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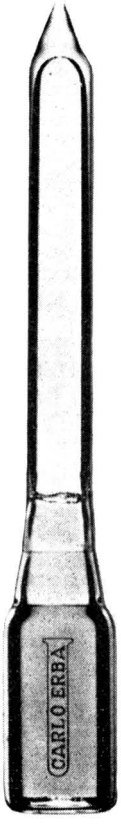

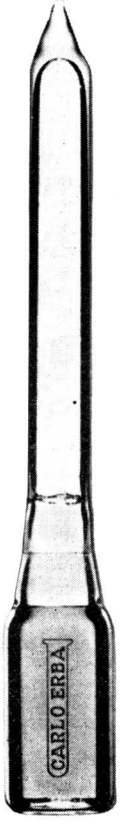

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Summaries of Papers in this Issue

A Fully Automated Method for the Determination of Chemical Oxygen Demand

A novel approach to the determination of chemical oxygen demand based on the use of a porous catalytic silver electrode is described. The conditions used in the digestion step are essentially the same as for the standard method, but the amount of oxidant (dichromate or permanganate) consumed is determined by allowing the excess of oxidant to react with hydrogen peroxide to liberate oxygen, which is measured coulometrically by the electrochemical sensor. The effectiveness of the present automated method as a detector of organic pollution is assessed by studying the oxygen absorbed values of synthetic sample solutions of several pure organic compounds. Percentage oxidation values are calculated and compared with those obtained with standard methods. Various aspects of interferences and their removal are also discussed.

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and J. TENYGL

Polarography Institute, Czechoslovak Academy of Sciences, Prague 1, Czechoslovakia.

Analyst, 1972, **97**, 321–333.

The Determination of Fluoride in Sugar Cane by Using an Ion-selective Electrode

A method is described for the determination of fluoride in sugar cane in which a fluoride ion selective electrode is used. Three methods for removing the interferences of silicon, aluminium and iron, which occur in high concentrations in sugar cane, were evaluated in detail: (1) direct complexation of the interfering elements with phosphoric acid; (2) separation of fluoride from the interfering elements by a microdiffusion technique; and (3) separation of fluoride from the bulk of the interfering elements by leaching from a sodium carbonate - zinc oxide fusion, followed by complexing residual trace elements with citrate.

The proposed method involves an adaptation of method (3) and yielded good accuracy and precision over a wide concentration range of fluoride (5 to 1000 p.p.m.) added to sugar-cane tissue. The method permits the analysis of six samples per working day per operator and can be applied to other types of plant tissues with which silicon, aluminium and iron cause interference.

C. W. LOUW and J. F. RICHARDS

Air Pollution Research Group, National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, South Africa.

Analyst, 1972, **97**, 334–339.

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A Fully Automated Method for the Determination of Chemical Oxygen Demand*

BY B. FLEET, A. Y. W. HO
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AND J. TENYGL
(Polarography Institute, Czechoslovak Academy of Sciences, Prague 1, Czechoslovakia)

A novel approach to the determination of chemical oxygen demand based on the use of a porous catalytic silver electrode is described. The conditions used in the digestion step are essentially the same as for the standard method, but the amount of oxidant (dichromate or permanganate) consumed is determined by allowing the excess of oxidant to react with hydrogen peroxide to liberate oxygen, which is measured coulometrically by the electrochemical sensor. The effectiveness of the present automated method as a detector of organic pollution is assessed by studying the oxygen absorbed values of synthetic sample solutions of several pure organic compounds. Percentage oxidation values are calculated and compared with those obtained with standard methods. Various aspects of interferences and their removal are also discussed.

THE importance of chemical methods for the determination of the oxygen demand of water and waste water can hardly be over-emphasised. Although chemical methods do not permit differentiation between biologically stable and unstable forms of organic matter, they are valuable as indicators of organic pollution, especially that caused by trade wastes. The latter often contain toxic substances and bactericides, which may render the results of a biochemical procedure meaningless. Further, chemical methods have the merits of being relatively simple and of giving quick results when compared with the biochemical method and are therefore of value in routine monitoring and control of water pollution, even when the sample effluent is free from bactericides.

The commonest two chemical methods used, the dichromate value (C.O.D.) method and the permanganate value method, are well documented in the literature and have been incorporated in several standard and recommended methods for the analysis of effluents.[1–5] These standard procedures usually consist of a digestion step in which the organic waste is oxidised followed by a titrimetric finish to determine the amount of oxidant consumed. Although these procedures are rapid compared with the biochemical oxygen demand (B.O.D.) test, they still require considerable time and manipulation. Consequently, increasing demands for such analyses could only be met by the introduction of automated procedures that provide increases in speed, economy and precision and also possibilities of continuous monitoring of the effluent stream. Conventional automated procedures differ from the standard procedures in that the determination step is based on the measurement of optical densities, either at the wavelength maxima of the reagent or of its reduction product.[6–8] Fleet, Ho and Tenygl[9] have recently described automated methods for the determination of permanganate and dichromate based on their reaction with hydrogen peroxide in acidic media to liberate oxygen, which, in turn, is monitored with a new type of coulometric oxygen sensor. The reactions can be represented by the following equations—

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 8H_2O + 5O_2 \quad .. \quad .. \quad (1)$$

$$\underset{\substack{\text{chromic}\\\text{acid}\\\text{anhydride}}}{2CrO_3} + H_2O_2 = \underset{\substack{\text{perchromic}\\\text{anhydride}}}{Cr_2O_7} + H_2O$$

$$Cr_2O_7 + 4H_2O_2 = Cr_2O_3 + 4H_2O + 4O_2 \quad .. \quad .. \quad (2)$$

* Presented in part at the Third SAC Conference, Durham, July 12th to 16th, 1971.

Electrode reactions—

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \text{ (Ag working electrode at } -0{\cdot}85 \text{ V } \textit{versus} \text{ Hg/HgO)}$$
$$4OH^- \rightarrow O_2 + 2H_2O + 4e \text{ (Pt counter electrode)} \quad .. \quad .. \quad .. \quad (3)$$

These methods provide an attractive automated finish to standard procedures for determining dichromate and permanganate values of effluents. The present paper describes an extension of the above semi-automated procedures into fully automated procedures. Most of the conditions used in the digestion step of the present procedures conform to those of standard methods; the unreacted oxidant, dichromate or permanganate, is then determined as described above. Both the non-integrated current response and the integrated signal ($Q = \int i dt$) can be used as analytical parameters. The choice depends on the availability of equipment and on whether continuous monitoring is anticipated.

Moore and co-workers[10,11] have investigated the theoretical-percentage oxidation of a large number of organic compounds by the standard dichromate reflux procedure. In the present study, common organic compounds comprising the following classes have been selected: branched-chain hydrocarbons, sugars, phenols, straight-chain acids and alcohols and benzene. The values for oxygen absorbed (both dichromate and permanganate) of synthetic sample solutions of these compounds were determined and the resultant theoretical-percentage oxidation values compared with those obtained by using standard methods. Such a comparison of the effectiveness of the present automated procedure with that of a standard method in the oxidation of various organic compounds provides a useful evaluation of the present technique for determining the oxygen demand of sewage and waste that contain complex organic compounds.

The main classes of interferences normally encountered when chemical methods are used for determining the oxygen demand of waste water have been discussed.[9] Two particular anions, nitrite and chloride, merit special attention because of their wide occurrence. Their interfering effects, removal and associated problems have been investigated in detail.

Experimental

Apparatus—

Sample introduction—Technicon AutoAnalyzer modules consisting primarily of a sampler and a proportioning pump with associated pump tubes and glass fittings were used. For procedures in which the integrated current response was used, the probe assembly and the sample plate drive of the sampler were altered. The altered probe assembly consisted of two probes, one dipping into a sample cup and the other into an oxidant (permanganate or dichromate) cup. The sample plate drive was then advanced two cup positions for each probe cycle, which was accomplished by replacing the standard Geneva gear with a double-acting gear.[12] The reason for using this altered sampler instead of supplying a constant stream of oxidant and introducing the sample with a standard sampler is discussed below. In both the dichromate and permanganate value methods for which the integrated current response was used as analytical signal, samples and oxidants were introduced at the rate of twenty per hour with a ratio of sample to water wash of 1:2. When the non-integrated current response was used as analytical signal, a sampling rate of ten per hour was used with a ratio of sample to water wash of 1:1.

The coulometric oxygen analyser consisting of a 3-electrode cell, a potentiostat and integrator was identical with that previously described.[9]

Carbon dioxide absorber—This was used to remove carbon dioxide produced by the oxidation of organic matter, which would shorten the life of the silver electrodes. In the present study, a simple carbon dioxide absorption device was introduced between the phase separator and the sensor. This consisted of a U-tube (i.d. 4 mm; total length 14 cm), three quarters of which was filled with soda-lime asbestos (Carbosorb, self-indicating granules, 12 to 30 mesh), the remaining quarter being filled with anhydrous calcium chloride. The water formed was also removed by the calcium chloride. It was found that this absorber functioned satisfactorily in the present procedure and when samples with a C.O.D. range of 50 to 100 were analysed, the absorber was less than 30 per cent. exhausted after a continuous run of 50 to 60 samples. Attempts to re-use the partially exhausted absorber tube on the next day, however, proved unsuccessful as the sodium carbonate formed tends to clog the absorption tube as soon as the continuous gas flow is stopped.

FLOW DIAGRAM—

The flow chart for the automated dichromate value method is shown in Fig. 1. The sample and dichromate - mercury(II) sulphate reagent are pre-mixed, segmented with nitrogen and joined in a water-cooled jacket tee by a stream of 75 per cent. v/v sulphuric acid containing silver sulphate, and the mixture is passed into a high-temperature heating bath. The bath was equipped with two 40-foot lengths of standard coils (i.d. 1·6 mm) in series and maintained at a temperature of 145 °C. The digested sample is cooled, re-pumped and mixed with hydrogen peroxide in a water-cooled mixing coil. The oxygen liberated in the reaction is carried along in the nitrogen stream and presented to the sensor after the liquid phase has been removed by passing the gas - liquid mixture through two consecutive phase separators. Except for the determination step, the manifold described differs in several respects from that used in Adelman's procedure.[7] Firstly, the dichromate is incorporated in the mercury(II) sulphate reagent rather than in the concentrated sulphuric acid. This makes it possible to prepare more easily and precisely the different strengths of digestants that are necessary to cover a wide range of C.O.D. values. It also has the advantage that it prevents the reduction of mercury(II) sulphate to mercury(I) sulphate, with precipitation of the latter, by highly reducing substances such as formaldehyde, which is present in photographic processing solutions[8] and other wastes. Secondly, it was found that streams of concentrated sulphuric acid (98 per cent. w/w) and aqueous solutions did not mix well even when using a coil filled with glass beads; 75 per cent. sulphuric acid, which gave more satisfactory results, was then used. The final acid concentration of the digestion mixture was approximately 55 per cent., which was lower than the 56 per cent. recommended by Adelman.[7] Boiling within the bath was, however, not observed at 145 °C. Thirdly, it was necessary to re-pump the digestion mixture after passing it through the high-temperature bath so that the small excess of pressure required for the silver working electrode to function correctly could be isolated and consequently not affect the remainder of the flow system.

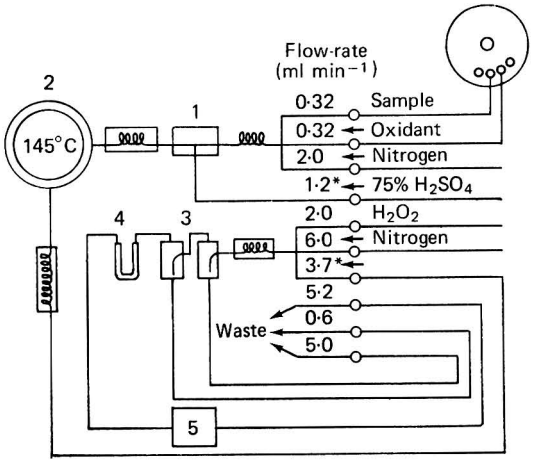

Fig. 1. Flow diagram for the automated dichromate value (C.O.D.) method (*Acidflex pump tubes): 1, jacketed T-piece; 2, heating bath; 3, phase separators; 4, CO_2 absorber; and 5, sensor

The flow chart for the automated permanganate value method is shown in Fig. 2. The sample, neutral permanganate solution, dilute sulphuric acid (10 N) and nitrogen are mixed and the reaction mixture is pumped through a standard double-coil heating bath set at 90 °C. The digested sample is then passed through a water-cooled mixing coil, re-pumped and the excess of permanganate is determined as described above for dichromate. The acidic permanganate solution is prepared in the system rather than introduced in a ready-made form, as neutral permanganate solutions are more stable.

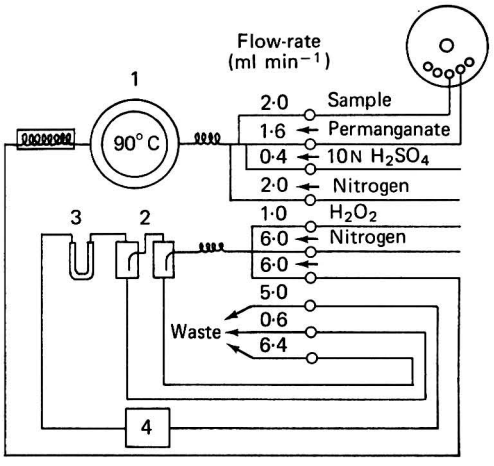

Fig. 2. Flow diagram for the automated permanganate value method: 1, heating bath; 2, phase separators; 3, CO_2 absorber; and 4, sensor

MATERIALS AND REAGENTS—

All chemicals used in this study were of analytical-reagent grade.

Potassium dichromate stock solution, 1N—Dried potassium dichromate (49·04 g) was dissolved in distilled water and the solution was made up to 1 litre with distilled water.

Dichromate - mercury(II) sulphate digestant solution—Mercury(II) sulphate (1 g) was slurried with a little concentrated sulphuric acid, 50 ml of dilute sulphuric acid (1 + 1) were then added followed by 5 ml of stock dichromate solution and the mixture was made up to 100 ml with distilled water. This digestant solution was then 0·05 N in dichromate and contained about 30 per cent. of sulphuric acid. Digestants of other strengths could readily be prepared by varying the volume of standard dichromate solution added.

Sulphuric acid (75 per cent.) containing silver sulphate—Silver sulphate (7·5 g) was dissolved in 1 litre of 75 per cent. sulphuric acid.

Potassium permanganate stock solution, 0·0625 N—This solution was prepared and standardised as previously described.[9]

The stock hydrogen peroxide solution, hydrogen peroxide working solution and purified nitrogen supply were prepared as previously described.[9]

RESULTS AND DISCUSSION

THE INTEGRATED AND THE NON-INTEGRATED CURRENT RESPONSE—

Both the integrated and non-integrated current response can be used as analytical parameters. In a recent publication,[9] we have described automated methods of determining dichromate and permanganate based on equations (1) and (2). A logical extension of these methods to determine the dichromate and permanganate values of sewage and effluents would be to supply a constant stream of oxidants (which are present in excess) while the samples were being introduced by using the standard sampler II. The oxygen consumed can then be calculated from the decrease in oxidant concentrations. It must be remembered, however, that diffusion within the sensor electrodes and carry-over between sample and wash cause considerable spreading of the current signal response, so that for a sampling time of 1 minute, the time required for the whole of the current response profile to appear may be as much as 2 minutes. Assuming a sampling time of 1 minute and an integration time of 2 minutes, the integrated response would be at least 50 recorder units, even though the

sample has completely reduced the oxidant [Fig. 3 (*b*)]. The useful recorder range is therefore limited to between 50 and 100 units. In the present study, therefore, a modified sampler consisting of two probes was used, one dipping into the sample cup and the other into an oxidant cup. The lengths of the tubings leading from the sampling probes were adjusted so that the two solutions merged at exactly the same instant. With this modified system, the signal-to-time response resembled that shown in Fig. 3 (*a*). Although the integration time was still considerably greater than the sampling time, this resulted only in an increased contribution of the background current giving rise to a larger blank, but the useful recorder range was not so greatly reduced as in the method in which the unmodified sampler is used.

The integrated method has the advantages of smaller sample requirements, faster sampling rate and greater precision. It has, however, the serious drawback that the integrator has to be operated manually. After initial studies with the integrated method and comparing the results with standard procedures, the possibility of using the non-integrated signal as an analytical parameter was investigated.

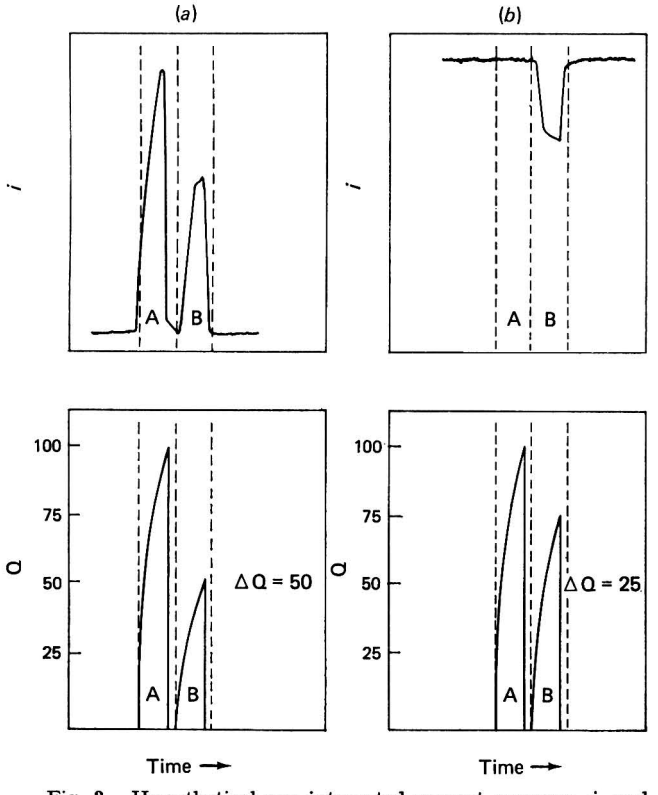

Fig. 3. Hypothetical non-integrated current response, *i*, and integrated signal, Q, obtained with (*a*) method in which sample and oxidant are introduced simultaneously by the modified sampler interspersed with water wash, and (*b*) method in which a constant stream of oxidant is supplied and the sample presented by an ordinary sampler: A, oxidant *plus* distilled water; and B, oxidant *plus* sample, which causes 50 per cent. reduction

Dichromate value method (C.O.D.)

Preparation of calibration graph—

The calibration graph was prepared by using distilled water in the sample cup and dichromate standard solutions of various concentrations (0·01 to 0·05 N) in the oxidant cups. A rectilinear relationship between the integrated signal and concentration over the range

studied was obtained (Fig. 4). This working curve can readily be used to calculate the C.O.D. of sewage, effluents and solutions of organic substances as illustrated below. Thus, if the sample causes a decrease in the integrated signal corresponding to a decrease in the normality (N) of dichromate from N_{bl} to N_s, then the C.O.D. of the sample, which is defined as the amount of oxygen in milligrams absorbed from dichromate by 1 litre of sample, is given by—

$$\text{C.O.D. (mg l}^{-1}) = (N_{bl} - N_s) \times V_o/V_s \times 8 \times 1000$$

where V_o and V_s are the volumes of oxidant (dichromate) and sample supplied per minute, respectively. In the manifold shown in Fig. 1, both the sample and oxidant flow-rates were 0·32 ml min^{-1} and therefore

$$\text{C.O.D. (mg l}^{-1}) = (N_{bl} - N_s) \times 8000$$

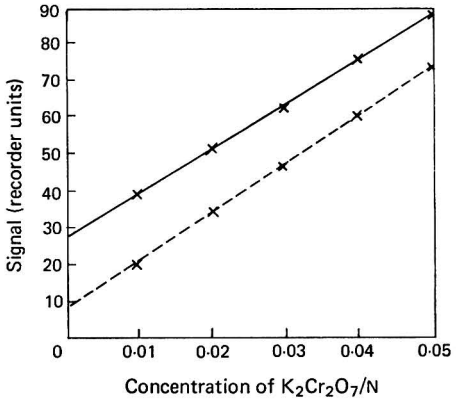

Fig. 4. Calibration graph for the automated dichromate value (C.O.D.) method: ——, integrated response; and – – –, non-integrated response

RANGE OF APPLICABILITY—

In practice, consumptions of oxidant of between 20 and 80 per cent. are permissible; the present manifold is therefore applicable to the C.O.D. range of 80 to 320. C.O.D. of lower ranges can be determined by increasing the sample flow-rate or decreasing the dichromate flow-rate, or both. The converse is true when designing a manifold for effluents of higher C.O.D. values. When varying the manifold, however, it is important to keep the acid concentration in the final digestion mixture above 55 per cent. so as to prevent boiling inside the heating bath.

C.O.D. OF PURE ORGANIC SUBSTANCES—

Moore and co-workers,[10,11] who had investigated the theoretical-percentage oxidation of various pure organic compounds by the standard dichromate reflux procedure, found that, in general, branched-chain hydrocarbons, sugars and phenolic compounds were readily oxidised but that straight-chain acids and alcohols and such compounds as benzene, pyridine and toluene were not. The oxidisabilities of straight-chain acids and alcohols, however, were later found to be markedly increased by using silver sulphate as a catalyst in the digestion mixture.[11,13,14] No attempt has been made in the present study to cover such a comprehensive selection of organic compounds. Examples from each of the above classes of organic compounds were chosen in this study to illustrate the effectiveness of the present automated technique, which conforms to the standard method,[1] by using silver sulphate as a catalyst in the digestion mixture and mercury(II) sulphate to mask the interfering chloride ion. The results obtained are summarised in Table I. The retention time in the heating bath was only 7 minutes with the manifold used (Fig. 1). It was astonishing, therefore, to note that the percentage oxidation of most of the compounds studied approached so closely those obtained with the standard method, which involves a 2-hour refluxing period. Continuous

TABLE I

OXIDATION OF SOME PURE ORGANIC COMPOUNDS BY THE AUTOMATED DICHROMATE VALUE METHOD AND THE STANDARD REFLUX METHOD

Compound	Theoretical oxygen demand* for a 100 p.p.m. solution	Concentration of sample, p.p.m.	Theoretical oxygen demand for sample	Observed oxygen demand (automated method)	Per cent. of theoretical	
					Automated method	Standard method
Acetic acid ..	106·7	200	213·4	102·4	48·0†	95·1‡
Benzene.. ..	307·7	87·7	269·2	10·4	4·0	8·1‡
Ethanol ..	208·7	79	164·8	102·4	61·8§	80·1‡
Benzyl alcohol ..	252·0	100	252·0	234·4	93·0	—
Glucose	107·0	200	214·0	222·4	104·0	96·9‖
Glycerol.. ..	122·0	200	244·0	222·4	91·1	100‖
Ascorbic acid ..	90·9	200	181·8	180·0	98·8	—
Urea	80·0	200	160·0	10·4	6·5	33·6‖
Phenol	238·0	100	238·0	216·0	90·8¶	100‖

* Theoretical oxygen demand calculated by the equation $C_xH_yO_z + \left[x + \frac{y-z}{2}\right] O_2 \rightarrow xCO_2 + yH_2O$, except for urea, which is oxidised according to the equation $CO(NH_2)_2 + 3O \rightarrow CO_2 + 2H_2O + N_2$.

† Value increased to 70 per cent. when retention time in heating bath increased to 13½ minutes.

‡ Ref. 15.

§ Value increased to 79 per cent. when retention time in heating bath increased to 13½ minutes.

‖ Ref. 16.

¶ Solution used after standing for 2 days; the relatively low value is probably caused by oxidation of phenol by air during that period.

agitation in the heating coils and the large exposed surface were possible factors accounting for this high oxidising efficiency. The value obtained for acetic acid was, however, much lower than that of the standard method. It was decided, therefore, to increase the retention time in the heating bath by reducing the flow-rate of the nitrogen stream used to segment the sample and dichromate to 1 ml min^{-1}. The retention time was then increased to 13½ minutes. The percentage oxidation of acetic acid was found to increase to 70 and that of ethanol to 79. The percentage oxidation of the other substances studied showed only a slight increase or none. Further increases in the retention time could be achieved by using wide-bore (4 mm) coils of 40-foot length, as suggested by Adelman.[7]

INTERFERENCE CAUSED BY CHLORIDE—

The interfering effect of chloride in C.O.D. determinations has been investigated[16] and Dobbs and Williams[17] recommended the use of 10 mg of mercury(II) salt to complex each 1 mg of chloride present. The low solubility of the mercury(II) salt in the digestant limits the amount that can be used and hence the amount of chloride that can be tolerated. Following Adelman,[7] a mercury(II) sulphate solution (1 g per 100 ml) was supplied at the rate of 0·32 ml min^{-1} in the present study, and the maximum amount of chloride in the sample that could be tolerated was therefore 1000 p.p.m. (with a sample flow-rate also of 0·32 ml min^{-1}). Two sets of solutions of organic substances were prepared, one of which contained 1000 p.p.m. of chloride, and their C.O.D. values were determined (Table II). Chloride was found to increase slightly the C.O.D. value of the urea solution but no interference was observed with the other compounds studied.

NON-INTEGRATED CURRENT RESPONSE—

As discussed above, it is difficult to automate the integrator part of the present procedure. It therefore became desirable to investigate the minimum sampling time required for the non-integrated current response to be analytically useful. A sampling rate of ten per hour with a ratio of sample to water wash of 1:1 was found to give satisfactory results provided that a pulse suppressor was introduced in the re-pumped digestant line at a point immediately before the sample was mixed with the hydrogen peroxide and nitrogen. A linear relationship between the current signal and the concentration of dichromate was obtained over the concentration range of 0·01 to 0·05 N (Fig. 4, broken line).

TABLE II

EFFECT OF CHLORIDE ON THE C.O.D. DETERMINATION

Mercury(II) sulphate (10 mg) used to mask each milligram of chloride ion

Compound	Concentration of sample, p.p.m.	Theoretical oxygen demand	Concentration of Cl^-, p.p.m.	Observed C.O.D. (automated method)	Per cent. of theoretical
Acetic acid	200	213·4	Nil	102·4	48·0
Acetic acid	200	213·4	1000	101·8	47·7
Benzene	87·7	269·2	Nil	10·4	4·0
Benzene	87·7	269·2	1000	10·4	4·0
Benzyl alcohol ..	100	252·0	Nil	234·4	93·0
Benzyl alcohol ..	100	252·0	1000	236·0	93·5
Glycerol	200	244·0	Nil	222·4	91·1
Glycerol	200	244·0	1000	219·0	90·0
Urea	200	160·0	Nil	10·4	6·5
Urea	200	160·0	1000	16·4	10·0

This method can be used to analyse discrete samples with the modified sampler in the same way as with the integrated method. A series of glucose solutions was therefore analysed (Fig. 5) and the results are summarised in Table III. All the results gave a percentage oxidation value of greater than 100 (mean 109, range 105 to 112). The most plausible explanation for this positive bias is that the C.O.D. calculations have been based on the assumption that both the sample and the oxidant pump tubes were delivering exactly 0·32 ml min^{-1}, but the guaranteed accuracy of delivery of such tubes was only of the order of 88 per cent. In order to render the C.O.D. values independent of the accuracy of the delivery rates of the pump tubes, it is preferable to construct a calibration graph by using the same dichromate oxidant and standard solutions of various concentrations of a pure organic substance such as glucose, which is 100 per cent. oxidised by the method used. The oxygen demand of the effluent sample can then be expressed in terms of glucose units (mg l^{-1}) or in the conventional manner by using the appropriate conversion factor. As an alternative to analysing discrete samples, a constant sample stream can be fed into the pump and dichromate supplied with a standard sampler at 3-minute intervals interspersed with a

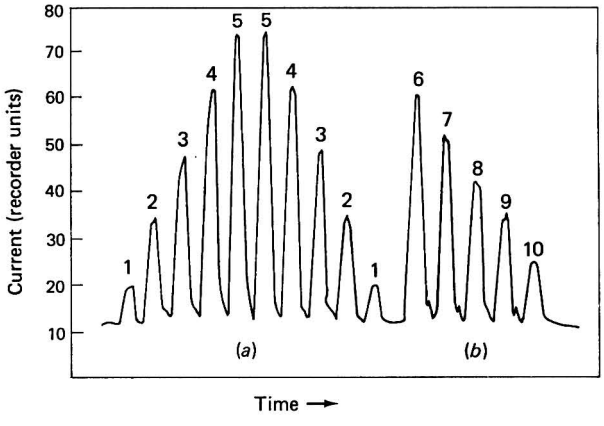

Fig. 5. Typical recording of the non-integrated current response obtained with the modified sample presentation method in which sample and oxidant were introduced simultaneously at the rate of ten per hour and interspersed with water wash. (*a*) Distilled water *plus* a series of dichromate standards: 1, 0·01; 2, 0·02; 3, 0·03; 4, 0·04 and 5, 0·05 N. (*b*) 0·05 N Dichromate *plus* a series of glucose solutions: 6, 50; 7, 100; 8, 150; 9, 200 and 10, 250 p.p.m.

3-minute wash with water. A series of current - time waves would be obtained, which varies in height with variation in the C.O.D. of the sample. Fig. 6 is a typical recording of the signals obtained when a 0·04 N dichromate solution was supplied at 3-minute intervals interspersed with a 3-minute wash with water. The first four waves correspond to signals obtained when a continuous stream of distilled water was supplied in lieu of sample. The next two sets of four waves each correspond to continuous streams of 100 and 150 p.p.m. glucose solutions. This method gives ten readings per hour when applied to the determination of the C.O.D. of an effluent stream and would be useful when there is no need for a minute-to-minute control of the system, and yet it is desirable to have some less rigorous system of continuous monitoring.

TABLE III

C.O.D. OF GLUCOSE SOLUTIONS DETERMINED BY THE AUTOMATED (NON-INTEGRATED) PROCEDURE

Concentration of glucose, p.p.m.	Theoretical oxygen demand	Current signal	N_s (× 0·01 N)	N_{bl}-N_s (× 0·01 N)	Observed C.O.D.	Theoretical percentage oxidation
50	53·5	62·0	4·10	0·75	60	112
100	107·0	52·0	3·35	1·50	120	112
150	160·5	42·0	2·75	2·10	168	105
200	214·0	33·0	1·90	2·95	234	109
250	267·5	24·0	1·25	3·60	288	107
Distilled water	—	72·0	4·85	—	—	—

PERMANGANATE VALUE METHOD

PREPARATION OF CALIBRATION GRAPH—

The calibration graph was prepared by using distilled water in the sample cup and permanganate standard solutions of various concentrations (0·0025 to 0·0125 N) in the oxidant cups. A rectilinear relationship was obtained between the integrated signal and concentration over the range studied (Fig. 7). This calibration graph can readily be used to calculate the permanganate value of samples of effluents and wastes as in the C.O.D. method above.

$$\text{Permanganate value (mg l}^{-1}) = (N_{bl} - N_s) \times V_o/V_s \times 8000$$

where the symbols N_{bl}, N_s, V_o and V_s have the same meanings as in the C.O.D. method.

RANGE OF APPLICABILITY—

In general, consumptions of the oxidant of between 30 and 70 per cent. are permissible for standard manual procedures.[18] It is not unreasonable to allow wider margins for auto-

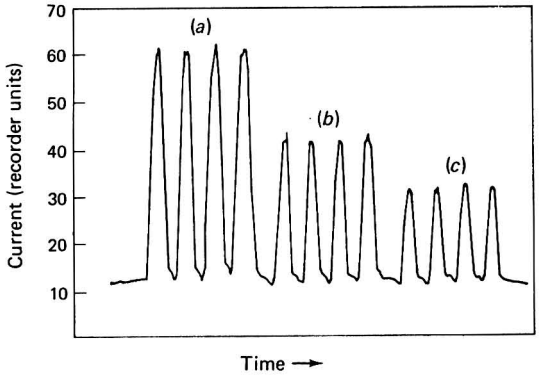

Fig. 6. Non-integrated current signals obtained when the sample was continuously supplied, whereas the oxidant, 0·04 N dichromate, was being supplied at the rate of ten per hour with a water wash ratio of 1 : 1. Sample used: (*a*) distilled water; (*b*) 100 p.p.m. glucose solution; and (*c*) 150 p.p.m. glucose solution

mated procedures in which the conditions are more strictly controlled. The present manifold (Fig. 2), with $V_0 = 1{\cdot}6$ ml min^{-1} and $V_s = 2$ ml min^{-1}, is therefore applicable to the range of permanganate values of 16 to 64 (reduction between 20 and 80 per cent.). It could be readily adapted to operate in other ranges of permanganate values by simply altering the sample flow-rate or the permanganate flow-rate, or both.

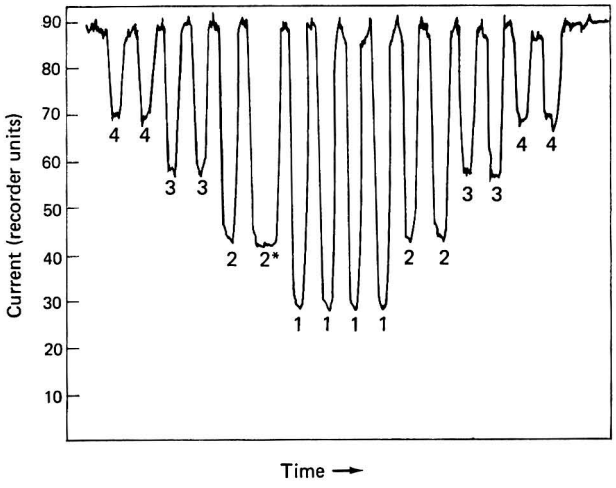

Fig. 7. Non-integrated current signals obtained when a series of permanganate standards (1–4) was presented at the rate of ten per hour, interspersed with a 0·0125 N $KMnO_4$ wash, at a wash ratio of 1:1. Concentration of standards: 1, 0·0025; 2, 0·0050; 3, 0·0075; and 4, 0·0100 N $KMnO_4$. *Standard 2 supplied for 6 minutes

PERMANGANATE VALUES OF PURE ORGANIC SUBSTANCES—

The standard 4-hour permanganate method, which involves incubation at 27 °C, does not cause effective oxidation of many organic compounds and hence little information is available in the literature on the theoretical-percentage oxidation of pure organic compounds by this method. By using the same organic compounds as those studied in the dichromate

TABLE IV

OXIDATION OF SOME PURE ORGANIC COMPOUNDS BY THE AUTOMATED PERMANGANATE VALUE METHOD AND THE STANDARD 4-HOUR METHOD

Compound	Concentration of sample, p.p.m.	Theoretical oxygen demand*	Observed C.O.D.		Per cent. of theoretical		
			Automated	Standard	Automated	Standard	4-Hour method
Acetic acid ..	20·0	21·3	Nil	Nil	Nil	Nil	(Nil)
Benzene	17·5	53·8	Nil	Nil	Nil	Nil	—
Ethanol	32·0	66·8	16·0	14·8	24·0	22·2	(26·0)
Benzyl alcohol ..	50·0	12·6	42·0	46·4	33·0	36·8	—
Glucose	40·0	42·8	40·8	5·6	95·3	13·0	—
Glycerol	20·0	24·4	25·4	8·4	104·0	34·4	(54·0)
Ascorbic acid ..	50·0	45·4	47·6	36·7	105·0	80·8	—
Urea	20·0	16·0	Nil	Nil	Nil	Nil	—
Phenol	20·0	47·6	49·0	39·2	103·0	82·3	(80·0)

* Theoretical oxygen demand calculated by assuming complete oxidation of sample according to the equation $C_xH_yO_z + \left[x + \frac{y-z}{2}\right] O_2 \rightarrow xCO_2 + yH_2O$.

