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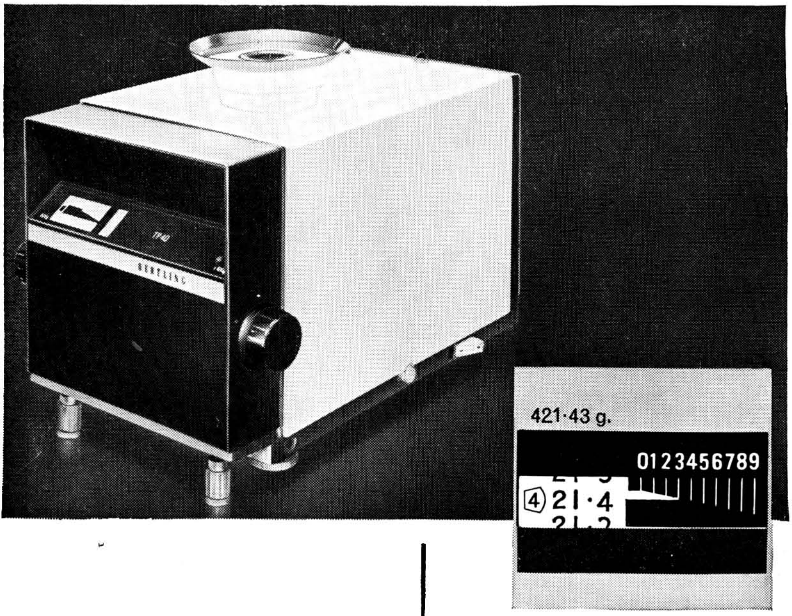
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Ion-selective Membrane Electrodes

A Review

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ERNÖ PUNGOR and KLÁRA TÓTH

Department of Analytical Chemistry, University of Chemical Industries, Veszprém, Hungary.

Analyst, 1970, **95**, 625–648.

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The Determination of Aliphatic Ketones by Polarography of their Girard T Hydrazone Derivatives

A method is described for the determination of a range of aliphatic ketones by polarography of their Girard T derivatives. The compound is formed *in situ* in a 75 per cent. ethanolic - acetate buffer (apparent pH 4·00) solution 0·1 M with respect to the Girard T reagent.

M. D. BOOTH and B. FLEET

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

Analyst, 1970, **95**, 649–651.

Automatic Titration by Stepwise Addition of Equal Volumes of Titrant

Part II. An Automatic Titration System

A fully automatic titration system is described. The system carries out transfer of the sample by pipette, and dilution, titration and washing of electrodes and titration vessels. Titrations are performed by adding titrant stepwise in equal volumes to the sample, with recording of potential after each addition. These results are used to calculate equivalence points. The system has a loading capacity of 200 samples, and an analysis rate of up to 30 samples per hour.

AXEL JOHANSSON and LENNART PEHRSSON

Department of Analytical Chemistry, Royal Institute of Technology, Stockholm, Sweden.

Analyst, 1970, **95**, 652–656.

The Use of Enthalpimetric Titration to Study the Reaction of Thiourea and its *N*-substituted Derivatives with Cerium(IV)

The oxidation of thiourea and its symmetrically *N*-substituted derivatives has been examined by enthalpimetric titrimetry. The initial reaction is considered to cause the formation of a disulphide and slower secondary oxidations of these products have been detected. Reaction rates are acid dependent and studies have been carried out in hydrochloric and sulphuric acids. In hydrochloric acid, thiourea and ethylenethiourea can be titrated to within ±0·3 per cent. of the theoretical value for the first reaction step over the acid range 0·3 to 0·2 M, while in sulphuric acid (0·3 to 0·6 M) the values for *N*,*N′*-diethylthiourea are within ±0·4 per cent. of the theoretical. Comparison is made with the titration method for the determination of thiourea by cerium(IV), which has been shown to be satisfactory within certain acidity ranges in sulphuric acid.

W. A. ALEXANDER, C. J. MASH and A. McAULEY
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1.

Analyst, 1970, **95**, 657–660.

Spectrophotometric Study of the Reaction of Uranium(VI) with a New Salicylazochromotropic Acid Derivative

On the basis of a study of substituted salicylic acid groups as functional analytical groups in the determination of uranium(VI), a new bissalicylazochromotropic derivative has been synthesised, *i.e.*, the 3,6-bis(4-carboxy-3-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid, as the tetrasodium salt. The reagent thus obtained gives a sensitive reaction with uranium(VI), which enables between 0·5 and 16 μg ml^{-1} of uranium to be determined. Uranium(VI) combines with the reagent in the ratio 1 : 2, and the instability constant of the compound is $1{\cdot}2 \times 10^{-9}$.

