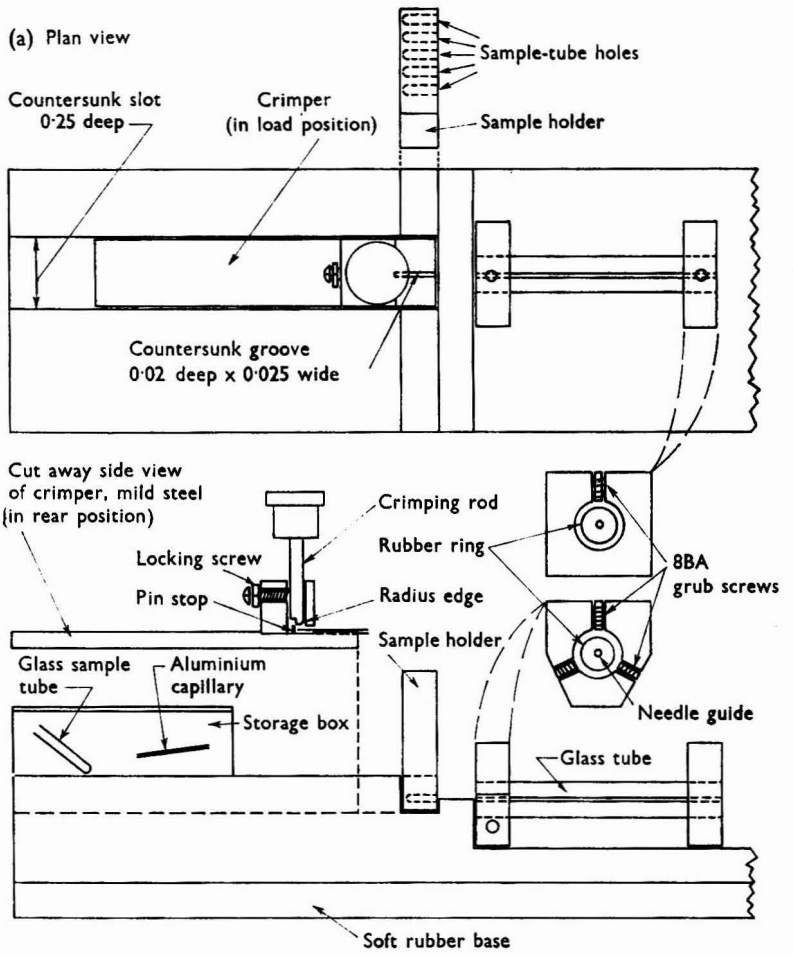

Fig. 2. Details of crimper, sample holder and needle guide. Construction material was Tufnol, except where indicated; all measurements are in inches

PROCEDURE FOR WEIGHING A SAMPLE—

Fill a melting-point sample tube three quarters full with sample and place the sample-holder tube in position. The holder is then put into position as shown in Fig. 2 (side view).

Slide the syringe fully forward and pump the syringe piston several times. When the air has been expelled from the needle draw the piston back to the required volume (this can be calculated from the sample density if it is already known), then draw the syringe back until the needle is clear of the sample tube, and withdraw the piston a further 0·1 μl.

Remove the sample holder from the stage, place a tared aluminium capillary in the crimper groove and slide the crimper into load position.

Slide the syringe fully forward and inject sample into the capillary, then depress the crimping rod. Withdraw the syringe and carefully reverse the capillary in the crimper groove with forceps; seal the capillary tube by depressing the crimping rod.

The capillary tube can then be transferred to a balance for weighing.

Received *August 30th*, 1967

Book Reviews

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1966. Volume LXIII. Pp. xvi + 834. London: The Chemical Society. 1967. Price 100s.

The "Annual Reports on the Progress of Chemistry for 1966," published by the Chemical Society, occupy 762 pages of text. Of these, 31 pages are devoted to Analytical Chemistry. The authors of this section of the report, Messrs. Anderson, Pierce, Stoddart and Wilson, have sought, within these 31 pages, to give a balanced account of the most significant developments in analytical chemistry in 1966. They feel that they have dealt with about 5 per cent. of the analytical papers published in the year and, in their selection, which cannot be free from personal bias, have dealt with items under the following main headings: Qualitative Analysis, Quantitative Organic Analysis, Electrochemical Methods, Radiochemistry, Spectroscopic Analysis, Methods of Separation, Gravimetric Analysis, Titrimetric Analysis, Reaction-Rate Methods and Thermal Methods.

In the view of the reviewer, who carried out similar work for 3 years, and who is well aware of some of the difficulties involved, the task is becoming almost impossible to perform satisfactorily.

In 31 pages, 453 references to original papers and other reviews have been covered; the average for each reference is less than 2½ lines of text. The analytical chemist seeking new ideas will be well advised to read this report very carefully indeed and try to find very brief notes that will lead him to original papers worthy of intensive study. He will, however, find himself beset with difficulties because of the large amount of ground that has had to be covered, for example, on page 678 it is said, with reference to a particular paper, "Reaction products from the oxidation or reduction of organic compounds in acetic acid may be isolated from the acetic acid by extraction with carbon disulphide." How many analytical chemists will be led to the original paper without knowledge of the chemical nature of the organic compounds that are being oxidised or reduced?

Similar examples of difficulty could be quoted, not as criticisms, but as evidence of the task that the authors have been set and with which they have tried admirably to cope.