For urea, the equation is $CO(NH_2) + 3O \rightarrow CO_2 + 2H_2O + N_2$. The percentage values in brackets were obtained by Cameron and Moore[16] by using 0·125 N $KMnO_4$.

value method, we have been able to compare the effectiveness of the oxidative process by the present automated procedure with that in which the standard 4-hour method is used. The results are summarised in Table IV. Almost all the organic substances studied (except benzyl alcohol) gave a higher theoretical-percentage oxidation value for the automated method compared with the standard procedure. The higher temperature (90 °C) used in the automated method is undoubtedly a major factor in its increased oxidising efficiency. Continuous agitation in the heating coils and the large exposed surface area are also factors that may account for this greater oxidising efficiency being achieved within a much shorter period (about 6 minutes compared with 4 hours). A manual procedure with an elevated temperature would give a higher percentage oxidation in a shorter period than the 4-hour standard method. However, the reproducibility of such methods is likely to be low as permanganate is readily decomposed if subjected to localised overheating. Also, the time of heating and cooling, and the extent of agitation, would have to be rigidly controlled to give reproducible results, which could only be achieved with an automated procedure similar to that used in the present study.

TABLE V

EFFECT OF CHLORIDE ION ON THE PERMANGANATE VALUE OF SOME ORGANIC COMPOUNDS (DILUTE SULPHURIC ACID USED)

Compound	Concentration of sample, p.p.m.	Concentration of Cl^-, p.p.m.	Theoretical oxygen demand	Observed oxygen demand (automated method)
Benzyl alcohol ..	50	Nil	126·0	42·8
Benzyl alcohol ..	50	1000	126·0	41·8
Phenol	20	Nil	47·6	49·0
Phenol	20	1000	47·6	49·0
Ethanol	32	Nil	66·8	15·8
Ethanol	32	1000	66·8	15·6
Acetic acid ..	20	Nil	21·3	Nil
Acetic acid ..	20	1000	21·3	Nil
Urea	40	Nil	32·0	Nil
Urea	40	400	32·0	2·0
Urea	40	800	32·0	6·0
Urea	40	1600	32·0	13·6

INTERFERENCE CAUSED BY CHLORIDE—

According to Roberts,[19] chloride interferes in the permanganate value method by forming chlorine, which acts on certain organic substances that are not normally oxidised by acidic permanganate. Cameron and Moore[16] have also studied the interference of chloride ion on the dichromate method and concluded that the presence of chloride enhances the oxidation of organonitrogen compounds such as urea. We have investigated the effect of chloride on the permanganate value of several organic substances and found that chloride up to 1000 p.p.m. has no effect on the permanganate value of all the carbonaceous compounds studied but that the oxidation of urea was enhanced (Table V). Roberts[19] has also suggested the use of phosphoric acid instead of sulphuric acid in the standard method to eliminate the chloride interference. As reported in a recent publication,[9] the reaction between permanganate and hydrogen peroxide proceeds with the same ease in both phosphoric and sulphuric acid media, Robert's modification could therefore be readily adapted to the present procedure. In the present study, however, it was found that although urea and possibly other nitrogenous organic matter were not reduced when a phosphoric acid medium is used to eliminate chloride interference, the over-all oxidising power of the permanganate appears to be lowered as well. As can be seen in Table VI, lower permanganate values were obtained for several organic compounds by both the automated and the standard methods when phosphoric acid was used instead of sulphuric acid. Caution must therefore be observed when phosphoric acid is substituted for sulphuric acid in the permanganate value method.

INTERFERENCE CAUSED BY NITRITE—

The Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents[4,5] has recommended the use of urea to decompose nitrite. As shown above, excess of urea

TABLE VI

USE OF PHOSPHORIC ACID TO REMOVE CHLORIDE INFLUENCE AND ITS EFFECT ON THE PERMANGANATE VALUE OF SOME ORGANIC COMPOUNDS

Compound	Concentration of sample, p.p.m.	Concentration of Cl^-, p.p.m.	Permanganate value			
			Automated method		Standard 4-hour method	
			Dilute H_2SO_4	Dilute H_3PO_4	Dilute H_2SO_4	Dilute H_3PO
Urea	40	Nil	Nil	Nil	Nil	Nil
Urea	40	2000	18·4	Nil	—	Nil
Benzyl alcohol ..	50	Nil	42·8	11·2	46·4	21·6
Benzyl alcohol ..	50	1000	41·8	11·2	—	22·8
Phenol	20	Nil	49·0	35·2	38·4	36·8
Glucose	40	Nil	40·8	3·2	6·0	1·6

does not interfere with the permanganate value provided that chloride is absent. The urea method can therefore be used in the present procedure for samples that do not contain chloride although the carbon dioxide generated in the reaction

$$2H^+ + 2NO_2^- + CO(NH_2)_2 = 2N_2 + CO_2 + 3H_2O$$

might shorten appreciably the life span of the carbon dioxide absorption tubes. As suggested in a recent publication,[9] the use of sulphamic acid would give more satisfactory results as both the reagent itself and the products of the reaction

$$H^+ + NO_2^- + {}^-O.SO_2.NH_2 = N_2 + HSO_4^- + H_2O$$

are not likely to affect the analytical signal or the electrode. The results of using sulphamic acid and other common reagents to eliminate nitrite are summarised in Table VII. Sodium azide, normally used to remove nitrite in the Alsterberg modification of the Winkler procedure for dissolved oxygen,[4,5] cannot be used in the present procedure because the excess of reagent reduces the permanganate.

TABLE VII

INTERFERENCE OF NITRITE ON THE PERMANGANATE VALUE METHOD AND ITS REMOVAL

Compound	Concentration of sample, p.p.m.	Concentration of NO_2^-, p.p.m.	Pre-treatment step	Permanganate value
Glucose	20	Nil	Nil	20·4
Glucose	20	100	Nil	52·8
Glucose	20	100	Urea method	21·0
Glucose	20	100	Sulphamic acid method	21·2
Glucose	20	100	Sodium azide method	80*

* Excess of sodium azide causes reduction of the permanganate.

THE NON-INTEGRATED RESPONSE—

As discussed in the dichromate value method, the non-integrated current response could be more useful for routine control purposes and for continuous monitoring. In practice, a constant sample stream is abstracted and mixed with a constant stream of 0·0125 N permanganate. The reaction mixture is then incubated and the excess of permanganate is allowed to react with hydrogen peroxide in the manner described in the integrated method. The recorder gives a continuous tracing of the current response, which provides an indication of the excess of permanganate unconsumed by the sample, which in turn is inversely proportional to the oxygen demand of the sample. For calibration purposes, a constant stream of distilled water is supplied in lieu of sample and a 0·0125 N permanganate solution is then fed in for a few minutes. A series of permanganate standard solutions of lower concentrations was then presented at the rate of ten per hour and interspersed with the 0·0125 N standard with a ratio of 1:1. A typical recording is shown in Fig. 7. A rectilinear relationship between the non-integrated signal and concentration was obtained over the range studied (Fig. 8, broken line).

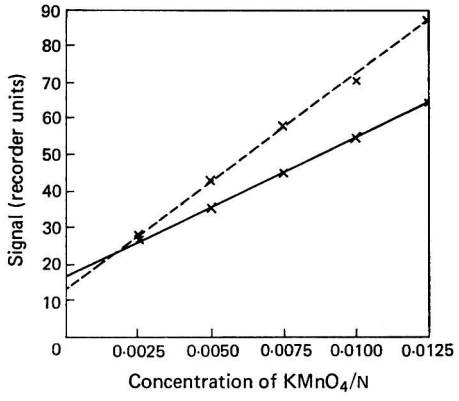

Fig. 8. Calibration graph for the permanganate value method: ——, integrated response; and – – –, non-integrated response

Conclusion

The present automated methods for the determination of chemical oxygen demand offer an attractive alternative to the existing automated colorimetric procedures, especially when the sample solution is coloured or turbid. By using appropriate reagents and varying the manifold design, it is possible to use the present instrumental set-up for automated C.O.D. procedures with oxidants other than permanganate and dichromate, such as sodium hypochlorite, cerium(IV) sulphate and iodic acid.

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The Determination of Fluoride in Sugar Cane by Using an Ion-selective Electrode*

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A method is described for the determination of fluoride in sugar cane in which a fluoride ion selective electrode is used. Three methods for removing the interferences of silicon, aluminium and iron, which occur in high concentrations in sugar cane, were evaluated in detail: (1) direct complexation of the interfering elements with phosphoric acid; (2) separation of fluoride from the interfering elements by a microdiffusion technique; and (3) separation of fluoride from the bulk of the interfering elements by leaching from a sodium carbonate - zinc oxide fusion, followed by complexing residual trace elements with citrate.

The proposed method involves an adaptation of method (3) and yielded good accuracy and precision over a wide concentration range of fluoride (5 to 1000 p.p.m.) added to sugar-cane tissue. The method permits the analysis of six samples per working day per operator and can be applied to other types of plant tissues with which silicon, aluminium and iron cause interference.

Fluoride is known to cause varying degrees of damage to different plant species.[1–3] Interest has arisen in such damage to sugar cane because of the erection of an aluminium smelter, a known source of fluoride, on a site adjacent to large fields of sugar cane in South Africa.

A wide variety of plants[2,4] have been analysed for fluoride but no results have thus far been published on sugar cane. Sugar cane contains higher concentrations of silicon (about 1 to 3 per cent. of silica), aluminium (about 0·004 to 0·3 per cent.) and iron (about 0·005 to 0·3 per cent.) than most other plants and, moreover, these elements are known to interfere in the determination of fluoride. Different methods of separation[5–12] have been used by other workers to eliminate interference from these elements. Three of these methods[8,10,12] were evaluated by us in detail by using the addition method and the results are reported in this paper. The fluoride ion selective electrode was used for the final step in the determination of fluoride because of its high selectivity[13] and wider linear range[11,14] compared with spectrophotometric methods.

Also described is a method developed for the determination of fluoride in sugar cane, which is an adaptation of the method of Edmond.[12]

Experimental

Apparatus—

A fluoride ion selective electrode (Orion, Model 94–09) and a single-junction reference electrode (Orion, Model 90–01) were used with an Orion, Model 801, digital pH meter to measure pF values.

A magnetic stirrer was modified so as to permit the stirring of both small (5 ml) and large (40 ml) volumes of solution. The electrically driven disc of the magnetic stirrer was fitted with a holder to take a 50-ml polythene beaker with dimensions 40 mm (base) × 50 mm (height). Stirring was accomplished by rotation of both the beaker and its contents.

Parafilm "M" (American Can Co., Marathon Products, Neenah, Wisconsin, U.S.A.) was used for covering the beakers so as to avoid losses from effervescence during the neutralisation of samples.

Nickel crucibles with dimensions 34 mm (base) × 38 mm (height) and capacity 40 ml were used for ashing and fusing plant samples. The crucibles had lips to facilitate the transfer of the extracts of the ashed and fused plant samples.

Rigid plastics rods, 12 cm × 2·5 mm o.d., were made from plastics-shielded knitting needles with one end closed off by careful heat-sealing of the plastics shield.

* Presented at the Third SAC Conference, Durham, July 12th to 16th, 1971.

REAGENTS—

All the reagents used were of analytical-reagent grade. All solutions were prepared with de-ionised water (specific resistance >4 MΩ cm).

Standard fluoride experimental solutions—Prepare solutions containing 0·05, 0·10, 1·0 and 10·0 p.p.m. of fluoride (adjusted to pH 6 with 1 M sodium citrate buffer solution) from standard fluoride stock solutions.

Sodium citrate buffer, 1 M solution[12]—Adjust the pH of the sodium citrate solution to 6 with concentrated hydrochloric acid by using a pH meter.

Sodium carbonate - zinc oxide fusion mixture—Mix 20 g of sodium carbonate and 2 g of zinc oxide thoroughly with a mortar and pestle. Pass the mixture through a sample divider several times, re-combining the fractions after each pass, and then stir it thoroughly with a spatula to homogenise it.

PROCEDURE—

Preparation of samples—Soil adhering to freshly harvested plant samples is removed carefully with a cotton-wool swab. Plant tissue is cut into small pieces, which are dried in separate paper bags at about 80 °C for 48 hours. Samples are allowed to cool and are ground to pass a 30-mesh B.S. sieve and then passed several times through a sample divider to give a homogeneous mixture. Aliquots of the samples are then ground to pass a 60-mesh B.S. sieve and finally sealed in plastics bags until required for analysis.

Moisture determination—Moisture determinations are carried out in duplicate, concurrently with sample analysis, on 1-g aliquots at 110 °C until constant weight (±0·003 g) is obtained.

Analysis—The dried and ground plant sample (500 mg) is treated in a nickel crucible with 2 to 3 ml of de-ionised water to form a slurry, 0·5 ml of 2·5 N sodium hydroxide solution is mixed thoroughly with the slurry and the mixture is dried on a hot-plate. When dry, the sample is ashed slowly over a Bunsen burner.

Sodium carbonate - zinc oxide fusion mixture (1·1 g) is mixed carefully with the ash by using a rigid plastics rod. The contents of the crucible are fused at bright red heat for 5 minutes with an air - gas blowtorch, and are then allowed to cool.

The fused mixture is extracted with 5 ml of de-ionised water on a steam-bath for 30 minutes and stirred with a plastics rod to break up the melt. An additional 1 ml of de-ionised water is added after heating the melt for 15 minutes. The crucible is removed from the steam-bath and the residue is allowed to settle. The outside of the crucible lip is greased lightly with silicone grease and the clear liquid is decanted through a plastics funnel containing a Whatman No. 42 filter-paper into a 50-ml calibrated polythene beaker. The extraction procedure is repeated with three 5-ml volumes of de-ionised water, heating for 15-minute periods on each occasion and passing all the contents of the crucible with the final extract through the filter-paper.

The crucible and the filter-paper are washed with 0·5 to 1-ml volumes of hot de-ionised water, rubbing the walls of the crucible with a rigid plastics rod to remove all adhering particles.

The filtrate is evaporated down to about 15 ml on a steam-bath and allowed to cool, and the beaker is covered with Parafilm "M." The filtrate is neutralised by adding 5 N hydrochloric acid with a Pasteur pipette through a small hole pierced in the Parafilm "M," with methyl orange as indicator. Twenty millilitres of 1 M sodium citrate buffer solution are added, and any droplets adhering to the Parafilm "M" are washed into the beaker.

The beaker with the filtrate is equilibrated at 20 °C, the volume is adjusted to 40 ml with de-ionised water, and the potential is determined with the fluoride-selective electrode while stirring the solution.

RESULTS AND DISCUSSION

EVALUATION AND ACCURACY OF DIFFERENT METHODS—

Phosphoric acid complexation method—The direct phosphoric acid complexation method suggested by Baumann[8] was found to be unsuitable because precipitation of silica occurred when phosphoric acid was added to an aqueous suspension of the ashed and fused cane sample. This could lead to co-precipitation of fluoride and thus result in low recoveries.

A filtration step was introduced prior to the addition of phosphoric acid to remove the undissolved material (mainly hydroxides of iron, magnesium, manganese and calcium) present in the aqueous suspension of the ashed and fused plant sample. It was thought that this undissolved material could serve as a nucleus for the precipitation of silica. The precipitation of silica was prevented but for levels of 50 p.p.m. of fluoride added to cane leaf and trash tissues the recoveries obtained were only about 50 per cent.

NOTE—
Cane-trash is the term used for those leaves which are allowed to die on the plant stem and eventually fall to the ground.

Microdiffusion method—The microdiffusion method investigated is a modified version of that suggested by Thomas and Amtower.[10] Firstly, the ashed plant sample was fused prior to microdiffusion because of its high silica content. Secondly, the ashed and fused sample was neutralised with perchloric acid before adding the amount of perchloric acid required for diffusion. Thirdly, the fluoride ion selective electrode was used for the final determination of fluoride in TISAB III[15] medium.

Erratic recoveries were obtained, however, and consequently several possible sources of error were investigated. Errors resulting from the addition of reagents, crucible contamination, adsorption and transfer losses were found to be negligible. The efficiency of the microdiffusion reaction itself was checked and found to be about 100 per cent. for amounts of fluoride ranging over three orders of magnitude (*i.e.*, 0·5, 5·0 and 50 μg of fluoride) provided that the lids of the microdiffusion vessels were tight fitting. Losses due to effervescence during neutralisation of the ashed and fused cane samples with perchloric acid were prevented by covering the microdiffusion vessel during this step.

We also investigated whether the optimum conditions had been used during ashing and fusion. The use of sodium hydroxide rather than calcium oxide as the fluoride fixing agent and the doubling of the amount of sodium hydroxide used in the fusion mixture (130 mg instead of 65 mg per 50 mg of plant sample) improved the reproducibility and recovery.

The recoveries finally obtained with the microdiffusion method are given in Table I. It was thought that the poorer reproducibility obtained with the leaf samples might have been due to the inhibition of the microdiffusion process as a result of the presence of large amounts of silica, aluminium and iron in these samples. Phosphoric acid[8] was therefore added as a complexing agent to the sample prior to microdiffusion. No improvement was obtained, however. It is unlikely that chloride, carbonate or bromide anions could have interfered in spite of the fact that no silver salt was added[11] to the perchloric acid used for microdiffusion. Bromide is not present in sugar cane and carbonate will be removed when the sample is acidified prior to microdiffusion. Chloride concentrations in sugar cane are too low to cause interference with the diffusion process.[11] Moreover, the number of gram-equivalents of sodium hydroxide used here for the adsorption of diffused fluoride is about ten times that used by Stuart,[11] who determined the extent of interference by these anions.

TABLE I

RECOVERIES OBTAINED WITH MICRODIFFUSION AND FUSION - LEACHING - COMPLEXATION METHODS

Method	Fluoride added, p.p.m. w/w	Plant tissue analysed	No. of determinations	Average recovery, per cent.*
Microdiffusion	10	Stalk,† trash	6	97 ± 20 (20·6)
	50	Leaf‡	6	90 ± 28 (31·4)
	1000	Stalk,† trash	6	90 ± 7·6 (8·5)
	5000	Leaf‡	6	92 ± 24 (25·7)
Fusion - leaching - complexation	5	Stalk,† leaf,‡ trash	23	102 ± 35 (33·7)
	10	Stalk,† leaf,‡ trash	12	97 ± 12 (12·4)
	100	Stalk,† leaf,† trash	14	98 ± 5 (5·1)
	1000	Stalk,† leaf,‡ trash	12	100 ± 4 (4·0)

* Relative standard deviations, *i.e.*, standard deviation expressed as a percentage of the mean, are given in parentheses.
† Stalk, middle section.
‡ Leaf, basal half.

Method involving fusion with sodium carbonate - zinc oxide and complexation with citrate— It was necessary to adapt this method[12] to yield optimum recoveries. Ashing of the samples was carried out over a Bunsen burner rather than in a muffle furnace so as to avoid contamination from the furnace linings.[9,16,17] It was found that it was necessary to use a considerably shorter fusion time than that suggested by Edmond[12] (15 minutes) for grass samples; longer fusion times incurred serious losses of fluoride; for 5 μg of fluoride the recovery was about 20 per cent. lower when 10-minute instead of 5-minute fusion periods were used.

The conditions required for efficient extraction of fluoride from the fusion mixture had to be determined experimentally, and the procedure outlined here is that which yielded optimum recoveries.

Furthermore, it was found imperative to rinse thoroughly and rub (with a rigid plastics rod) the nickel crucible so as to remove fluoride that remained adsorbed on the inside surface of the crucible after the final extraction step. The recovery for 5 μg of fluoride was increased by about 15 per cent. by thoroughly rubbing the crucible. It was found necessary to apply silicone grease to the outside of the crucible lip to prevent the extract from running down the outside of the crucible when the contents were decanted.

The use of platinum instead of nickel crucibles was also investigated as other workers[16,18] had experienced small losses of fluoride when nickel crucibles were used. No better recovery could be obtained, however.

The final results are given in Tables I and II. The variations reported in Table II are due primarily to inherent variations in electrode readings (see the discussion on electrode response and reproducibility, below). It is evident from these results that the fusion - leaching - complexation method permits the determination of a wide range of fluoride concentrations with good accuracy and precision.

TABLE II

SENSITIVITY AND PRECISION OBTAINED WITH FUSION - LEACHING - COMPLEXATION METHOD

Fluoride added to plant tissue*		No. of determinations	Precision, p.p.m.
p.p.m. w/w	μg†		
5	2·5	23	±1·7
10	5·0	12	±1·2
100	50	14	±5·0
1000	500	12	±40·0

* Stalk, leaf and trash tissue.
† Determination on a 500-mg plant sample.

It should be pointed out that large variations in results have been reported[18] in a recent inter-laboratory study in which the techniques used were basically steam distillation followed by spectrophotometric determination. Between-laboratory relative standard deviations ranged from 12·7 to 25·4 per cent. for samples of alfalfa, citrus, gladiolus, pine and orchard grass containing 53 to 118 p.p.m. of fluoride. Within-laboratory precision varied considerably and appeared to improve when more than 60 μg of fluoride in the samples were measured.

RESPONSE AND REPRODUCIBILITY OF THE FLUORIDE ION SELECTIVE ELECTRODE—

The response time of the fluoride-selective electrode varied from 2 to 5 minutes over the concentration range 0·05 to 10·0 p.p.m. of fluoride in de-ionised water, TISAB III or citrate buffer media (a reading was regarded as constant when it did not change by more than 0·3 mV in 1 minute). Samples and standards were read in increasing order of concentration because, according to the manufacturers,[13] this technique promotes a more rapid response. Samples were always stirred when measurements were made as this accelerates the response time.[13] Accordingly, the Orion microsampling dish was not used for small volumes, and instead the modified magnetic stirrer was used for volumes as small as 5 ml.

Typical readings and variations obtained at 20 °C for the electrode in de-ionised water, TISAB III and citrate buffer media are given in Table III. It is evident that the electrode displays a larger fluctuation in the citrate buffer medium than in de-ionised water and TISAB III media.

TABLE III

REPRODUCIBILITY OF FLUORIDE-SELECTIVE ELECTRODE IN DIFFERENT SOLUTION MEDIA AT 20 °C

	De-ionised water				TISAB III				Citrate buffer, 1 M			
Fluoride in standard solution, p.p.m.	No. of determinations	Average reading/mV	Standard deviation/mV	Relative standard deviation*	No. of determinations	Average reading/mV	Standard deviation/mV	Relative standard deviation*	No. of determinations	Average reading/mV	Standard deviation/mV	Relative standard deviation*
0·05	6	165·7	0·63	0·38	6	174·0	0·53	0·30	10	157·1	2·18	1·39
0·10	6	146·1	0·25	0·17	6	156·6	0·30	0·19	10	147·0	2·35	1·60
1·0	6	83·5	0·29	0·35	6	97·4	0·24	0·25	10	95·9	1·23	1·28
10·0	6	24·2	0·09	0·37	6	35·9	0·16	0·45	10	34·9	1·28	3·65

* Standard deviation expressed as percentage of the mean.

It was stated above that the variations in the recoveries obtained with the leaching - fusion - complexation method are due primarily to inherent variations of the electrode under the experimental conditions used. This can be seen from the following example.

A 500-mg sample of cane to which 2·5 μg of fluoride was added (≡ 5·0 p.p.m. w/w) should theoretically give a reading of 0·063 p.p.m. of fluoride in the final solution (volume 40 ml). In practice, a reading of about 0·12 p.p.m. is obtained, this higher reading being due to the presence of fluoride in the reagents (average fluoride content 0·025 p.p.m.) and in the plant tissue (average fluoride content 0·030 p.p.m.). The variation of the electrode reading in parts per million at the concentration level of 0·12 p.p.m. can be found approximately by converting the standard deviation (in millivolts) for a solution of 0·10 p.p.m. of fluoride in 1 M citrate buffer solution (Table III) into parts per million by using the relevant standard graph. This variation is 0·014 p.p.m., and is equivalent to 1·1 p.p.m. at the level of 5 p.p.m. of fluoride in the plant tissue. The actual variation found in the recovery at the 5-p.p.m. level was ±1·7 p.p.m. Likewise, the variations at the levels of 100 and 1000 p.p.m. were determined and found to be approximately 4·0 and 40 p.p.m., respectively. These variations compare favourably with those reported in Table II. Therefore, these findings demonstrate that the variations obtained are due primarily to inherent variations of the electrode under the experimental conditions used.

The reproducibility at low concentration levels can be improved by using a smaller final volume, say 5 ml, but at the cost of a considerable increase (about 20 per cent.) in the time required for analysis, so that a complete analysis in one working day will no longer be possible. This is due to the evaporation on the steam-bath being relatively slow, which prevents the liquid from boiling and hence losses due to splashing.

APPLICATION OF THE METHOD—

The fusion - leaching - complexation method described here was used for the determination of fluoride in sugar cane plants that had been grown under natural conditions as well as plants that had been fumigated with various levels of hydrogen fluoride. The fumigation equipment used was similar to that used by other workers.[3,19,20]

The results given in Table IV show that sugar cane grown under natural conditions contains small amounts of fluoride, and that fluoride accumulates mainly in the leaves and the trash while comparatively little is taken up by the stalk of the plant. The latter result is in agreement with those reported for other plants.[1–3,20,21]

CONCLUSION

The method described for the determination of fluoride in sugar cane is applicable over the concentration range 5 to 1000 p.p.m. of fluoride (2·5 to 500 μg of fluoride) and permits the analysis of six samples per working day per operator.

It is believed that this method can also be applied to other types of plant tissues, particularly those which contain high concentrations of silicon, aluminium and iron.

TABLE IV

DISTRIBUTION OF FLUORIDE IN NATURAL AND FUMIGATED SUGAR CANE

Sugar cane	Treatment*	Average fluoride concentration in cane tissue,† p.p.m. (dry weight basis)					
		Stalk			Leaves		
		Lower section	Middle section	Top section	Basal half	Terminal half	Trash
Natural cane, sample 1	—	0·16	1·96‡	0·25	0·82‡	3·46	13·2§
Natural cane, sample 2	—	0·00	0·00	1·52	0·00	1·18	4·55
Fumigated cane	3·6 p.p.b. of HF for 7 days	0·99	0·00	0·25	13·9	22·1	43·0
	3·6 p.p.b. of HF for 7 days and 17 p.p.b. of HF for 7 days	0·31	0·32	0·34	17·1	97·1	181·0
	3·6 p.p.b. of HF for 7 days, 17 p.p.b. of HF for 7 days and 30 p.p.b. of HF for 7 days ..	0·95	5·1	2·4	43·0	284·0	509·0

* The hydrogen fluoride fumigation levels are well above the average ambient concentrations of 0·1 to 0·5 p.p.b. recorded in the U.S.A.[19,22] The average ground-level atmospheric fluoride concentrations (expressed as hydrogen fluoride) measured in the environment of some aluminium smelters range from 0·38 to 1·3 p.p.b. depending on the distance from the factory. Maximum fluoride levels (expressed as hydrogen fluoride) range from 2·5 to 13 p.p.b., depending on the distance from the factory. (p.p.b. = parts per 10^9.)

† Determinations carried out in triplicate, except where indicated.

‡ Determinations carried out in sextuplicate.

§ Determinations carried out in duplicate.

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Biamperometric Determination of Platinum in Some Technical Products

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A method is described for the determination of platinum based on the reduction of platinum(IV) to platinum(II) with an excess of copper(I) chloride and titration of the resulting solution with a strong oxidant, such as cerium(IV). The reaction proceeds in two steps, the first corresponding to oxidation of an excess of copper(I), and the second to oxidation of platinum(II). The electrochemical characteristics of the systems involved appear to be ideal for biamperometric titration. Up to the first end-point the reversible system copper(II) - copper(I) is present, after which the next system, platinum(IV) - platinum(II), formed in the course of further additions of the titrant, is strongly irreversible. An excess of the oxidant in acidic solution forms a reversible cerium(IV) - cerium(III) couple. In these systems a double-bend titration curve is formed when a small voltage (100 mV) is applied. The only standardised solution required is cerium(IV) sulphate and removal of oxygen is, in general, unnecessary. The reaction is much faster at elevated temperatures and it is therefore convenient to warm the solution up to 80 °C before titration.

Depending on the concentration of the titrant (0·1 or 0·01 M) an amount of platinum from 5 to 50 mg can be determined with a relative standard deviation of about 0·14 per cent. This method has been applied to the determination of platinum in platinum - nickel alloys and platinum catalysts.

PLATINUM and its compounds play an important rôle in various industrial problems and therefore the need exists for rapid, precise and accurate methods for determining them. In view of the concentration range and precision required, we attempted to find a titrimetric method, preferably one involving instrumental end-point detection. The most promising area of investigation seemed to be the use of redox reactions in which divalent and quadrivalent platinum are involved. The standard redox potential for this redox couple in a chloride medium is 0·72 V *versus* N.H.E.; however, this system is known to be highly irreversible.

Known titrimetric redox methods for determining platinum are based on two principles (apart from direct titration, which is rather inconvenient). In the first group of methods the reducing agent is added in excess, the excess is then decomposed and platinum is oxidimetrically titrated from the platinum(II) to the platinum(IV) state. In the second group a known excess of a standard solution of the reductant is added and back-titrated without oxidation of the platinum, which is usually inert at room temperature. In both groups the accuracy is poor as the reactions often do not reach the stoicheiometric end-point.

Reductants used in the above methods include the following: copper(I) chloride, iron(II) salts, ascorbic acid, potassium iodide and potassium ferrocyanide. Their standard potentials vary in the range from +0·45 to +0·65 V *versus* N.H.E. This value is important, because at potentials close to that of the normal hydrogen electrode further reduction to the elemental state can occur. The principal problem is therefore to choose a reductant such that no direct reduction of quadrivalent platinum to metal occurs owing to kinetic factors. The thermodynamic data here are insufficient because the standard potentials of both reactions (reduction to the metal and divalent state) are very close.

The excess of reductant can in some instances be removed by oxidation with air; copper(I) chloride is an example of such an instance. If oxidation is incomplete positive errors are observed, whereas prolonged oxidation causes oxidation of platinum(II) to platinum(IV). Theoretically the excess of reductant can be back-titrated; for example, with potentiometric end-point detection, recording the difference between the first and second potential jumps facilitates calculation of the amount of platinum present. This is, in practice, difficult because the difference in standard potentials is not large enough to give a

distinct end-point. Nevertheless, Ryabtchikov[1] has proposed a method based on this principle although it has several disadvantages. The first end-point is only in the tens of millivolts range, and decreases significantly when the concentration of the oxidised form of the reductant is too large. The second one, on the contrary, is very sharp, so that titration must be carried out with small increments of the titrant to detect the end-point accurately. Further, the indicated temperature is too low to give an acceptable time of titration.

It is perhaps surprising that until recently no amperometric[2,3] or biamperometric titration method for platinum has been available. The latter method, especially, is promising because of the high degree of irreversibility of the platinum(IV) - platinum(II) couple when the couple is formed by the excess of reductant and the oxidising titrant. Such systems are formed with copper(I) chloride in an acidic medium as reductant and cerium(IV) sulphate as oxidant.

Experimental

Reagents—

Copper(I) chloride, 1 to 2 per cent. solution—Dissolve an accurately weighed amount of analytical-reagent grade copper(I) chloride [containing no sulphur dioxide or iron(II)] in 20 ml of concentrated hydrochloric acid and dilute the solution to 100 ml. This solution will remain stable for 1 day.

Cerium(IV) sulphate, 0·1 M solution—Dissolve 40·5 g of cerium(IV) sulphate in 500 ml of hot 2 M sulphuric acid and dilute the solution to 1000 ml. The solution is standardised by titration against samples of pure (99·99 per cent.) platinum. When a 0·01 M solution is required the stock solution is diluted accordingly.

Sulphuric acid, concentrated.

Hydrochloric acid, concentrated.

Nitric acid, concentrated.

The above three acids are used for sample dissolution.

Apparatus—

Standard equipment for biamperometric titration was used. Platinum-wire electrodes, each with a surface area of 0·1 cm^2, were purified by anodising and later cathodising them in a solution containing 30 g of sodium hydroxide, 100 g of sodium carbonate decahydrate and 10 g of sodium phosphate per 1000 ml. When not in use the electrodes were short-circuited and kept in a 0·2 M solution of ammonium iron(II) sulphate in 2 M sulphuric acid. Before readings were taken the electrodes were anodised (with a graphite counter electrode) for 15 s with an applied voltage of 4·5 V and were then left for several minutes in this solution.

The titration solutions were mixed by use of a magnetic stirrer, stirring at a rate of 400 r.p.m.

Voltammetry of the systems—

To establish the best conditions for the determination, the current - potential curves were recorded at different stages of the titration by using standard equipment with a platinum-foil electrode in a mixed solution of reductant and oxidant (Fig. 1). These curves confirm the excellent reversibility in an acidic medium of the copper(II) - copper(I) system (the titration parameter, f, is equal to −0·1). The cerium(IV) - cerium(III) system is not so reversible, as is shown by the slope of the curve for an excess of the titrant (f is equal to 1·1). The anodic branch of this curve almost coincides with the curve for the anodic oxidation of water. The curves for the platinum couple indicate its highly irreversible character; the cathodic part slowly increases, while on the anodic part a pronounced maximum is observed. This maximum is not stable for any length of time, nor is its height proportional to the concentration of platinum(II) but is connected with the oxidation of platinum(II) by oxygen chemisorbed on the electrode, or with disturbance of the diffusive transport of ions to the electrode. When the electrode is anodised beforehand the height of this maximum significantly decreases. In the absence of platinum(II) no maximum is observed and the system is highly irreversible (f is equal to 1·0).

A clear indication of the optimum conditions for electrode polarisation is obtained when the current is plotted against the applied voltage (Fig. 2). To decrease the current between the points $f = 0$ and $f = 1$ the applied voltage should not be greater than 0·2 V.