GH. BAIULESCU, D. MARINESCU and C. GREFF
Department of Analytical Chemistry, University of Bucharest, Romania.

Analyst, 1970, **95**, 661–664.

Determination of Sulphate Ion by Replacement of Iodate in Iodine-131 Labelled Barium Iodate

Between 2 and 100 μmoles of sulphate (60 to 3200 μg of sulphur) can be determined in aqueous solution, by passing the solution through a column of iodine-131 labelled barium iodate and counting the filtrate. The blank can be reduced by using 20 per cent. methanol. Each determination takes only a few minutes, and the precision is ±2·5 per cent. The apparatus required is simple and inexpensive, apart from the counting equipment. The method has been tested with standard kale, and has been applied to the determination of sulphur in fruticose lichens.

H. J. M. BOWEN
Chemistry Department, Reading University, Whiteknights, Reading, Berks.

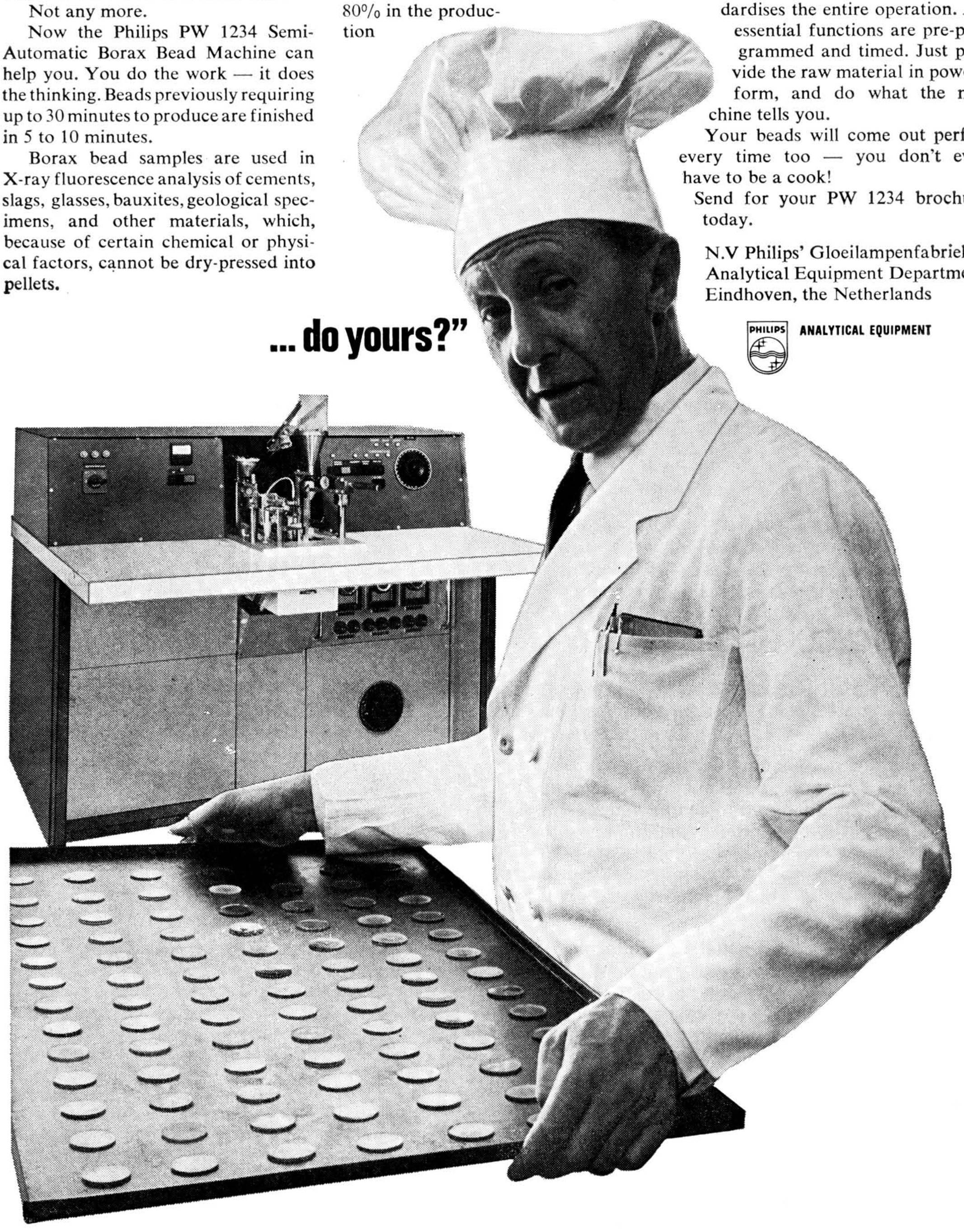
Analyst, 1970, **95**, 665–667.