The introductory part of this report gave the present reviewer the most pleasure because here the authors try to point out the trends in analytical work as a result of their study of innumerable papers. They draw attention to the procedures that are being used less frequently and to those that are developing fast, to the importance of automation of analytical methods and to the very welcome changes that are taking place in the attitudes adopted by commercial manfacturers to the instruments they sell.

J. HASLAM

COLORIMETRIC METHODS OF ANALYSIS INCLUDING PHOTOMETRIC METHODS. By FOSTER DEE SNELL, Ph.D., Sc.D., and CORNELIA T. SNELL, Ph.D. Volume IVA. Pp. x + 645. Princeton, New Jersey, Toronto and London: D. Van Nostrand Company Inc. 1967. Price 140s.

If you are in need of a colour reaction with which to determine a particular organic compound or group of compounds, your first action will almost certainly be to consult Snell. The six books that make up the third edition of "Colorimetric Methods of Analysis," by Foster D. Snell and Cornelia T. Snell offer the analyst a quick and reliable means of making a first search for suitable colour reactions, and every competent organic analyst must surely be familiar with them.

Volume IV, which was published in 1954, contained sixteen chapters, each one covering a compact group of compounds, mostly nitrogenous in composition: Volume IVA is a supplement to the first six chapters of volume IV (the authors, in their preface, say, seven, but this appears to be an error) and its effect is both to up-date and to expand considerably the material given in the earlier volume. The information given is, of course, taken directly from the literature, and although the reviews are accompanied in all cases by detailed instructions for carrying out the determinations, no claim is made that they have been confirmed by the authors, and the reader must recognise that the responsibility for examining the methods critically falls upon his shoulders. Nevertheless, it is clear from the references, which are given at the foot of each page, that the authors have cast their net widely in their search for up-to-date and dependable analytical methods.

The first chapter covers nitrites, nitrates and nitro compounds, and includes methods for determining several nitrobodies that are commonly used for preservation and pest control in agricultural products. In the subheadings, these are named with their chemical and with their commercial names, but their constitutional formulae do not appear, and although it is generally possible to write them down after a moment's thought, I am sure that most people would welcome the inclusion of structural formulae for the compounds that are described.

Chapter 2 is devoted to aliphatic amines and amides, and includes methods for distinguishing between primary, secondary and tertiary amines. Sometimes the text is difficult to follow; for example, on p. 74, dibeprin, 8-(10-dioxodiindeno[3,2-*b* : 2′,3′-*e*]pyrid-11-yl)-1-naphthoyl chloride, is described as "a reagent for primary amines: the reagent is yellow, but gives a blue-violet colour with unsubstituted and monosubstituted amides in ethanolic alkaline solution. Esters and disubstituted amides do not give the colour." What about the amines then? And on page 77, in the working instructions for carrying out the determination of primary amines by reaction with dibeprin, the important step of adding the reagent has been omitted. The latter part of this chapter has a decidedly biochemical flavour, through the inclusion of several drugs, amino-acids and metabolites.

Chapter 3 deals in a much more detailed way with amino-acids, allotting 92 pages to this group of substances, and Chapter 4 is devoted to the determination of proteins, such as globulin, albumin, lipo- and muco-proteins, fibrinogen and gelatin in tissues, serum, cerebrospinal fluid and other biological or natural products.

The fifth chapter reverts to the subject of primary, secondary and tertiary amines and amides, this time of the aromatic series, and the final chapter covers a selection of azo compounds, heterocyclics (barbiturates, pyridine derivatives and indoles), purines and vitamin B_{12}.

One cannot say much that is original about a volume of this kind; those who frequently use this work will probably have the previous volumes of the third edition, and will wish to keep the series complete. Colorimetric methods of determination have, of course, declined in importance as a result of the revolution in spectroscopy and chromatography that has taken place in recent years, but there are some fields of analysis that are, as yet, only lightly touched by these powerful techniques, and one has only to remember the successes that have been achieved in the mechanisation of clinical analysis to recognise the important part that colorimetry still plays in modern analytical science.

H. E. STAGG

DÜNNSCHICHT-CHROMATOGRAPHIE. EIN LABORATORIUMSHANDBUCH. Edited by EGON STAHL. Second Edition. Pp. xx + 979. Berlin, Heidelberg and New York: Springer-Verlag. 1967. Price DM 98; $24.50.

The expansion from the first to this revised (German) edition of Stahl's book fittingly marks recent advances in thin-layer chromatography. The compendium is a credit to the thoroughness of editor, publisher and printer. The many authors contribute authoritative chapters on twenty-six topics, physical, organic and inorganic; the classification is based, with little overlap, on chemical features (essential oils, steroids, lipids, alkaloids, indole derivatives, amines, amino-acids, nucleotides and nucleic acids, sugars and inorganic ions), and on biological action or technical utility (vitamins, synthetic drugs and dyestuffs, antibiotics, foodstuffs and additives, fine chemicals and hydrophilic plant substances). Materials and apparatus are fully described, as well as special methods, electrophoresis, gas-chromatographic adjuncts, documentation, quantitative methods, application of isotopes and clinical tests (forensic methods are not gathered into one chapter). The literature is covered into 1965, which dates the volume on preparative chromatography and on the ready-made plates now on sale. The volume ends with an updated list of 246 spray reagents, a glossary of terms in English, French and German, an international list of suppliers of equipment and a copious index. It is well produced and illustrated, but some of the pages have the shiny surface that marred those of the first edition.

The modern analyst works with pure standard samples and is regaled with a spate of commercial literature; with a little wit and resource he can solve many of his problems and establish the sensitivity of his methods in less time than it takes to consult the literature or a compendium. Much of the effort devoted to this book may, therefore, be lost to the average user of the methods.