The difference between the reversibility of the two couples, before the first equivalence point (f is less than 0) and after the second (f is greater than 1), influences the slope of the titration graph (Fig. 3). If a galvanometer of high sensitivity is used (curve 2 in Fig. 3) the first part of the curve is too steep to be plotted accurately, whereas in the case of a galvanometer of low sensitivity (curve 1 in Fig. 3) the last part is too flat to permit accurate extrapolation. Of the two possibilities, changing the galvanometer sensitivity or changing the applied voltage, the former was considered to be more promising. Making the change led to the final titration graph, indicated in Fig. 3 by a solid line.

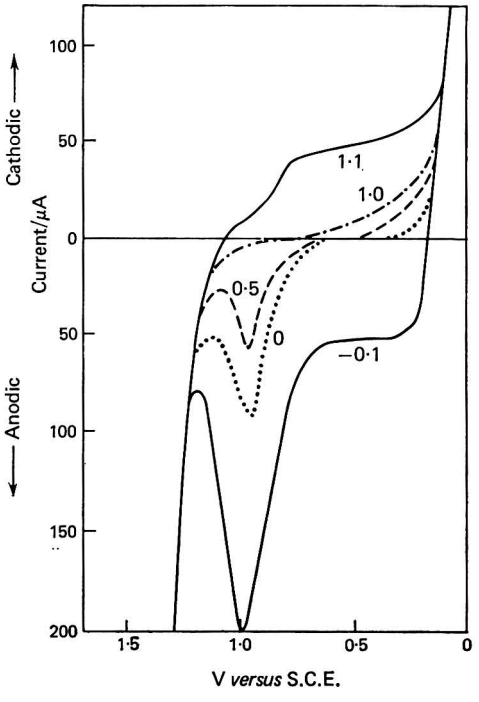

Fig. 1. Current *versus* potential graphs at different stages of platinum titration. Numbers indicate the value of the titration parameter f: −0·1, copper(II)/(I) *plus* platinum(II); 0, copper(II) *plus* platinum(II) *plus* cerium(III); 0·5, copper(II) *plus* platinum(IV)/(II) *plus* cerium(III); 1·0, copper(II) *plus* platinum(IV) *plus* cerium(III); and 1·1, copper(II) *plus* platinum(IV) *plus* cerium(IV)/(III). All graphs were obtained with a platinum electrode polarised from the zero current potential

SOLUTION COMPOSITION AND INTERFERENCES—

When the amount of copper(I) chloride added as a reductant is too small it is impossible to obtain enough points to carry out an accurate extrapolation of the first equivalence point. Too large an excess is also inconvenient but has no effect on the titration curve and precision of titration. The best choice is therefore about a 10 per cent. excess. In dilute solutions oxidation of copper(I) chloride by dissolved oxygen proceeds rapidly. It is therefore advantageous either to add the titrant in equal portions at equal time intervals, or to remove oxygen with the nitrogen gas (even in an open beaker). Nevertheless, if the platinum concentration is higher than 1 mg ml^{-1} this is not important.

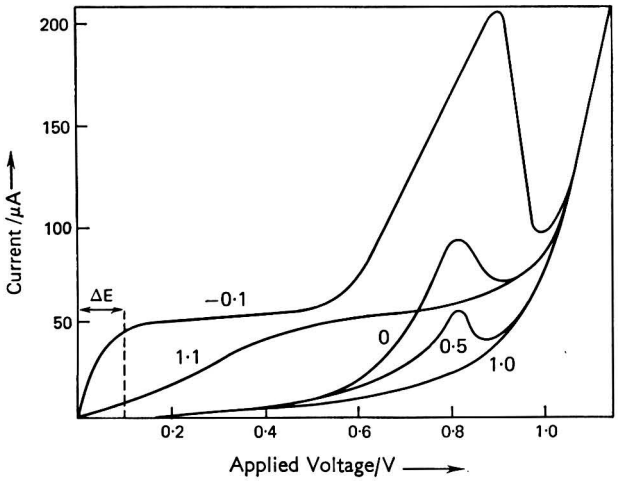

Fig. 2. Current *versus* applied voltage graphs at different stages of platinum titration. Numbers indicate the value of the titration parameter, f, and refer to systems given under Fig. 1

In the instance when the stirred solution, containing an excess of copper(I) chloride, is left for several minutes all of the reductant is oxidised and titration can be started directly from the first inflection point. Such a titration should be carried out under controlled conditions because after 30 minutes a negative error of about 1 per cent. has been observed, caused by oxidation of the platinum. When the sample contains large concentrations of salts, which is the case in the analysis of catalysts, no oxidation of copper(I) chloride occurs.

In any practical application of the method the effect of different solution components is important. The titrated solution always contains a certain concentration of chloride, which is added with the solution of the reductant. Chlorides do not interfere when their concentration is below 0·5 M (calculated as hydrochloric acid). An increase in chloride concentration

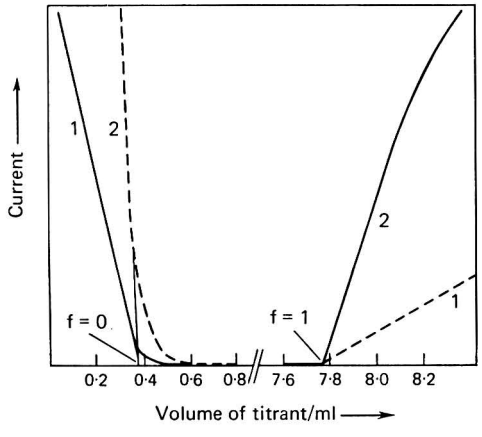

Fig. 3. Biamperometric titration graphs obtained at lower (curve 1) and higher (curve 2) galvanometer sensitivities. The solid line represents the final titration graph. For all determinations the applied voltage was 100 mV. Curve 1, 250 μA; curve 2, 50 μA per full scale

above this limit makes both end-points indistinct, and when the concentration is about 2 M, cerium(IV) ions oxidise the chloride, thus rendering the titration impossible. The best end-points are obtained in sulphuric acid solutions; however, when the acid concentration is above 2 M the reversibility of the cerium couple decreases and the effect of chloride ions increases. The presence of nitrate is undesirable and it should be removed by preliminary evaporation with sulphuric or hydrochloric acid.

Interferences in the determination can be expected from metals that are reduced at potentials more positive than +0·4 V, at which level they are re-oxidised by cerium(IV) sulphate. Among these metals are iron, vanadium, gold and ruthenium. Molybdenum, palladium, rhodium and iridium do not interfere when present in amounts comparable with that of platinum.

PRECISION OF THE METHOD—

The expected high precision of the method has been confirmed with a pure standard solution of platinum prepared from metal of 99·99 per cent. purity. The results summarised in Table I indicate that for two 550-mg samples, four aliquots of each being analysed, the standard deviation was equal to 0·076 mg, which corresponds to a relative standard deviation of 0·14 per cent. This is good precision, even for the determination of platinum in pure solutions, and none of the currently used methods for this concentration range can compete with the given procedure.

TABLE I

BIAMPEROMETRIC TITRATION OF STANDARD PLATINUM SOLUTION

Amount of platinum/mg		Error	
Taken	Found	mg	per cent.
56·46	56·60	+0·14	+0·24
	56·50	+0·04	+0·07
	56·46	0·00	0·00
	56·44	−0·02	−0·04
54·59	54·55	−0·04	−0·07
	54·51	−0·08	−0·14
	54·69	+0·10	+0·18
	54·55	−0·04	−0·07

Standard deviation, 0·076 mg.
Relative standard deviation, 0·14 per cent.
Applied voltage, 100 mV; temperature, 70 °C; Volume, 40 ml.

ANALYSIS OF TECHNICAL PRODUCTS—

To determine platinum in a platinum - nickel alloy a sample of 0·5 to 0·8 g was dissolved in aqua regia and evaporated until the first crystals appeared, and then three times with concentrated hydrochloric acid. Following the last evaporation the crystals were dissolved in water and an aliquot containing 50 to 80 mg of platinum was taken for the determination. To this sample 3 to 6 ml of 2 per cent. copper(I) chloride solution were added, the exact

TABLE II

DETERMINATION OF PLATINUM IN TECHNICAL PRODUCTS

Sample weight/ g	Platinum found/ mg	Number of determinations	Average content, per cent.	Standard deviation, per cent.	Relative standard deviation
Nickel - platinum alloy—					
0·053 50	49·11	4	91·59	0·07	0·0014
0·075 18	68·75	5			
0·074 70	68·40	3			
0·061 53	56·34	4			
Platinum - alumina catalyst—					
1·0651	5·510	1	0·5180	0·0015	0·0029
1·1097	5·756	1			
0·9745	5·061	1			
0·8912	4·631	1			
0·9580	4·944	1			

amount being dependent on the concentration of unoxidised copper(I) salt. The total time of analysis is not greater than 3 hours and the titration takes only 15 minutes.

In the determination of platinum in catalysts the principal difficulty is dissolution of the sample, which usually contains about 0·5 per cent. of platinum. Of the various acid mixtures possible, the sulphuric acid - hydrochloric acid mixture was found to be the best. The sample was completely dissolved in a short time (not exceeding 2 to 3 hours) and the composition of the solution was found to be adequate for titration. The 1·0 to 1·5-g sample solution was then heated on a sand-bath until a clear, yellow solution was obtained, which was diluted with water and evaporated to dryness several times with re-dissolution of the residue. The solution prepared in this way contained approximately 5 mg of platinum and was titrated at 60 to 80 °C with 0·01 M cerium(IV) sulphate solution, following the addition of 1 to 2 ml of 1 per cent. copper(I) chloride solution. The total time of analysis was under 4 hours and, as before, the contribution of the titration time was small.

The results of the determination of platinum in the materials mentioned are given in Table II. They indicate very good precision in the instance of platinum - nickel alloy and slightly less good precision for the determination of platinum in catalysts, which is attributable to variable moisture content and inhomogeneity of the materials.

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The Enhancement of Acidity in Non-aqueous Solvents

Part I. An Improved Procedure for the Determination of Short-chain Carboxylic Acids in the Presence of their Anhydrides*

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Weak short-chain carboxylic acids can be determined potentiometrically in the presence of their acid anhydrides after enhancement of their acidity by reaction with alkaline earth perchlorates. The method is particularly suitable for the determination of acid contents in the range 0·5 to 5 per cent. Of five electrode systems examined, glass - modified calomel and platinum - in-stream platinum combinations gave responses exceeding 500 mV per millilitre of titrant at the end-point. Both acetonitrile and acrylonitrile are satisfactory solvents, but the latter is generally preferable for non-aqueous titration because, while it leads to equally sharp end-points, it is more readily available in a pure, acid-free form.

INDIRECT methods for the determination of carboxylic acids in the presence of their anhydrides are based on measurements of the difference between the contents of anhydride and total acid after hydrolysis.[1,2] Such methods suffer from lack of precision, particularly when the acid content is low, and are time consuming, and consequently attention has been focused on direct methods of determination. Siggia and Floramo[3] used a tertiary amine in acetone for the potentiometric titration of carboxylic acids in mixtures with their anhydrides with a glass - calomel electrode combination. In ketonic solvents, good potential breaks at the end-point were obtained with carboxylic acids having pK values of 3 or less. Phthalic and maleic acids can be determined, but only one of their carboxyl groups is sufficiently acidic to be titrated. Acids having pK values greater than 3, including acetic acid, cannot be determined. Wharton[4] subsequently reported a titration procedure in which lithium chloride was used to enhance the acidity of weak carboxylic acids (HA) in acetonitrile solution. It is claimed that the reaction

$$HA + LiCl \overset{CH_3CN}{\rightleftharpoons} LiA + HCl$$

is displaced to the right, forming the weakly dissociated lithium carboxylate and hydrochloric acid. This, stronger, acid can then be titrated with the tertiary amine and, in this way, fatty acids can be determined in the presence of their anhydrides.

The lithium chloride enhancement technique suffers from two major disadvantages. Firstly, although the titration graph is sharp for long-chain fatty acids, only poor precision and accuracy are obtained with fatty acids of low molecular weight. For example, the potential break at the equivalence point for acetic acid obtained by Wharton[4] was only 75 mV per millilitre of 0·05 M titrant, which is at the lower limit for useful practical results.[5] Secondly, the low solubility of lithium chloride in acetonitrile (a saturated solution at room temperature is about 0·035 M) limits the volume of acid that can be titrated in practice, especially as a considerable excess over the stoicheiometric amount of the salt was found to be necessary for complete enhancement.

McClure, Roder and Kinsey,[6] who had earlier reported a lack of success in attempts to titrate acetic acid in acetic anhydride potentiometrically, obtained a value for the acetic acid content by using methyl red as a visual indicator. However, the colour change from orange to red at the end-point was difficult to assess, especially with dark-coloured samples. An alternative thermometric method suggested by these authors produced good results over

* Based in part on a paper presented at a meeting of the Society for Analytical Chemistry, Birmingham, May 7th and 8th, 1970.

the range 0·8 to 5·5 per cent. w/w of acid in its anhydride, but calibration was necessary and the accurate determination of the amount of acid present in standard mixtures was difficult.

In this work, a detailed study of the enhancement of the acidity of weak acids by the addition of salts such as alkali metal and alkaline earth halides and perchlorates was carried out with acetonitrile and acrylonitrile as solvents. A brief evaluation has also been made of several other solvents, including benzonitrile, phenylacetonitrile, dimethyl sulphoxide, tetrahydrothiophen-1,1-dioxide (sulpholane), dimethylformamide and acetone, but these were less effective than acetonitrile and acrylonitrile in the enhancement process. The aim was to improve the precision of the analytical method, especially when it is applied to the anhydrides of aliphatic acids of low molecular weight containing small amounts of free acid and, ultimately, to elucidate the mechanism of salt enhancement.

When the enhancement technique is applied to acid - anhydride mixtures the enhancing salt must, of course, be completely anhydrous or the anhydride may be hydrolysed, thus producing high results. Alkaline earth perchlorates were effective for enhancement but calcium perchlorate (suggested tentatively by Wharton[4]) and magnesium perchlorate are both difficult to dehydrate completely. In contrast, barium and strontium perchlorates are available in the anhydrous form and the former can be dried by heating at 140 °C.[7]

In acetonitrile and acrylonitrile, the exchange reaction

$$2CH_3COOH + Ba(ClO_4)_2 \rightleftharpoons Ba(O.COCH_3)_2 + 2HClO_4$$

is, apparently, immediately displaced to the right. Barium perchlorate is highly soluble in these solvents and the stoicheiometric amount is sufficient for quantitative enhancement. Perchloric acid is known to be a stronger acid than hydrochloric acid in acetonitrile and gives sharp inflexions in non-aqueous potentiometric titration.[8]

In this work, particular attention was paid to the titration of acetic acid in acetonitrile and acrylonitrile solvents with barium perchlorate as the enhancing salt and tripropylamine in acetone as the titrant. It has been suggested[9] that the use of a platinum - pre-polarised platinum electrode pair may result in particularly sharp potential breaks in non-aqueous titrations, and this system has been compared with the glass - modified calomel, glass - platinum and antimony - platinum electrode systems.

Experimental

Reagents—

Acetone—Analytical-reagent grade acetone was dried over molecular sieve 4A before use.

Acetonitrile—Laboratory-reagent grade acetonitrile was dried over molecular sieve 4A before use.

Acrylonitrile, 99 per cent.—This was used as received.

Other solvents were used as received.

Anhydrous barium perchlorate, 99 per cent.—This was dried at 140 °C before use.

Tripropylamine, 0·25 M solution in acetone—Standardise this solution against analytical-reagent grade succinic acid (25 to 30 mg) or benzoic acid (50 to 60 mg) in acetonitrile (30 ml) containing anhydrous barium perchlorate (0·2 g) by potentiometric titration (as under Procedure, below). The temperature should be noted.

Apparatus—

Conventional potentiometric titration apparatus with a 10-ml burette (0·02-ml divisions) is used, and a closed, magnetically stirred, 100-ml titration cell with an inlet and an outlet for inert gas.

The calomel electrode in the glass - calomel system contained methanol saturated with sodium chloride and had a porous ceramic membrane. The glass electrode was conditioned in the solvent for 30 minutes before use,[10] and was stored in distilled water after use.

The platinum - platinum, glass - platinum and antimony - platinum systems had a platinum electrode in the titrant stream and were based on a design by Brooks and Maher[11] in which the titrant and titration solution make electrical contact through a flamed porosity 4 sintered-glass membrane. The platinum electrodes were pre-polarised by applying a potential of 5 V for 1 minute across two platinum wires immersed in 1 per cent. sulphuric acid solution.[12] The anode wire was used as the pre-polarised electrode. Electrodes were wiped with tissue-paper and rinsed with the solvent before use.

PROCEDURE—

Titration—Weigh a sample expected to contain 1 to 4 mequiv of acid into a dry 100-ml calibrated flask, dissolve it in the titration solvent, and make the volume up to the mark with the same solvent. Transfer 25 ml of the solution with a pipette into the titration cell, displace the air with dry nitrogen, add about 0·2 g of anhydrous barium perchlorate or an appropriate amount of another salt, stir the mixture for 2 minutes to allow the exchange reaction to proceed, and titrate the solution potentiometrically with the standard tripropylamine, taking readings 1 minute after each addition of titrant. With efficient stirring, the precipitate usually does not interfere with the sharpness of the end-point. If the temperature differs from that obtaining during standardisation of the titrant, an appropriate correction to the titrant volume is made.[13] Blank titrations on solvents are made by using 50 ml of solvent and the above titration procedure.

Measurement of the potential shift (mV)—Measure the potential (P_1 mV) established with a glass electrode in 25 ml of acetonitrile made 0·05 M in acetic acid, relative to the modified calomel electrode. Add an amount of enhancing salt in excess of the stoicheiometric amount (about 0·2 g, in all, is sufficient), stir the mixture for 2 minutes, note the new potential reading (P_2 mV) and record the value $P_2 - P_1$ as ΔmV.

RESULTS AND DISCUSSION

Fig. 1 indicates the improvement in the sharpness of the end-point obtained when barium perchlorate in acetonitrile or acrylonitrile is used instead of lithium chloride in acetonitrile as the medium for the enhancement of acidity in the potentiometric titration of acetic acid. Lithium chloride is almost insoluble in acrylonitrile and consequently its enhancing properties in this solvent cannot be assessed.

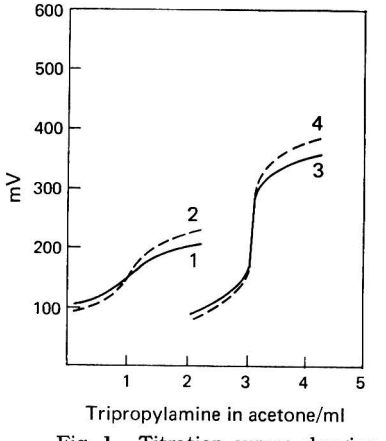

Fig. 1. Titration curves showing the effect on end-point sharpness of salt enhancement of acidity of acetic acid in acetonitrile and acrylonitrile (glass - modified calomel electrodes): 1, titrant 0·05 M, saturated solution of LiCl in acetonitrile; 2, titrant 0·25 M, saturated solution of LiCl in acetonitrile; 3, titrant 0·25 M, 1 per cent. $Ba(ClO_4)_2$ in acetonitrile; and 4, titrant 0·25 M, 1 per cent. $Ba(ClO_4)_2$ in acrylonitrile

The five electrode combinations investigated are compared in Table I. Barium perchlorate in acetonitrile and acrylonitrile is used as the enhancing salt. In the titration of acetic acid, the pre-polarised platinum - in-stream platinum and glass - modified calomel systems give sharpnesses of the end-point of the same order, when expressed as millivolts per millilitre of titrant, but the values with the former electrode system were more variable,

TABLE I

COMPARISON OF ELECTRODE SYSTEMS USED IN THE TITRATION OF ACETIC ACID IN ACETONITRILE AND ACRYLONITRILE WITH TRIPROPYLAMINE IN ACETONE

Conditions—0·3 mequiv of acetic acid in 50 ml of solvent; 0·25 M tripropylamine in acetone; saturated solution of lithium chloride; 0·025 M solution of barium perchlorate in solvent

Electrode system	Solvent	Enhancing salt	Potential range ±0·5 ml of equivalence/mV	$[\Delta mV/\Delta ml]_{max}$
Glass - modified calomel ..	CH_3CN	LiCl	100	170
	CH_3CN	$Ba(ClO_4)_2$	240	650–1100
	C_2H_3CN	$Ba(ClO_4)_2$	250	700–1400
Pt - in-stream Pt	CH_3CN	$Ba(ClO_4)_2$	70	400
Pre-polarised Pt - in-stream Pt	CH_3CN	LiCl	100	100
	CH_3CN	$Ba(ClO_4)_2$	220	400–1100
	C_2H_3CN	$Ba(ClO_4)_2$	240–320	400–1500
Glass - in-stream Pt ..	C_2H_3CN	$Ba(ClO_4)_2$	200	600–700
	CH_3CN	$Ba(ClO_4)_2$	200	330–340
Sb - in-stream Pt ..	CH_3CN	$Ba(ClO_4)_2$	80	120

probably because pre-polarisation is difficult to reproduce and "ages" erratically. The other three electrode systems are less effective. Acrylonitrile is marginally superior to acetonitrile in terms of sharpness of the end-point and is generally preferable to the latter because it is more readily available in a pure, dry, acid-free form; its main drawback is probably its lower efficiency, compared with acetonitrile, as a solvent for inorganic salts, although it is satisfactory with barium perchlorate.

TABLE II

POTENTIOMETRIC TITRATION OF ACETIC ACID WITH TRIPROPYLAMINE IN THE PRESENCE OF ACETIC ANHYDRIDE AND BARIUM PERCHLORATE

Conditions—Solvent, acetonitrile (25 ml); titrant, 0·25 M tripropylamine in acetone; 0·025 M solution of barium perchlorate in the solvent. Duplicate samples for the acid - anhydride mixtures were taken from prepared solutions in the reaction solvent

Sample: Acetic acid: Added/mg	Acetic acid: In acetic anhydride/mg	Acetic anhydride/g		Acetic acid found: mg	Acetic acid found: per cent.	Acetic acid taken (columns 1 + 2), per cent.
32·0	—	0		31·7	99·1	100·0
32·0	—	0		32·1	100·3	100·0
53·4	40·1	5·3400		99·6	1·85	1·73
53·4	40·1	5·3400		104·6	1·94	1·73
62·3	45·0	6·0017		105·6	1·74	1·77*
62·3	45·0	6·0017		114·0	1·88	1·77*
42·3	15·8	2·1120		61·9	2·87	2·70
42·3	15·8	2·1120	(a)	61·9	2·87	2·70
129·9	45·0	6·0016		159·1	2·59	2·85*
129·9	45·0	6·0016		178·8	2·92	2·85*
58·0	8·1	1·0740		66·3	5·86	5·84
58·0	8·1	1·0740		65·3	5·77	5·84
0	—	6·0000		43·6	0·73	—
0	—	6·0000	(a)*	45·2	0·75	—
0	—	6·0000		45·7	0·76	—
0	—	6·0000		44·2	0·74	—
0	—	6·0130	(b)*	107·2	1·78	—
0	—	6·0130		105·6	1·76	—

(*a*) and (*b*)—Different sources of analytical-reagent grade acetic anhydride; source (*a*) has an acetic acid content of 0·75 per cent. w/w.

* Acrylonitrile (25 ml) as solvent.

In Table II results are given for titrations of acetic acid - acetic anhydride mixtures in acetonitrile with barium perchlorate as enhancing salt. Accuracies are better than 1 per cent. for acetic acid alone when 25-mg samples are used, and of the order of 2 per cent. for 5 per cent. of the acid in the anhydride and 10 to 20 per cent. for 1 per cent. of the acid in the anhydride. The free acetic acid content of a sample of AnalaR acetic anhydride was found to be 0·75 per cent. w/w; this compares with the value of 0·745 per cent. w/w obtained by using the spectrophotometric method of Mitra, Ghosh and Palit.[14] The latter method, a relative one, requires calibration with mixtures of known composition or the use of a special technique involving twelve separate measurements for the initial determination.[14] Our method, an absolute one, is probably more suitable for "one-off" or referee analyses and for the determination of calibration standards.

A convenient method for determining approximately the enhancing power of a salt - solvent system for a given acid is to measure the potential change ("mV shift") that occurs when the salt is added to a solution of the acid in the solvent of interest, in which a glass - modified calomel electrode pair is immersed. The shift is probably a measure of the extent to which the enhancement reaction has proceeded. The test is satisfactory for salts that are freely soluble in acetonitrile, but for sparingly soluble salts it is difficult to make a valid comparison without a further investigation of other solvents. The potential shifts produced with some salts of Group IA and IIA metals in acetonitrile were as follows—

Salt	LiCl	NaCl	KCl	$LiClO_4$	$NaClO_4$	$Mg(ClO_4)_2$	$Ca(ClO_4)_2$	$Sr(ClO_4)_2$	$Ba(ClO_4)_2$
mV shift (±10 per cent.)	85	5	5	90	5	270	250	210	180

The superior enhancing power of alkaline earth perchlorates is evident, with magnesium perchlorate showing the largest potential shift. Unfortunately, as already noted, this salt cannot be used for titrations when anhydrides are present. Furthermore, in an actual titration the sharpness of the end-point was found to be inferior to that obtained with barium perchlorate. This may have been due to a reduction in electrode response caused by a gelatinous precipitate, peculiar to magnesium perchlorate, which forms a film on the surface of the electrode. Typical titration curves obtained with the alkaline earth perchlorates are shown in Fig. 2.

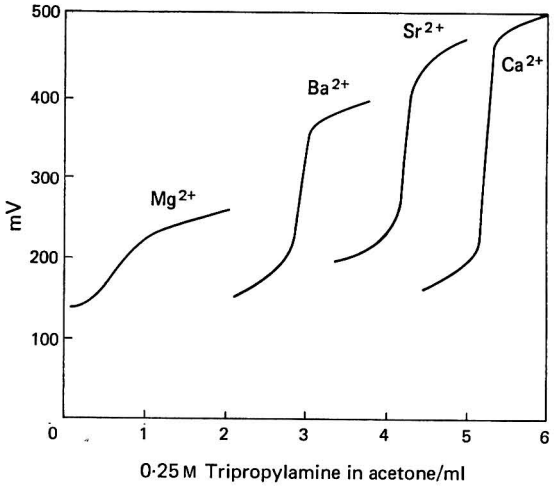

Fig. 2. Potentiometric titration of acetic acid in acetonitrile with alkaline earth perchlorates as enhancing salts

Higher fatty acids (propionic and butyric acids) and also benzoic, phthalic and succinic acids were determined alone or in the presence of their anhydrides by using the enhancement technique. In general, the end-points were as sharp as or sharper than those obtained with acetic acid; typical results are given in Table III.

TABLE III

POTENTIOMETRIC TITRATION OF SAMPLES OF ACIDS AND OF ACIDS IN ANHYDRIDES IN THE PRESENCE OF BARIUM PERCHLORATE

Conditions—as in Table II, with acrylonitrile (50 ml) as solvent

Compound	Taken/g	Acid found		Potential range ±0·5 ml of equivalence/mV	$[\Delta mV/\Delta ml]_{max.}$ ±10 per cent.
		mg	per cent.		
Propionic anhydride ..	5·6426	36·6	0·65	270	750
	5·6430	37·2	0·66		
Succinic anhydride ..	0·6762	14·4	2·14	350	2500
	0·7709	15·7	2·04		
Phthalic anhydride ..	0·4424	6·8	1·54	390	5000
	1·8443	28·5	1·55		
Butyric acid	0·0302	30·4	100·7	220	780
	0·0331	32·8	99·1		
Benzoic acid	0·0549	Standardisation of titrant		280	1180
	0·0566				

CONCLUSIONS

Anhydrous barium perchlorate in acetonitrile or, preferably, acrylonitrile, enhances the acidity of short-chain carboxylic acids, thus making possible their direct determination in the presence of their anhydrides by non-aqueous potentiometric titration with a tertiary amine in a non-hydroxylic solvent.

The method has the advantages of speed and simplicity, as well as accuracy, over indirect methods. The sharpness of the end-point with barium perchlorate is much better than that obtained with lithium chloride as enhancing salt and, in addition, acrylonitrile can be used as the solvent when barium perchlorate is used.

Glass - modified calomel and pre-polarised platinum - in-stream platinum electrodes both give satisfactory results, but with the former combination they are more reproducible.

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The Determination of the Non-volatile Acidity of Rain Water by a Coulometric Procedure

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A precise and accurate method for the determination of the non-volatile acidity of rain water or of any dilute acid solution (10^{-4} to 10^{-6} M) is described. The method is based on the coulometric titration of a sample from which carbon dioxide has been removed by bubbling nitrogen through it. The end-point is detected by potentiometry with a glass electrode by using Gran's theory. The acidity from both strong and weak acids is determined. The average standard deviation is ± 5 per cent. and the limit of sensitivity 0·1 μg ml^{-1} (calculated as sulphuric acid).

THE determination of acidity in rain water is of great interest in studies of the environment of a certain area; it is usually recorded in terms of the pH value. In studies of pollution the acidity due to strong acids is of specific interest, but the pH measured for a strong acid might not correspond to its true concentration if weak acids are present and the pH of the rain water is above 4. An alkalimetric procedure, with methyl red as the indicator, has been used to avoid this disadvantage,[1] but the accuracy is rather poor for low hydrogen ion concentrations.

This paper describes a precise and sensitive method for the determination of acidity. The procedure is based on the coulometric titration of rain-water samples from which carbon dioxide has previously been removed by bubbling nitrogen through them. The end-point of the titration is detected by potentiometry with a glass electrode, by use of Gran's theory.[2,3] This theory facilitates the evaluation of the acidity due to strong and to weak acids.

THEORY

An acidic rain-water sample is titrated by cathodic generation of hydroxyl ions at constant current in a galvanic cell of the type

(−) reference electrode | test solution | glass electrode (+)

Hydroxyl ions are liberated at a platinum electrode—

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^-$$

whereas at the anode (a silver - silver bromide electrode) silver bromide is formed—

$$Ag + Br^- \rightarrow AgBr + e^-$$

The e.m.f. of the cell (E) is given by—

$$E = E'_o + \frac{2{\cdot}3\,RT}{F} \log [H^+]\,\gamma_H + E_j \qquad (1)$$

where E'_o includes the potential of the reference half-cell and the normal potential of the probe half-cell, E_j is the liquid junction potential and γ_H is the activity coefficient of the hydrogen ion. For any value of time t, corresponding to the generation of $it F^{-1}$ equivalents of hydroxyl ion before the equivalence point, the following equation holds—

$$[H^+] = \frac{V_o[H]_o - itF^{-1}}{V_o} \qquad (2)$$

where V_o ml is the volume of solution that is titrated, $[H_o]$ is the initial molar hydrogen-ion concentration from strong acids, i mA is the current, t s is the time and F is Faraday's constant.

From equations (1) and (2) the following is obtained—

$$E = E'_0 + \frac{2{\cdot}3\,RT}{F}\log\left(\frac{V_0[H]_0 - it\mathrm{F}^{-1}}{V_0}\right) + \frac{2{\cdot}3\,RT}{F}\log\gamma_H + E_j$$

As the ionic strength is kept almost constant by the addition of potassium bromide and the initial hydrogen-ion concentration of the sample is generally lower than 10^{-4} M, γ_H and E_j do not change appreciably during the titration.

By plotting the function $\psi = 10^{E\frac{F}{2{\cdot}3RT}}$ *versus* t a straight line is obtained. This graph intercepts the abscissa at a value t_e that corresponds to the end-point of the titration.

The initial hydrogen-ion concentration, $[H]_0$, from strong acids, is obtained from the relationship—

$$[H]_0 = \frac{it_e}{FV_0}$$

Continued generation of OH^- beyond the equivalence point can supply additional information if the function $\psi' = 10^{-E\frac{F}{2{\cdot}3RT}}$ is plotted *versus* the generation time. By drawing a line through the experimental points a new intercept, t'_e, is obtained, from which an $[H]'_0$ value is calculated; this value represents the acidity caused by strong and weak non-volatile acids that may be present in the rain sample [*e.g.*, HSO_3^- and hydrolysable cations such as $Fe(H_2O)_6^{3+}$, $Al(H_2O)_6^{3+}$, etc.].

Regarding sulphur dioxide, it should be pointed out that if the initial pH of the sample water is below 4, sulphur dioxide will be set free by bubbling a stream of nitrogen through the cell, while at pH values higher than 4, the sulphur dioxide, which is present as HSO_3^- ions, will be titrated as a monoprotic weak acid.

The $[H]_0$ value coincides with that of $[H]'_0$ in the absence of weak acids. In this instance the graphs of the two functions give straight lines, which intercept each other on the abscissa. When the solution contains a weak non-volatile acid, the graphs of the two functions are curved; the extrapolations of the straight portions of these curves do not give the same intercept on the abscissa and the difference between the two intercepts gives a value for the acidity from weak acids.

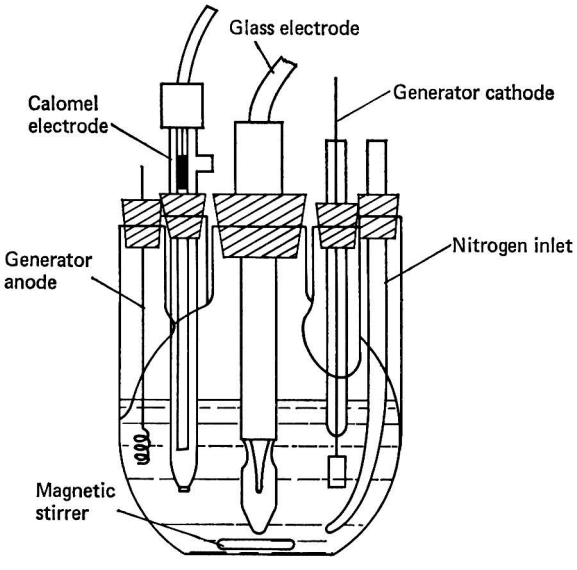

Fig. 1. Measuring cell for coulometric titration

Experimental

Apparatus—

A measured sample of rain water (50 to 75 ml) was transferred to a five-necked cell (Fig. 1). One neck held the working electrode, polarised to act as a cathode, which was made of a platinum sheet (1·25 × 0·65 cm); the anode, a coiled silver wire, was set in another neck. The glass indicator electrode and the reference electrode were placed in two of the remaining necks of the flask, the last neck being used as an entry for the nitrogen that was bubbled through the solution in order to render it carbon dioxide free.

A coulometric microtitrator (Amel, Milan) was used as a constant-current generator operating in the range 0 to 10 mA.

Potentiometric measurements were made with a Jonosis potentiometer pHz (S.I.S., Milan) by means of a glass electrode and a conventional fibre-type reference electrode.