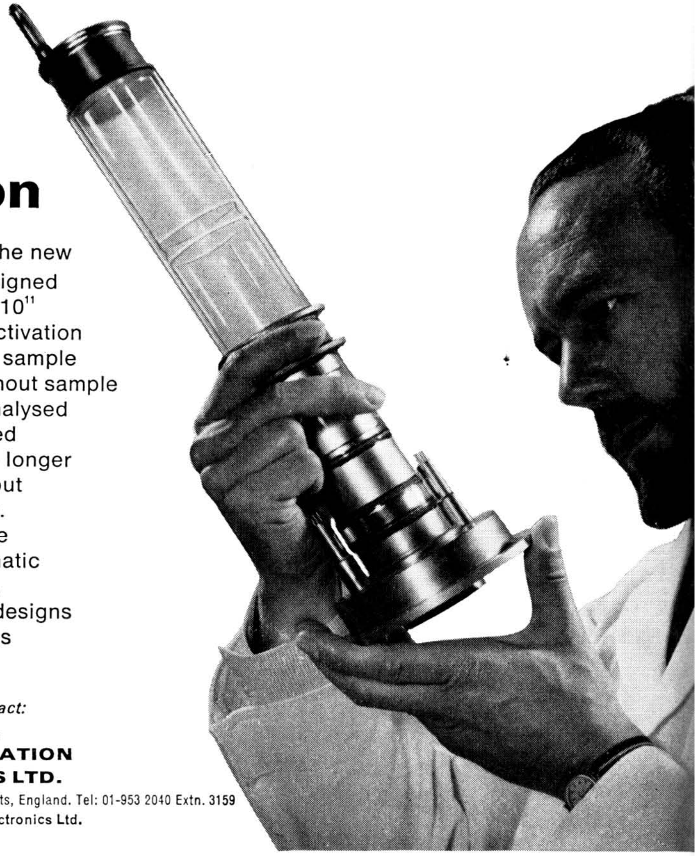
Comparison of Low Temperature Radiofrequency Ashing with Other Methods of Organic Sample Oxidation for the Determination of Sodium in an Acrylic Fibre

Acrylic fibre samples can be prepared for sodium determination by low temperature radiofrequency ashing, by ignition in air and by wet oxidation with a mixture of sulphuric and nitric acids or sulphuric acid and hydrogen peroxide. The sodium is determined by flame photometry. A minimum of eleven determinations by each technique allows a statistical examination of the results. It is demonstrated that low temperature radiofrequency ashing offers advantages in both precision of analysis and simplicity of sample handling.

R. COOMBER and J. R. WEBB
Ministry of Technology, Royal Aircraft Establishment, Farnborough, Hants.

Analyst, 1970, **95**, 668–669.





JULY, 1970 Vol. 95, No. 1132

THE ANALYST

Ion-selective Membrane Electrodes

A Review*

BY ERNÖ PUNGOR AND KLÁRA TÓTH

(Department of Analytical Chemistry, University of Chemical Industries, Veszprém, Hungary)

SUMMARY OF CONTENTS

SINCE the supposition that membranes separating cells play an important rôle in the vital functions of the organism, the behaviour of various membranes has been studied in detail. This has led to the discovery of the electrical phenomena of membranes in electrolytes. The purpose of this paper is to summarise the electrical behaviour of ion-selective membranes that are used as electrodes.

From an electrochemical point of view, the membranes can be divided into the following groups.

Porous membranes—Membrane layers that separate electrolytes and permit the diffusion of both cations and anions, this diffusion being hindered only by the size of the pores of the membrane. The potential developed across the membrane layer is a diffusion one.

Perm-selective membranes—Membranes containing a matrix with fixed ionic groups, so-called fixed charges, which allow the transport of the oppositely charged ions in certain concentration ranges. The upper limit of the concentration range is always determined by the concentration of fixed charges in the matrix. The perm-selective membranes do not differentiate between the individual ions, and the potential developed on the membrane surface is caused by the ion-exchange and diffusion phenomena of the membrane.

Porous and perm-selective membranes have been studied in detail.[1,2,3]

Ion-specific membranes—Membranes with specific exchange properties and perfect semi-permeability.

Classification can also be made on the basis of the structure of membranes.

Homogeneous membranes—Membranes containing only the material that is responsible for the electrochemical behaviour of the membranes. They can be polymerised further, pressed from amorphous particles or polycrystals or grown as a single crystal.

Heterogeneous membranes—Membranes consisting of an electrochemically active material and a supporting material.