The authority of Stahl's book reiterates the significance of the composition of layers and of factors in methods of detection. Ultraviolet examinations may strain the eyes of observers unless they stand behind a suitable screen and wear glasses. Some spray reagents contain highly toxic substances; all spraying should be carried out in a fume-cupboard. Layers may contain dangerous constituents, such as uranyl salts, and the silica and alumina presumably form dangerous dusts (the tenacious layers now on sale reduce this hazard).

It is surprising that more progress has not been made on mass-spectrographic examinations of substances volatilised direct from the area of the layer in which they have been detected.

Stahl's new "Dünnschicht-chromatographie" is described, like its predecessor, as a laboratory handbook, although it has grown into a tome costing over £8. It is an eligible compendium for libraries.

ALAN LONG

RAMAN SPECTROSCOPY, THEORY AND PRACTICE. Edited by HERMAN A. SYZMANSKI. Pp. x + 255. New York: Plenum Press. 1967. Price $12.50.

This book consists of seven chapters, each by different authors. The Preface makes interesting reading; the preparation of the book was obviously not trouble-free! Its intention, as stated on the dust cover, is to act both as an introduction for the beginner and to assist established workers in the field. Such divergent duality is always difficult to achieve satisfactorily in any relatively short, single work.

The General Introduction by L. A. Woodward is elegantly composed and presented. It discusses the nature of the Raman effect and the necessary underlying theory, as well as pointing out applications as they naturally arise at the various theoretical phases of the chapter. I cannot see many readers, previously unfamiliar with group theory, being able to apply it to vibrations from the condensed presentation here, but it will surely act as an incentive to the reader to look further afield; it is a pity that the reference suggested for further study is not pitched at a more elementary level. There is one unfortunate printing error on page 24 where transitions appears in place of translations.

The section, Advances in Raman Instrumentation and Sampling Technique, by J. R. Ferraro, considers most of the recording Raman spectrometers, about which details have been published, but does not, unfortunately, manage to give much detail of the recently praised APC Laser Raman Model 81. This section is not constructive or critical enough in the reviewer's opinion. The second half of the chapter is mainly devoted to sampling techniques for investigating solids, and is marred by some appalling photographic illustrations and an annoying lack of phase between the text and the diagrams.

Laser Raman Spectroscopy, by J. A. Konigstein, presents a comparison between laser and Toronto-arc spectra, and then describes a variety of experiments in which laser sources have been used, some of them specifically requiring laser properties. The article is well written, but one feels that many of the comments are out of date.

Raman Intensities and the Nature of the Chemical Bond, by R. E. Hester, gives a usefully detailed theoretical introduction and discusses results that have been published on the relationship between Raman intensity and bond nature. The data are critically assessed, and experimental and theoretical dangers exposed, the final section on intermolecular interaction in liquids being particularly useful in this respect.

Ionic Melts, by G. J. Janz and S. C. Wait, jun., and Observed Resonance Raman Spectra, by J. Behringer, provide excellent up-to-date specialist reviews. Raman Spectroscopy of Complex Ions in Solution, by D. E. Irish, is curious in that it is written at a much more elementary level than the rest of the book. For this reason, and because it refers to the most commonly used aspect of the Raman effect, it would have been better placed as the earliest applications chapter.

This book has a place in a chemical library, but it is not indispensable at the work bench; at its high price it cannot be recommended to students. PETER L. GOGGIN

ULTRA VIOLET AND VISIBLE SPECTROSCOPY. CHEMICAL APPLICATIONS. By C. N. R. RAO, D.Sc., Ph.D., F.R.I.C., F.A.Sc. Second Edition. Pp. xiv + 200. London: Butterworths. 1967. Price 50s.

The first edition (1961, reprinted 1964) of this monograph met a need, and the opportunity has now been taken to revise the work thoroughly. The section on quantitative analysis has been much enlarged and the treatment of far ultraviolet spectra has been extended. The chapter on fluorescence has been modified and the treatment of charge-transfer spectra is now more comprehensive. There is a new chapter on the absorption spectra of amino-acids, proteins and related compounds.

Although the revision has made the book more up to date, the very real merits of the first edition have been retained and the treatment has been kept concise. R. A. MORTON

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Notes on the writing of papers for *The Analyst*

Manuscripts should be in accordance with the style and usages shown in recent copies of *The Analyst*.* Conciseness of expression should be aimed at: clarity is increased by adopting a logical order of presentation, with suitable paragraph or section headings.

Descriptions of new methods should be supported by experimental results showing accuracy, precision and selectivity.

The recommended order of presentation is as indicated below—

(*a*) Synopsis.

(*b*) Statement of object of investigation and, if necessary, historical introduction and account of preliminary experimental work; these need be no longer than is necessary for the understanding of the new material.

(*c*) Description of method. When working details are given, they should, if possible, be given in the imperative mood. Well known procedures must not be described in detail.

(*d*) Presentation of results.

(*e*) Statistical analysis of results. Any statistical evaluation of results should be in accordance with accepted practice.

(*f*) Discussion of scope and validity.

(*g*) Summary and conclusions.