Procedure—

The titration is carried out in the following way. The solution under test is magnetically stirred and made 0·02 M with respect to bromide by the addition of solid potassium bromide. Nitrogen is then bubbled through it and the e.m.f. of the cell is measured. The potential becomes constant after a certain period, the exact length of which depends on the carbon dioxide concentration. When the electrolysis current (1 to 5 mA) is started the e.m.f. of the cell is read at intervals of 20 to 30 s and the results are used to construct graphs by use of Gran's theory.

Results and discussion

The method has been checked with dilute sulphuric acid solutions in the concentration range 10^{-4} to 10^{-6} N and with a variety of rain samples. In Fig. 2 the experimental graphs resulting from the titration of 50 ml of 10^{-5} N sulphuric acid are plotted. As no weak acids are present, the intercepts corresponding to the functions ψ and ψ' *versus* time coincide.

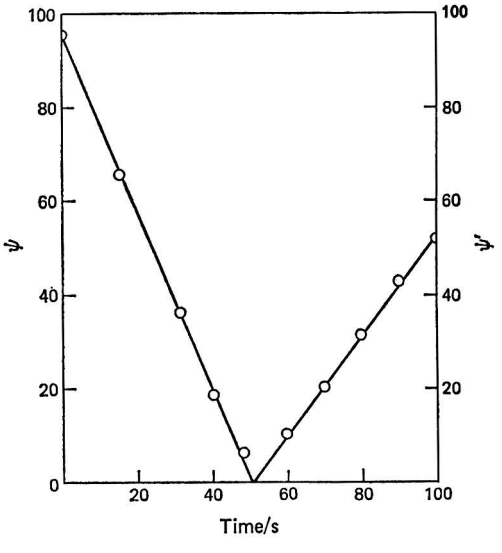

Fig. 2. Graphs resulting from Gran's theory for ψ *versus* time and ψ' *versus* time for the coulometric titration of 50 ml of 10^{-5} N sulphuric acid. The current was 1 mA

A typical titration graph for a rain-water sample is shown in Fig. 3. The experimental results are shown in Table I. From the intercept of line 1 the concentration due to strong acids is calculated; the intercept of line 2, obtained in alkaline solution, gives the sum of

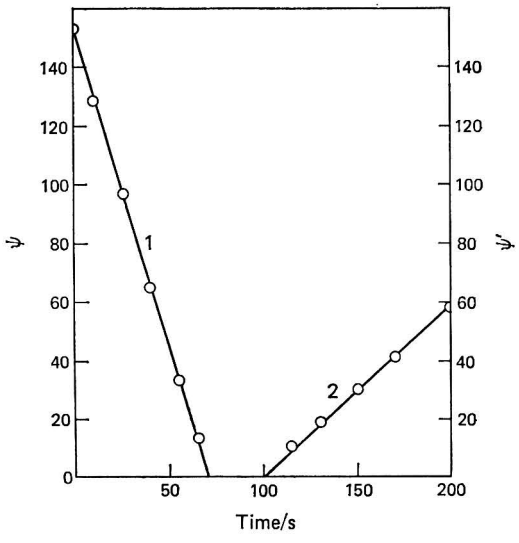

Fig. 3. Use of graphs resulting from Gran's theory for ψ *versus* time (line 1) and ψ' *versus* time (line 2) for the detection of the end-point of the coulometric titration of a rain-water sample

the concentrations due to strong and non-volatile weak acids. The difference between the two intercepts indicates the content of non-volatile weak acids in the sample. To evaluate the reproducibility of this method a large rain-water sample with a pH of 4·92 was taken and ten 50-ml sub-samples were analysed. The average strong acid concentration was 46 μg per 50 ml, expressed as sulphuric acid. The relative standard deviation was ± 5 per cent., $[H]_o$ being about 10^{-5} M.

TABLE I

TITRATION OF A 50-ml RAIN-WATER SAMPLE

Potassium bromide added, 120 mg; temperature, 25 °C; current, 1 mA; $2{\cdot}3RT/F = 59{\cdot}15$ mV

Time/s	Potential/mV	$\psi = 10^{E/59{\cdot}15}$	$\psi' = 10^{-E/59{\cdot}15}$
0	129·2	153·0	—
10	124·7	128·6	—
25	117·5	96·8	—
40	107·1	64·8	—
55	90·0	33·2	—
65	67·0	13·6	—
115	−60·1	—	10·4
130	−75·9	—	19·2
150	−87·7	—	30·4
170	−95·4	—	41·0
200	−104·3	—	58·0

Results: $[H]_o = 1{\cdot}47 \times 10^{-5}$ M (strong acidity).
$[H]_o' = 2{\cdot}03 \times 10^{-5}$ M (strong and weak non-volatile acidity).
$[H]_o' - [H]_o = 0{\cdot}56 \times 10^{-5}$ M (weak non-volatile acidity).

Regarding the accuracy of the determination, the standard error, determined from the coulometric titration of seven solutions containing the same amounts of sulphuric acid (100 μg in 50 ml), was 1·7 μg.

The lowest concentration of strong acid detectable in a sample is about 0·1 μg ml^{-1}, corresponding to a 10^{-6} M sulphuric acid solution. Below this value the change in hydrogen-ion concentration at the equivalence point is so small as to prevent any evaluation of the end-point.

Conclusions

The coulometric method yields satisfactory and reliable results for the determination of the acidity of atmospheric precipitations, this acidity being caused by the presence of strong and weak non-volatile acids. It is necessary only to set weak volatile acids free before the titration. The method can also be used for the titration of any very dilute acid solution with a high degree of accuracy; specifically, it could be applied to the titration of aqueous extracts of airborne particulate matter.

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A Kinetic Method for the Determination of Arsenic(III), Antimony(III) and Ascorbic Acid

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A simple and rapid method is described for the determination of arsenic(III) over a wide concentration range down to 0·005 p.p.m. in 20 ml of solution. The technique, which was also applied to the determination of antimony(III) and ascorbic acid, compares favourably with other titrimetric and coulometric methods for these determinations.

NUMEROUS papers have described the determination of arsenic(III), antimony(III) and ascorbic acid by reaction with one of a number of oxidising agents. The methods that have been proposed include many titration techniques in which the addition of titrant may be volumetric or by coulometric generation, and the end-point of the titration is detected by visual, potentiometric, amperometric or spectrophotometric methods. A number of such methods involve bromine as the oxidising agent, generated either coulometrically[1,2] or by the reaction of bromate with bromide ions.[3]

A simple and novel kinetically controlled method has been proposed by Burgess and Latham[4] for the determination of phenol and substituted phenols. In their method, bromine is generated homogeneously at a controlled rate by the reaction of bromate with bromide in acidic solution—

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad .. \quad .. \quad .. \quad (1)$$

The rate of this reaction is given by the well established rate law[3,5–7]—

$$+\frac{d[Br_2]}{dt} = k_4[BrO_3^-][Br^-][H^+]^2 \quad .. \quad .. \quad .. \quad (2)$$

where the value of the fourth-order rate constant, k_4, which is dependent on the ionic strength (μ) of the solution,[5,7] has a value of 489 l^3 mol^{-3} min^{-1} at 25 °C and $\mu = 1$ M (Tuladhar and Ottaway, unpublished work). The bromine generated reacts with the phenol and completion of the monobromination of the phenols is indicated by the bleaching of methyl orange, which is used as an indicator. The time taken for bleaching to take place is proportional to the initial concentration of phenol.

This procedure is equally applicable to the determination of other suitable reducing agents that react very slowly with bromate but rapidly with bromine, and as a further illustration of the technique, this paper reports the determination of arsenic(III), antimony(III) and ascorbic acid. The procedure is analogous to a coulometric titration procedure except that the rate of generation of bromine is controlled by suitable selection of the concentrations of bromate, bromide and hydrogen ions instead of the current. The general possibilities afforded by this technique have been investigated, in particular with respect to the sensitivity that may be attained, and the advantages and disadvantages of the technique compared with the other common titration procedures are discussed.

EXPERIMENTAL

REAGENTS—

Analytical-reagent grade chemicals were used throughout.

Bromate - bromide solution—The required weights of potassium bromate and potassium bromide were dissolved in distilled water to give a solution 0·1 M in potassium bromate and 0·2 M in potassium bromide.

Arsenic(III) solution, 0·02 M—After drying the appropriate amount of arsenic(III) oxide at 110 °C for 2 hours, it was dissolved in the minimum volume of sodium hydroxide solution, and the resulting solution neutralised with dilute sulphuric acid before dilution to volume.

The other solutions, 0·3045 M sulphuric acid, 0·01 per cent. methyl orange, 0·02 M potassium antimony(III) tartrate and 0·02 M ascorbic acid, were prepared by dissolving the appropriate amounts of the reagents in water.

PROCEDURES—

Visual method—As will be explained, the method can be applied to a wide range of reductant concentrations. For routine analysis it is convenient to avoid long time intervals and to ensure that, for any particular concentration range, the reaction times are of the order of 2 to 10 minutes. This can be easily accommodated by selection of the appropriate working conditions with respect to the concentrations of bromate, bromide and hydrogen ions. The conditions (A to F) found convenient for various concentration ranges of arsenic(III) are shown in Table I and the procedure is then as given below.

Dilute the stock solutions of sulphuric acid, methyl orange and bromate - bromide to the levels given in Table I. Transfer by pipette sulphuric acid (10 ml), methyl orange (10 ml) and a suitable aliquot of the stock or unknown arsenic(III) solution into a 100-ml calibrated flask and dilute to the mark with distilled water. Transfer 10 ml of this solution, again by pipette, into a clean, dry boiling-tube and similarly add 10 ml of the appropriate bromate - bromide solution to a second tube, placing both tubes in a temperature-controlled water-bath at 25·00 ± 0·05 °C for 30 minutes. Then mix the contents of the tubes thoroughly by transferring the mixture from one tube to the other three times and simultaneously start a stop-watch. For visual determinations, place the tube containing the reaction mixture back in the water-bath over a white tile and measure the time taken for the colour of the indicator to disappear completely. In a blank experiment with arsenic absent, determine the time taken to decolorise the indicator itself. This varies from 6 s with conditions A to 27 s with conditions C. Subtract this time from the observed reaction times.

For conditions F, a melting ice bath was used to maintain the temperature near 0 °C. The procedure did not then require the use of a thermostat but a higher concentration of the bromate - bromide solution was required in order to compensate for the lower rate of reaction (1) at this temperature. For calibration purposes the above procedure was found to be most convenient, but when using unknown arsenic solutions it was more convenient to add the arsenic directly to the final reaction mixture in the first boiling-tube; this was easily arranged by a slight modification to the procedure.

TABLE I

WORKING CONDITIONS FOR THE DETERMINATION OF DIFFERENT CONCENTRATIONS OF ARSENIC(III)

Conditions	Arsenic(III) concentration range*/mol l^{-1}	Concentration of sulphuric acid stock solution/ mol l^{-1}	Concentration of methyl orange stock solution, per cent.	Bromate - bromide solution	
				Concentration of bromate/ mol l^{-1}	Concentration of bromide/ mol l^{-1}
A	1 to 7 × 10^{-4}	0·3045	0·005	0·02	0·04
B	2 to 12 × 10^{-5}	0·3045	0·002	0·01	0·02
C	0·4 to 2 × 10^{-5}	0·3045	0·002	0·005	0·01
D	0·8 to 4 × 10^{-6}	0·2030	0·002	0·005	0·01
E	2 to 10 × 10^{-7}	0·1015	0·001	0·005	0·01
F	0·8 to 4 × 10^{-6}	0·2030	0·002	0·02	0·02

* Concentrations in this instance only refer to the final reaction solution (20 ml).

Photometric method—At very low concentrations of arsenic(III), such as those under conditions E (Table I), the rate of generation of bromine had to be made quite slow and the indicator blank, even with a smaller concentration, therefore became much larger (127 s). The indicator was decolorised over a considerable time interval, making visual observation of the end-point difficult and imprecise. In this instance, photometric detection of the end-point was carried out by use of an Evans Electroselenium Limited photometric titration unit. The procedure followed was as described above except that one of the reaction tubes was replaced by a 40-ml titration cell that was supplied with the instrument. After mixing the solutions, the reaction mixture was placed in the titration cell, which was replaced in

the water-bath. When the indicator started to decolorise, the cell was removed from the bath, its exterior was dried rapidly with a tissue and it was then placed in position on the titrator unit. Measurements of the absorbance at three or four time intervals by using a 604 filter allowed the end-point (taken as the complete decolorisation of the methyl orange) to be located by normal extrapolation techniques.

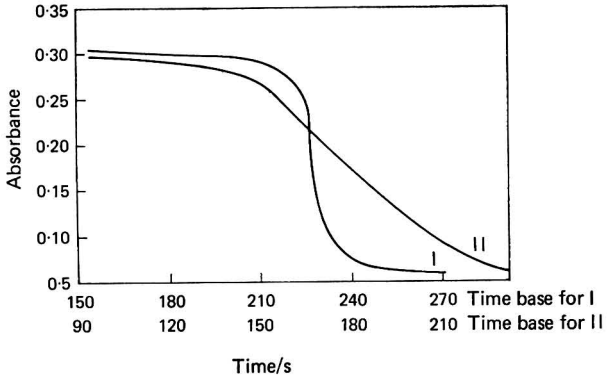

Fig. 1. Titration graphs for the determination of:
I, $0{\cdot}8 \times 10^{-4}$ M arsenic(III) with conditions B; and
II, 10×10^{-7} M arsenic(III) with conditions E

Two typical photometric titration graphs are shown in Fig. 1, and these show the increased indicator blank time with conditions E and the necessity of using the photometer for precise location of the end-point under these conditions. The error involved in using the solution on the titrator when the temperature is not thermostatically controlled is negligible, as the cell is only out of the bath for approximately 1 minute and should, in any event, be at a temperature near to room temperature. At the concentration level involved here the error from this source is insignificant.

It is, of course, possible to use any standard visible spectrophotometer in a similar way, and we have used a Unicam SP800 with a constant-temperature cell compartment and obtained comparable results.

Potentiometric method—Measurements of potential were made by using a platinum-wire electrode - saturated calomel reference electrode couple and a Pye Dynacap pH meter. After mixing the reaction solutions the electrodes were dipped into the mixture and the change in potential with time was observed.

Results and discussion

Some typical results obtained at different concentrations of arsenic(III) by using the various procedures and conditions specified in Table I are given in Table II. Linear calibration graphs of arsenic(III) concentrations against time were obtained in all instances. To ensure that linear calibration graphs are obtained it is essential that the rate of generation of bromine, given by equation (2), should be constant throughout the reaction. This condition is fulfilled provided the concentrations of bromate, bromide and hydrogen ions are in reasonable excess over the initial concentration of arsenic(III), so that there is a negligible consumption of bromate or hydrogen ions and negligible generation of additional bromide ions from the reduction of bromate.

The method was satisfactorily reproducible over a wide range of arsenic(III) concentrations, shown by the values for the rate of disappearance of reductant given in Tables II and III. The standard deviation of the results varied from 0·96 per cent. under conditions A and 0·90 per cent. under conditions C, to 19 per cent. under conditions E. These figures include all the results in each instance and therefore also include any variation from the blank determination. The limit of detection, defined as four times the standard deviation

TABLE II

TYPICAL RESULTS FOR THE DETERMINATION OF ARSENIC(III)

Concentration of arsenic(III)/ mol l^{-1}	Conditions	Indicator blank time/s	Analysis time/s	Average time/s	Rate of disappearance of arsenic(III)/ mol l^{-1} s^{-1}
7×10^{-4}	A	6	511, 512	511·5	$1·37 \times 10^{-6}$
4×10^{-4}	A	6	290, 290	290	$1·38 \times 10^{-6}$
2×10^{-4}	A	6	143, 144	143·5	$1·39 \times 10^{-6}$
1×10^{-4}	A	6	71, 72	71·5	$1·40 \times 10^{-6}$
8×10^{-5}	B	7	220, 221	220·5	$3·63 \times 10^{-7}$
6×10^{-5}	B	7	165, 165	165	$3·64 \times 10^{-7}$
4×10^{-5}	B	7	110, 111	110·5	$3·62 \times 10^{-7}$
2×10^{-5}	B	7	55, 56	55·5	$3·60 \times 10^{-7}$
$1·6 \times 10^{-5}$	C	27	163, 161	162	$9·88 \times 10^{-8}$
$1·2 \times 10^{-5}$	C	27	120, 122	121	$9·94 \times 10^{-8}$
8×10^{-6}	C	27	80, 81	80·5	$9·94 \times 10^{-8}$
4×10^{-6}	C	27	41, 39	40	$10·00 \times 10^{-8}$
$3·2 \times 10^{-6}$	D	61	64, 63	63·5	$5·04 \times 10^{-8}$
$2·4 \times 10^{-6}$	D	61	45, 46	45·5	$5·40 \times 10^{-8}$
$1·6 \times 10^{-6}$	D	61	32, 33	32·5	$4·92 \times 10^{-8}$
8×10^{-7}	D	61	17, 18	17·5	$5·75 \times 10^{-8}$
$1·25 \times 10^{-7}$	E	151·5	9·5, 9·0, 2·5, 10·5	8·0	$1·56 \times 10^{-8}$
$2·5 \times 10^{-7}$	E	151·5	13·5, 12·5, 16·5, 17·5	15·0	$1·67 \times 10^{-8}$
5×10^{-7}	E	151·5	23·5, 24·5 24·5, 24·5	24·5	$2·04 \times 10^{-8}$
10×10^{-7}	E	151·5	61·5, 62·5, 63·5, 62·5	62·5	$1·60 \times 10^{-8}$
$3·2 \times 10^{-6}$	F	38	61, 63, 64	62·5	$5·12 \times 10^{-8}$
$2·4 \times 10^{-6}$	F	38	50, 51, 48	49·5	$4·85 \times 10^{-8}$
$1·6 \times 10^{-6}$	F	38	37, 36, 35	36	$4·44 \times 10^{-8}$
8×10^{-7}	F	38	21, 22, 23	22	$4·58 \times 10^{-8}$

of the blank in the lowest concentration range, which was similar to the standard deviation of the results at any particular concentration in that range, was found to be 6×10^{-8} M or 0·005 p.p.m. of arsenic(III). As can be seen from the tables, the results are more reproducible at higher concentration levels. A melting ice bath (conditions F) can be used in the interests of simplicity, if desired, and the results are just as satisfactory (Table II).

Similarly reproducible results were obtained for antimony(III) and ascorbic acid and a few typical results are given in Table III. Solutions of both of these reagents deteriorate on

TABLE III

RESULTS FOR THE DETERMINATION OF ANTIMONY(III) AND ASCORBIC ACID

Concentration of reductant/ mol l^{-1}	Conditions	Indicator blank time/s	Analysis time/s	Average time/s	Rate of disappearance of reductant/ mol l^{-1} s^{-1}
Antimony(III)—					
4×10^{-5}	B	11	103, 103, 103	103	$3·88 \times 10^{-7}$
8×10^{-5}	B	11	206, 206, 206	206	$3·88 \times 10^{-7}$
12×10^{-5}	B	11	309, 309, 309	309	$3·88 \times 10^{-7}$
8×10^{-6}	C	54	74, 75, 76	75	$1·07 \times 10^{-7}$
16×10^{-6}	C	54	148, 149, 150	149	$1·07 \times 10^{-7}$
24×10^{-6}	C	54	225, 227, 226	226	$1·06 \times 10^{-7}$
Ascorbic acid—					
1×10^{-4}	A	5	73, 73, 73	73	$1·37 \times 10^{-6}$
2×10^{-4}	A	5	145, 146, 145·5	145·5	$1·37 \times 10^{-6}$
3×10^{-4}	A	5	220, 219, 219·5	219·5	$1·37 \times 10^{-6}$
4×10^{-5}	B	10	100, 100, 100	100	$4·00 \times 10^{-7}$
8×10^{-5}	B	10	203, 202, 202·5	202·5	$3·95 \times 10^{-7}$
12×10^{-5}	B	10	301, 300, 300·5	300·5	$3·99 \times 10^{-7}$

standing[8,9] and it is more convenient to use standard arsenic(III) solutions for calibration purposes. The method therefore appears to be generally applicable to all reducing agents that react with bromine and may have very wide applications.

Potentiometric indication of the end-point can be used instead of methyl orange and a typical graph of the reaction is shown in Fig. 2. The normal sharp break in the arsenic(III) - bromine titration graph[3] is obtained and this is a very good indication of the end-point. At low concentrations, the platinum electrode response in the presence of excess of arsenic(III) becomes sluggish and premature end-points might be expected in this form of continuous titration. Satisfactory results are still obtained, however, as the bromine generation in this instance is homogeneous and the electrode response is not therefore affected by local excesses of bromine, which normally impair the accuracy of volumetric or coulometric titrations.

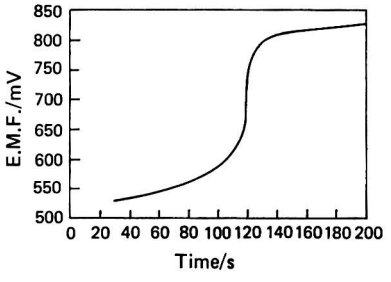

Fig. 2. Titration graph for the determination of $1{\cdot}6 \times 10^{-4}$ M arsenic(III) with potentiometric indication of the end-point. Conditions A, temperature 25 °C

For the indicator method to be satisfactory, it is essential that the generated bromine should react with arsenic(III) in preference to methyl orange. The reaction of arsenic(III) with bromine—

$$\text{As(III)} + \text{Br}_2 \xrightarrow{k_1} \text{As(V)} + 2\text{Br}^- \quad .. \quad .. \quad .. \quad (3)$$

is extremely fast and unpublished results by the present authors indicate that the second-order rate constant described by the rate law

$$-\frac{\text{d[As(III)]}}{\text{d}t} = k_1[\text{As(III)}][\text{Br}_2] \quad .. \quad .. \quad .. \quad (4)$$

has a value in excess of 10^{10} l mol^{-1} min^{-1}. The reaction of methyl orange with bromine has recently been studied[10] and has a rate law of the form

$$-\frac{\text{d[M]}}{\text{d}t} = \frac{k_2 K_m[\text{M}][\text{Br}_2]}{[\text{H}^+](1 + \text{K}[\text{Br}^-])} \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where K_m is the ionisation constant of methyl orange and K the formation constant of the tribromide ion, Br_3^-. The effective second-order rate constant, k_2', for this reaction, given by $k_2K_m[H^+](1 + K[Br^-])$, has a value of the order of 3×10^5 l mol^{-1} min^{-1} for the conditions used here, *i.e.*, 0·03 M with respect to sulphuric acid and 0·01 M with respect to bromide. The methyl orange reaction is therefore significantly slower than the arsenic(III) reaction and fulfils the above condition. As the active bromine concentration in both equations (4) and (5) will be the same steady-state concentration, dependent on the rate of generation by reaction (1) and the rate of consumption by reaction with arsenic and methyl orange or arsenic alone, the general condition for the satisfactory application of methyl orange as an indicator will be that

$$k_1[\text{As(III)}] \gg k_2'[\text{M}]$$

or, for any reductant, Red,

$$k_1[\text{Red}] \gg k_2'[\text{M}]$$

Provided that k_1 is much greater than k_2', the concentration terms in these equations will be relatively unimportant, as in the present instance, but if k_1 is not much greater than k_2',

or if k_1 is only one or two orders greater than k_2', then difficulties will be encountered with premature bleaching of the methyl orange as the concentration of arsenic(III) or other reductant is reduced towards the end of the reaction. No premature bleaching was noticed in the determination of either arsenic(III) or antimony(III) at any concentration level, indicating that in these cases k_1 is much greater than k_2', but some curvature of the initial, flat part of the photometric titration graph was obtained at lower concentrations of ascorbic acid, indicating that in this instance k_1 is not very much greater than k_2'. In principle, the sensitivity of the method would be limited by these considerations alone, but in practice it is limited by these and by the ability to detect accurately the disappearance of the colour due to methyl orange by visual or photometric means.

The direct titration of arsenic(III) or antimony(III) with potassium bromate in an acidified bromide medium can be carried out with high precision.[3] However, difficulties are encountered at low concentration levels with either visual or potentiometric indication of the end-point. Most bromometric indicators are to a greater or lesser extent irreversible, and attacks on the indicator by local excesses of bromine titrant formed during the adding - mixing process will become very serious at low levels of titrand concentration; indicator blanks will also become much more significant. Potentiometric indication methods will become very tedious at low arsenic(III) or antimony(III) concentrations as the reaction of either of these systems at a platinum electrode is very slow. Also, the electrode responds to small amounts of bromine formed momentarily in the solution, giving high potentials. The electrode takes a long time to reach its equilibrium value for points before the end-point under these conditions and the titration may take well in excess of 30 minutes. Coulometric generation with either of these methods of end-point detection suffers from the same disadvantage and would almost certainly have to be discontinuous if precise results were required at low concentrations. Clearly the kinetic method, which provides homogeneous generation of bromine titrant, is advantageous, particularly at the lower concentration levels, and needs no stirring apart from the initial mixing of the reactant solutions. Thus, the method is rapid, determinations can be accomplished in any selected time at any concentration level, and it is very cheap to carry out as virtually no apparatus, except a stop-watch and thermostat, is required.

In this paper the sensitivity of the technique has been established, and with a limit of 0·005 p.p.m. of arsenic(III), it compares favourably with many trace techniques for arsenic determinations. The same is true for antimony. The method is non-selective with respect to reducing agents that react with bromine, and in this sense it is analogous to volumetric and coulometric titration methods. In many analytical applications this may be considered no great disadvantage.

We wish to thank the Principal and the Head of the Chemistry Department of the Stow College of Engineering, Glasgow, for providing the facilities with which part of this work was carried out.

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A Field Test for the Determination of Some Ketone Vapours in Air

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A field test is described for the determination in air of those ketones most commonly used industrially, in concentrations up to twice their current threshold limit values. The vapour, the nature of which must be known, is collected in water and the solution allowed to react with acidic 2,4-dinitrophenylhydrazine solution. The addition of methanolic potassium hydroxide results in the formation of a red coloration, which is compared visually with standards after 10 minutes. A common series of standards is used for all the ketones, the volume of absorbent used and the size of sample taken being dependent on the identity of the ketone present in the atmosphere. Both the apparatus and method used are simple and the time required for a complete determination is between 25 and 50 minutes.

KETONES are used widely in industry as solvents and chemical intermediates. Although not normally considered toxic, their vapours can have a strong irritant and narcotic effect on man and in some instances can form flammable and explosive mixtures with air. A simple field test was required to determine the concentrations in air of the most commonly used ketones at about their threshold limit values,[1] the current values of which are given in Table I. The wide range of values covered precluded the development of a single test to cover all the ketones satisfactorily and it was decided to devise specific tests for as many as possible and a general test for the remainder. Specific tests developed for propan-2-one (acetone),[2] 3,5,5-trimethylcyclohex-2-en-1-one (isophorone),[3] cyclohexanone and commercial methylcyclohexanone[4] have been described previously. A test for butan-2-one (ethyl methyl ketone), described by Böhme and Eichler[5] and based on its conversion into dimethylglyoxime, which was detected with nickel ions, was investigated but found to be unsuitable for field use without considerable modification.

TABLE I

VOLUMES OF POTASSIUM DICHROMATE, COPPER(II) SULPHATE AND COBALT(II) SULPHATE SOLUTIONS REQUIRED PER 100 ml TO PRODUCE KETONE FIELD TEST COLOUR STANDARDS

Standard	Blank	A	B	C
Yellow component/ml	4·0	4·0	3·6	2·0
Blue component/ml	3·8	4·4	6·0	0·2
Red component/ml	3·0	6·0	13·6	48·0

The standards A, B and C represent the following concentrations (p.p.m.) of ketone vapour in air when sampled and determined as described—

Ketone	Concentration of ketone, p.p.m. A	B*	C
Propan-2-one	500	1000	2000
Butan-2-one	100	200	400
4-Methylpentan-2-one	50	100	200
4-Hydroxy-4-methylpentan-2-one	25	50	100
4-Methylpent-3-en-2-one	12·5	25	50
Cyclohexanone	25	50	100
Methylcyclohexanone	50	100	200

* The B standard corresponds to the current threshold limit values.[1]

Earlier work in this laboratory resulted in the development of a modified method[2] based on 2,4-dinitrophenylhydrazine reagent for the determination of carbonyl compounds. Further experiments with solutions of ketones suggested that this method could be used as a basis for a general test for ketones.

Experimental

Preparation and calibration of standard atmospheres—

Atmospheres containing known concentrations of the various ketones were required so as to assess the efficiency of the sampling technique and for use in the development of the field test. With the exception of propan-2-one and 4-hydroxy-4-methylpentan-2-one (diacetone alcohol), these were prepared by using the permeation technique devised in this laboratory.[3,4,6]

Propan-2-one and 4-hydroxy-4-methylpentan-2-one—Atmospheres of these two ketones were prepared by an injection - atomisation technique similar to that described elsewhere.[2] With 4-hydroxy-4-methylpentan-2-one some difficulty was experienced in obtaining stable atmospheres at the higher levels as complete volatilisation was not taking place at the injection rate required. This problem was overcome by placing a heating coil round the atomiser to prevent condensation of the liquid.[7]

Calibration—The atmospheric concentrations thus obtained were checked by quantitatively absorbing the vapour in a suitable solvent, usually water, and determining the ketone content by an iodimetric method.

Colorimetric determination of ketones—

For field work, controlled-temperature reactions are to be avoided when possible. The modified 2,4-dinitrophenylhydrazine method[2] was investigated for possible use at ambient temperatures, 22 °C being chosen as an arbitrary reference temperature. Calibration graphs for each of the ketones under consideration were plotted in the range 0 to 250 $\mu g\ ml^{-1}$, at this temperature, by using solutions prepared by diluting with water aliquots of stock solutions made up with water, methanol or methanol - water as necessary. The sensitivity was found to be generally lower and more temperature dependent than that of the normal reaction temperature of 50 °C. The response for each ketone was different, being highest for propan-2-one and lowest for 3,5,5-trimethylcyclohex-2-en-1-one. Temperature had a significant effect above 30 °C and below 15 °C, and in any field test it would be necessary to specify limits between which the reaction should be carried out. Colour development was not affected by temperature.

As the final colour obtained with each ketone appeared to be similar, it seemed reasonable to assume that a sampling scheme might be devised whereby the same optical density was obtained for all the ketones at each of their respective half, one and two threshold limit value concentrations.

An optical density of 0·200 measured against the reagent blank was chosen as reasonable for atmospheric concentrations at the threshold limit value and was obtainable with all the ketones except 3,5,5-trimethylcyclohex-2-en-1-one, which, under the proposed test conditions, reached a maximum optical density of 0·090 at a concentration of about 200 $\mu g\ ml^{-1}$. As a specific test was already available for this particular ketone,[3] it could, if necessary, be eliminated from the general test.

The colours obtained with solutions of each ketone at a concentration necessary to give an optical density of 0·200 were compared visually and found to be similar, as were the spectra obtained with these solutions when plotted on a recording spectrophotometer over the range 400 to 650 nm. The final colour was unstable, slowly becoming more yellow. However, for field work, no significant errors should occur provided comparison with standards is carried out within a reasonable time.

Reliability of reagents—

A comparison was made of 2,4-dinitrophenylhydrazine and methanol from various manufacturers and of different batches from the same manufacturer. Negligible differences were noted for 2,4-dinitrophenylhydrazine. Widely differing blanks were found with samples of unpurified methanol from various manufacturers and often with different batches from the same manufacturer. Some grades, however, did give blanks of the same order as that of the purified material. It would be necessary, therefore, to specify the highest tolerable blank in order that unpurified methanol could be used if possible.

COLLECTION OF KETONES—

Of the ketones initially under investigation 5-methylheptan-3-one (threshold limit value 25 p.p.m. v/v) was known to be the least soluble in water and consequently it was chosen for preliminary work on collection efficiency. Samples of an atmosphere (concentration 260 mg m^{-3}) were collected in three absorbers in series each containing 5 ml of water. Equal amounts, approximately 10 per cent. of the theoretical atmosphere, were collected in each absorber. Variation of the sampling rate, in the range 50 to 500 ml min^{-1}, and of the volume of water used for collection made little difference to the results obtained. Also, no improvement in collection efficiency was apparent when different types of inlet tube were used. Of a variety of other solvents tried, dioxan, ethylene glycol, methanol and dimethyl sulphoxide, all ensured the collection of more than 85 per cent. of the theoretical atmosphere in a single bubbler. Both dioxan and ethylene glycol were rejected as unsuitable, the former giving an exceptionally high blank. The latter was too viscous for accurate volume measurements and addition of water to reduce its viscosity markedly reduced the collection efficiency. Use of methanol was to be avoided if possible because of evaporation during the sampling period and the known difficulty in obtaining material with a low and constant blank. Under the proposed field test conditions, with reaction restricted to that at room temperature, it was found that the responses of all the ketones in dimethyl sulphoxide were greatly reduced and for 5-methylheptan-3-one a maximum optical density of 0·125 was reached at a concentration of about 250 μg ml^{-1}.

As 5-methylheptan-3-one has relatively little use in industry compared with the other ketones under consideration, it was decided that it could, if necessary, be excluded from the general field test scheme. Then, possibly, water could be used as the collecting agent for the other ketones under study.

Samples of standard atmospheres of the various ketones at levels approximately equal to twice their current threshold limit values were each collected, at 22 °C, in a single absorber containing the appropriate volumes of water, as shown in Table II. Virtually 100 per cent. absorption was achieved with propan-2-one, 4-hydroxy-4-methylpentan-2-one, cyclohexanone and 3-methylcyclohexanone; about 95 per cent. with butan-2-one; 80 per cent. with 4-methylpent-3-en-2-one (mesityl oxide) and 70 per cent. with 4-methylpentan-2-one (isobutyl methyl ketone). Over the temperature range 5 to 45 °C, the temperature had a negligible effect on collection efficiency except with 4-methylpentan-2-one. With the latter, efficiency decreased with increasing temperature; up to about 35 °C the effect was well within the acceptable field test tolerance of one quarter of the threshold limit value. In the final test an upper temperature limit for collection of 30 °C was selected.

TABLE II

SAMPLING CONDITIONS FOR THE DETERMINATION OF VARIOUS KETONES BY THE PROPOSED FIELD METHOD

Ketone	Volume of water in absorption tube/ml	Air sample volume/ml	Collection time at 125 ml min^{-1}/minutes
Propan-2-one	25	125	1
Butan-2-one	20	625	5
4-Methylpentan-2-one	5	750	6
4-Hydroxy-4-methylpentan-2-one ..	5	1625	13
4-Methylpent-3-en-2-one	5	1375	11
Cyclohexanone	15	1125	9
Methylcyclohexanone	15	500	4

SAMPLING SCHEME—

The proposed test envisaged the use of different volumes of collecting agent and sample to give the same optical density regardless of the ketone being determined. For convenience it was desirable to use the same collection vessel, solvent and sampling rate for all the ketones. The all-glass absorber shown in Fig. 1, which would accommodate liquid volumes of 2 to 25 ml, was considered suitable with water as collecting agent. A sampling rate of 125 ml min^{-1} was chosen because this rate could be obtained by using a rubber bulb hand aspirator.