Naturally all membrane types mentioned previously can be used as electrochemical sensors, *i.e.*, potentiometric electrodes, but electrodes selective to individual ions can only be formed from ion-specific membranes. The ion-selective electrodes can be sub-divided into glass, salt membrane and special ion-exchange electrodes on the basis of the electrode material.

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

Salt membrane electrodes consist of slightly soluble materials, at which a solubility equilibrium is established on the surface of the membrane.

Special ion-exchange electrodes have fixed ionic groups, which ensure the selective ion-exchange reaction with the particular ion.

The first step in the development of ion-selective electrodes was the discovery of the pH glass electrode at the beginning of this century.[4,5] This led to many theoretical and practical studies which resulted in a new interpretation[6] of glass electrode potential on the basis of ion exchange. The electrochemical behaviour and composition of glass membranes were studied in detail by Lengyel and Blum,[7] whose work led to the development of alkali-sensitive glass electrodes. The development of various glass-electrode theories is given by Eisenman[8] and more detailed studies of glass electrodes were made by Bates[9] and Eisenman.[10]

Various clay materials and precipitates have been used as membrane electrodes.[11 to 16] These electrodes responded to the change in the electrolyte concentration, but their response was not selective. At the beginning of the sixties an advance was made in ion-selective electrodes with the introduction of the highly selective silver iodide based iodide electrode.[17] This work directed attention to precipitates that ensure a rapid precipitate exchange reaction on their surfaces. Since then the research on ion-selective electrodes has been carried out in three ways.

In the first method precipitates are prepared with crystal defects or doped crystals and are incorporated in a suitable supporting material such as silicone rubber, and the second method involves preparation of slightly soluble single or pressed crystals with crystal defects or which have been doped. These form the group of solid-state electrodes. The third method is the synthesis of special ion exchangers with certain selectivity to individual ions, examples of which are the liquid ion exchangers for copper and calcium.

There is at present a rapid increase in the number of publications on ion-selective electrodes, which indicates the great interest of chemists in this field. However, various contradictory and supplementary hypotheses have been put forward, thus the aim of this study is to give a summary of the present knowledge of ion-selective electrodes.

THEORY

PRECIPITATE-BASED ION-SELECTIVE (SALT) MEMBRANE ELECTRODES—

The papers on precipitate-based ion-selective membrane electrodes that have so far appeared in the literature discuss the electrochemical behaviour of heterogeneous and solid-state membrane electrodes separately.[18,19,20,21] However, on the basis of experimental results this differentiation is not necessary because they differ from each other only in mechanical and not in electrochemical respects, so in this paper they are treated together.

For the theoretical interpretation of the behaviour of precipitate-based ion-selective electrodes, silver halide based membrane electrodes were chosen because silver halide salts have been extensively examined. As far as precipitate-based membrane electrodes are concerned with the particle size, the defect structure of the precipitate and the adsorption phenomena on its surface are of great importance. The particle size of the silver iodide precipitate was studied by Schulek, Pungor and Guba.[22] The examination of the adsorption of the related Cl^-, Br^-, SCN^- and other ions (SO_4^{2-} and PO_4^{3-}) on silver iodide showed that halide and pseudo-halide ions adsorb without their hydrate shell, while the other ions adsorb with 6 to 8 moles of water.[23,24] This was concluded from the results of titrations that were carried out in the presence of organic dyes that adsorb on the surface of silver iodide precipitate, and behave as surface acid - base indicators, when the surface charge of the precipitate is changed. This reaction did not take place on the surface of any other silver halide precipitates, or if it did, then only to a very slight degree. This phenomenon can be used for the determination of the adsorbed amount of other anions forming precipitates with silver on the surface of the silver iodide precipitate if a solution containing the iodide and this other anion is titrated with silver nitrate in the presence of *p*-ethoxychrysoidin. The proton uptake and the proton loss of the organic dye was detected with a pH glass electrode. The end-point, corresponding to the amount of the iodide ion present, was shifted depending on the type and concentration of the other ion titrated.

The ratio of the shifts of the end-points corresponding to the iodide determined in the presence of various halide and pseudo-halide ions was inversely proportional to the square of the ratio of the radii of the anions investigated.

With a knowledge of the surface area determined by electron microscopy, and the amount of ions adsorbed, the place occupied by one ion was calculated. These phenomena are important with respect to the formation of the membrane potential.

The rate of precipitate exchange reaction for silver halide precipitates has been found to be fast, which is important because of the response time of the electrodes.

Many papers[25,26,27] deal with the defective structure of silver halide precipitates, from which it can be concluded that in equilibrium the distribution of the space charge is an exponential function of the distance counted from the surface of the precipitate. On the surface of a precipitate the space charge is given on the electrolyte side by the partly or fully hydrated ions, and on the solid side by the lattice defects.