SI Units—In 1960, the Conférence Générale des Poids et Mesures formally approved the metric system of units known as SI (Système International d'Unités). Its main features are (1) that there are six basic units—

physical quantity	*name of unit*	*symbol for unit*
length	metre	m
mass	kilogramme	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	degree Kelvin	°K
luminous intensity	candela	cd

(2) that the unit of force, the newton (kg m s^{-2}) is independent of the Earth's gravitation, so that the introduction of g into equations is no longer necessary; (3) that the unit of energy is the joule (newton × metre) and of power the joule per second (watt), so that the variously defined calories, the kilowatt-hour, the B.t.u. and the horse-power are all superseded; (4) that "electrostatic" and "electromagnetic" units are replaced by SI electrical units; and (5) that multiples of units are normally to be restricted to steps of a thousand and fractions similarly to steps of a thousandth. In SI there are two supplementary dimensionless units, plane angle (radian, rad) and solid angle (steradian, sr). The following derived SI units have special names—

name of unit	*symbol for unit*	*physical quantity*	*definition of unit*
joule	J	energy	kg m^2 s^{-2}
newton	N	force	kg m s^{-2} = J m^{-1}
watt	W	power	kg m^2 s^{-3} = J s^{-1}
coulomb	C	electric charge	A s
volt	V	electric potential difference	kg m^2 s^{-3} A^{-1} = J A^{-1} s^{-1}
ohm	Ω	electric resistance	kg m^2 s^{-3} A^{-2} = V A^{-1}

* Rules for nomenclature in "Handbook for Chemical Society Authors 1961" (price 21s. from the Chemical Society, Burlington House, London, W.1) are followed. The Shorter Oxford English Dictionary is followed for spelling, and some of the alternative spellings are used.

name of unit	*symbol for unit*	*physical quantity*	*definition of unit*
farad	F	electric capacitance	$A^2 s^4 kg^{-1} m^{-2} = A s V^{-1}$
weber	Wb	magnetic flux	$kg m^2 s^{-2} A^{-1} = V s$
henry	H	inductance	$kg m^2 s^{-2} A^{-2} = V s A^{-1}$
tesla	T	magnetic flux density	$kg s^{-2} A^{-1} = V s m^{-2}$
lumen	lm	luminous flux	cd sr
lux	lx	illumination	$cd sr m^{-2}$
hertz	Hz	frequency	cycles per second
degree Celsius	°C	customary temperature, t	$t/°C = T/°K - 273{\cdot}15$

Examples of other derived SI units are—

physical quantity	*SI unit*	*symbol for unit*
area	square metre	m^2
volume	cubic metre	m^3
density	kilogramme per cubic metre	$kg m^{-3}$
velocity	metre per second	$m s^{-1}$
angular velocity	radian per second	$rad s^{-1}$
acceleration	metre per second squared	$m s^{-2}$
pressure	newton per square metre	$N m^{-2}$
magnetic field strength	ampere per metre	$A m^{-1}$
luminance	candela per square metre	$cd m^{-2}$

Certain units will be allowed in conjunction with SI, *viz.*—

physical quantity	*name of unit*	*symbol for unit*	*definition of unit*
area	barn	b	$10^{-28} m^2$
	hectare	ha	$10^4 m^2$
volume	litre	l	$10^{-3} m^3 = dm^3$
pressure	bar	bar	$10^5 N m^{-2}$
mass	tonne	t	$10^3 kg = Mg$
kinematic viscosity, diffusion coefficient	stokes	St	$10^{-4} m^2 s^{-1}$
dynamic viscosity	poise	P	$10^{-1} kg m^{-1} s^{-1}$
magnetic flux density (magnetic indication)	gauss	G	$10^{-4} T$
radioactivity	curie	Ci	$37 \times 10^9 s^{-1}$
energy	electronvolt	eV	$1{\cdot}6021 \times 10^{-19} J$

The common units of time (e.g., minute, hour, year) and the angular degree (°) will continue to be used in appropriate contexts.

Fractions and multiples have the following names and symbols (for use as prefixes)—

10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f			
10^{-18}	atto	a			

In addition the fractions 10^{-1} (deci, d) and 10^{-2} (centi, c), and multiples 10 (deka, da) and 10^2 (hecto, h) are available, but their use should be avoided if possible.

Compound prefixes (*e.g.*, mμm) should not be used; 10^{-9} metre = 1 nm. Until such time as a new name may be adopted for the kilogramme, the gramme will continue to be used, both as an elementary unit (g) to avoid the absurdity of mkg, and in association with prefixes, *e.g.*, μg.

The effect on current style of papers for *The Analyst* includes the following—

(*a*) dimensions should preferably be given in metres or in mm, although cm will be permitted in special cases;

(*b*) temperatures should be expressed in °C (NOT °F);

(*c*) wavelengths should be expressed in nm (which equals 10 Å and replaces mμ);

(*d*) frequency should be denoted in Hz (or kHz, etc.), NOT in c/s or c.p.s.; rotational frequency can be denoted by use of s^{-1};
(*e*) radioactivity will continue to be expressed in curies (or millicuries or microcuries), but the symbol will be Ci (mCi; μCi), NOT C;
(*f*) the micron (μ) will NOT be used; 10^{-6} m will be 1 μm.

Abbreviations—SI units as recommended by The Royal Society Conference of Editors should be used, with exceptions as already indicated. Normality and molarity are generally expressed as decimal fractions (*e.g.*, 0·02 N, 0·375 M). Abbreviational full stops are omitted after the common contractions of metric units (*e.g.*, ml, g, μg, mm) and other units represented by symbols; litre and metre, when without prefixes, are printed in full.

Abbreviations other than those of recognised units should be avoided in the text; symbols and formulae are not used instead of the names of elements and compounds in the text, but may be used in addition to names when they are necessary to avoid ambiguity, *e.g.*, to specify crystalline composition, as in $CuSO_4.5H_2O$, to show structure or in equations.