With the widely different sensitivities of the ketones to the test, it was apparent that some compromise would be necessary in respect of the volume of absorbent used and the sample taken. The sampling time at the fixed rate should preferably be to the nearest minute and not too long. There should also be as few different volumes of absorbent as possible, and each should be capable of measurement with a readily obtainable pipette. The scheme finally adopted, which is given in Table II, was devised as follows: if T μg l^{-1} is the threshold limit value of the ketone, V ml is the volume of absorbent, E per cent. is the collection efficiency and X μg ml^{-1} is the concentration of the ketone in the final reaction solution, which gives an optical density of 0·200, then the volume of the sample required is $\frac{X \times V \times 100}{TE}$ litres.

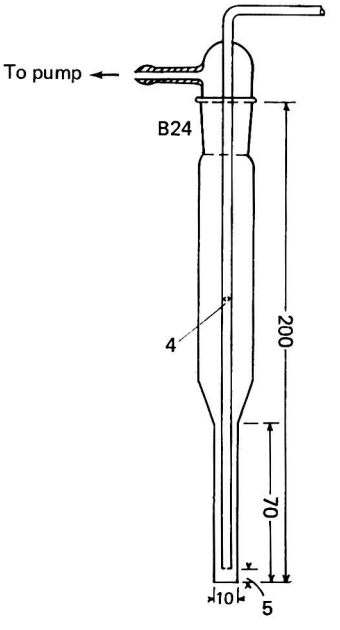

Fig. 1. All-glass absorber (all measurements are in millimetres)

To check the validity of the sampling scheme, samples of standard atmospheres of each of the various ketones were taken by the proposed field method and a graph plotted of the optical density of the final test solution against the current threshold limit value of the appropriate ketone. For completeness, 5-methylheptan-3-one was included, but with methanol free from carbonyl compounds as the collecting agent. 3,5,5-Trimethylcyclohex-2-en-1-one could not be included because, although sensitivity to the test was increased by using methanol as solvent, the calibration graph was non-linear and the optical density reached a maximum value below that required for an atmosphere of twice the threshold limit value. The graph (Fig. 2), which for clarity includes only a selection of the results obtained, showed the proposed method to be capable of estimating the concentrations of the atmospheres of the various ketones to within the acceptable field test limit of one quarter of their respective threshold limit values.

PREPARATION OF COLOUR STANDARDS—

Aqueous solutions of acetone were used for the preparation of colour standards. Solutions of concentration sufficient to give optical densities of 0·100, 0·200 and 0·400 with respect to the reagent blank were allowed to react with 2,4-dinitrophenylhydrazine reagent prepared

from the purified methanol and the colours obtained were matched with mixtures of solutions of inorganic salts. Good visual differentiation between the prepared standards was possible when viewed through 50 mm of the liquid. Details of the preparation of these colour standards are given later.

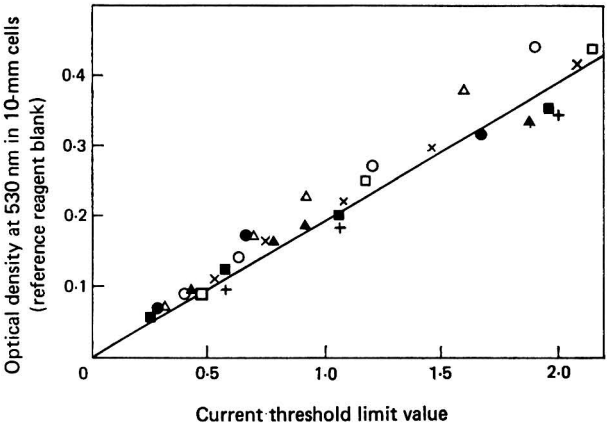

Fig. 2. Relationship between the optical density of the 2,4-dinitrophenylhydrazine complexes formed and the current threshold limit values[1] of ketones when atmospheres were sampled by the proposed field test procedure: ×, propan-2-one; ○, butan-2-one; □, 4-methylpentan-2-one; △, 4-hydroxy-4-methylpentan-2-one; +, 4-methylpent-3-en-2-one; ●, cyclohexanone; ■, 3-methylcyclohexanone; and ▲, 5-methylheptan-3-one

As mentioned above, the reagent blank could vary considerably, depending on the methanol used for preparing the 2,4-dinitrophenylhydrazine reagent. It was decided that an over-estimation not greater than one quarter of a threshold limit value was permissible, which would be equivalent to an optical density of 0·050. Because the average optical density of a reagent blank, with purified methanol, was about 0·07 with respect to water, the blank standard was produced with an optical density of 0·100 with respect to water. The blank standard is intended as a guide to selecting methanol suitable for use in the test; its use as a zero standard could result in the under-estimation of concentrations below one half of a threshold limit value.

Results obtained when ketone atmospheres of known concentrations were sampled by the proposed field test, and the levels assessed by the colour standards, are given in Table III.

To simulate industrial conditions the test was checked in the laboratory by using static atmospheres of each of butan-2-one and methylcyclohexanone (Sextone B). Parallel samples of the generated atmosphere were taken from a single sampling point by the proposed field test and by collection in water for analysis by the iodoform method. The results obtained are given in Table IV.

INTERFERENCES—

The effect of possible interference with the proposed field test by substances likely either to be used with ketones or to react in a similar way was examined. Solutions of these compounds were prepared with water or methanol free from carbonyl compounds and 1 ml of each solution, which was treated by the proposed field method, was compared with the blank colour standard. Initially these solutions were of a concentration ($\mu g\ ml^{-1}$) equivalent to ten times the threshold limit value of the compound under consideration (*e.g.*, if the threshold limit value is $x\ \mu g\ l^{-1}$, the test solution would contain $10x\ \mu g\ ml^{-1}$). When a red coloration was observed, the concentration of the solution was successively reduced to a level at which the coloration was no longer discernible. Of the compounds studied, which included hydrocarbons, alcohols, aldehydes, halogenated hydrocarbons, esters and ethers, only aldehydes

TABLE III

ESTIMATION BY THE PROPOSED FIELD TEST PROCEDURE OF THE CONCENTRATION OF STANDARD KETONE ATMOSPHERES

Ketone	Ketone concentration, p.p.m. v/v: Actual	Found by field test
Propan-2-one	517	500+*
	750	500 to 1000
	980	1000
	1083	1000+
	1183	1000 to 2000
	2040	2000+
Butan-2-one	73	100—
	88	100—
	125	100+
	247	200+
	389	400+
4-Methylpentan-2-one	45	0 to 50
	61	50+
	117	100+
	183	200—
	214	200+
4-Hydroxy-4-methylpentan-2-one	16	0 to 25
	33	50—
	38	50—
	49	50+
	79	100—
	130	>100
4-Methylpent-3-en-2-one	11	0 to 12·5
	14	12·5—
	25	25—
	27	25
	50	50—
Cyclohexanone	15	0 to 25
	20	25—
	35	25 to 50
	52	50+
	84	50 to 100
	139	>100
3-Methylcyclohexanone	27	0+
	56	50+
	105	100
	195	200—
	276	>200

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

showed any positive interference, the extent of which would depend on the ketone for which the test was being carried out. The concentrations at which the first discernible red coloration was observed were 3 and 90 μg ml^{-1} for formaldehyde and acetaldehyde, respectively. Table V shows the concentration of these aldehydes necessary to produce a positive interference if present with the ketone for which the test is being carried out. These concentrations are generally well above the current threshold limit values for the aldehydes and they would themselves therefore constitute hazards. The relative humidity in the range 18 to 78 per cent. at 25 °C was found to have no apparent effect on the method.

TABLE IV

COMPARISON OF THE RESULTS OF ANALYSIS OF BUTAN-2-ONE AND METHYLCYCLOHEXANONE ATMOSPHERES BY THE PROPOSED FIELD TEST AND IODOFORM METHOD

Ketone	Ketone concentration found, p.p.m. v/v: By iodoform method	Estimated by field test
Butan-2-one	16	0
	47	0 to 100
	62	0 to 100
	170	200—*
	290	200 to 400
	340	400
Methylcyclohexanone (Sextone B)	26	0
	39	0 to 50
	56	50+
	79	100—
	112	100 to 200
	131	100 to 200

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

TABLE V

EFFECT ON THE PROPOSED TEST OF FORMALDEHYDE OR ACETALDEHYDE PRESENT IN ATMOSPHERE BEING SAMPLED

Ketone sampled	Concentration of co-contaminant to give first discernible red coloration, p.p.m. v/v*	
	Formaldehyde (2 p.p.m.)†	Acetaldehyde (200 p.p.m.)†
Propan-2-one	400	10000
Butan-2-one	63	1600
4-Methylpentan-2-one	13	333
4-Hydroxy-4-methylpentan-2-one	6	153
4-Methylpent-3-en-2-one	7	183
Cyclohexanone	27	666
Methylcyclohexanone	60	944

* Assuming 100 per cent. absorption in trapping agent.
† Current threshold limit value.[1]

PROPOSED FIELD METHOD FOR THE DETERMINATION OF KETONE VAPOURS IN AIR

The method can be used for the determination of any one of the following seven ketones: propan-2-one, butan-2-one, 4-methylpentan-2-one, 4-hydroxy-4-methylpentan-2-one, 4-methylpent-3-en-2-one, cyclohexanone and methylcyclohexanone. The identity of the ketone must be known before applying the test.

APPARATUS—

All-glass absorber—Of the shape and dimensions shown in Fig. 1.

Sampling pump—Capable of drawing air through the apparatus at the rate of 125 ml min^{-1}.

Flow meter—Capable of measuring a flow-rate of 125 $\pm$ 5 ml min^{-1}.

Control valve—Suitable for control at a flow-rate of 125 $\pm$ 5 ml min^{-1}.

Reaction tubes—Glass test-tubes (approximate volume 20 ml) fitted with a ground-glass stopper.

Glass comparator tubes—Optically matched, approximately 10 mm i.d., calibrated with a mark at 50 mm.

NOTE—

The pump, flow meter and valve can be replaced by a suitable aspirator bulb for sample volumes of up to 500 ml.

REAGENTS—

For this test it is essential that the methanol used for the preparation of the 2,4-dinitrophenylhydrazine reagent should be free from carbonyl compounds. When the test is carried out as given under Procedure, but with 1 ml of distilled or de-ionised water instead of the ketone solution, the colour obtained should not be more intense than that of the blank standard (see preparation of colour standards, Table I). A few commercially available methanols (*e.g.*, some spectrographic and other high purity grades) have been found to conform to this requirement, but a method of preparing suitable material is given below.

All other reagents should be of analytical-reagent grade.

Methanol, free from carbonyl compounds—Using all-glass apparatus, reflux 1 litre of methanol with 5 g of 2,4-dinitrophenylhydrazine and 5 drops of concentrated hydrochloric acid for 2 hours. Distil the methanol twice, rejecting the first 100 ml and final 150 ml of distillate from each distillation. The purified methanol can be used for about 2 weeks if stored in a well stoppered, dark glass bottle.

2,4-Dinitrophenylhydrazine reagent—Dissolve 0·10 g of 2,4-dinitrophenylhydrazine in about 75 ml of the above methanol containing 0·40 ml of hydrochloric acid (sp. gr. 1·18) and dilute to 100 ml with the methanol. Prepare fresh daily.

Potassium hydroxide solution—Dissolve 100 g of potassium hydroxide in 200 ml of distilled or de-ionised water, cool and dilute to 1 litre with methanol. (The use of the purified material is unnecessary.)

This reagent can be used for several weeks if stored in a well fitting screw-topped polythene bottle.

NOTE—

All reagents and the distilled or de-ionised water used for collection of samples should be stored and dispensed in a ketone-free atmosphere. In the interests of safety, pipette fillers should be used to dispense the reagents used in this test.

PROCEDURE—

Transfer with a pipette the volume of water, as indicated in Table II for the appropriate ketone, into the absorption tube. Insert the inlet tube and connect it to the aspiration assembly. Transfer the apparatus to the sampling site and collect the required volume of sample (see Table II) at the rate of 125 ± 5 ml min^{-1}. During the sampling period the temperature should not exceed 30 °C (see Note 1). Transfer the apparatus to a ketone-free atmosphere, remove the inlet tube and, with a pipette, transfer 1 ml of the ketone solution to the reaction tube. Add 1 ml of the 2,4-dinitrophenylhydrazine reagent, stopper the tube and mix the solutions by gentle swirling. Allow the solution to stand at a temperature of between 18 and 25 °C (see Note 1) for $10 \pm 0{\cdot}5$ minutes, then add 5 ml of the potassium hydroxide reagent (see Note 2), replace the stopper and mix the contents of the tube by inverting it several times. After about 8 minutes, transfer the solution into a comparator tube up to the calibration mark and, 10 minutes (see Note 3) after addition of the potassium hydroxide reagent, compare the colour of the solution with that of the colour standards (contained in similar tubes) by viewing through the depth (50 mm) of the liquids in daylight against a white background.

NOTES—

1. Except in extreme temperature conditions, the permissible range can normally be maintained by placing the absorbers or reaction tubes in water previously adjusted to about 22 °C.

2. The addition of potassium hydroxide reagent results initially in the formation of a dense black precipitate that slowly dissolves to give a clear solution.

3. The red coloration is unstable and slowly changes to yellow. Comparison with standards must be completed within 1 minute.

PREPARATION OF COLOUR STANDARDS—

Yellow component—Dissolve 3·00 g of potassium dichromate in water and dilute to 1 litre.

Blue component—Dissolve 300 g of copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$) in water, add 25 ml of concentrated hydrochloric acid (sp. gr. 1·18) and dilute to 1 litre.

Red component—Dissolve 300 g of cobalt(II) sulphate heptahydrate ($CoSO_4.7H_2O$) in 850 ml of water.

Prepare the colour standards by mixing these solutions in the proportions shown in Table I, diluting each to 100 ml with water and mixing thoroughly. As an alternative to the above colour standards a series of permanent glass standards in a comparator disc is available from Tintometer Ltd.

DISCUSSION AND APPLICATION OF METHOD

The method described has been developed for use as a field test and is not intended for the accurate determination of ketones or as a means of identification; in fact, the test is based on the assumption that the identity of the ketone is known. The test can be extended to include other carbonyl compounds provided an atmosphere of known concentration is available to determine the collection efficiency of the absorbent. From a calibration graph plotted at 22 °C, the temperature at which the colour standards were prepared, the concentration required to give an optical density of 0·200 with respect to the reagent blank can be found. The sample required can be calculated as described above.

Assessment of the proposed method has been carried out under field conditions at industrial sites where butan-2-one is used in large amounts together with toluene and Cellosolve acetate or with propan-2-ol. Parallel samples of the contaminated atmospheres were taken by the field method and by collection in water for analysis by the iodimetric method. Good agreement was obtained between the results.

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

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Quantitative Determination of the Pungent Principle (Capsaicin) of Ceylon Chillies (*Capsicum* Species)

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There is a remarkable variation in the pungency of different varieties of capsicum and this investigation describes a method for the determination of the total capsaicin content in the fruits of *Capsicum* species. The extraction procedure is based on a method by which phenolic interference is reduced to a minimum by selective solubility. During the various stages of extraction, before any extract is rejected, thin-layer chromatography is used as a monitoring device. The spectrophotometric determination of the total capsaicin content is based on the colour reaction of capsaicin with tungstophosphoric acid - molybdophosphoric acid reagent. The relative concentrations of capsaicin (milligrams per 100 g dry weight) in different varieties of capsicum are calculated by reference to a calibration graph.

Many methods for the colorimetric determination of capsaicin are recorded in the literature. In 1931 Fodor[1] developed a method in which capsaicin gave a blue colour with vanadyl(V) chloride. Schulte and Kruger[2] developed a method based on the reaction of diazobenzenesulphonic acid with the phenolic group, which gave rise to a red colour. Karawya, Balbaa, Girgis and Youssef[3] used the same colour reaction for the determination of capsaicin in capsicum fruits by thin-layer chromatographic techniques while the Folin - Denis reagent was used by North[4] for the colorimetric determination of capsaicin. In this last method phenolic interference was reduced to a minimum by selective solubility. Ananthasamy, Kamat and Pandija[5] used this method in a comparative study of the capsaicin contents of different varieties of chillies. The method currently required by the British Pharmaceutical Codex 1968 is based on the report of the Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry on Methods of Assay of Crude Drugs.[6]

In this paper a method is described for the determination of the total capsaicin content of samples of *Capsicum* species that have different degrees of pungency. The method is based on the extraction procedure of North[4] followed by the spectrophotometric determination of the capsaicin content with reference to a standard solution of capsaicin.

Experimental

Materials—

Two brands of packeted chillie powder (*Capsicum annuum* L. variety *acuminatum*) were obtained from commercial sources. Samples of *Capsicum frutescens* L. variety *minima*, *Capsicum annuum* L. variety *longum* and *Capsicum annuum* L. variety *grossum* were obtained from the local market.

Reagents—

All reagents should be of analytical-reagent grade, if available.

Kerosene (Ceylonese Lanka grade, sp. gr. 0·820)—Purify commercial grade material by re-distilling it with concentrated sulphuric acid and collecting the fraction in the boiling range 200 to 250 °C.

Acetone - water (3 + 2)—Dilute 600 ml of acetone to 1 litre with distilled water.

Diethyl ether, peroxide-free.

Light petroleum (boiling range 60 to 90 °C).

Standard capsaicin solution—Dissolve 0·200 g of capsaicin in 1 litre of distilled water, containing 0·03 per cent. of 1 N sodium hydroxide solution, and leave the solution overnight to ensure that the capsaicin is completely dissolved.

Tungstophosphoric acid - molybdophosphoric acid—To 100 g of pure sodium tungstate add 20 g of molybdophosphoric acid, 100 g of syrupy phosphoric acid (85 per cent.) and 700 ml of distilled water. Boil the mixture, cool it, filter the resulting solution through a Whatman No. 7 filter-paper and make the final volume up to 1 litre with distilled water.

Sulphanilic acid.

Sodium carbonate solution—Saturated aqueous solution.

Sodium hydroxide.

Sodium nitrite.

Hydrochloric acid (sp. gr. 1·18).

Diazotised sulphanilic acid—Prepare the reagent by the method of Stahl.[7]

EXTRACTION PROCEDURE—

Place the capsicums in a dryer at 60 °C under a vacuum of 700 mm of mercury until the moisture and other volatile matter content is less than 1 per cent. w/w. Determine the moisture content by the solvent distillation method[8] on another portion of the same batch of dried capsicum material. Grind the material to a moderately fine powder (to pass through a 40-mesh sieve) and extract 5 g of the powder three times with 50-ml portions of peroxide-free diethyl ether in a Waring blender, filtering the extracts through a No. 1 sintered-glass filter. Evaporate the combined extracts in a rotary evaporator under reduced pressure, then dissolve the oleoresin obtained in 30 ml of purified kerosene and transfer the solution to a 250-ml Squibb separating funnel. Next, re-extract the original residue with 50 ml of purified kerosene and transfer this also to the Squibb separating funnel. Pour into the funnel 80 ml of the acetone - water (3 + 2) mixture containing sodium chloride (1 g per 80 ml). Shake the liquids gently for 30 minutes on a mechanical shaker. On standing, two sharply defined layers separate; remove the lower layer and re-extract the kerosene fraction with further 20-ml portions of the acetone - water solution until no capsaicin can be detected in the kerosene fraction by use of the thin-layer chromatographic method described below.

Transfer the combined acetone fractions to a 100-ml calibrated flask containing 0·5 g of Celite. Stopper the flask and shake it mechanically for 30 minutes. Dilute the solution to 100 ml and filter it through a Whatman No. 542 filter-paper to obtain a clear filtrate.

Transfer the entire clear filtrate by pipette into a 250-ml beaker and remove the acetone from the solution by evaporating it on a water-bath at 65 °C. Cool the liquid to room temperature and add 10 ml of 0·5 N sodium hydroxide solution, stirring until the oily sediment is dissolved. Transfer the contents to a 250-ml Squibb separating funnel and wash the beaker with two 5-ml portions of 0·5 N sodium hydroxide solution. Pour the combined washings into the separating funnel. Add 5 g of sodium hydrogen carbonate, then 100 ml of light petroleum (boiling-range 60 to 80 °C). For *Capsicum annuum* L. variety *grossum*, a larger volume of the solvent may be necessary. Shake the mixture gently by hand and leave it overnight to obtain a sharp separation. Use thin-layer chromatography for monitoring the completeness of extraction of the capsaicin into the upper layer. On completion of the extraction reject the lower layer and carefully filter the upper layer. Wash the funnel with two 10-ml portions of light petroleum. A yellow precipitate, which separates only in the instance of the large capsicum, *Capsicum annuum* L. variety *grossum*, was excluded. Shake the light petroleum layer with 10 ml of 0·5 N sodium hydroxide solution and add 10 drops of 95 per cent. v/v ethanol. Allow the mixture to stand for 10 minutes, by which time two layers have separated. Test the upper layer for residual capsaicin by using thin-layer chromatography as a monitoring device. If the test is positive, carry out another washing with 0·5 N sodium hydroxide solution, adding this to the initial extract. Filter the lower layer into a 50-ml calibrated flask and extract the light petroleum extract again with up to three 10-ml portions, successively, of distilled water. Filter each extract into the calibrated flask, finally adjusting it to volume with distilled water.

THIN-LAYER CHROMATOGRAPHY—

A thin-layer chromatographic method for the determination of capsaicin in ground paprika has been reported by Spanyár and Blazovich.[9] It was observed in our laboratories that the lowest limit of sensitivity for capsaicin when using the diazotised sulphanilic acid reagent was 0·5 μg, and at this concentration capsaicin gave a yellow colour instead of the usual pink madder lake colour. Thin-layer chromatography was used as a monitoring device

to detect capsaicin during the extraction procedure and tests were carried out at every stage of the extraction procedure before any extract was rejected. If any test was found to be positive extra washings were carried out until further tests proved negative. The tests could be carried out quickly by placing the plates in one solvent system only.

Glass plates (20 × 20 cm) were coated with a matrix of silica gel G (E. Merck A.G., Darmstadt, Germany) 0·35 mm thick. The plates were air dried for 1 hour and activated for 30 minutes at 100 °C just before use. A 100-μl portion of the extract was then subjected to thin-layer chromatography in the solvent system chloroform - ethyl acetate (4 + 1). The plates were air dried for 10 minutes and sprayed with diazotised sulphanilic acid reagent, following which a pink madder lake colour was obtained. Co-chromatography showed that this compound was identical with authentic capsaicin (obtained from Fluka A.G., Buchs, S.G., Switzerland).

SPECTROPHOTOMETRIC DETERMINATION—

A calibration graph was prepared by making use of standard solutions of authentic capsaicin at concentrations ranging from 0 to 100 μg.

The test solution (5 ml) was transferred by pipette into a 50-ml calibrated flask and 5 ml of tungstophosphoric acid - molybdophosphoric acid reagent were added. The contents were mixed by gently rotating the flask and the solution was made up to the 50-ml mark with saturated sodium carbonate solution. The solutions were mixed thoroughly for 30 minutes by using a shaking machine, and then filtered. The optical density of each was determined at 735 nm in a Unicam SP500 spectrophotometer against a blank consisting of the reagent mixture and distilled water containing 0·05 per cent. of 1 N sodium hydroxide solution instead of the test solution. (Aliquots of 3 ml in 1-cm cuvettes were used for the assay.) All readings were made in duplicate. The concentration of capsaicin in each of the test solutions was found by reference to the calibration graph and the capsaicin contents of the original extracts of capsicum were calculated from these results.

RESULTS AND DISCUSSION

Table I shows the relative concentrations of capsaicin in the various *Capsicum* species.

The unripe fruits of *Capsicum frutescens* L. variety *minima* contained the highest concentration of capsaicin (1216·6 mg per 100 g dry weight) while the unripe fruits of *Capsicum annuum* L. variety *grossum* contained the lowest concentration of capsaicin (186·1 mg per 100 g dry weight). It was observed that certain commercial packeted varieties of *Capsicum annuum* L. variety *acuminatum* (ripe and dried) contained a comparatively low concentration of capsaicin (250·2 mg per 100 g dry weight). The low values obtained in this instance may be caused, in part, by the reduction of the capsaicin content during ripening and drying, as shown by Ananthasamy, Kamat and Pandija.[5]

During the extraction procedure it was observed that many interfering compounds were eliminated. Appreciable amounts of polyphenolic compounds were present in the light petroleum extract of samples of *Capsicum annuum* L. variety *grossum*. These compounds

TABLE I

QUANTITATIVE DETERMINATION OF CAPSAICIN IN CEYLON CHILLIES WITH REFERENCE TO PURE CAPSAICIN

Variety	Average length of pod/mm	Average breadth of pod/mm	Capsaicin content/ mg per 100 g dry weight
C. frutescens L. variety *minima* ..	21·66	8·50	1216·6 1186·0 1120·1
C. annuum L. variety *longum* ..	67·80	8·80	540·0 472·6 507·3
C. annuum L. variety *acuminatum* (packeted samples)	69·00	18·50	262·5 250·2 304·1
C. annuum L. variety *grossum* ..	88·75	26·00	186·1 212·5 196·1

gave a red colour with the diazotised sulphanilic acid reagent but gave different R_F values from that of capsaicin on the chromatoplate. The presence of polyphenolic compounds in the extracts of paprika had already been shown by Zitko and Durigover,[10] who detected the occurrence of hydroxycinnamic acid and four unidentified flavanoid compounds.

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A Possible Method for the Identification of Canned Fish by Separation of its Carbonyl Constituents

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A method for the identification of canned fish, based on the thin-layer chromatographic patterns of the 2,4-dinitrophenylhydrazine derivatives of the carbonyl compounds in fish, is described. By using this technique it is possible to distinguish between canned sprats, brisling, sardines, salmon, tuna, cod, haddock and plaice. The dinitrophenylhydrazone patterns of these canned products are presented.

ELECTROPHORETIC methods exist for the objective identification of fish species in the raw[1] and cooked states.[2] As these methods depend on the presence of sufficiently unchanged protein fragments they are restricted to fish cooked under atmospheric pressure and are not applicable to the identification of canned products. The carbonyl components present in canned fish have been studied in relation to fish quality by Hughes[3] and McLay.[4]

This paper describes the use of a procedure for the separation of 2,4-dinitrophenylhydrazine derivatives of carbonyl compounds into classes as a possible means of identification of canned fish products. The experimental techniques are based on the methods of Schwartz and co-workers[5,6] with some modifications.

METHODS

SAMPLES—

Cans of fish were obtained from several commercial sources. All cans of white fish were prepared in our own laboratory together with some cans of British sprats. The latter, *Clupea sprattus*, are also known as "sild sardines." In this paper the term sardine is used for fish of the species *Sardina pilchardus*. Norwegian brisling is summer-caught *Clupea sprattus*.

SOLVENTS—

All solvents were freshly distilled and rendered free from carbonyl compounds.

RECOVERY OF CARBONYL COMPOUNDS AS 2,4-DINITROPHENYLHYDRAZONES—

Remove as much oil or sauce as possible from the fish. Extract 50 g of fish with three 50-ml volumes of hexane and filter the combined extracts. Pass the extract through a Celite column bed impregnated with 2,4-dinitrophenylhydrazine, orthophosphoric acid and water according to the procedure of Schwartz, Haller and Keeney[5] so as to convert the carbonyl compounds into their 2,4-dinitrophenylhydrazones. Wash the column with 100 ml of hexane, pass the extract through the column once more and wash the column with 250 ml of hexane. Combine the hexane extract with the washings and pass the mixture through a Buchner funnel with a filter bed composed of 50 g of bentonite and 50 g of Celite. Discard the hexane and elute the adsorbed hydrazones with methanol. Add a few crystals of the antioxidant butylated hydroxytoluene (2,6-di-t-butyl-*p*-cresol), and evaporate the methanol to dryness under vacuum at room temperature. Dissolve the residue in 10 ml of chloroform.

CLASS SEPARATION—

Prepare thin-layer chromatographic plates by spreading on them a coating consisting of a mixture of 14 g of Celite 535, 6 g of magnesium oxide (light) and 85 ml of 0·75 per cent. potassium hydroxide solution to a thickness of 0·25 mm. Leave the plates overnight at 20 °C before using them.

Apply 50 μl of the chloroform solution to the plate and develop it with hexane - chloroform (95 + 25).

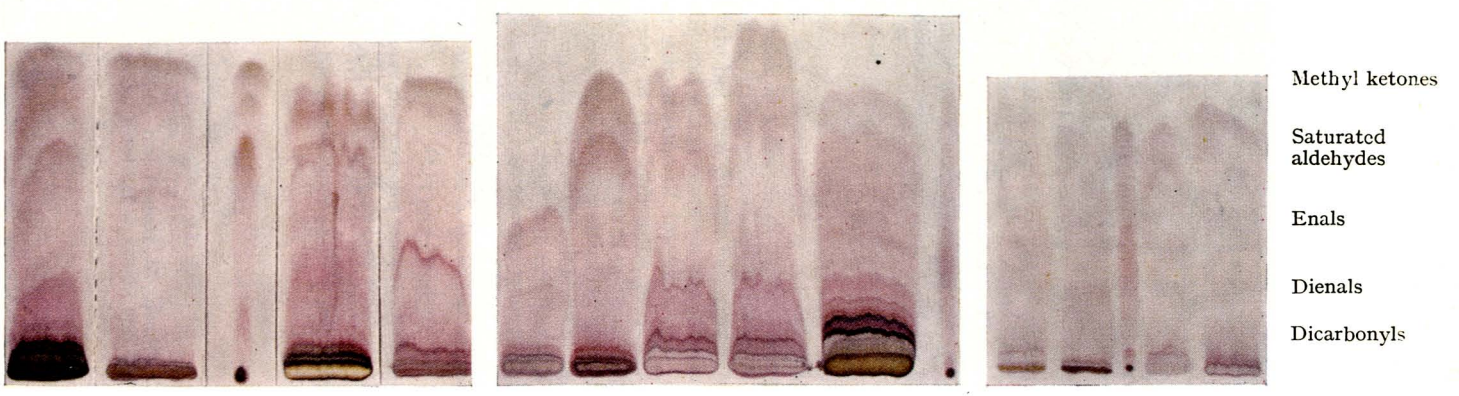

Fig. 1. Thin-layer patterns of dinitrophenylhydrazones of fish. The samples are commercially canned in oil unless otherwise stated. (*a*) Raw Norwegian brisling; (*b*) raw British sprat; (*c*) Norwegian brisling; (*d*) experimental British sprat; (*e*) Danish sprat; (*f*) British sprat; (*g*) and (*h*) British sprat (experimental); (*j*) Norwegian brisling; (*k*) Norwegian brisling in tomato; (*l*) Norwegian brisling in oil; (*m*) British sprat in tomato; (*n*) British sprat in oil; and (*s*) standard mixture

[To face page 376

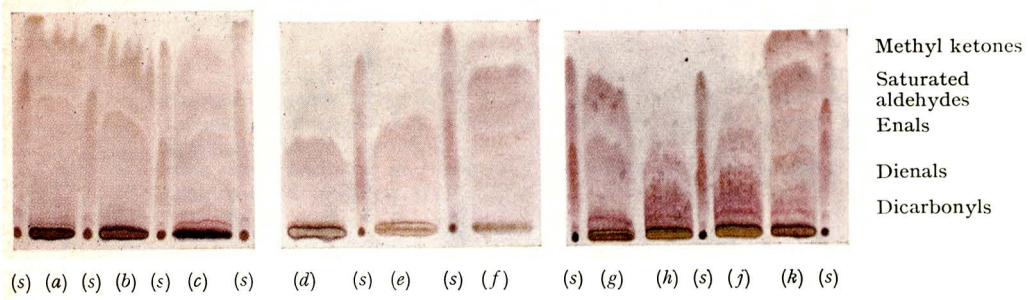

Fig. 2. Thin-layer patterns of dinitrophenylhydrazones of fish. (*a*) Canned pink salmon; (*b*) canned cohoe salmon; (*c*) canned sockeye salmon; (*d*) raw cod; (*e*) raw haddock; (*f*) raw plaice; (*g*) canned cod in oil; (*h*) and (*j*) canned haddock in oil; (*k*) canned plaice in oil; and (*s*) standard mixture. The cod, haddock and plaice were canned in the laboratory

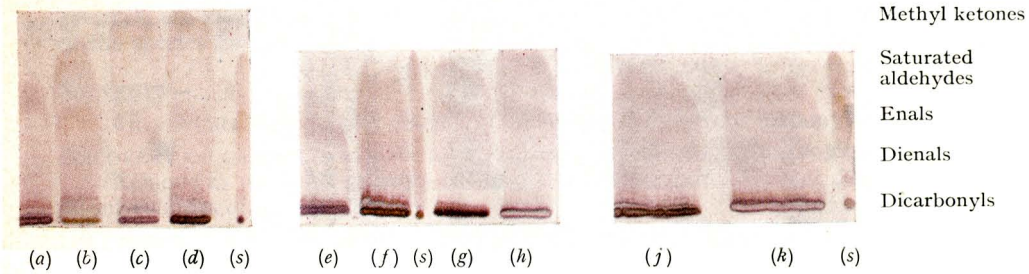

Fig. 3. Thin-layer patterns of dinitrophenylhydrazones of commercially canned sardines (in oil unless otherwise stated). (*a*) Spanish; (*b*) Moroccan; (*c*) Moroccan; (*d*) Portuguese; (*e*) British sprats; (*f*) Norwegian brisling; (*g*) Portuguese; (*h*) Moroccan; (*j*) Moroccan in tomato; (*k*) Portuguese in tomato; and (*s*) standard mixture

To face page 377]

RESULTS AND DISCUSSION

The thin-layer patterns of the 2,4-dinitrophenylhydrazones of carbonyl compounds in the main imported types of canned fish, some samples of raw fish and also a few types of canned fish produced in the laboratory are given in Figs. 1, 2 and 3. Because of variations in the thickness and moisture content of the thin-layer plates it is difficult to obtain exact replicas of any sample, therefore testing of unknown samples should be carried out if possible together with known samples. In addition, the differences between similar types, *e.g.*, Portuguese and Moroccan sardines, and pink and cohoe salmon, are very slight. There are variations in hydrazone patterns within commercial types, *e.g.*, sardines. Samples of Moroccan sardines [Fig. 3 (*b*) and (*c*)] are dissimilar and again are different from a Portuguese sample [Fig. 3 (*d*)]; however, all three samples are sufficiently similar to each other, and dissimilar to British sprats or Norwegian brisling, to permit their identification. None the less, by adjusting the concentration and the length of time of development it is possible to identify the commercial types shown in Figs. 1 to 3 from the thin-layer patterns. Small numbers of samples only were examined for Danish sild, Spanish sardines, salmon and the white fish. However, the sprats, brisling and sardines were sampled fifty times from a wide variety of commercial sources.