By using either a heterogeneous or a homogeneous ion-selective electrode at zero current in a solution containing the ion to which the electrode is reversible, the equilibrium between the solution and solid phase is attained when the difference of the electrochemical potentials of the solvated ion and the ion bonded to the solid phase is equal to zero. If the electrochemical potential of the appropriate i-th ion in the solution is

$$\eta_s = \mu_s + z_i F \Psi_s \quad \ldots \quad (1)$$

while in the membrane

$$\eta_m = \mu_m + z_i F \Psi_m \quad \ldots \quad (2)$$

where η is the electrochemical potential,
μ is the chemical potential,
Ψ the Galvani potential,
z is the valency, F is the Faraday constant,
s and m are subscripts denoting the solution and membrane phase, respectively.

In equilibrium η_s is equal to η_m.

$$\mu_s + z_i F \Psi_s = \mu_m + z_i F \Psi_m$$

$$z_i F(\Psi_m - \Psi_s) = \mu_s - \mu_m = \mu_s^{\circ} - \mu_m^{\circ} + RT \ln \frac{(a_i)_s}{(a_i)_m} \quad \ldots \quad (3)$$

$$E = E_0 + \frac{RT}{z_i F} \ln \frac{(a_i)_s}{(a_i)_m} \quad \ldots \quad (4)$$

where E is the electrode potential,
E_0 is the standard electrode potential,
μ° is the standard chemical potential and
$(a_i)_s$ and $(a_j)_m$ are the activities of the i-th ion in the solution and in the membrane phase, respectively.

In this deduction of the electrode potential the ion diffusion across the membrane was not considered as it normally has no effect on the membrane potential at zero current. However, Buck[20] has pointed out that if Eisenman's concept,[28] *i.e.*, the phase boundary processes are combined with the diffusion of the particles and defects in the membrane, is used here, then the behaviour of the electrode can also be interpreted in solutions containing the appropriate ion and an ion forming a less soluble salt with the cation of the precipitate used in the electrode than the appropriate ion (ion composing the precipitate in the membrane). Furthermore, Buck stated that the mixed adsorption of the ions can also be used for the interpretation of the electrode potential in bi-ionic solutions.

If the concentration of the appropriate ion is relatively low in the solution examined, then the electrode potential approaches a limiting value, which can be expressed for univalent ions in the following way[29]—

$$E = E_0 + \frac{RT}{F} \ln \frac{\sqrt{S_{ji}} + \sqrt{S_{ji} + 4(a_i)_s^2}}{2} \quad \ldots \quad (5)$$

where S_{ji} is the solubility product of the precipitate used as electrode.

In a solution containing not only the ion to which the electrode is reversible but another ion, which also forms a precipitate with one of the components of the membrane matrix, the following precipitate exchange reaction is established—

$$\mathrm{AgI} + \mathrm{K} \rightleftharpoons \mathrm{AgK} + \mathrm{I} \quad \ldots \quad (6)$$

$$K_{ik} = \frac{(a_i)_s\,(a_k)_m}{(a_k)_s\,(a_i)_m} \quad \ldots \quad (7).$$

On the basis of this exchange equilibrium the following equation can be derived for the potential of the membrane electrode if the intra-membrane diffusion phenomena are neglected.

$$E = E_0 + \frac{RT}{z_iF} \ln (a_i)_s \sum_n K_{ik} \frac{(a_k)_s}{(a_i)_s} = E_0 + \frac{RT}{z_iF} \ln (c_i)_s \sum_n K_{ik} \frac{(c_k)_s}{(c_i)_s} . f\pm \quad .. \quad (8)$$

where a_i,c_i and a_k,c_k are the activities and concentrations of i-th and k-th ions, respectively

n is the number of ions taking part in the exchange reaction,

$f\pm$ is the mean activity coefficient, and

K_{ik} is the selectivity constant of the electrode.

The selectivity constant can be deduced from the exchange equilibrium and has the general form—

$$K_{ik} = \frac{S_{ji}^{1/a}}{S_{jk}^{1/n}} = \frac{e(a_i)_s^{b/a}}{e(a_k)_s^{m/n}} \quad .. \quad .. \quad .. \quad .. \quad (9)$$

where $e(a_i)$ and $e(a_k)$ are equilibrium activities of the ions taking part in the precipitate exchange reaction, which is measured when co-precipitation starts,

a, b, n, m are the stoicheiometric constants of the precipitates built in the membrane or formed during the exchange reaction, and

S_{ji} and S_{jk} are the appropriate solubility products.