Percentage concentrations of solutions should be stated as "per cent. w/w" (alternatively "g per 100 g"), as "per cent. w/v" (alternatively "g per 100 ml") or as "per cent. v/v." Concentrations of solutions of the common acids, however, are often conveniently given as dilutions of the concentrated acids, such as "diluted hydrochloric acid (1 + 4)," which signifies 1 volume of the concentrated acid mixed with 4 volumes of water. This avoids the ambiguity of 1:4, which might be equivalent to *either* 1 + 4 *or* 1 + 3.

Tables, diagrams, etc.—The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns may often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables must be supplied with titles and be so set out as to be understandable without reference to the text.

Tables or graphs may be used, but not both for the same set of results, unless important additional information is given by so doing.

In general, graphs should have a reasonable number of co-ordinate lines, and not only the two main axes. The information given by a straight-line calibration graph can usually be conveyed adequately as an equation in the text.

Diagrams and graphs should be drawn in Indian ink on Bristol board, stout paper or tracing cloth, not larger than foolscap size and with at least 1-inch margins all round. The use of squared paper should be avoided. All lettering should be inserted lightly in black lead pencil at the appropriate place in the diagram, and will be replaced by type in block-making. All lines in Indian ink should be firmly drawn and sufficiently thick to stand reduction.

Drawings should be specially prepared for submission to *The Analyst*, as they cannot normally be returned and may be modified or cut in the course of block-making.

Three sets of illustrations should be provided, two sets of which may be photographic or dyeline copies of the originals, or pencil sketches, for transmission to the referee; there is no need to prepare Indian-ink duplicates.

Photographs—Photographs should only be submitted if they convey essential information that cannot be shown in any other way. They should be submitted as glossy prints made to give the maximum detail. Colour photographs can only be accepted when a black-and-white photograph fails to show some vital feature.

References—References should be numbered serially in the text by means of superscript figures, *e.g.*, Wilson and Duff,[1] Mendoza, Wales, McLeod and McKinley[2] or Jolly,[3] and collected in numerical order under "REFERENCES" at the end of the paper. They should be listed, with the authors' initials, in the following form (doubled-spaced typing)—

1. Wilson, H. N., and Duff, G. M. S., *Analyst*, 1967, **92**, 723.
2. Mendoza, C. E., Wales, P. J., McLeod, H. A., and McKinley, W. P., *Ibid.*, 1968, **93**, 173.
3. Jolly, S. C., *Editor*, "Supplement to Official, Standardised and Recommended Methods of Analysis," The Society for Analytical Chemistry, London, 1967, p. 77.

For books, the edition (if not the first), the publisher and the place and date of publication should be given, followed by the volume or page number, or both if required.

The entry of "personal communications" in the reference list is not justified; full acknowledgment of such unpublished sources should be made in the text or in the acknowledgments at the end of the paper.

Authors must, in their own interest, check their lists of references against the original papers; second-hand references are a frequent source of error. The number of references must be kept to a minimum.

Summaries of Papers in this Issue

The Application of Atomic-absorption Spectrophotometry to the Analysis of Iron and Steel

A Review

Atomic-absorption spectrophotometry is a useful technique for the determination of many of the minor elements commonly present in iron and steel. It is rapid and relatively free from most of the troublesome inter-element effects associated with alternative techniques such as colorimetric and polarographic analysis. This paper reviews published and certain unpublished information dealing specifically with the analysis of iron and steel by atomic-absorption spectrophotometry.

P. H. SCHOLES

BISRA, The Inter-Group Laboratory of the British Steel Corporation, Chemical Analysis Section, Metallurgy Division, Hoyle Street, Sheffield S3 7EY.

Analyst, 1968, **93**, 197–210.

The Spectrographic Determination of Nickel in Molten Steels

A prerequisite for the direct spectrographic analysis of molten steels in industrial furnaces is the knowledge that good quality spectra can be obtained from molten steel surfaces, and that precise quantitative determinations can be made by using such spectra.

The emission-spectrographic determination of nickel from a molten steel surface at 1600° C under an argon atmosphere has, therefore, been investigated. When a condensed spark between a graphite electrode and the molten steel surface was used, spectra of good quality were produced. The standard deviations in the error for the determination of 0·7 to 1·8 per cent. of nickel in molten and solid steel samples, analysed under similar conditions, were 0·045 and 0·022 per cent., respectively.

J. B. HEADRIDGE and A. K. LAMBERT

Department of Chemistry, The University, Sheffield 10.

Analyst, 1968, **93**, 211–213.