The hydrazones of the various classes of carbonyl compounds ran in the following order: saturated methyl ketones (fastest), saturated aldehydes, 2-enals, 2,4-dienals and dicarbonyl compounds (slowest). The different classes of hydrazones gave characteristic colours on alkaline plates: blue for dicarbonyl compounds, rose red for 2,4-dienals, pinkish red for 2-enals, tan for saturated aldehydes and grey - brown for methyl ketones. These colour differences, particularly those between the hydrazones of the 2,4-dienals and dicarbonyl compounds, assist considerably in the identification of samples.

Carbonyl compounds are almost certainly breakdown products of the oxidative degradation of fatty acids and the Strecker degradation of amino-acids. As these processes are continuous during storage and processing it is difficult to understand why their composition is constant enough to be used as a means of identification. It is impossible to say whether it is the species that are being differentiated or the various treatments accorded to the species. It is possible to differentiate between frozen raw sprats and brisling; however, the patterns for sprats after canning depend much more on the process than those for brisling [Fig. 1 (*a*), (*b*), (*c*), (*d*) and (*f*)]. The substitution of tomato sauce for oil in canned Norwegian brisling makes a noticeable difference to the hydrazone pattern but does not affect the pattern for commercial British canned sprats. The type of oil used in canning does not alter the hydrazone pattern significantly, nor does the size or shape of can or period of maturation. However, the composition of the can has an effect. Brisling in tin cans has a relatively larger dicarbonyl fraction than brisling in aluminium cans but not enough to prevent its identification.

One can each of Polish and Baltic sprats, tuna and herring gave distinctive hydrazone patterns that were different from any of those shown in Figs. 1 to 3. It therefore appears that the technique may be applicable to a wide variety of types of canned fish.

CONCLUSION

Thin-layer chromatography of the 2,4-dinitrophenylhydrazones of carbonyl compounds in canned fish appears to be a promising method for the identification of canned fish products.

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Fungicide Residues

Part I. The Detection, Identification and Determination of Residues of Quintozene in Tomatoes, Lettuces and Bananas by Gas Chromatography

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A simple method for determining residues of quintozene in tomatoes, lettuces and bananas is presented. After extraction with hexane, quintozene is separated from interfering co-extractives by a partition process with dimethylformamide followed by chromatography on an alumina column, and is quantitatively determined by electron-capture gas - liquid chromatography. A confirmatory chemical test for quintozene is also described.

QUINTOZENE (pentachloronitrobenzene) is used mainly as a soil fungicide or seed or transplant dressing for the control of many root-rotting and damping-off diseases; it is also applied directly to foliage for botrytis control, especially on lettuce grown under glasshouse conditions. It is a persistent compound, retaining its fungicidal properties for a considerable time,[1] but in moist soil it is slowly reduced to pentachloroaniline,[2] which is also stable and shows lower fungicidal activity. Quintozene is generally regarded as being non-systemic in action.

Methods of analysis for residues of quintozene have been reviewed by Zweig.[3] The three principal methods described are colorimetric,[4,5] polarographic[5] and gas chromatographic with either microcoulometric[5,6] or electron-capture detectors.[7,8] This last procedure is widely used for the determination of residues of organochlorine insecticides and consequently is suitable for the detection and determination of residues of quintozene on a routine basis.

The report of the F.A.O./W.H.O. Joint Meeting in 1969 expressed a desire for further work on the development of analytical methods with greater sensitivity and their evaluation for regulatory purposes. The procedure described in this paper has therefore been devised to provide suitable extraction, clean-up and gas-chromatographic conditions for the detection, identification and determination of residues of quintozene and its degradation product pentachloroaniline in tomatoes, lettuces and bananas, these crops being taken as representatives of the types of product on which quintozene may be used.

EXPERIMENTAL

The samples used in this work were obtained from retail sources and therefore had unknown histories of treatment except for some control lettuces, obtained by courtesy of the Glasshouse Crops Research Institute, Littlehampton, which were known not to have been treated with quintozene. The procedure of a partition process with dimethylformamide followed by clean-up on an alumina column has been used successfully in this laboratory for many years for the determination of residues of organochlorine insecticides in a wide variety of sample substrates.[9] A similar procedure was therefore applied to samples to which quintozene had been added in various concentrations, and gas-chromatographic determinations of the cleaned-up extract were carried out on several stationary phases. Of the columns tested, that containing 5 per cent. of EGSS-X on Chromosorb G (100 to 120 mesh) was found to be the most suitable for quantitative determinations. For confirmatory purposes, the SE-52 and Apiezon L columns used for organochlorine compounds[10] were found to be suitable. Table I gives the relative retention times of quintozene and pentachloroaniline under the operational conditions.

Both quintozene and pentachloroaniline have very short retention times on the columns (Table I) that are normally used in the determination of organochlorine pesticides, and to avoid interferences from co-extracted materials that are generally also eluted rapidly from the column, all the reagents used in the method must be carefully purified before use (see under Reagents). Many interfering peaks were initially obtained from the batches of sodium sulphate and alumina used owing to inadequate heat treatments. In any chromatographic analytical procedure, in which a chemical species is "identified" by measuring its retention

TABLE I

RETENTION TIMES OF QUINTOZENE AND PENTACHLOROANILINE RELATIVE TO DIELDRIN (= 1·00)

Column	Column temperature/°C	Relative retention time	
		Quintozene	Pentachloroaniline
EGSS-X	200	0·24	0·53
	170	0·19	0·48
SE-52..	200	0·25	0·37
Apiezon L	196	0·26	0·37

time (relative to a standard pure compound) on at least three columns with widely differing polarities, it is preferable that at some stage during the analysis the species is unambiguously characterised. This is usually achieved by either (*a*) isolating the chromatographic fraction corresponding to the "identifying" retention time and then characterising the species chemically or by using instrumental methods of analysis (*e.g.*, infrared or mass spectrometry), or (*b*) chemically pre-treating the injected solution to give a suitable derivative that is chromatographically distinguishable from the parent material under the same conditions. The latter approach has been used to provide a chemical confirmatory test for quintozene, namely, reduction with lithium aluminium hydride in diethyl ether to form pentachloroaniline in high yield. Formation of pentachloroaniline can be confirmed by its removal by shaking with sulphuric acid. However, this confirmatory test is complicated by the fact that pentachloroaniline is also a natural metabolite of quintozene[4,6] and consequently vegetable samples that contain quintozene may also contain pentachloroaniline. Therefore, in applying this chemical test for quintozene, all traces of pentachloroaniline present in the untreated sample must first be removed by treatment with sulphuric acid. In all the vegetable samples examined, no co-extracted materials gave rise to peaks that interfered with the gas-chromatographic determination of quintozene. In both retail and control lettuce samples, a peak having a retention time similar to that of pentachloroaniline was observed, but as this peak disappeared after reduction of the sample with lithium aluminium hydride no interference occurred in the identification and determination of pentachloroaniline formed during the confirmatory test for quintozene. Lettuce samples, however, which were known to have been treated with thiram and zineb (*i.e.*, control lettuces) showed several additional peaks in the vicinity of that of pentachloroaniline. These peaks were probably due to sulphur-containing degradation products derived from the added fungicides and were easily removed from the organic extract by elution through a silver nitrate - alumina column prior to carrying out the confirmatory test. By using carefully purified reagents, and following the extraction and clean-up procedures described above to remove interfering co-extractives, this method allows the chemical identification and quantitative determination of quintozene in vegetable materials at the required residue level.

REAGENTS—

Analytical-reagent grade materials should be used whenever possible.

Hexane—Distil hexane from sodium hydroxide solution and, to check its suitability, concentrate a 50-ml volume to 1 ml and examine the product by gas - liquid chromatography.

Sodium sulphate—Heat anhydrous sodium sulphate at 500 °C for 36 hours and allow it to cool in a desiccator.

Alumina—Heat alkaline aluminium oxide (100 to 240 mesh) for 4 hours at 500 °C. Allow it to cool in a desiccator, add 5 per cent. w/w of water dropwise and shake the mixture for 2 hours; store the product in a tightly stoppered bottle.

Dimethylformamide—Laboratory-reagent grade material is used.

Quintozene—Recrystallise technical quintozene from ethanol and dry it in a desiccator (m.p. 142 °C; literature value,[2] 143·6 °C).

Pentachloroaniline—Add 0·3 g of lithium aluminium hydride to 1 g of recrystallised quintozene in 30 ml of dry diethyl ether. Destroy the excess of reagent by adding water dropwise, separate the ethereal layer, dry it over anhydrous sodium sulphate, filter it and evaporate it to dryness. Recrystallise the product from ethanol and purify it by sublimation (m.p. 228 °C; literature value,[11] 232 °C). The infrared spectrum of the product in a Nujol mull was identical with the published spectrum of pentachloroaniline.[4]

APPARATUS—

Gas chromatograph—The detector was of the tritium-foil electron-capture type; the columns, used isothermally, were as follows.

1. 1·6 m × 4 mm i.d. glass column containing 5 per cent. of EGSS-X on Chromosorb W (100 to 120 mesh), operated at 170 or 200 °C.
2. 1·8 m × 3 mm i.d. glass column containing 1·3 per cent. of SE-52 and 0·15 per cent. of Epikote 1001 on silanised Chromosorb G (60 to 80 mesh), operated at 200 °C.
3. 1·2 m × 3 mm i.d. glass column containing 1 per cent. of Apiezon L and 0·15 per cent. of Epikote 1001 on silanised Chromosorb G (60 to 80 mesh), operated at 196 °C.

For all columns, oxygen-free nitrogen was used as the carrier gas at a flow-rate of about 100 ml min^{-1}.

Homogeniser.

Evaporator—A Kuderna-Danish instrument, of 500-ml capacity, was used.

PROCEDURE—

Quantitative procedure—To 10 g of sample (taken from a 100 to 120-g batch of well mixed sample) add 50 ml of hexane and 30 g of anhydrous sodium sulphate and blend the mixture in the homogeniser for 2 minutes. Filter the solution through a short column of anhydrous sodium sulphate into the Kuderna-Danish evaporator and repeat the extraction three times with 25 ml of hexane. Reduce the volume of the combined hexane extracts to approximately 5 ml on a steam-bath. Make the volume up to 20 ml with hexane in a 100-ml separating funnel and extract the solution with 10 ml of dimethylformamide saturated with hexane. Transfer the lower dimethylformamide extract into a second 100-ml separating funnel and extract the remaining hexane phase twice with 10 ml of dimethylformamide saturated with hexane. Wash the combined extracts with 10 ml of hexane saturated with dimethylformamide and transfer the dimethylformamide extract into a 500-ml separating funnel. Wash the residual hexane solution with 10 ml of dimethylformamide saturated with hexane and add the mixture to the first extract. To the combined extracts, add 300 ml of a 2 per cent. w/v sodium sulphate solution, shake the mixture well and allow the hexane layer to separate. Fill a chromatographic column (30 cm × 13 mm) with a slurry of 10 g of alumina in hexane, allow it to settle and drain off the hexane until the solvent level reaches the top of the alumina. Discard the aqueous layer from the separating funnel and slowly run the hexane solution on to the column. Wash the separating funnel twice with 2 ml of hexane and add the washings to the column. Elute the column with hexane and collect 100 ml of the eluate. Examine a 5-μl volume of the eluate by gas - liquid chromatography and then adjust the volume to give a quintozene concentration of approximately 0·1 μg ml^{-1}. Calculate the concentration of the quintozene present by comparing the peak height with that obtained from a 5-μl injection of a standard solution (0·1 μg ml^{-1}) of quintozene in hexane. A calibration graph, prepared by injecting 5-μl volumes of standard solutions and plotting the resultant peak height against the weight of quintozene taken, showed that the detector response was linear over the range 0·1 to 1·0 ng. With a signal-to-noise ratio of 3:1 the limit of detection for quintozene was found to be 5 pg on the 10-g sample taken.

Reduction of quintozene—To 1 ml of a solution of pure, recrystallised quintozene in dry diethyl ether (1 μg ml^{-1}) in a 10-ml calibrated test-tube, add a small amount of lithium aluminium hydride and shake for 0·5 minute. Add 5 ml of distilled water, dropwise, with shaking, and centrifuge the mixture if necessary. Add diethyl ether to give a total volume of the ether of 1 ml and examine a 5-μl volume of the ethereal extract by gas - liquid chromatography on each of the columns specified above. Calculate the concentration of pentachloroaniline present by comparison with a standard solution of pure pentachloroaniline in diethyl ether (1 μg ml^{-1}). The detector response for pentachloroaniline was shown to be linear over the range 1 to 5 ng injected, and the limit of detection (with a signal-to-noise ratio of 3:1) was 50 pg on the 10-g sample taken. It should be noted that if the reduction stage is allowed to continue for longer than the stated time, the yield of pentachloroaniline obtained is decreased owing to competing side reactions. By using the above procedure, three separate experiments gave yields of 105, 87 and 83 per cent. of pentachloroaniline.

Confirmatory test for quintozene in vegetable samples—After the extraction and clean-up procedures have been carried out on the vegetable sample, the quintozene content of the hexane extract is determined gas chromatographically and the quintozene is confirmed chemically by the following procedure.

Dissolve 0·75 g of recrystallised silver nitrate in a mixture of 0·7 ml of water *plus* 3 ml of acetone. Add the solution obtained to 10 g of alumina, shake the mixture well and warm it in a current of air to remove the acetone. Fill a chromatographic column (4 cm × 6 mm) with a slurry of 1 g of the prepared alumina in hexane and drain off the hexane until the solvent level reaches the top of the alumina. Run 1 ml of the hexane extract of the vegetable (0·1 μg ml^{-1}) on to the column, elute it with hexane and collect 20 ml of the eluate. Concentrate the eluate to 2 ml, add 0·5 ml of concentrated sulphuric acid and shake the mixture well to remove any pentachloroaniline that is already present. Evaporate 1 ml of the hexane phase to dryness in a gentle stream of air. Add 1 ml of diethyl ether to the residue and reduce the quintozene with lithium aluminium hydride as described above. Determine the concentration of pentachloroaniline in the reduced extract by gas - liquid chromatography. A final test can be made by shaking the reduced ethereal extract with a further 0·5 ml of concentrated sulphuric acid (to remove the pentachloroaniline formed from the reduction of quintozene) and examining the organic phase by gas - liquid chromatography. A completely clean trace should be obtained.

Results and discussion

Quintozene was added to tomato samples to give concentrations from 0·005 to 0·1 mg kg^{-1}. The recoveries obtained are listed in Table II. All blank determinations carried out on untreated samples, prior to recovery experiments, were in the range 0·0006 to 0·001 mg kg^{-1} and are substantially lower than the recommended tolerance level[12] (0·1 mg kg^{-1}) set for quintozene in tomatoes.

Similarly, Table III lists the recoveries obtained from the skins and fruits of bananas spiked separately with quintozene to give concentrations from 0·01 to 5·0 mg kg^{-1}. Blank

Table II

Recovery of quintozene added to tomatoes

Quintozene added/mg kg^{-1}	Quintozene recovered	
	Range, per cent.	Mean, per cent.*
0·1	87–106	94
0·05	79–92	83
0·025	88–92	90
0·01	81–93	87
0·005	85–102	91

* Average of three determinations on each sample.

Table III

Recovery of quintozene added to bananas

Sample	Quintozene added/mg kg^{-1}	Quintozene recovered	
		Range, per cent.	Mean, per cent.*
Skin	5·0	75–79	77
Fruit	5·0	75–90	82
Skin	1·0	79–87	83
Fruit	1·0	77–84	80
Skin	0·5	75–76	75
Fruit	0·5	75–76	75
Skin	0·1	74–80	77
Fruit	0·1	75–86	81
Skin	0·05	76–81	79
Fruit	0·05	75–79	77
Skin	0·01	85–99	92
Fruit	0·01	95–110	103

* Average of three determinations on each sample.

TABLE IV

RECOVERY OF QUINTOZENE ADDED TO CONTROL LETTUCES

Quintozene added/mg kg^{-1}	Quintozene recovered	
	Range, per cent.	Mean, per cent.*
5·0	98–101	99
1·0	96–107	100
0·5	97–101	99
0·1	110–113	111
0·05	86–94	90
0·01	95–125	108

* Average of three determinations on each sample.

determinations were carried out on all banana skins and fruits used and the amounts of quintozene residues found were in the range 0·006 to 0·01 mg kg^{-1} for banana fruits and 0·008 to 0·01 mg kg^{-1} for banana skins. The majority of the banana samples examined contained quintozene residues that were well below the recommended tolerance levels[12] set for quintozene, *i.e.*, 0·01 mg kg^{-1} for banana fruits and 1·0 mg kg^{-1} for whole bananas.

Recovery experiments were carried out on control lettuces, which were then treated with quintozene to give concentrations from 0·01 to 5·0 mg kg^{-1}. The results obtained are shown in Table IV. Blank determinations were in the range 0·012 to 0·018 mg kg^{-1}. The distribution of quintozene residues in retail lettuces is shown in Table V and, as expected, most of the applied fungicide was found to reside on the outermost leaves of the plant. Residue levels were found to be in the range 0·78 to 2·6 mg kg^{-1} for retail lettuces of Dutch origin (Table V) and 0·70 to 1·2 mg kg^{-1} for four English retail lettuces. All the retail lettuce samples examined contained quintozene residues that were above the recommended tolerance level[12] of 0·3 mg kg^{-1} set for lettuces; even the hearts of three out of four samples contained amounts of quintozene that exceeded this level.

TABLE V

DISTRIBUTION OF QUINTOZENE RESIDUES IN RETAIL LETTUCES*

Outer leaves†/ mg kg^{-1}	Inner leaves†/ mg kg^{-1}	Heart†/ mg kg^{-1}	Weighted average per lettuce/mg kg^{-1}
2·92	1·52	1·00	1·99
1·00	0·80	0·21	0·78
1·62	0·98	0·37	1·10
4·85	1·27	0·40	2·60

* Imported lettuces of Dutch origin.
† For a 10-g sample.

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Permission to publish this paper has been given by the Government Chemist.

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A Simplified Method for the Determination of Selenium in Soils and Sediments

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A method is described for the determination of low levels of selenium in soils. An extract of the soil in nitric acid and orthophosphoric acid is prepared. An aliquot is oxidised with potassium persulphate at 100 °C, at which temperature the loss of selenium is minimal. The excess of nitric acid is removed by evaporation and 50 per cent. hydrochloric acid is added to reduce selenate. The selenite produced is complexed with 2,3-diaminonaphthalene and the resulting 4,5-benzopiazselenol is extracted with cyclohexane. Sodium sulphate is added to remove interfering substances and the selenium complex is determined fluorimetrically. Selenium in soils down to 0·04 p.p.m. can be determined to within ±0·1 p.p.m.

Many of the methods for the determination of selenium in soils have been used primarily in studies of the relationship between high levels of selenium in soils and toxicity problems in animals. There is, however, an increasing interest in the rôle of selenium as an essential trace element in animal nutrition.

Schwarz and Foltz[1] and Patterson, Milstrey and Stokstad[2] showed that a selenium-containing factor was effective in the prevention of exudative diathesis in poultry. Since then other workers[3,4] have demonstrated that a low dietary intake of selenium is associated with white muscle disease in lambs and with certain myopathic conditions in other species.

In the course of studies of white muscle disease in lambs and goat kids in Turkey, geological considerations are often taken into account for defining areas in which elemental deficiencies are likely to be encountered. Consequently, the need has arisen for a simplified method for determining the selenium content of soils that are inherently low in selenium. To meet this requirement, the method proposed in this paper was developed primarily as a "screening" procedure and the empirical extraction processes are considered to be adequate for this purpose. By expanding these operations to exhaustive extractions, the method can be rendered precise for determining total selenium in soils. Correspondingly, if precautions are taken to prevent loss of selenium during evaporation, the method can be applied to the determination of selenium in water or for the determination of "available" selenium in aqueous extracts of soils. The oxidative capacity of the digestion procedure evolved for routine use is limited to soils or residues that contain less than 20 per cent. of "organic matter," and, as a guide, the method can be applied only to dry materials in which the level of selenium in relation to "organic matter" exceeds 0·2 p.p.m. By making suitable reductions in the initial weight of sample taken, it has been possible to determine the selenium in a variety of materials of high organic contents, including dried kidney. If fat is present it can be removed after the preliminary digestion without affecting the result.

Hall and Gupta[5] have pointed out that losses of selenium may occur under certain conditions when perchloric acid is evaporated from digestion mixtures. The proposed method involves extraction and digestion procedures intended to minimise such losses. After conversion to selenite, the selenium is subsequently determined fluorimetrically by a procedure similar to those described by Parker and Harvey,[6] Allaway and Cary,[7] Watkinson,[8,9] Ewan, Baumann and Pope[10] and Lindberg.[11] This procedure involves the addition of 2,3-diaminonaphthalene at pH 2 to form 4,5-benzopiazselenol, which is extracted with cyclohexane and determined fluorimetrically. Additionally, it has been found necessary to add sodium sulphate to the extract to remove interfering substances prior to fluorimetry.

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METHOD

APPARATUS—

Fluorimeter—An instrument that is capable of excitation at 366 nm and measurement at 525 nm is required, and a Beckman Ratio Fluorimeter, Model 772, fitted with UG II (1-mm) primary filters and a combined CS 3–70 (Part No. 97612) and CS 4–97 (Part No. 97614) secondary filter, was used in this work. The phosphor sleeve was set at the 360-nm position. Extracts were compared in matched 12 × 75-mm Pyrex culture tubes (Part No. 101579).

REAGENTS—

Analytical-reagent grade materials should be used whenever possible, and de-ionised water.

Nitric acid, sp. gr. 1·42—Re-distil it from glass apparatus if necessary. Bromide should be absent.

Hydrochloric acid, approximately 5·5 M—Dilute hydrochloric acid, sp. gr. 1·18, with an equal volume of water.

Hydrochloric acid, approximately 0·1 M—Dilute 10 ml of hydrochloric acid (sp. gr. 1·18) to 1 litre with water.

Orthophosphoric acid, sp. gr. 1·71.

Potassium persulphate.

Ethylenediaminetetraacetic acid, diammonium salt, approximately 0·04 M *solution*—Dissolve 7·6 g of EDTA, diammonium salt, in 500 ml of water.

Ammonia solution, approximately 7 M—Add 150 ml of de-ionised water to 100 ml of ammonia solution, sp. gr. 0·91.

Cresol red indicator—Dissolve 0·02 g of cresol red in 100 ml of water containing 0·2 ml of 7 M ammonia solution.

Sodium sulphate—Anhydrous, powdered.

Aluminium oxide—Chromatographic grade, alkaline, Brockmann activity I, 100 to 200 mesh.

Cyclohexane—Pass cyclohexane through an active column of aluminium oxide and re-distil it.

Chloroform.

Decolorising charcoal—Norit NK (Hopkin and Williams).

Hydroxylammonium chloride.

2,3-Diaminonaphthalene.

Purification of 2,3-diaminonaphthalene—The general precautions for handling laboratory chemicals of this type should be observed.

Prepare a lump-free slurry of 5 g of 2,3-diaminonaphthalene in 20 ml of chloroform. Transfer the slurry, by using additional chloroform, to a 1-litre flask fitted with a reflux condenser. Make the total volume up to 360 ml with chloroform. Add a few antibumping granules and reflux the solution gently for 10 to 15 minutes on a hot-plate. Remove the flask from the heater and, when boiling ceases, add a slurry of about 6 g of decolorising charcoal in 20 ml of chloroform. Continue to boil the mixture under reflux for 2 minutes. Prepare a filter consisting of a 1-cm bed of sodium sulphate loosely packed on a 7-cm sintered glass Buchner funnel of No. 3 porosity. Place a Whatman No. 1 filter-paper on top of the sodium sulphate and warm the assembly to 80 °C in an oven. Filter the boiling solution rapidly under slightly reduced pressure in diffused light. Cool the filtrate in cold water while swirling it. Keep the filtrate at −20 °C for 2 to 3 hours to allow the 2,3-diaminonaphthalene to crystallise further. Filter the crystals through a pre-cooled sintered-glass funnel, covered with a filter-paper, and wash the crystals with two 20-ml volumes of chloroform previously cooled to −20 °C. Remove the solvent under slightly reduced pressure and dry the 2,3-diaminonaphthalene in a desiccator over calcium chloride in the dark. The yield should be about 60 per cent. Store it in a cool place in an amber bottle with an air-tight stopper. Except for the most precise work, solutions freshly prepared with 2,3-diaminonaphthalene that has been purified in this manner do not require further purification before use. Blanks should be checked periodically, however.

Working solution of 2,3-diaminonaphthalene (1 *mg ml*$^{-1}$)—Just before use and in restricted light add 100 mg of purified 2,3-diaminonaphthalene to 100 ml of 0·1 M hydrochloric acid

containing 1 g of hydroxylammonium chloride. Warm the mixture to 50 °C for not more than 25 minutes to facilitate dissolution.

Standard selenite solutions—Dissolve 0·1634 g of selenous acid (H_2SeO_3), free from selenate, in 0·1 M hydrochloric acid and dilute the solution to 1 litre with 0·1 M hydrochloric acid. This stock standard solution contains 100 μg ml^{-1} of selenium.

Dilute 5 ml of the stock standard selenite solution to 500 ml with 0·1 M hydrochloric acid to give a solution containing 1·0 μg ml^{-1} of selenium. Prepare a working standard solution containing 0·2 μg ml^{-1} of selenium in 0·1 M hydrochloric acid.

NOTE—

A series of standard solutions in nitric acid in the range 0 to 1 μg ml^{-1} of selenium were also prepared from the stock standard solution for use in recovery and "ashed" standard determinations. The action of nitric acid on certain plastics stoppers was found to release measurable amounts of selenium; all-glass containers should be used for these solutions.

PREPARATION OF THE SAMPLE—

A representative sample of not less than 500 g of soil should be spread out on a suitable tray and allowed to air dry. A light flow of air at 30 to 35 °C can be used to facilitate drying, but sunlight should be avoided. Sieve the sample to remove stones and debris. If necessary, crush a sub-sample of the soil mechanically. Sieve the sample through a nylon or stainless-steel sieve of 2-mm mesh and collect about 100 g for storage. Mix the samples well before taking sub-samples for analysis.

DIGESTION OF SOIL—

Use safety pipettes for the additions of corrosive or poisonous solutions. Conduct all operations in which volatile oxidation products are present in an efficient fume cupboard.

Weigh 1·0 g of soil and transfer it to a dry 20-cm boiling-tube having a B24 ground-glass neck and stopper. Add carefully 5 ml of nitric acid, ensuring that material from frothing does not rise more than 6 cm in the tube. Swirl the tube to mix the contents. Fit a 20-cm air condenser and, by using a microburner, reflux the mixture in a fume cupboard for 15 minutes with occasional swirling. In the latter stages "bumping" may occur and the tubes should be of good quality and securely held. Run 5 ml of orthophosphoric acid down the condenser and continue to reflux the mixture for 15 minutes. Allow the tube to cool, remove the air condenser, swirl the mixture gently to mix in any surface condensate, then fit a stopper to the tube and allow it to stand at room temperature until a clear liquid results. By using a safety pipette, withdraw aliquots, usually 2·0 ml, from about 1 cm below the surface (to avoid any floating matter) and take care not to disturb the sediment. Alternatively, a clear extract can be obtained by centrifuging or by filtration of the mixture through a glass sinter.

Transfer 2·0 ml of the clear acidic extract of the soil into a 50-ml squat-form beaker, then add 0·3 g of potassium persulphate. Swirl the beaker to mix the contents. Place it on a boiling water bath in a fume cupboard until the nitric acid has evaporated, which usually takes 45 minutes. Add 1·0 ml of 5·5 M hydrochloric acid, mix the contents and continue to heat the beaker on the water-bath until this acid has evaporated. Add 10 ml of 0·1 M hydrochloric acid down the inside of the beaker and continue to heat it for a further 5 minutes. Remove the beaker from the water-bath and transfer the contents to a 20-cm boiling-tube and complete the transfer with two 10-ml volumes of 0·1 M hydrochloric acid. Mix the contents of the tube and fit a stopper. At this stage, the solution can be set aside until it is convenient to proceed further.

Undigested blanks and standards containing 1 ml of orthophosphoric acid can now be incorporated into the series if desired.

COMPLEXING WITH 2,3-DIAMINONAPHTHALENE—

Prepare the working solution of 2,3-diaminonaphthalene about 30 minutes before it is required. From this stage the work should continue without interruption and in diffused light until all of the excess of 2,3-diaminonaphthalene is removed from the reaction mixture.

Add 8·0 ml of EDTA, diammonium salt, solution to each tube containing the digested soil extract and mix the contents. Solutions containing iron will become yellow. Add 3 drops of cresol red solution to one of the colourless preparations (*i.e.*, the "ashed" blank) and titrate it to a pale orange colour with 7 M ammonia solution contained in a 25-ml burette.

Cool the solution to room temperature before adjusting the final end-point. Note the volume of ammonia solution required, add a similar volume to each of the remaining tubes and immediately mix each solution to avoid precipitation of metal hydroxides. It is assumed that, within the accuracy required, the amount of residual acid from similar aliquots of soil extract is uniform. Separate titrations will be necessary if different aliquots have been taken. Add 5·0 ml of the working solution of 2,3-diaminonaphthalene and mix. Fit stoppers to the tubes and place them in a water-bath at 50 °C for 25 minutes. Remove the tubes from the bath, cool them, add 10 ml of cyclohexane and shake them vigorously for 60, 30 and 15 s at 2 to 5-minute intervals.

Transfer the mixture to a 100-ml separating funnel that is free from grease (PTFE keys are convenient), allow the organic solvent to separate and discard the aqueous layer. Add 20 ml of 0·1 M hydrochloric acid to the extract, shake the mixture for 10 s, and discard the aqueous layer. Wash the extract again with 20 ml of 0·1 M hydrochloric acid and remove the aqueous layer. Add about 1 g of anhydrous sodium sulphate to the separating funnel and shake it to remove any residual water in the organic extract. Pour the extract into a centrifuge tube having a C14 stopper and containing 1·5 to 2 g of anhydrous sodium sulphate. Fit a stopper to the tube, shake it and place it in a refrigerator or cold room overnight. Remove the stoppers and centrifuge the tubes at 2000 r.p.m. for 1 minute. Pour the extract, at room temperature, into a matched tube for measurement of the fluorescence.

Fluorimetry and results

Use an undigested blank and standard for setting the instrument. Suitable settings for low selenium soils are—

Opaque bar	Set at 0
Blank (after adjusting the standard)	Set at 2·0
Standard (≡ 0·20 μg of selenium)	Set at 82·0

From time to time, a permanent standard and an unashed standard should be compared at a fixed temperature to ensure inter-series continuity. From eighteen such measurements, with a mean reading of 59·6, the standard deviation was 1·2. Standards and extracts should be in temperature equilibrium while readings are made and instrument settings should be checked at least once during each series. Some typical results are shown in Table I.

Table I

Recovery of selenium in digests of soil extracts

Sample digested	Aliquot for selenium determination	Selenium determined/μg	Selenium in soil, p.p.m.	Recovery, per cent.
0·2 μg of selenium	⅕ (0·04 μg of Se)	0·038	—	95
0·4 μg of selenium	⅕ (0·08 μg of Se)	0·077	—	96
0·6 μg of selenium	⅕ (0·12 μg of Se)	0·116	—	97
0·8 μg of selenium	⅕ (0·16 μg of Se)	0·152	—	95
1·0 μg of selenium	⅕ (0·20 μg of Se)	0·190	—	95
2·0 μg of selenium	⅕ (0·40 μg of Se)	0·379	—	95
4·0 μg of selenium	⅕ (0·80 μg of Se)	0·764	—	95
1 g of soil 1071	⅕ (0·20 g of soil)	0·015	0·08	—
1 g of soil 1071 + 1·0 μg of selenium	⅕ (0·20 g of soil + 0·2 μg of Se)	0·203	—	94
1 g of soil 7427	⅕ (0·20 g of soil)	0·068	0·34	—
1 g of soil 7427 + 0·5 μg of selenium	⅕ (0·20 g of soil + 0·10 μg of Se)	0·166	—	98
1 g of soil "A"	1/10 (0·10 g of soil)	0·120	1·20	—
1 g of soil "A"	⅕ (0·20 g of soil)	0·242	1·21	—

Discussion

The use of a comparatively large initial weight of soil is an advantage in reducing sampling errors and the subsequent analysis of an aliquot of an acidic extract is considered to be valid for the purposes for which the method was developed. Initially, refluxing with nitric acid alone was tried as the means of extracting the selenium from the soil. However, recoveries of added selenium were low from some soils. The addition of orthophosphoric acid to the

refluxing mixture greatly improved these recoveries and served as a non-volatile reaction medium and buffer for the digest after dilution.

Centrifuging the cyclohexane extracts containing the 4,5-benzopiazselenol failed to eliminate co-extracted material when the method was applied to soils. A final removal of water from these extracts with anhydrous sodium sulphate caused interfering matter to be retained on its surface. As local ambient temperatures in the laboratory often exceed 32 °C in the summer, evaporation of the solvent (which freezes at about 6 °C) is minimised by keeping the tubes in a cool place. The dehydrating action of the sodium sulphate is also improved at a temperature nearer to the freezing-point of the solvent.

In this laboratory the oxidation procedure has proved safe. Solid oxidants such as potassium persulphate should not, however, be added to hot acids and no attempt should be made to grind or break up such oxidants during the procedure. Precautions similar to those recommended for perchloric acid digestion should be observed.

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Determination of Total Mercury in Sediments and Soils

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A highly sensitive and precise procedure has been developed for the quantitative determination of total mercury in sediments and soils. Undried samples are treated with concentrated nitric and sulphuric acids, potassium permanganate and potassium persulphate in order to digest and oxidise all forms of mercury to mercury(II) ions, which are subsequently determined by flameless atomic-absorption spectrophotometry. Recovery of mercury, added as mercury(II) chloride, methylmercury chloride, phenylmercury hydroxide or phenylmercury acetate to a lake sediment, ranged from 98 to 105 per cent. The procedure developed by us resulted in the extraction of more mercury from sediments and soils than did extraction with concentrated nitric acid. Drying at 60 °C caused a significant loss of organomercury compounds from a lake sediment.