When univalent ions form the precipitates, then equation (9) reduces to—

$$K_{ik} = \frac{S_{ji}}{S_{jk}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10).$$

The validity of equation (8) was proved experimentally with an iodide-selective electrode. The slope of the linear part of the graph of E *versus* log a_i is, theoretically, 60·1 mV at 30° C, for which 60 mV was found experimentally. The difference is within the limits of experimental error.

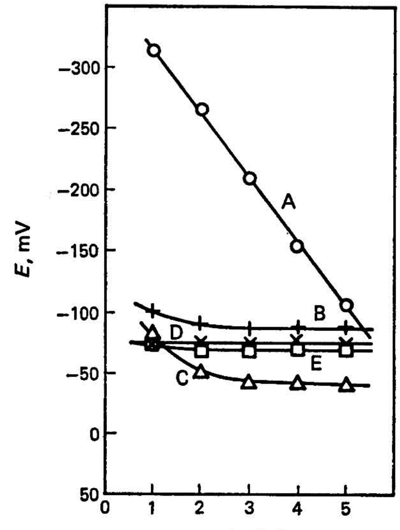

Fig. 1. Potentiometric selectivity of I⁻ membrane electrode to I⁻ in I⁻ - Cl⁻ and I⁻ - Br⁻ binary mixtures. Reference electrode Ag - AgCl (0·1) electrode with KNO_3 salt bridge: A, calibration graph for I⁻ electrode; B, 10^{-5} M KI in Br⁻ solution; C, 10^{-6} M KI in Br⁻ solution; D, 10^{-5} M KI in Cl⁻ solution; and E, 10^{-6} M KI in Cl⁻ solution; when X is Cl⁻ or Br⁻

The potentiometric determination of the selectivity constant also underlines the validity of the theory based on precipitate exchange reactions. The determination of the selectivity constant can be carried out by a direct or indirect method. The activity of the appropriate ion is constant and relatively low, while that of the interfering ion varies when the direct method is used. The opposite is found with the indirect method.

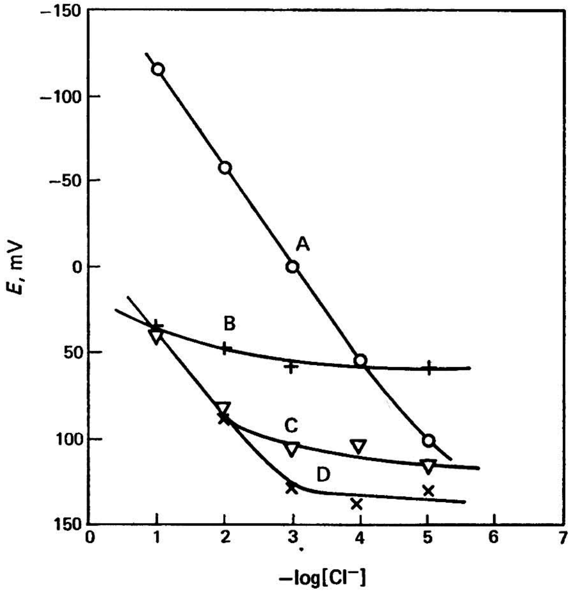

Fig. 2. Potentiometric selectivity of Br^- membrane electrode to Br^- in Br^- - Cl^- binary mixtures. Reference electrode Ag - AgCl (0·1) with KNO_3 salt bridge: A, calibration graph for Br^- electrode; B, 10^{-4} M Br^- in Cl^- solution; C, 10^{-5} M Br^- in Cl^- solution; and D, 10^{-6} M Br^- in Cl^- solution

The graphs obtained with the direct method for iodide and bromide-selective electrodes, presented in Figs. 1 and 2, were the basis of the determination of the selectivity constants of these electrodes. The break-points of the extrapolated lines gave the activities of the interfering ions, where they disturb the appropriate halide determination, while the activity of the appropriate ion was calculated from the concentration of the sample. The ratio of these activities gave the selectivity constant.

It must be emphasised[30] that the solution tested should contain both the appropriate and other ions when either the direct or indirect method for the determination of the selectivity constant is used. Alternatively, if the method devised by Eisenman[28] for glass electrodes[8] is used for other ion-selective electrodes, then the conditions of the potential measurement are not well defined because the potential measurement is carried out in the absence of the appropriate ion. The values obtained for selectivity constants therefore agree only in magnitude with the theoretical values. The results obtained by Rechnitz, Kresz and Zamochnick[31] and Rechnitz and Kresz,[32] who measured the selectivities of halide-selective electrodes in this way, can only be treated as apparent values.