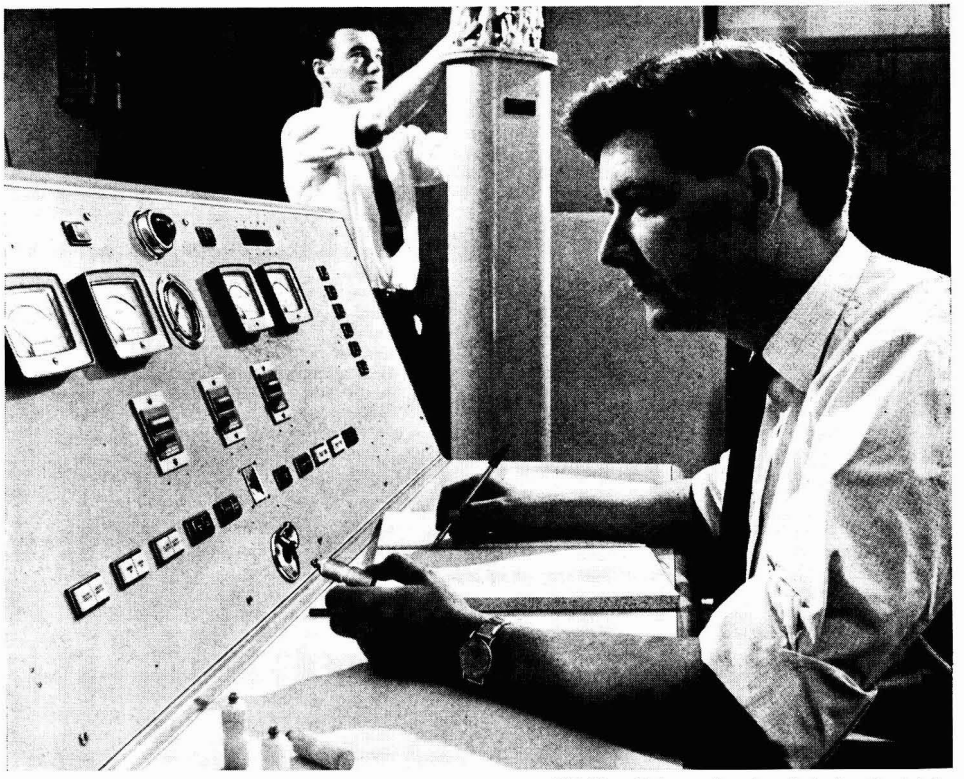
Spectrophotometric Determination of Small Amounts of Tin in Lead and Antimonial Lead Alloys

A method is described for the determination of 0·001 to 0·10 per cent. of tin in lead and antimonial lead alloys. The sample (0·25 to 2·5 g) is dissolved in a mixture of nitric and citric acids. After addition of EDTA and ammonium chloride, the pH of the solution is adjusted to 5·5 with ammonia solution before passing it through a column containing silica gel. Tin is adsorbed on the column, while lead, antimony and other metals pass through. After elution with hydrochloric acid solution the tin is determined spectrophotometrically with gallein. The standard deviation on samples containing 0·0051 and 0·038 per cent. of tin is $\pm$0·0005 and $\pm$0·002, respectively. At least eight determinations can be carried out in 1 day.

J. C. H. JONES

Associated Lead Manufacturers, Research Laboratories, 7 Wadsworth Road, Perivale, Greenford, Middlesex.

Analyst, 1968, **93**, 214–218.



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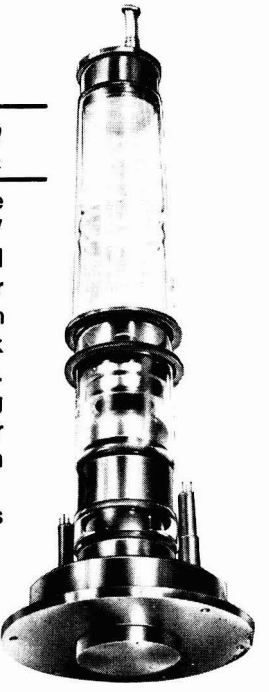

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The Polarographic Determination of Some Dithiocarbamates and their Heavy Metal Complexes

Procedures for the determination of monoalkyl- and dialkyldithiocarbamates and some of their metal complexes that are used as pesticides are described. The methods are based on a detailed investigation of the polarographic behaviour of these compounds, and are suitable for the analysis of pesticide preparations and residues.

D. J. HALLS, A. TOWNSHEND and P. ZUMAN
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15.

Analyst, 1968, **93**, 219–223.

A Selective Amplification - Titration Procedure for the Determination of Microgram Amounts of Phosphate

Phosphate is converted into phosphomolybdic acid, which is separated from excess of molybdate by extraction. The phosphomolybdate is back-extracted into aqueous solution, and the twelve molybdate ions accompanying each phosphate ion are reduced on a silver reductor column and titrated with 10^{-3} M cerium(IV) by use of a 50-ml burette. Other heteropoly acid-forming elements, *e.g.*, arsenic, antimony, germanium and silicon do not interfere, and there is no interference from a wide range of other ions. The method is both precise and rapid, and has been applied to the submicro determination of phosphorus in a standard organic compound.

G. F. KIRKBRIGHT, A. M. SMITH and T. S. WEST
Chemistry Department, Imperial College, London, S.W.7.

Analyst, 1968, **93**, 224–227.

The Determination of Actinium-227 in Urine

A method is described for the determination of actinium-227 in urine. After oxidation of the urine sample with nitric acid, actinium is co-precipitated on barium sulphate. The barium sulphate is converted into carbonate, dissolved in acid and the actinium co-precipitated on iron(III) hydroxide to remove barium and radium. The iron(III) hydroxide precipitate is dissolved in a mixture of nitric and hydrochloric acids and the solution passed through an anion-exchange column upon which iron, thorium and protactinium are absorbed. The column effluent, which contains the actinium, is essentially free from solids. Sources for α-counting may be prepared either by evaporation or by electro-deposition. Actinium recoveries of about 80 per cent. are obtained, with good decontamination from protactinium, thorium, radium, polonium and lead.

P. J. GOMM and J. D. EAKINS
Health Physics and Medical Division, A.E.R.E., Harwell, Didcot, Berks.

Analyst, 1968, **93**, 228–234.

Loss of Polonium-210 on Dry Ashing Rat Tissues in a Muffle Furnace

The losses of polonium-210 during dry ashing of rat tissues are reported, and it is shown that losses occur at lower temperatures than generally referred to in the literature.