Evaluation of the extent of mercury pollution of natural waters necessitates the use of methods that will provide accurate determinations of the total amount of mercury in sediments and soil materials entering streams, rivers and lakes. Because of the complex nature of the components in sediments and soils that retain mercury, quantitative determinations of total mercury are more difficult with these materials than with biological materials for which several methods are available (see reviews by Jonasson,[1] Keckes and Miettinen,[2] U.S. Geological Survey,[3] Wood[4] and Wallace, Fulkerson, Shults and Lyon[5]).

Neutron-activation analysis has been used for the determination of total mercury in ores,[6] biological materials,[7–10] fish[11] and in waters and soils.[12,13] Although neutron-activation analysis is precise and sensitive, it is also time consuming, expensive and requires the use of a nuclear reactor.

Recent developments in atomic-absorption spectrophotometry have resulted in an increased application of this technique to the determination of mercury in extracts of a wide range of materials. Flameless atomic-absorption spectrophotometry is less specific than neutron-activation analysis for the determination of mercury because certain chemical compounds, such as sulphur dioxide, nitrogen dioxide and several volatile organic compounds, absorb radiation at the same wavelength as mercury. With adequate precautions, however, flameless atomic-absorption spectrophotometry can be made to provide sensitive and accurate mercury determinations and it is less expensive and time consuming than neutron-activation analysis.

Sample digestion constitutes a critical step in the quantitative determination of total mercury. Errors can arise during digestion as a result of incomplete extraction of mercury, non-quantitative conversion of organomercury into mercury(II) ions or loss of mercury vapour. A wide range of digestion procedures has been proposed. Sulphuric acid and hydrogen peroxide have been used with soils and rocks[14]; sulphuric and nitric acids in the presence of selenium with soils[15]; sulphuric acid, potassium permanganate and hydrogen peroxide with soils and grain[16]; aqua regia[17] and sulphuric acid, nitric acid, potassium permanganate and potassium persulphate[18] with natural and industrial waters; and sulphuric acid and potassium permanganate with fish.[19]

The purpose of this paper is to report on a procedure developed in our laboratory that gives reliable results for total mercury in sediments and soils. The procedure involves the wet digestion of the sample and determination of mercury in the extract by flameless atomic-absorption spectrophotometry.

Method

Reagents—

Sulphuric acid, 1 and 36 N.
Nitric acid, 11 N.

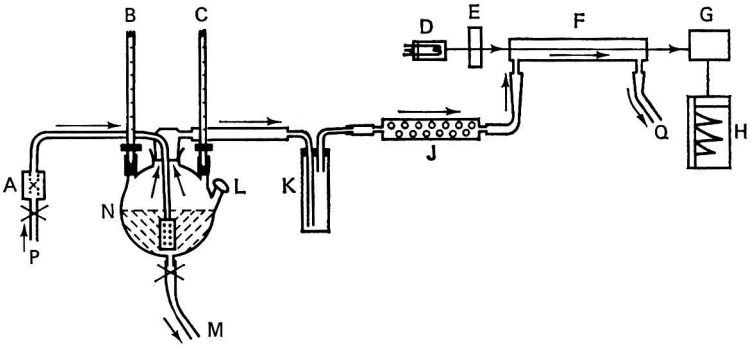
Hydrochloric acid, 6 N.
Tin(II) chloride solution—A 20 per cent. w/v solution in 6 N hydrochloric acid.
Potassium permanganate, 5 *per cent. w/v solution.*
Potassium persulphate, 5 *per cent. w/v solution.*

MATERIALS AND APPARATUS—

The materials used in this investigation were from Wisconsin, U.S.A., and included grab samples of two sediments from the Wisconsin River, designated Wisconsin River High (sampled close to an industrial operation) and Wisconsin River Low (sampled in a rural area), a grab sample of sediment from the Fox River and from Lake Pickerel, and three soils, namely Plainfield sand, Poygan silty clay loam and a muck peat.

The digestion can be carried out in 100-ml glass centrifuge tubes or 125-ml Erlenmeyer flasks previously rinsed with concentrated nitric acid and then distilled water. The use of plastics-ware should be avoided because of surface adsorption of mercury.[20,21]

The flameless atomic-absorption spectrophotometric apparatus is similar to that described by Rathje[22] except that the reaction flask is modified (Fig. 1). The modifications include side inlets for the addition of nitric acid and tin(II) chloride solution, a stoppered inlet on the front for sample addition and an outlet at the bottom to remove the sample after analysis. These modifications allow for a shorter analysis time for each sample and for the addition of tin(II) chloride to the closed system, thereby preventing any loss of mercury vapour, which might occur if tin(II) chloride solution was added to an open flask.



A = Flow meter
B = Nitric acid
C = Tin (II) chloride solution
D = Mercury lamp
E = Monochromator
F = Borosilicate glass tube with quartz windows
G = Detector
H = Recorder
J = Drying tube containing magnesium perchlorate
K = Trap
L = Sample inlet
M = Outlet
N = Bubbler flask
P = Air inlet
Q = Air and mercury vapour outlet

Fig. 1. Apparatus used for the determination of mercury by flameless atomic-absorption spectrophotometry

Compressed air at a flow-rate of 2 l min^{-1} was used to sweep the metallic mercury out of the reaction flask, through a magnesium perchlorate filter (to remove water vapour) and into a borosilicate glass absorption tube (21 cm long by 2·5 cm diameter) with quartz end-windows. The tube was held in the light path of a Jarrell-Ash atomic-absorption unit by an aluminium bracket attached to the burner support. The absorption of the mercury vapour was measured at a wavelength of 253·7 nm.

PROCEDURE

EXTRACTION—

To a known weight of wet sediment or soil (equivalent to an oven-dry weight of approximately 1 g) contained in a glass centrifuge tube or flask add 15 ml of a 2 + 1 mixture of concentrated sulphuric and nitric acids. Mix well and place the mixture in an ice-bath to prevent volatilisation of mercury. For calcareous samples, the acid mixture should be added dropwise with continuous shaking until the evolution of carbon dioxide has subsided. With samples of high organic matter content, additional acid (about 10 ml) may be needed to ensure complete digestion.

Place the flask or tube in a water-bath maintained at 50 to 60 °C (again, higher temperatures may result in volatilisation of mercury) and allow digestion to continue until the suspension is clear (usually after 2 to 3 hours). Remove the tube or flask from the water-bath and cool the contents by transferring the flask to an ice-bath. Add 5 ml of 5 per cent. potassium permanganate solution with gentle stirring and allow the mixture to stand for 15 minutes. Next, add additional potassium permanganate solution until the purple colour of the permanganate ion persists for at least 15 minutes, followed by 2 ml of 5 per cent. potassium persulphate solution to ensure complete oxidation of organomercury.[18] Allow the mixture to stand for at least 4 hours, preferably overnight. If necessary, dilute the extract with 6 N hydrochloric or nitric acid. A reagent blank should be carried through with each batch of samples.

DETERMINATION—

Transfer an aliquot of the digestion extract containing not more than 0·5 μg of mercury to the reaction flask (see Fig. 1) and dilute it to 30 ml with distilled water. Add 3 ml of concentrated nitric acid, followed by 3 ml of 20 per cent. tin(II) chloride solution, and begin aeration. A standard curve is prepared in the working range of 0 to 0·5 μg of mercury.

The reproducibility of total mercury determination by the developed procedure was evaluated by analysing duplicate samples of Wisconsin River Low sediment on eight different days.

To investigate the recovery of mercury added in various forms to Lake Pickerel sediment, the following standard solutions were prepared.

Mercury(II) chloride—Dissolve 0·1354 g of mercury(II) chloride in 100 ml of 1 N sulphuric acid. The solution contains 1000 μg ml^{-1} of Hg^{2+} and is stable for at least 2 months.

Methylmercury chloride—Dissolve 31·3 mg of methylmercury chloride in 250 ml of water. The solution contains 100 μg ml^{-1} of mercury.

Phenylmercury acetate—Dissolve 41·9 mg of the acetate in 250 ml of 1 N acetic acid. The solution contains 100 μg ml^{-1} of mercury.

Working solutions containing either 0·1 or 1·0 μg ml^{-1} of mercury were prepared from the above stock solutions.

The effect on the recovery of added mercury of drying the sediment prior to determination was investigated by adding mercury(II) chloride, methylmercury chloride, phenylmercury hydroxide or phenylmercury acetate solutions to a series of Lake Pickerel sediment samples and drying the treated samples at 60 °C for 16 hours. The mercury in the samples was subsequently extracted and determined by the above procedure.

RESULTS AND DISCUSSION

Two major considerations essential to the successful application of a quantitative analytical procedure for the determination of total mercury in sediments and soils are the completeness of recovery of mercury when it is added in various forms and the completeness of extraction of native mercury from the sample. Although quantitative recovery of added mercury does not necessarily indicate that the extraction of native mercury is complete, it does indicate that mercury is not lost during the digestion procedure or prior to aeration of the extract for determination by atomic-absorption spectrophotometry. Because digestion and determination errors invariably lead to low mercury recoveries, extraction - digestion procedures can be evaluated on the basis of maximum values of native mercury obtained.

Upon aeration of the digested sample or standard solutions containing mercury as Hg^{2+}, and in the absence of tin(II) chloride solution, volatilisation was appreciable unless a prior

TABLE I

EFFECT ON THE RECOVERY OF ADDED MERCURY OF THE ADDITION OF POTASSIUM PERMANGANATE TO SOLUTIONS CONTAINING VARIOUS AMOUNTS OF CONCENTRATED NITRIC ACID AND 20 PER CENT. TIN(II) CHLORIDE

Volume of concentrated nitric acid/ml	Volume of 20 per cent. tin(II) chloride/ml	Recovery from solution 1,* per cent.	Recovery from solution 2,† per cent.
0	0	87	0
8	0	87	0
10	0	50	0
11	0	27	0
12	0	17	0
15	0	17	0
0	2	100	100
2	2	100	100

Hg added = 0·2 μg, added as $HgCl_2$.
* Hg added to 2 ml of concentrated H_2SO_4 diluted to 100 ml with 0·5 N H_2SO_4.
† Hg added to 2 ml of concentrated H_2SO_4 *plus* 1 ml of 5 per cent. $KMnO_4$ solution diluted to 100 ml with 0·5 N H_2SO_4.

addition of potassium permanganate solution was made. Loss of organomercury was not observed under similar conditions. In the absence of potassium permanganate and tin(II) chloride solutions, recovery of Hg^{2+}, added to sulphuric acid, decreased with increasing additions of concentrated nitric acid (Table I). The addition of 1 ml of 5 per cent. potassium permanganate solution eliminated the loss of mercury in the absence of tin(II) chloride and when tin(II) chloride solution was added, either in the presence or absence of potassium permanganate, the mercury added as Hg^{2+} was recovered quantitatively. This finding indicates that erroneous results may be obtained unless potassium permanganate is added to prevent volatilisation of mercury prior to the addition of tin(II) chloride solution. Increasing the amount of tin(II) chloride added from 2 to 10 ml did not significantly affect the recovery of added mercury (results not presented). The use of 3 ml of 20 per cent. tin(II) chloride solution in 6 N hydrochloric acid is preferred to ensure reduction of excess of potassium permanganate.

The recovery of all forms of mercury added to undried samples of Lake Pickerel sediment was essentially quantitative (Table II) over a wide range of mercury additions. The recovery of added mercury ranged from 98 to 105 per cent. This finding indicates that

TABLE II

RECOVERY BY THE DEVELOPED PROCEDURE OF MERCURY ADDED IN VARIOUS FORMS TO UNDRIED LAKE PICKEREL SEDIMENT

Form in which mercury was added	Amount of mercury added*/μg	Amount of mercury recovered/μg	Recovery, per cent.
Mercury(II) chloride	1·0	1·0	100
	3·3	3·4	103
	10·0	10·3	103
	30	31	103
	50	51	102
Methylmercury chloride.. ..	0·80	0·80	100
	2·4	2·5	104
	8·0	8·0	100
	24	25	104
	40	42	105
Phenylmercury hydroxide ..	0·70	0·72	103
	2·0	2·0	100
	6·8	6·7	98
	20	20·8	104
	34	35	103
Phenylmercury acetate	0·70	0·71	101
	2·8	2·7	98
	7·4	7·7	101
	29	29	100
	48	48	100

* Added to 2 g of sediment.

mercury is not lost by volatilisation during digestion with a mixture of nitric and sulphuric acids and that recovery from the digestion extract was complete during the reduction - aeration step. Separate experiments have shown that metallic mercury added to soils is recovered quantitatively by digestion as described in this procedure, or with concentrated nitric acid, but not by digestion with concentrated sulphuric acid.

The developed procedure enabled more mercury to be extracted from the materials investigated than did extraction with concentrated nitric acid (Table III), although in some instances the difference was small. Although the greatest difference between the amounts of mercury extracted by the two procedures was obtained with the muck peat, which also had the highest organocarbon content, there was no obvious relationship between the recovery of mercury and the organic matter content of the other samples investigated. A second extraction with nitric and sulphuric acids or with nitric acid removed small amounts of mercury from the samples. Extraction with a mixture of nitric and sulphuric acids following extraction with nitric acid alone also removed small additional amounts of mercury. The Wisconsin River High sediment contained an unusually large amount of mercury; this was related to the discharge of mercury from a nearby "chlor-alkali" plant. These findings suggest that the developed procedure gives a reliable estimate of total mercury in sediments and soils.

TABLE III

TOTAL MERCURY IN SEDIMENTS AND SOILS DETERMINED BY NITRIC ACID EXTRACTION, NITRIC ACID - SULPHURIC ACID EXTRACTION (DEVELOPED PROCEDURE) AND COMBINATIONS OF THESE TWO PROCEDURES

		Total mercury (μg g^{-1}) found after						
		HNO_3 extraction			HNO_3 extraction followed by HNO_3 - H_2SO_4 extraction	HNO_3 - H_2SO_4 extraction		
Sample	Organo-carbon,* per cent.	1st	2nd	Sum		1st	2nd	Sum
Sediments—								
Wisconsin River High	7·6	774	3·2	777	791	792	8·5	801
Wisconsin River Low	12·2	1·60	—	—	—	1·61	—	—
Fox River	12·4	1·71	—	—	—	2·27	—	—
Lake Pickerel	1·0	0·15	0·07	0·22	0·25	0·23	0·03	0·26
Soils—								
Plainfield	0·6	0·19	0·01	0·20	0·23	0·24	0·01	0·25
Poygan	3·6	0·17	0·01	0·18	0·20	0·20	0·01	0·21
Muck peat	25·3	0·23	—	—	—	0·44	—	—

* Determined by the method of Konrad, Chesters and Keeney.[23]

An additional advantage of the developed procedure is that organic matter, which may be a major component of sediments and soils, is effectively destroyed during digestion with nitric and sulphuric acids. Partially oxidised organic matter, which may be present in some samples after digestion with nitric acid alone, causes foaming during the aeration step in the atomic-absorption determination, and low recoveries of mercury may result. Although the use of antifoaming agents has been proposed,[22] their use may lead to a low recovery of mercury (results not presented). In an experiment involving the addition of octanol to standard mercury solutions or to digestion extracts, it was found that the recovery of mercury consistently decreased and that the relationship between the recovery of mercury and the amount of octanol added was not always constant. Consequently, the use of antifoaming agents is not recommended. Complete destruction of organic matter in the sample must be effected to alleviate foaming and this technique is preferred to the use of antifoaming agents such as octanol.

Sample pre-treatment is an additional important consideration in the quantitative determination of total mercury in sediments and soils. It is much more convenient to transport, store and analyse dried samples of sediments and soils. The effect of drying on mercury recovery was therefore evaluated. Whereas the recovery of mercury added in various forms to samples of an undried sediment was essentially quantitative (Table II), drying the same sediment at 60 °C for 16 hours following additions of the various forms of

mercury had the effect of varying the recoveries obtained (Table IV). The recoveries of methylmercury chloride and phenylmercury hydroxide were the most affected by drying (16·8 and 11·7 per cent. loss, respectively), presumably because of volatilisation. Loss of mercury from phenylmercury acetate was low (2·3 per cent.) and that from Hg^{2+} negligible (0·2 per cent.). It is recommended that undried samples be used for the determination of total mercury in sediments and soils.

TABLE IV

EFFECT OF DRYING AT 60 °C FOR 16 HOURS ON THE RECOVERY OF MERCURY ADDED IN VARIOUS FORMS TO LAKE PICKEREL SEDIMENT

Form in which mercury was added	Amount added/μg g^{-1}	Amount recovered/μg g^{-1}	Loss of mercury, per cent.
Mercury(II) chloride	5·00	4·99	0·2
Methylmercury chloride	4·05	3·87	16·8
Phenylmercury hydroxide ..	3·35	3·00	11·7
Phenylmercury acetate	3·60	3·50	2·3

The sensitivity of this procedure is largely dependent on sample size as other parameters that control sensitivity (*viz.*, aeration rate, temperature, adsorption, cell volume and sample flask volume) are constant. A 1-g sample containing 0·01 μg of total mercury necessitates a probable lower detection limit of 10 parts per 10^9. The normal working range would be higher, as background levels for soils and sediments are generally greater than 50 parts per 10^9 of mercury. If increased sensitivity is required, signal amplification by means of recorder scale expansion is possible. Standard curves for a scale expansion of 10$\times$ have been obtained (not reported) which increase sensitivity to 1 part per 10^9.

The precision of the method is indicated by the low standard deviation (0·033 p.p.m.) in results for the determination of mean total mercury content (1·61 p.p.m.) of the Wisconsin River Low sediment obtained on eight different days.

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The Determination of Niobium in Steel by Atomic-absorption Spectrophotometry

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The determination of niobium by atomic-absorption spectrophotometry is complicated by many matrix effects. For the determination of niobium in steels, the interference effects were avoided by separating the niobium and re-dissolving it in ammonium sulphate - sulphuric acid and adding tartaric acid to stabilise the solution. Potassium sulphate was added as an ionisation suppressant to all the solutions containing niobium. An aqueous solution of niobium must have a concentration in the range 100 to 1000 μg ml^{-1} to give satisfactory absorption results.

NIOBIUM is added to many types of steel, including pipeline steel, which is of current interest in the gas industry. As the determination of niobium by classical chemical analysis is difficult and tedious, we decided to investigate the possibilities of atomic-absorption spectrophotometry for its determination in a variety of steels. Kirkbright, Smith and West[1] have developed an indirect method for determining niobium in which molybdoniobophosphoric acid is formed and its molybdenum content is determined by atomic-absorption spectrophotometry.

Niobium in steel has been determined directly by Welcher and Kriege[2,3] and Schiller[4] but their methods required the use of hydrofluoric acid. As our apparatus is not equipped with a PTFE-lined nebuliser, we decided to develop a method that does not require the use of this acid. Three methods of dissolving steels were considered so as to find the most suitable method for our purpose.

EXPERIMENTAL

APPARATUS—

A Techtron AA4 atomic-absorption spectrophotometer was used, equipped with an AB50 50-mm slot burner and a niobium hollow-cathode lamp made by Atomic Spectral Lamps Ltd.

The instrument settings were as follows—

Wavelength	334·9 nm
Slit width	25 μm (0·08 nm optical slit width)
Lamp current	20 mA
Nitrous oxide pressure	138 kN m^{-2}
Nitrous oxide flow-rate	9·6 l min^{-1}
Acetylene flow-rate	Set to give a luminous flame, being finally adjusted to give maximum response (3·55 l min^{-1})

REAGENTS—

The acids used both for interference studies and for dissolving the samples were of Aristar grade. All other reagents were of analytical-reagent grade. The niobium pentoxide used for the standard solutions was Johnson Matthey JMC "High Purity Material," grade 1.

Standard niobium solution—A stock solution containing 1000 μg ml^{-1} of niobium was prepared from niobium pentoxide. A 1·4305-g amount of the oxide was weighed into a 100-ml beaker and 14 g of ammonium sulphate and about 22 g of concentrated sulphuric acid were added.[5] The mixture was heated on a hot-plate until the clear yellow solution obtained had evaporated almost to dryness. A 100-g amount of tartaric acid was weighed out and a portion was added to the cooled niobate residue followed by a small volume of water such that there was an excess of solid tartaric acid present. To avoid hydrolysis of the niobium compound, the niobate was allowed to dissolve in this saturated solution of tartaric acid without heating. The niobate solution, to which the remainder of the tartaric acid had

been added, was made up to 1 litre with water. This stock solution of niobium was found to be stable and was diluted to give various concentrations of niobium without further addition of tartaric acid. Potassium sulphate, at a potassium concentration of 2500 μg ml^{-1}, was added to the working standards as an ionisation suppressant.

Choice of fuel and absorption lines—

An acetylene-rich flame was used, so as to give maximum absorbance. The most sensitive position for the beam from the hollow-cathode lamp was found to be 5 mm above the top of the burner.

Four niobium lines are listed in "Hollow Cathode Lamp Data,"[6] *viz.*, 334·9, 358·0, 408·0 and 405·9 nm. The first two lines are of almost equal sensitivity but the 358·0-nm line occurs in a region of high CN emission,[7] whereas the 334·9-nm line occurs in a region of low emission and is the best line to use. The 405·9-nm line, although less sensitive than the 408·0-nm line, is particularly strong and, as only a small potential is required on the photomultiplier tube, it is very stable and useful for scale expansion.

Sensitivity—

The sensitivity (defined as the concentration of metal to give 1 per cent. absorption) of niobium at a wavelength of 334·9 nm is usually quoted[6] as 20 μg ml^{-1}. Manning[7] found a value of 40 μg ml^{-1}, and this is the value we found with our apparatus.

Study of interferences—

The effects of a number of ions and compounds on the niobium absorption were investigated. The solutions contained 500 μg ml^{-1} of niobium and 5000 μg ml^{-1} of a foreign ion or amounts of different acids such that their concentrations were 5 or 3 N. The metals were added as sulphates or nitrates and the anions as the potassium salts. The results are shown in Tables I, II and III.

Table I

Interference of metal and ammonium ions

Potassium concentration, 2500 μg ml^{-1}; niobium concentration, 500 μg ml^{-1}

Foreign ion at a concentration of 5000 μg ml^{-1}	Niobium absorption in the presence of interfering ion, per cent.	Foreign ion at a concentration of 5000 μg ml^{-1}	Niobium absorption in the presence of interfering ion, per cent.
None	9·8	Manganese	9·8
Iron	7·5	Titanium	2·0
Cobalt	3·0	Zinc	6·5
Nickel	3·0	Cadmium	8·0
Chromium	5·5	Lithium	1·0
Aluminium	18·8	Sodium	9·8
Lanthanum	1·0	Magnesium	9·8
Copper	3·0	Uranium	2·0
		Ammonium	9·0

Table II

Interference of anions

Potassium concentration, 2500 μg ml^{-1}; niobium concentration, 500 μg ml^{-1}

Foreign anion at a concentration of 5000 μg ml^{-1}	Niobium absorption in the presence of interfering ion, per cent.	Foreign anion at a concentration of 5000 μg ml^{-1}	Niobium absorption in the presence of interfering ion, per cent.
None	9·8	Acetate	9·8
Fluoride	9·8	Phosphate	7·5
Chloride	9·8	Dichromate	6·5
Bromide	9·8	Iodate	9·8
Iodide	9·8	Permanganate	9·8
Sulphate	9·8	Vanadate	1·0
Nitrate	9·8	Molybdate	9·8
		Tungstate	9·8

TABLE III

INTERFERENCE OF ACIDS

Potassium concentration, 2500 μg ml^{-1}; niobium concentration, 500 μg ml^{-1}

Acid	Niobium absorption in the presence of interfering acid, per cent.
None	9·8
Hydrochloric acid, 5 N	9·8
Sulphuric acid, 5 N	6·5
Nitric acid, 5 N	9·8
Acetic acid, 5 N	13·0
Sulphuric acid, 3 N	9·8
Acetic acid, 3 N	11·0

EFFECT OF ALUMINIUM ON THE NIOBIUM ABSORPTION—

As the presence of aluminium almost doubled the niobium absorption, this effect was studied further, including the influence of aluminium on the interferences of other metals.

With a niobium concentration of 500 μg ml^{-1}, an aluminium concentration of 5000 μg ml^{-1} and an interfering metal concentration of 5000 μg ml^{-1}, it was found that the matrix effects due to cobalt, nickel, chromium, uranium and lithium were reduced but not completely overcome. The aluminium had little effect on the niobium absorption in the presence of titanium and vanadium, but the matrix effect of iron was completely eliminated. The results are shown in Table IV.

TABLE IV

EFFECT OF ALUMINIUM

Potassium concentration, 2500 μg ml^{-1}; niobium concentration, 500 μg ml^{-1}; aluminium concentration, 5000 μg ml^{-1}

Foreign cations and vanadate at a concentration of 5000 μg ml^{-1}	Niobium absorption in the presence of interfering ion and aluminium, per cent.
None	18·8
Iron	18·8
Cobalt	13·0
Nickel	11·0
Chromium	13·0
Titanium	3·0
Lithium	11·0
Uranium	12·0
Vanadate	3·0

Table V shows the effect of aluminium concentration on a solution containing 200 μg ml^{-1} of niobium.

TABLE V

EFFECT OF ALUMINIUM CONCENTRATION

Aluminium concentration/μg ml^{-1}	Niobium absorption, per cent.
0	4·5
100	7·5
200	9·8
300	9·8
400	9·8

ANALYSIS OF STEEL—

The steels used for this investigation were niobium standard steels (Table VI) and some mild steels previously analysed by X-ray fluorescence spectrometry.

Three methods of dissolving the steels were investigated.

Method 1—In the method of Schiller[4] steel is dissolved in 3 N sulphuric acid, leaving niobium carbide as a residue. By using this method we were unable to dissolve the three standard steels completely. The residue was examined by X-ray diffraction and was found to consist mainly of unattacked steel. The filtrates were also examined by this method and found to be free from niobium. As we were unable to spray hydrofluoric acid through

our instrument, we fused the above residue with ammonium sulphate - sulphuric acid and dissolved the melt in tartaric acid as described under *Standard niobium solution*. The results obtained for niobium concentration were invariably low, presumably owing to the depressant effects of iron, nickel and chromium on the niobium absorption.

With the low-niobium mild steels, for which a large weight of sample, *e.g.*, 10 to 20 g, was necessary, the bulk of the steel was dissolved by this method. The sulphuric acid solution was filtered off and examined by X-ray fluorescence spectrometry for niobium, which was not found. The residue was dissolved in a mixture of hydrochloric and nitric acids, as described under *Method III*, and the niobium was precipitated by diluting the acidic solution.

TABLE VI

CERTIFIED VALUES OF THE STANDARD STEELS OBTAINED FROM BRITISH CHEMICAL STANDARDS

Austenitic stainless steel No. 337		Niobium-stabilised stainless steel 261/1		Alcomax III No. 365	
Element	Content, per cent.	Element	Content, per cent.	Element	Content, per cent.
C	0·081	C	0·09	C	0·025
Si	0·50	Si	0·50	Si	0·34
S	0·018	P	0·017	S	0·18
P	0·016	Mn	0·83	Mn	0·11
Mn	0·87	Cr	17·4	Ni	13·5
Cr	17·80	Ni	13·1	Cu	2·7
Ni	9·52	Nb	0·91†	Co	24·7
Nb	1·02*	Ta	0·006	Al	8·1
Ta	0·04	Mo	0·11	Nb	0·57‡
Pb	0·0012	Cu	0·12	Ta	0·033
		Co	0·050	Fe	49·3
		As	0·016		

* Average of 1·01, 1·00, 1·02, 1·06, 1·03, 1·00, 1·04 and 1·01 per cent.
† Average of 0·91, 0·91, 0·92, 0·90, 0·89, 0·93, 0·90 and 0·89 per cent.
‡ Average of 0·55, 0·55, 0·59, 0·57 and 0·58 per cent.

Method II—The method of Krasil'schchikov and Popova,[8] in which the steel is dissolved in 1 + 1 hydrochloric acid - water *plus* a few drops of 1 + 4 nitric acid - water, was investigated. After the sample had dissolved, the solution was diluted and heated with sodium sulphite to hydrolyse the niobium compounds. The precipitate was fused with ammonium sulphate - sulphuric acid, as described under *Standard niobium solution*, and the niobate was dissolved in tartaric acid solution. This method worked well on Alcomax but the results on stainless steels that contained niobium tended to be low.

Method III—The most satisfactory method of dissolving the standard steels[9] is by heating them in an acidic mixture consisting of 750 ml of concentrated hydrochloric acid, 250 ml of concentrated nitric acid and 1000 ml of water; 25 ml of this mixture were used for each 2 g of steel. With Alcomax (a 2 to 4-g sample is suitable) the bulk of the acid was boiled off and the solution was diluted to 100 to 200 ml (depending on the sample weight). The precipitated niobium compounds were filtered off and then fused with ammonium sulphate - sulphuric acid. X-ray fluorescence spectrometry showed that there was no niobium in the filtrate.

With the high-chromium stainless steels, dissolution was not complete when the mixture of hydrochloric and nitric acids was used. The steel (2 g) was boiled with 25 ml of the mixture of acids until no further dissolution appeared to take place. The solution was filtered and the residue was examined by X-ray diffraction and shown to consist of undissolved steel and niobium nitride. The residue was dissolved by heating it with 10 ml of aqua regia and then heated with 25 ml of perchloric acid to oxidise the chromium to dichromate. The perchloric acid was evaporated off and the solution was diluted to 100 ml with water and filtered. X-ray fluorescence spectrometry showed that all the filtrates were free from niobium.

The unattacked niobium nitrides were fused with 1 g of ammonium sulphate *plus* 2 ml of concentrated sulphuric acid. The resulting mixture was heated on a hot-plate until a clear yellow solution was obtained. On cooling this solution, a clear glassy substance was obtained, the ammonium sulphate and the bulk of the sulphuric acid having been evaporated

off. The glassy substance was dissolved in the cold in tartaric acid solution as described under *Standard niobium solution*, and the solution was made up to 100 ml with water. The niobium concentration was read off from a calibration graph.

The results for the three standard steels are given in Table VII. The variations were no greater than those on which the certified values, shown in Table VI, were based.

TABLE VII

NIOBIUM CONTENTS OF THE THREE STANDARD STEELS

Steel	Certified niobium content, per cent.	Niobium content determined, per cent.
Austenitic stainless steel No. 337	1·02	1·00
		1·00
		0·95
		0·99
		0·96
Niobium-stabilised stainless steel 261/1	0·91	0·89
		0·90
		0·90
Alcomax III	0·57	0·54
		0·54
		0·60
		0·58
		0·55
		0·59
		0·58

Method III is therefore the recommended procedure for steels that contain more than 0·25 per cent. of niobium. A sample weight of about 4 g should be used for a steel with a niobium content of 0·25 per cent. and correspondingly smaller sample weights for steels with higher niobium contents.

For the analysis of mild steels with a niobium content of 0·05 per cent. or lower, a 20-g sample weight was taken. The bulk of the steel was dissolved in 3 N sulphuric acid as described under *Method I*. The residue was dissolved in hydrochloric acid - nitric acid as described under *Method III* and the niobium was precipitated by diluting the solution. The niobate was fused with ammonium sulphate - sulphuric acid and dissolved in tartaric acid solution. Aluminium nitrate was added to the niobate solution so that the concentration of aluminium was at least twice the expected concentration of the niobium and at least equal to the concentration of any foreign metals. A similar amount of aluminium was added to the solutions used for obtaining the standard calibration graph.

Table VIII shows the results of the analysis of two mild steels.

TABLE VIII

NIOBIUM CONTENTS OF MILD STEELS

	Niobium content	
	by atomic-absorption spectrophotometry, per cent.	by X-ray fluorescence spectrometry, per cent.
Steel A	0·023	0·024
Steel B	0·052	0·051

DISCUSSION

Tables I to IV show that considerable matrix effects occur in the determination of niobium.

The increase in absorption by metals when acetic acid is added has been noted by other workers, particularly Sachdev, Robinson and West.[10] They concluded that the effect was similar to that of organic solvents; presumably the acetic acid lowers the viscosity of the solution. When vanadium was used they found a considerable increase in absorbance when aluminium and titanium were present. We found that aluminium almost doubled the niobium absorption but that titanium depressed it. Sachdev, Robinson and West suggested

that the enhancement of absorption is due to the competition for oxygen between vanadium and the metals, which form very stable oxides. It is probable that a similar reaction takes place between niobium and aluminium. The equilibrium

$$2Nb + 5O \rightleftharpoons Nb_2O_5$$

is shifted in favour of free niobium atoms in the presence of aluminium. When the amounts of aluminium and niobium present were equal, the niobium absorption was doubled; increasing the amount of aluminium had little further effect. The matrix effect of iron was eliminated and other matrix effects could be reduced but not completely eliminated by the addition of aluminium.

Conclusions

The determination of niobium by atomic-absorption spectrophotometry is greatly influenced by the presence of other elements; the matrix effects can be eliminated by separating the niobium and re-dissolving it. This is the most time-consuming step in the determination. Provided a large enough steel sample is available, very low concentrations of niobium can be determined (*e.g.*, 0·01 per cent.). The absorption can be increased by adding aluminium.

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The Determination of Tungsten and Silicon in Highly Alloyed Materials by Atomic-absorption Spectroscopy

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Tungsten and silicon are determined in the presence of large amounts of iron, nickel, cobalt, molybdenum and other constituents of highly alloyed materials by means of atomic-absorption spectrophotometry with a nitrous oxide - acetylene flame. Complete dissolution is effected in a mixture of aqua regia and hydrofluoric acid, which necessitates the entire use of plastics-ware. Inter-element effects are both numerous and complex, and the method of standard addition is recommended for calibration purposes.

The classical gravimetric methods for determining tungsten, such as that described by Westwood and Mayer,[1] are tedious and require a high degree of skill on the part of the operator if satisfactory results are to be obtained in the presence of large amounts of molybdenum, silicon, titanium or chromium. The various colorimetric methods have recently been discussed by Fogg, Marriott and Thorburn Burns,[2] who state that even in their own final procedure difficulties are introduced by the presence of large amounts of molybdenum. Similarly, large amounts of tungsten and the other metals cause great difficulties in the gravimetric determination of silicon, and the corrosion resistance of many modern alloys renders their dissolution difficult under conditions suitable for the subsequent colorimetric determination of this last element. Price and Roos[3] have described a general method for the determination of silicon in many materials by atomic absorption, but the solution method recommended by them will not effect complete dissolution of many of the heat and corrosion-resistant alloys now in use.

A need arose recently in our laboratory to carry out determinations of both tungsten and silicon in a wide range of such alloys, and it became apparent that if the work was to be performed economically the traditional methods were inadequate. In addition to the work of Price and Roos referred to above, the atomic-absorption spectroscopy of tungsten has been described,[4,5] although few methods in which this technique is used have been described. The most likely explanation for this is the relatively poor sensitivity shown by this element, but this is not a drawback if significant alloying amounts are to be determined.