If the selectivity constant is measured by the indirect method, then the potentiometric titration curve is a basis for the determination. The activity of the appropriate ion at the point at which co-precipitation starts can be calculated from the potential difference established between the well defined start and the break-point of the titration graph. The activity of the interfering ion is known from the composition of the solution tested. The titration method is generally applicable, but it is assumed that the activity of the appropriate ion at the break-point can always be calculated from the Nernst equation. The ratio of the activities of the appropriate and other ion established when co-precipitation starts gives the selectivity constant. However, this assumption has limitations. If the mean activity coefficient in the solution is not constant during the titration then the use of the Nernst equation for the calculation of the activities is not correct. Furthermore, if mixed crystals are formed during the co-precipitation, then the activities of the appropriate ion at the break-point cannot be used for the calculation of the real selectivity constant. Despite this, the method is useful for the approximate determination of the selectivity constant.

In our experience the direct method only gives correct values when the selectivity constant is not lower than 10^{-5}.

Table I gives a comparison between the theoretically calculated and experimentally measured selectivity constants of iodide and bromide-selective electrodes. The theoretical values were calculated[30] by using equation (10), the validity of which is proved by the good agreement obtained. Table I contains the apparent selectivity constant of the bromide-selective electrode to chloride found by Rechnitz and Kresz,[32] the value of which is 10^{-2}. This differs from the theoretical selectivity constant.

TABLE I

COMPARISON OF SELECTIVITY CONSTANTS

Anion pair		Log of selectivity constant		
$[Br^-]$	$[Cl^-]$ at the break	real	apparent*	calculated
10^{-6}	$7{\cdot}11 \times 10^{-4}$	2·85		
10^{-5}	$5{\cdot}6 \times 10^{-3}$	2·75	2·0	2·6
10^{-4}	$5{\cdot}6 \times 10^{-2}$	2·75		
$[I^-]$	$[Br^-]$ at the break			
10^{-6}	5×10^{-3}	3·7	—	3·75
10^{-5}	$4{\cdot}25 \times 10^{-2}$	3·63	—	

* Measurement carried out by Rechnitz and Kresz.[32]
Data taken at 25° C.

PRECIPITATE-BASED ION-SELECTIVE MEMBRANE ELECTRODES IN THE PRESENCE OF COMPLEXING AGENTS—

For the discussion of this phenomenon, silver halide electrodes were chosen as the example. It was experimentally ascertained that all silver halide membrane electrodes responded to complexing agents such as cyanide or thiosulphate in solutions containing both the appropriate halide ion and the complexing agent. Further, it was also found that the response of the halide-selective electrodes to a complexing agent had started when the activity reached that of the appropriate halide ion (Fig. 3). Naturally all cyanide measure-

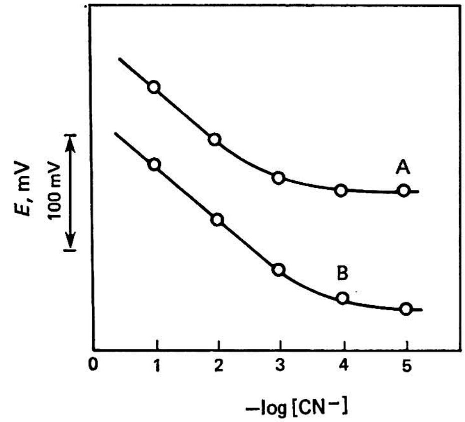

Fig. 3. Direct cyanide measurements with a Br^- and I^- selective electrode in the presence of I^- and Br^-, respectively. Reference electrode S.C.E. with KNO_3 salt bridge: A, 10^{-3} M $I^- + CN^-$; and B, 10^{-4} M $Br^- + CN^-$

ments were carried out[33] in solutions of pH higher than 11, and the life of the electrodes depended partly on the activity of the cyanide investigated and the time for which the electrode was used.

All halide electrodes, however, showed the same selectivity to various anions in the presence of cyanide as in the presence of the appropriate halide ion. Table II shows this comparison for silver iodide based cyanide electrode.

TABLE II

SELECTIVITY OF I^- MEMBRANE ELECTRODE TO VARIOUS IONS IN THE PRESENCE OF CN^- AND I^- AT 25° C

Ion	Selectivity constant in the presence of	
	CN^-	I^-
Cl^-	10^{-5} to 10^{-6}	10^{-6}
Br^-	10^{-3} to 10^{-4}	10^{-4}
I^-	1	—
CN^-	—	1
NH_4^+	10^{-5} to 10^{-6}	10^{-6}
SO_4^{2-}	10^{-5} to 10^{-6}	10^{-6}

Although the theoretical understanding of the behaviour of ion-selective electrodes in the presence of complexing agents is far from complete, those theoretical aspects which have been proved experimentally are summarised. The interpretation is based on the dissolution of silver halide salts by complexing agents. In the Orion catalogue[34] the same principle was used and the response of the iodide-selective electrode was explained with the effect of silver ion in equilibrium with the cyanide complex. The potential established on the surface of the cyanide membrane electrode is the result of the continuous dissolution of the silver halide precipitate and the exhaustion of the electrode by time is therefore understandable. However, as this interpretation does not answer the selectivity problem of the electrodes mentioned previously, it seems favourable to discuss the behaviour of the halide electrodes in the presence of complexing agents on the basis of the exchange reaction used for precipitate forming ions. In this discussion, the diffusion phenomena are neglected and the following interpretation, given for the behaviour of the electrodes responding to complexing agents, can be considered as a zero-order approximation.