J. J. CLEARY and E. I. HAMILTON
Radiological Protection Service, Clifton Avenue, Belmont, Sutton, Surrey.

Analyst, 1968, **93**, 235–236.

The Determination of Ferrocyanide and Related Compounds in Commercial Sodium Chloride

Ferrocyanide [hexacyanoferrate(II)] in commercial sodium chloride can be determined spectrophotometrically as its iron complex in the range 0·013 to 50·0 p.p.m. of $[Fe(CN)_6]^{4-}$. The iron complex is concentrated from a large volume of sample solution by filtration on kieselguhr, and a reproducible Prussian blue colour formed in a small volume under controlled conditions. Aquopentacyanoferrate can be determined simultaneously, and the amounts of each complex present are found by a simple calculation. Some interference is caused by carbonylpentacyanoferrate, which only partially reacts under the conditions of the procedure but the amount present can be determined and allowance made. The precise determination of carbonylpentacyanoferrate is carried out by using a similar principle of concentration, but with different reagents to develop the iron complex. No interference is caused by the presence of other stable iron - cyanogen complexes, or by the usual impurities and additives in commercial salts.

R. F. ROBERTS and R. H. WILSON

Research Department, Imperial Chemical Industries Limited, Mond Division, Northwich, Cheshire.

Analyst, 1968, **93**, 237–243.

Micro Determination of Carbonate in Dental Enamel

A method is described for the micro determination of carbonate in 50-μg particles of human dental enamel. The technique is rapid and more sensitive than previous procedures. Amounts of carbonate from 0·5 to 3·0 μg have been determined with an accuracy of 4 to 7 per cent. (standard deviation). Carbon dioxide is liberated by dissolving enamel particles in acid. The gas forms a single bubble, flattened into a 100-μ thick disc between the parallel glass surfaces of a Neubauer haemocytometer. The area of the flattened bubble is measured and the volume of gas calculated. By using this technique in combination with a recently developed sampling procedure, it has proved possible to measure variations in carbonate concentration within thin sections of dental enamel.

J. A. WEATHERELL and C. ROBINSON

Biological Research Unit, Dental School and Hospital, University of Leeds.

Analyst, 1968, **93**, 244–248.

The Titrimetric Determination of Molybdenum in Ammonium Molybdate, Molybdic Acid and Molybdenum Trioxide with Sodium Hydroxide

Titrimetric methods have been developed for the determination of molybdenum in ammonium molybdate, molybdic acid and molybdenum trioxide, based on their reactions with sodium hydroxide.

D. THORBURN BURNS, P. DEADMAN

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

and J. A. CLARK

Hopkin and Williams Ltd., Freshwater Road, Chadwell Heath, Essex.

Analyst, 1968, **93**, 249–251.

Fumigant Residues in Wheat and Flour: Solvent Extraction and Gas-chromatographic Determination of Free Methyl Bromide and Ethylene Oxide

Methods are described for the cold solvent extraction and analysis of traces of the fumigants methyl bromide and ethylene oxide present in flour and wheat after treatment, and for determining the efficiency of extraction, in which a combination of gas-chromatographic and chemical techniques is used.

Results are given showing the loss of fumigant caused by reaction with cereal constituents before recovery, and a method for correcting this is described. Recoveries generally of 95 per cent., or more, were obtained with a lower detection limit of about 0·3 p.p.m. The application of the method to other volatile compounds is indicated.

S. G. HEUSER and K. A. SCUDAMORE

Agricultural Research Council, Pest Infestation Laboratory, London Road, Slough, Bucks.

Analyst, 1968, **93**, 252–258.

The Determination of Quebracho in Mixtures with Some Other Tannin Extracts and Related Materials

A spectrophotometric method is described for the determination of quebracho in mixtures with other tannin extracts and related materials. The accuracy of the method is to within a range of ± 10 per cent. A method is also described for the identification of quebracho.

K. FIELD and B. E. KENT

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

Analyst, 1968, **93**, 259-261.

A Simple Device for Delivering an Approximately Metered Amount of a Powdered Catalyst Mixture into a Sample Boat

A device for delivering a metered amount of a powdered catalyst mixture into a sample boat is described. The design of the dispenser ensures that the hygroscopic mixture is stored and dispensed under clean conditions.

M. ELLISON

Fisons Ltd., Cambridge Division, Chesterford Park Research Station, Near Saffron Walden, Essex.

Analyst, 1968, **93**, 262–263.

Accurate Dispensing of Small Volumes of Volatile Liquids with a Micro Syringe and Aluminium Capillary Tubes

A device for delivering and sealing accurate volumes of volatile liquids into aluminium capillary tubes is described.

M. ELLISON

Fisons Ltd., Cambridge Division, Chesterford Park Research Station, Near Saffron Walden, Essex.

Analyst, 1968, **93**, 264–265.

Notice to authors

An extensively revised Notice to authors appears on pages 269 to 272.

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THE SOCIETY FOR ANALYTICAL CHEMISTRY

FOUNDED 1874. INCORPORATED 1907.

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry and of all questions relating to the analysis, nature and composition of natural and manufactured materials by promoting lectures, demonstrations, discussions and conferences and by publishing journals, reports and books.