Experimental

The atomic-absorption behaviour of tungsten in alkaline and acidic solution was checked, and no major difficulties were encountered. A very fuel-rich nitrous oxide - acetylene flame was required, and the sensitivity obtained was slightly lower than that claimed by Amos and Willis[4]; it is probable that this was caused by the rather wider spectral band pass used by us, the maximum resolution of our instrument being 0·15 nm, as opposed to the 0·08-nm band pass used by the earlier workers. The behaviour of silicon was already known to us, and is in any case well documented.

The choice of solution conditions was rather restricted for the alloys in which we were interested as most of them were not attacked by reducing acids and the reaction with aqua regia often ceased after a short period because of coating of the sample with insoluble tungsten, silicon or molybdenum compounds. Early attempts to hold tungsten in solution by incorporating phosphoric acid into the solvent proved abortive because such mixtures showed a greatly reduced rate of attack on the samples. Also, molybdenum and silicon still gave rise to insoluble coatings on the sample, even in such mixtures. Eventually, it was decided that a mixture that included hydrofluoric acid would be necessary, and that the difficulties known to be attendant upon its use would have to be tolerated. Some investigations were carried out along the lines followed by Price and Roos, whereby excess of fluoride is complexed with boron, but the amount of fluoride required to dissolve the samples completely was too high for this approach to be successful. It became evident that the line of approach most likely to yield satisfactory results was the simplest and most direct, and a method involving the use of aqua regia *plus* hydrofluoric acid as the solvent mixture was decided upon.

The availability of beakers made from PTFE has made this type of method practicable, and the fairly recent introduction of calibrated ware made from polypropylene has removed most of the remaining difficulties. Experiments showed that the mixture used in the procedure described below readily attacked most types of sample, and the effect of this solvent on the atomic-absorption spectrophotometer was investigated. No difficulties were encountered, and attack on the burner and nebuliser was found to be sufficiently slow with the dilute acids actually sprayed. The burner of our own instrument is constructed entirely from En 58J stainless steel (a 3 per cent. molybdenum - niobium stabilised grade) and it is possible that burner systems containing other materials may be more susceptible to attack. We would suggest in particular that titanium burner heads may suffer from attack by our acid mixture, and that this aspect should be checked before extensive use is made of this method on an instrument with such components.

The effects of other possible constituents of the type of alloy being studied on the atomic-absorption behaviour of both tungsten and silicon were investigated, and a number of suppression and enhancement effects found. These are summarised in Table I. It is noteworthy that the effects of two or more elements cannot be easily predicted from the single-element effects, and it became apparent that standardisation must be made under conditions as similar as possible to those obtaining in the sample solution. After a number of attempts to reproduce these conditions by means of synthetic mixtures, it was finally decided to use the method of standard addition.

TABLE I

INTER-ELEMENT EFFECTS

1-g synthetic samples of indicated composition, containing the equivalent of 5 per cent. of tungsten and 1 per cent. of silicon

Sample composition	Tungsten absorbance	Silicon absorbance
Nil	85·5	46
100 per cent. Ni	95	56
100 per cent. Mo	98	57
100 per cent. Fe	95·5	52·5
100 per cent. Cr	94	83·5 (very noisy)
1 + 1 Ni - Mo	94	53·5
1 + 1 Ni - Fe	93·5	53·5
1 + 1 Ni - Cr	87	57
1 + 1 Mo - Fe	90	52
1 + 1 Mo - Cr	79·5	53·5
1 + 1 Fe - Cr	86	50·5
1 + 1 + 1 Ni - Mo - Fe	97	53·5
1 + 1 + 1 Ni - Fe - Cr	95	51·5
1 + 1 + 1 Ni - Mo - Cr	90	62·5
1 + 1 + 1 Fe - Mo - Cr	92	60
1 + 1 + 1 + 1 Ni - Mo - Fe - Cr	89	59
As above + 1 per cent. of Mn + 1 per cent. of Cu	89	59

No significant background absorption was found with pure metal solutions at the 100 per cent. concentration level; silicon absorption had no effect on tungsten, but the effect of 10 per cent. of tungsten on pure silicon solution at the 1 per cent. concentration level was to increase the absorption from 46 to 56 arbitrary units. All solutions contained 10 ml of 2·5 per cent. w/v sodium chloride solution.

Standard addition methods should be inherently less precise than direct standardisation methods, but provided that certain criteria are satisfied, the former methods can give precision levels adequate for the contents dealt with in this work. The most important of these criteria are that the volumetric measurements should be of sufficient accuracy, that the addition should not materially affect the final solution conditions and that the final absorbance value obtained should lie within the linear portion of the calibration graph; all of these criteria can be fairly readily satisfied in this instance.

APPARATUS—

PTFE beakers—Squat-form beakers of 150-ml capacity were used (Baird & Tatlock Ltd., London).

Polypropylene calibrated flasks—Flasks of 100-ml capacity were used (X-Lon Products Ltd., London).

Atomic-absorption spectrophotometer—A spectrophotometer with a burner for nitrous oxide - acetylene flames and light sources suitable for determinations of silicon and tungsten is necessary. Our own instrument was a Southern Analytical A3000, with lamps from Varian Techtron and Southern Spectral Sources Ltd.

REAGENTS—

AnalaR grade reagents were used throughout, although the amounts used are such that general laboratory-grade reagents should be adequate. All the usual precautions associated with the handling of hydrofluoric acid solutions must be observed, and the initial solvent mixture is exceptionally corrosive. It is recommended that rubber gloves should be worn throughout the work and not removed until the final solutions have been used and discarded and the flasks rinsed out at least once. Even dilute hydrofluoric acid solutions are capable of inflicting unpleasant sores on the skin, especially with young or female operators. Solutions of hydrofluoric acid, or any other toxic substance, should not be aspirated into a flame without the provision of good ventilation, including the use of a forced draught. It is sometimes suggested that particular burner designs remove the need for such ventilation systems, but no burner design can prevent the discharge of the burnt gases and spent sample into the laboratory atmosphere. Fluoride vapours are highly toxic and should be regarded as being very dangerous.

STANDARD SOLUTIONS—

Fuse 1·262 g of freshly ignited tungsten(VI) oxide or 2·140 g of freshly ignited silica with about 5 g of sodium hydroxide in a silver crucible, extract the melt with water and make the volume up to 100 ml. One millilitre of this solution contains 10 mg of tungsten or silicon, which is equivalent to 1·00 per cent. with a 1-g sample.

METHOD—

Weigh 1 g of sample, in finely milled form, into a PTFE beaker and dissolve it in 10 ml of hydrochloric acid (sp. gr. 1·18) *plus* 5 ml each of nitric acid (sp. gr. 1·42) and 40 per cent. hydrofluoric acid. The order of addition of the acids is immaterial from the point of view of the final results, but it will often be found advantageous to attempt dissolution of particular samples with part of this mixture initially. For example, nickel - molybdenum or Monel-type alloys dissolve more readily in nitric acid than in aqua regia, and the other two acids can be added later to dissolve any precipitated silica, etc.; for high chromium alloys, the presence of aqua regia initially is often useful, the hydrofluoric acid being added when the reaction subsides, but for the most complex alloys the full mixture, with gentle heating, is necessary. Care must be taken to ensure that the solution does not boil or some loss of silicon may ensue.

When the sample has completely dissolved, transfer the solution carefully to a 100-ml calibrated plastics flask. Care is essential, as it is usual to find small particles of undissolved sample in the bottom of the beaker because, with the combination of opaque beakers, very dark sample solutions and very acid-resistant samples, it is difficult to be certain that dissolution is complete. If this difficulty arises, add about 5 ml of the acid mixture and warm the mixture to dissolve the solid particles. The method is quite tolerant of variations in the total acid concentration, between 10 and 25 ml of acid mixture in the final solution producing no significant change in the results. Next, add 10 ml of 2·5 per cent. sodium chloride solution to ensure that sufficient alkali metal is present to enhance fully the silicon absorption, dilute the solution to 100 ml and spray it into the burner under conditions appropriate to the element and the particular instrument in use. Our own conditions are given in Table II as a guide for other users of similar equipment but, in general, optimum conditions for any atomic-absorption determination should always be determined on the particular instrument in use.

CALIBRATION—

From the standard solutions prepare dilute tungsten and silicon solutions in the same concentrations of acid and sodium chloride as for the samples, containing various concentrations of each element up to 1 mg ml^{-1} of tungsten and 0·5 mg ml^{-1} of silicon. These maximum

concentrations correspond to 10 per cent. of tungsten and 5 per cent. of silicon in the sample, and on our instrument represent the top of the linear portion of the relevant calibration graph; the optical densities obtained were 0·5 and 0·73, respectively, and these values should not be exceeded in any subsequent determination or standardisation. Scale expansion can, of course, be used to give better precision of reading.

TABLE II

OPERATING CONDITIONS OF THE SOUTHERN ANALYTICAL A3000 ATOMIC-ABSORPTION SPECTROPHOTOMETER

		Tungsten	Silicon
Wavelength/nm		255·1	251·6
Band pass/nm		0·15	0·3
Burner height	Position	3	1
	Distance below axis/cm	0·85	1·4
N_2O flow	Indicated/l min^{-1}	6·5	6·5
	True/l min^{-1}	9·9	9·9
C_2H_2 flow	Indicated/l min^{-1}	7·5	7·3
	True/l min^{-1}	6·0	5·9

Samples will usually be analysed in batches of similar material, and our normal practice is to measure the optical densities for both elements on all sample solutions and then to re-weigh the sample (or samples) that gives the lowest reading. From the calibration graphs for the pure standard solution the amount of the element that must be added to double approximately the original reading is calculated, taking care that the final reading does not exceed the permitted maximum value, and the requisite amount is then added to the sample. The procedure, as given above, is followed and the instrument is set on this solution as standard; the sample solutions are then read against it and the tungsten and silicon contents calculated. This procedure allows the measurement of contents up to about 6 per cent. of tungsten and about 3 per cent. of silicon, while still retaining sufficient margin to allow the addition of a satisfactory volume of standard solution to give good calibration. For the determination of tungsten contents between 5 and 10 per cent., 0·5-g samples are taken, as they are for silicon contents of from 3 to 5 per cent. For contents greater than 10 per cent., the method, in our opinion, gives results that are insufficiently precise for reference work, although by using 0·25-g samples it may give results that are adequate for control purposes.

An alternative method of standardisation is to use standard samples of the same over-all composition as the actual samples, and this would be the method chosen for a laboratory that frequently analyses similar types of material. It was not available to us because work was received irregularly, and was not, therefore, regarded as routine.

RESULTS

The method has been applied to a number of samples that have also been analysed by gravimetric methods, and, in general, the agreement is considered to be satisfactory. Details of the samples and results are given in Table III.

The coefficients of variation as determined on the most complex alloy encountered, the nickel - iron - copper - chromium - molybdenum alloy, were 1·5 per cent. relative for silicon and 2·3 per cent. relative for tungsten. From the sensitivities quoted above and these precision figures, it would seem likely that the absolute lower limits for the method are about 0·05 per cent. of either element. These would give optical densities of only 0·003 and 0·007 for tungsten and silicon, respectively, and, with a single-beam instrument at least, we would not claim significance for these results on the basis of such readings. For levels below 0·2 per cent. of tungsten and 0·1 per cent. of silicon alternative methods will be superior. This method has been used successfully for mild and alloy steels, Monels, copper-base alloys and Nimonic-type alloys, usually for silicon alone as alloys of these types contain only trace amounts of tungsten. The time required for a batch of six determinations of both elements is about 1½ hours, or 1 hour if previously analysed standards are available.

For many of the simpler alloys mentioned above, other methods for determining silicon are perfectly adequate, *e.g.*, atomic-absorption methods not involving the use of hydrofluoric acid, absorption spectrophotometric methods and conventional gravimetric methods. The

TABLE III

RESULTS ON SOME TYPICAL SAMPLES AND AGREEMENT WITH GRAVIMETRIC RESULTS

Alloy	Silicon, per cent.	Tungsten, per cent.
Ni alloy, 30% *Mo*—		
Mean gravimetric results	0·66	4·20
Atomic-absorption results	0·68, 0·68	4·20, 4·10
B.C.S. steels—		
220/1 certificate value	0·30	6·74
Atomic-absorption results	0·32, 0·30	6·76, 6·80
241/1 certificate value	—	19·61
Atomic-absorption results	—	19·6, 19·8
Ni alloy, 6% *Fe*, 6% *Cu*, 6% *Mo*, 25% *Cr*—		
Mean gravimetric result	2·77	1·22
Atomic-absorption results	2·78, 2·80	1·20, 1·21
Duplicate determinations		
Ni alloys, 30% *Mo*—		
1	0·62, 0·63	1·73, 1·78
2	0·89, 0·85	1·44, 1·36
3	0·98, 1·08	—
4	0·96, 0·97	—
5	0·89, 0·93	—
Ni alloys, *Fe* - *Cu* - *Mo* - *Cr as above*—		
1	2·49, 2·51	2·81, 2·72
2	3·02, 3·05	2·74, 2·75
3	3·20, 3·26	2·68, 2·88
4	2·44, 2·47	0·61, 0·57
5	2·48, 2·47	1·84, 1·86
6	3·07, 3·10	3·50, 3·40
Monels—		
1 Gravimetric results	0·99	—
Atomic-absorption results	1·01, 1·10, 1·05	—
2 Gravimetric result	2·73	—
Atomic-absorption results	2·72, 2·72	—
3 Gravimetric result	4·65	—
Atomic-absorption results	4·66, 4·72	—
Carbon steels—		
1 Gravimetric result	0·60	—
Atomic-absorption results	0·59, 0·57	—
2 Gravimetric result	0·17	—
Atomic-absorption results	0·17, 0·18	—
3 Gravimetric result	1·06	—
Atomic-absorption results	1·03, 1·04	—

results given in Table III were obtained on samples of these types that were required to be analysed to determine silicon at the same time as the more difficult samples, and it was convenient to use the same method. In such a situation the method can be used to advantage.

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Volatility of Organic Microanalytical Standards

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It is sometimes convenient for samples that are to be decomposed by the oxygen-flask method to be weighed on the afternoon before the day on which they are to be burned. If this procedure is to be used with confidence, one must be sure that no loss of sample occurs by volatilisation during the time the sample remains standing.

A preliminary check of the volatilities of a range of materials of interest to microanalysts indicated that microanalytical standard compounds containing the trifluoromethyl group can undergo a significant loss in weight by volatilisation when they are left overnight. It would be difficult to measure absolute rates of evaporation, and the conditions used to store samples before oxygen-flask combustion vary, so we have compared the rates of evaporation of different substances under reproducible, arbitrary conditions. These comparisons clearly depend on the specific surface areas of the samples; we have not attempted to allow for this effect but have aimed to use samples that are typical of normal microanalytical practice.

Experimental and results

Weighed samples of dried microanalytical standard compounds (about 5 mg) were spread in the bottoms (about 11 × 4 mm) of conventional platinum microcombustion boats, which were placed on stainless-steel cooling blocks (4 cm in diameter and 1 cm high). Each block was placed on one half of a Petri dish (diameter about 10 cm) and covered with a crystallisation dish (about 8 cm in diameter and about 4 cm deep). The volume of air over the boat was then about 150 ml. These test units were stored in a balance room at about 24 °C and the weights were checked over a period of 40 days. A Mettler M5 microbalance was used for the weighings.

Duplicate tests were carried out on acetanilide, *S*-benzylthiuronium chloride, *p*-bromobenzoic acid, *p*-chlorobenzoic acid, *p*-fluorobenzoic acid, *o*-iodobenzoic acid, 2-methylbenzimidazole, 2,2-bis(ethylsulphonyl)propane (sulphonal), triphenylphosphine and 3-methoxy-4-hydroxybenzaldehyde (vanillin); these compounds showed no significant changes in weight (<5 μg day^{-1}). Benzoic acid (included only for comparison), trifluoroacetanilide and *m*-trifluoromethylbenzoic acid were examined in a similar manner and showed appreciable losses in weight. When the loss in weight was plotted against time, the following slopes (in μg day^{-1}) were obtained: benzoic acid, 15 (average of 2 tests); trifluoroacetanilide, 88 (average of 3 tests); and *m*-trifluoromethylbenzoic acid, 14 (average of 3 tests).

Because trifluoroacetanilide showed such a large loss in weight, further tests were carried out with this compound. Small platinum crucibles (1 cm in diameter and 1 cm deep) were used in place of the boats and they were stored, containing weighed amounts of the standard (about 5 mg), in corked sample tubes (5 × 1·5 cm), *i.e.*, under conditions that were nearer to those under which we store our samples for oxygen-flask combustion. The smaller container and better seal caused a marked reduction in the rate of loss in weight. A mean of three tests gave a rate of loss in weight of 16 μg day^{-1}.

The trifluoromethyl compounds are very useful standards for the oxygen-flask method and the above observations will therefore be of importance to anyone interested in planning their weighing schedules ahead of the day on which the actual analyses are to be carried out.

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Communication

Material for publication as a Communication must be on an urgent matter and be of obvious scientific importance. Manuscripts must not exceed 300 words; rapidity of publication precludes the use of diagrams, but tables or formulae may be included if the length of text is reduced appropriately. Communications should not be simple claims for priority. This facility for rapid publication is intended for brief descriptions of work that has progressed to a stage at which it is likely to be valuable to workers faced with similar problems. A fuller paper may be offered subsequently, if justified by later work.

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

A NOVEL SEPARATION MEDIUM

RESEARCH is being carried out into the chemical and physical nature of material generated as a result of wear in oil-washed surfaces. This work is aimed at improving conventional health monitoring techniques for engines and machinery.

A basic problem in this type of analysis is the difficulty of separating very small amounts of finely divided insoluble matter from a large volume of oil so that detailed examinations of the separated material can be made. The particles, which range in size from fractions of a micrometre upwards, cannot be separated in a reasonable time by centrifuging. Modern membrane filters retain all but the finest matter, but the range of solvents that can be used is limited and furthermore the milligram or so of solid is not easily separated from the membrane. Short columns of silica or alumina of the grades used for chromatography effect a clean separation but the material of interest is then inextricably mixed with the column material. The purpose of this communication is to report a novel approach to this problem, which involves the use of a filtration column made of a material that readily sublimes. After filtration, the particles of interest can then be isolated by applying gentle heat to remove the accompanying column material.

The first two readily available materials for trial were ammonium carbonate (sublimation temperature 58 °C) and metaldehyde (112 °C). The former proved to be difficult to purify to the required degree—iron was the chief element of interest in the wear samples. Metaldehyde was purified by heating it *in vacuo* and condensing it on to a cold finger. A filtration bed 1 cm in diameter and 2 cm deep was prepared by pouring in a slurry of the purified material in cyclohexane. The wear-oil sample was then aspirated through the bed and washed with cyclohexane, after which the bed was transferred to a dish and heated gently under vacuum. The residue of wear products was removed for chemical analysis.

Longer columns of metaldehyde have been used in chromatography to separate several components of the wear products from a synthetic turbine oil. Elution successively with light petroleum, isobutyl methyl ketone and acidified isobutyl methyl ketone (10^{-4} N in hydrochloric acid) removed three quite distinct amounts of iron. A fourth fraction remained totally insoluble. The chemical nature of these fractions is the subject of further experimentation.

This communication is published with the approval of the Director, Admiralty Materials Laboratory.

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Book Reviews

INFRARED SPECTROSCOPY. EXPERIMENTAL METHODS AND TECHNIQUES. By JAMES E. STEWART. Pp. xviii + 636. New York: Marcel Dekker Inc. 1970. Price $36.50; £17·35.

This is a good book, but its title is liable to be extremely misleading and it is therefore important that the scope of its contents be clearly understood. It was written because the author became convinced that "the new spectroscopist needed a book devoted to the spectrophotometer so that he could understand his instrument and use it in an optimum manner . . . moreover, the more experienced spectroscopist could also benefit from a better understanding of his instrument, its workings and its limitations." The result is a book heavily biased towards optics, electronics and mathematical considerations of topics that are correctly the province of the instrument designer.

Following short introductory chapters on infrared spectroscopy and the spectrophotometer, chapters are devoted to the elements of geometric and physical optics; optical components and systems of spectrophotometers; interference spectroscopy; mechanics of spectrophotometers; elements of electronics; infrared detectors; and electronic systems, electromechanical transfer functions and the photometric accuracy of infrared spectrophotometers. The level of treatment of these chapters ranges widely, from the elementary, *e.g.*, a description of the principle of the thermionic diode, to the complex, such as the spread function due to diffraction for a rectangular aperture and incoherent radiation. Much of this is pretty heavy going—the chances of it being of any direct benefit to either the new or the experienced spectroscopist mentioned above appear to be remote, to put it in the most favourable terms.

For the everyday practising spectroscopist, the greatest interest is likely to lie in the final four chapters, which deal with experimental methods of infrared transmission, reflection and emission spectroscopy and with advanced methods. The last of these chapters discusses topics such as electron beams and plasmas, measurements of optical constants and the spectroscopy of remote objects; unfortunately, it does not refer to any work more recent than 1967. This criticism can be extended to the book as a whole; only eight of the eighteen chapters give references to work published in 1968 and only four chapters contain anything as recent as 1969.

There are appendices dealing with the properties of Fourier and Laplace transforms and with the selection of operating parameters of infrared spectrophotometers. The author and subject indices are very comprehensive and the standard of production of the book is first class; in all, only three minor misprints were detected, although greater care could have been given to the punctuation used in the lists of references cited at the end of each chapter.

The over-all conclusion is that this is not, particularly at the price asked, a book for the modern practical analytical chemist; it may, however, be of some interest to specialists in optics, instrument designers or those dealing with fundamentals in spectroscopy.

D. M. W. ANDERSON

PRACTICAL HINTS ON INFRA-RED SPECTROMETRY FROM A FORENSIC ANALYST. By M. J. DE FAUBERT MAUNDER. Pp. vi + 239. London: Adam Hilger. 1971. Price £5·20.

The author claims that this book is an unashamed attempt to bring back an element of craftsmanship and critical appraisal of results. "The inverse respect paid to craftsmanship is one of the strange anachronisms of a technical age—a climate hostile to manual skill." For this reason alone, great credit is due.

This is a fascinating book, written in an entertaining yet instructive style by a down-to-earth, thoroughly experienced spectroscopist. It must be regarded as the infrared companion handbook to Leopold May's "Spectroscopic Tricks" and to "Practical Hints on Absorption Spectrometry" by the late Dr. J. R. Edisbury, and it is a pleasure to say that there should be a copy in every laboratory that has an infrared spectrometer.

The contents can be regarded as falling neatly into three distinct sections. The first four chapters deal with practical aspects of fundamental techniques—solid sampling, other basic techniques, anomalous spectra, and allied techniques. Then there are three chapters that are quite specialised, dealing with recommended analytical procedures for pharmaceuticals, characteristic absorptions of certain classes of drugs, and practical examples of spectra selected to illustrate the importance of technique and some of the more obvious pitfalls. It is a little unfortunate,

perhaps, that these three chapters in the middle of the book should be oriented quite so pharmacologically and forensically, the spectra being almost entirely restricted to those of methylamphetamine, diamorphine hydrochloride, phenmetrazine hydrochloride and promethazine hydrochloride; in all, some 47 pages are devoted to this.

Then there are three chapters on different aspects of information retrieval—27 pages in all, and the book ends with 11 pages of questions to which, thank heaven, answers are given. I do not think that analysts other than specialists in pharmaceuticals could identify at sight the spectra of methylphenobarbitone, methaqualone ("from a major supplier in the U.S.A."), dihydrocodeine hydrogen tartrate or isoprenaline hydrochloride. There is certainly one analytically redeeming feature of ethanol of reputable Scottish origin—the spectrum is simpler!

This book, however, makes excellent bed-time reading, with gems such as "One breath of exhaled air will undo many hours of patient work—people who naturally breathe through their mouths and thereby direct exhaled air straight at the object of their attention, rather than away as through the nose, are anathema as far as infrared work is concerned and need special tuition." "No amount of clean apparatus and purified reagents is of use if the worker is scruffy. An attitude of mind as well as technique is involved." "You may be lucky and get away with it first time, but, in most work, luck and infrared spectrometry do not often go together." "Ninety per cent. of analytical chemistry is knowing when to stop." The same applies to book reviewers!

D. M. W. ANDERSON

TREATISE ON ANALYTICAL CHEMISTRY. Part II. ANALYTICAL CHEMISTRY OF INORGANIC AND ORGANIC COMPOUNDS. Volume 14. Edited by I. M. KOLTHOFF and PHILIP J. ELVING. Pp. xviii + 444. New York, London, Sydney and Toronto: Wiley-Interscience. 1971. Price £11·75.

The three Parts of this comprehensive treatise on analytical chemistry deal with *Theory and Practice* (Part I), *Analytical Chemistry of Inorganic and Organic Compounds* (Part II) and *Analytical Chemistry in Industry* (Part III), and all are under the same co-editorship. Each of the volumes that make up these three Parts contains sections by individual authors who are well known for their competence in the field of their assignment.

This volume has two main sections—*B-1: Organic Analysis, I. The Elements*; and *B-2: Organic Analysis, II. Functional Groups*. Section B-1 has the sub-title *Chlorine, Bromine and Iodine*, and Section B-2 has the sub-titles *Unsaturation, Determination of Acyl Groups*, O-*Alkyl*, N-*Alkyl and* S-*Alkyl, Determination of Ethers and Epoxides*, and *Determination of Organic Peroxides*.

The first section of this volume occupies only 20 pages, and it is not surprising that methods for the satisfactory decomposition of organic materials, as a preliminary to determining the halogens, receive special attention.

Section B-2 is dealt with under such headings as *Properties, Detection and Identification*, and *Recommended Methods*, but this random selection of sub-titles is not, by any means, indicative of the wide coverage of this section.

With such a wealth of expertise collated to produce the entire text—it also has two additional section advisors—a comprehensive coverage of each subject heading has, understandably, been achieved.

This is undoubtedly a first-class publication, and a worthy companion to earlier volumes in the series that I have seen and, no doubt, to subsequent volumes to be issued. It is well reinforced with supporting references, neatly bound and uniformly presented; indeed, a book that the organic analyst is likely to treasure.

W. T. ELWELL

LECTURES AND COURSES

Biamperometric Determination of Platinum in Some Technical Products

A method is described for the determination of platinum based on the reduction of platinum(IV) to platinum(II) with an excess of copper(I) chloride and titration of the resulting solution with a strong oxidant, such as cerium(IV). The reaction proceeds in two steps, the first corresponding to oxidation of an excess of copper(I), and the second to oxidation of platinum(II). The electrochemical characteristics of the systems involved appear to be ideal for biamperometric titration. Up to the first end-point the reversible system copper(II) - copper(I) is present, after which the next system, platinum(IV) - platinum(II), formed in the course of further additions of the titrant, is strongly irreversible. An excess of the oxidant in acidic solution forms a reversible cerium(IV) - cerium(III) couple. In these systems a double-bend titration curve is formed when a small voltage (100 mV) is applied. The only standardised solution required is cerium(IV) sulphate and removal of oxygen is, in general, unnecessary. The reaction is much faster at elevated temperatures and it is therefore convenient to warm the solution up to 80 °C before titration.

Depending on the concentration of the titrant (0·1 or 0·01 M) an amount of platinum from 5 to 50 mg can be determined with a relative standard deviation of about 0·14 per cent. This method has been applied to the determination of platinum in platinum - nickel alloys and platinum catalysts.

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Analyst, 1972, **97**, 340–345.

The Enhancement of Acidity in Non-aqueous Solvents
Part I. An Improved Procedure for the Determination of Short-chain Carboxylic Acids in the Presence of their Anhydrides

Weak short-chain carboxylic acids can be determined potentiometrically in the presence of their acid anhydrides after enhancement of their acidity by reaction with alkaline earth perchlorates. The method is particularly suitable for the determination of acid contents in the range 0·5 to 5 per cent. Of five electrode systems examined, glass - modified calomel and platinum - in-stream platinum combinations gave responses exceeding 500 mV per millilitre of titrant at the end-point. Both acetonitrile and acrylonitrile are satisfactory solvents, but the latter is generally preferable for non-aqueous titration because, while it leads to equally sharp end-points, it is more readily available in a pure, acid-free form.

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Analyst, 1972, **97**, 346–351.

The Determination of the Non-volatile Acidity of Rain Water by a Coulometric Procedure

A precise and accurate method for the determination of the non-volatile acidity of rain water or of any dilute acid solution (10^{-4} to 10^{-6} M) is described. The method is based on the coulometric titration of a sample from which carbon dioxide has been removed by bubbling nitrogen through it. The end-point is detected by potentiometry with a glass electrode by using Gran's theory. The acidity from both strong and weak acids is determined. The average standard deviation is ± 5 per cent. and the limit of sensitivity 0·1 μg ml^{-1} (calculated as sulphuric acid).

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Analyst, 1972, **97**, 352–356.

A Kinetic Method for the Determination of Arsenic(III), Antimony(III) and Ascorbic Acid

A simple and rapid method is described for the determination of arsenic(III) over a wide concentration range down to 0·005 p.p.m. in 20 ml of solution. The technique, which was also applied to the determination of antimony(III) and ascorbic acid, compares favourably with other titrimetric and coulometric methods for these determinations.

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Analyst, 1972, **97**, 357–362.

A Field Test for the Determination of Some Ketone Vapours in Air

A field test is described for the determination in air of those ketones most commonly used industrially, in concentrations up to twice their current threshold limit values. The vapour, the nature of which must be known, is collected in water and the solution allowed to react with acidic 2,4-dinitrophenylhydrazine solution. The addition of methanolic potassium hydroxide results in the formation of a red coloration, which is compared visually with standards after 10 minutes. A common series of standards is used for all the ketones, the volume of absorbent used and the size of sample taken being dependent on the identity of the ketone present in the atmosphere. Both the apparatus and method used are simple and the time required for a complete determination is between 25 and 50 minutes.

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Analyst, 1972, **97**, 363–371.

Quantitative Determination of the Pungent Principle (Capsaicin) of Ceylon Chillies (*Capsicum* Species)

There is a remarkable variation in the pungency of different varieties of capsicum and this paper describes a method for the determination of the total capsaicin content in the fruits of *Capsicum* species. The extraction procedure is based on a method by which phenolic interference is reduced to a minimum by selective solubility. During the various stages of extraction, before any extract is rejected, thin-layer chromatography is used as a monitoring device. The spectrophotometric determination of the total capsaicin content is based on the colour reaction of capsaicin with tungstophosphoric acid - molybdophosphoric acid reagent. The relative concentrations of capsaicin (milligrams per 100 g dry weight) in different varieties of capsicum are calculated by reference to a calibration graph.

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Analyst, 1972, **97**, 372–375.

A Possible Method for the Identification of Canned Fish by Separation of its Carbonyl Constituents

A method for the identification of canned fish, based on the thin-layer chromatographic patterns of the 2,4-dinitrophenylhydrazine derivatives of the carbonyl compounds in fish, is described. By using this technique it is possible to distinguish between canned sprats, brisling, sardines, salmon, tuna, cod, haddock and plaice. The dinitrophenylhydrazone patterns of these canned products are presented.

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Analyst, 1972, **97**, 376–377.

Fungicide Residues

Part I. The Detection, Identification and Determination of Residues of Quintozene in Tomatoes, Lettuces and Bananas by Gas Chromatography

A simple method for determining residues of quintozene in tomatoes, lettuces and bananas is presented. After extraction with hexane, quintozene is separated from interfering co-extractives by a partition process with dimethylformamide followed by chromatography on an alumina column, and is quantitatively determined by electron-capture gas - liquid chromatography. A confirmatory chemical test for quintozene is also described.

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Analyst, 1972, **97**, 378–382.

A Simplified Method for the Determination of Selenium in Soils and Sediments

A method is described for the determination of low levels of selenium in soils. An extract of the soil in nitric acid and orthophosphoric acid is prepared. An aliquot is oxidised with potassium persulphate at 100 °C, at which temperature the loss of selenium is minimal. The excess of nitric acid is removed by evaporation and 50 per cent. hydrochloric acid is added to reduce selenate. The selenite produced is complexed with 2,3-diaminonaphthalene and the resulting 4,5-benzopiazselenol is extracted with cyclohexane. Sodium sulphate is added to remove interfering substances and the selenium complex is determined fluorimetrically. Selenium in soils down to 0·04 p.p.m. can be determined to within $\pm 0{\cdot}1$ p.p.m.

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Analyst, 1972, **97**, 383–387.

Determination of Total Mercury in Sediments and Soils

A highly sensitive and precise procedure has been developed for the quantitative determination of total mercury in sediments and soils. Undried samples are treated with concentrated nitric and sulphuric acids, potassium permanganate and potassium persulphate in order to digest and oxidise all forms of mercury to mercury(II) ions, which are subsequently determined by flameless atomic-absorption spectrophotometry. Recovery of mercury, added as mercury(II) chloride, methylmercury chloride, phenylmercury hydroxide or phenylmercury acetate to a lake sediment, ranged from 98 to 105 per cent. The procedure developed by us resulted in the extraction of more mercury from sediments and soils than did extraction with concentrated nitric acid. Drying at 60 °C caused a significant loss of organomercury compounds from a lake sediment.

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Analyst, 1972, **97**, 388–393.

The Determination of Niobium in Steel by Atomic-absorption Spectrophotometry

The determination of niobium by atomic-absorption spectrophotometry is complicated by many matrix effects. For the determination of niobium in steels, the interference effects were avoided by separating the niobium and re-dissolving it in ammonium sulphate - sulphuric acid and adding tartaric acid to stabilise the solution. Potassium sulphate was added as an ionisation suppressant to all the solutions containing niobium. An aqueous solution of niobium must have a concentration in the range 100 to 1000 μg ml^{-1} to give satisfactory absorption results.

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Analyst, 1972, **97**, 394–399.

The Determination of Tungsten and Silicon in Highly Alloyed Materials by Atomic-absorption Spectroscopy

Tungsten and silicon are determined in the presence of large amounts of iron, nickel, cobalt, molybdenum and other constituents of highly alloyed materials by means of atomic-absorption spectrophotometry with a nitrous oxide - acetylene flame. Complete dissolution is effected in a mixture of aqua regia and hydrofluoric acid, which necessitates the entire use of plastics-ware. Inter-element effects are both numerous and complex, and the method of standard addition is recommended for calibration purposes.

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Analyst, 1972, **97**, 400–404.

Volatility of Organic Microanalytical Standards

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Analyst, 1972, **97**, 405.

A Novel Separation Medium

Communication

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Analyst, 1972, **97**, 406.

Notice to Authors

The Editor welcomes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Papers are submitted to referees, who will advise on their suitability for publication.

Intending authors should consult the current Notice to Authors, last published in full in *The Analyst*, 1968, **93**, 269–272, reprints of which can be obtained on application to The Editor, *The Analyst*, 9/10 Savile Row, London, W1X 1AF.

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