The Society includes members of the following classes:—(*a*) Ordinary Members who are persons of not less than 21 years of age and who are or have been engaged in analytical consulting or professional chemistry; (*b*) Junior Members who are persons between the ages of 18 and 27 years and who are or have been engaged in analytical, consulting or professional chemistry or *bona fide* full-time or part-time students of chemistry. Each candidate for election must be proposed by three Ordinary Members of the Society. If the Council in their discretion think fit, such sponsorship may be dispensed with in the case of a candidate not residing in the United Kingdom. Every application is placed before the Council and the Council have the power in their absolute discretion to elect candidates or to suspend or reject any application. Subject to the approval of Council, any Junior Member above the age of 21 may become an Ordinary Member if he so wishes. A member ceases to be a Junior Member on the 31st day of December in the year in which he attains the age of 27 years. Junior Members may attend all meetings, but are not entitled to vote.

The Entrance Fee for Ordinary Members is £1 1s. and the Annual Subscription is £4 for Ordinary Members taking *The Analyst* and *Proceedings of the Society for Analytical Chemistry* only, or £9 for Ordinary Members taking *Analytical Abstracts* in addition to *The Analyst* and *Proceedings*. Junior Members are not required to pay an Entrance Fee and their Annual Subscription is £1 1s. No Entrance Fee is payable by a Junior Member on transferring to Ordinary Membership. The Entrance Fee (where applicable) and first year's Subscription must accompany the completed Form of Application for Membership. Subscriptions are due on January 1st of each year.

Scientific Meetings of the Society are usually held in October, November, December, February, April and May, in London, but from time to time meetings are arranged in other parts of the country. Notices of all meetings are sent to members by post.

All members of the Society have the privilege of using the Library of The Chemical Society. Full details about this facility can be obtained from the Librarian, The Chemical Society, Burlington House, Piccadilly, London, W.1.

The Analyst, the Journal of the Society, which contains original and review papers, information about analytical methods and reviews of books, and has a world-wide distribution, and *Proceedings of the Society for Analytical Chemistry*, in which are reported the day-to-day activities of the Society, are issued monthly to all Ordinary and Junior Members. In addition, any Ordinary Member may receive *Analytical Abstracts*, providing a reliable index to the analytical literature of the world, on payment of the higher Annual Subscription.

Forms of application for membership of the Society may be obtained from the Secretary, The Society for Analytical Chemistry, 9/10 Savile Row, London, W.1.

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THE North of England, Scottish, Western, Midlands and North East Sections were formed to promote the aims and interests of the Society among the members in those areas.

Specialised Groups within the Society are concerned with the study of various branches of analytical chemistry of specialised or topical interest. Groups dealing with such topics as Microchemical Methods, Biological Methods, Atomic-Absorption Spectroscopy, Chromatography and Electrophoresis, Thermal Analysis, Automatic Methods, Particle Size Analysis, Radiochemical Methods and a Special Techniques Group, covering very new developments and specialised physical methods, are at present active—and further Groups are formed from time to time as the need arises.

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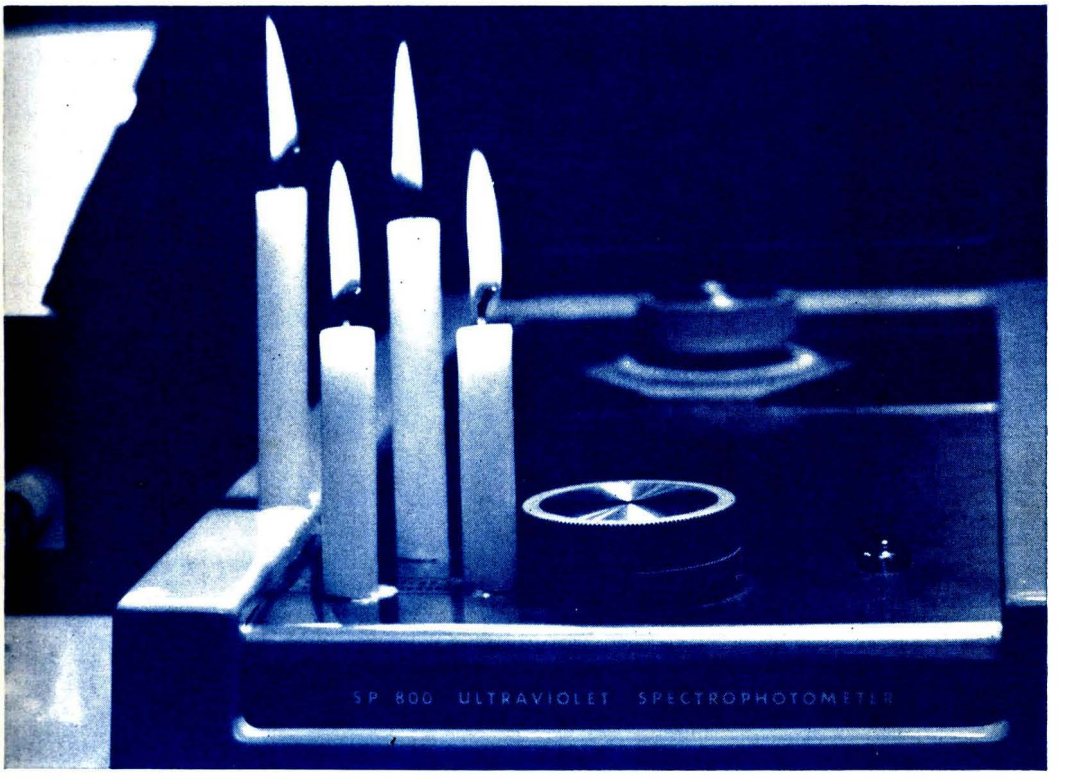

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THE ANALYST

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