The basic reaction is—

$$AgX + 2CN^- \rightleftharpoons Ag(CN)_2^- + X^- \quad .. \quad .. \quad .. \quad (11)$$

which is hindered by the adsorption of the liberated halide on the surfaces of the silver halide particles. It is assumed that the liberated halide ions determine the inter-facial potential of the membrane electrodes. A further assumption is that the dissolution of the silver salts results in an equilibrium, the equilibrium constant of which is as follows—

$$K_{X,CN} = \frac{a_{Ag(CN)_2} \cdot a_X^2}{a^2_{CN^-} \cdot a_{AgX}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12).$$

From this, the following equation was derived for the potential of the silver halide based cyanide electrode in solutions containing halide and cyanide ions—

$$E = E_0 + 0{\cdot}059 \log (a_X + a_X^* + K_{X,CN}\, a_{CN}^2) \quad .. \quad .. \quad .. \quad (13)$$

where a_x is the activity of the appropriate halide ion in the solution,
a_X^* is the activity of halide ion released by cyanide in the membrane layer,
a_{CN} is the activity of cyanide in the solution and
$K_{X,CN}$ is the dissolution constant of an AgX electrode to cyanide ions.

Naturally, if the solution contains only cyanide ions then equation (13) reduces to—

$$E = E_0 + 0{\cdot}059 \log (1/2a_{CN} + K_{X,CN}\, a_{CN}^2) \quad .. \quad .. \quad .. \quad (14).$$

From equations (13) and (14) it is clear that the original composition of the ion-selective membrane electrode is responsible for the selectivities of the electrodes to various other ions.

The validity of equation (13) was proved experimentally in the range of 10^{-4} to 2 M cyanide concentration. All solutions were made 2 M with respect to sodium hydroxide. The results are summarised in Fig. 4, where the theoretical curve is calculated according to equation (13). The value of the dissolution constant is 0·1.

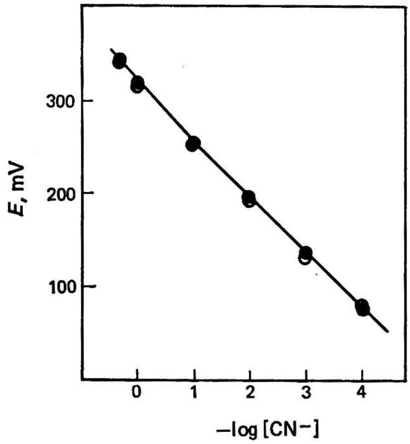

Fig. 4. Calibration graph for CN^-: —●—●— theoretical graph; and ○ points found experimentally

The interpretation given for cyanide is valid generally for complexing agents and it can also explain qualitatively the phenomenon observed in the presence of thiosulphate. In this instance, when a silver iodide membrane electrode is used, the concentration ratio at which the thiosulphate has a marked effect on the electrode is not 0·1 but about 100 (Fig. 5). This is because the $Ag(S_2O_3)_2$ complex is less stable than the $Ag(CN)_2$ complex.

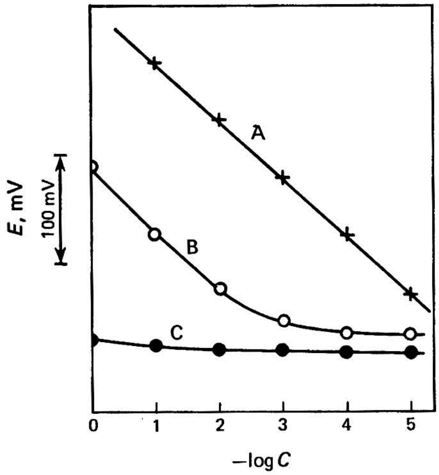

Fig. 5. Response of a CN^- selective electrode to cyanide in the presence of NH_4^+ and $S_2O_3^{2-}$ ions. Reference electrode S.C.E. with KNO_3 salt bridge: A, CN^-; B, 10^{-4} M $CN^- + S_2O_3^{2-}$; and C, 10^{-4} M $CN^- + NH_4^+$

Another problem is how metal ions forming complexes with the appropriate anions influence the behaviour of the halide electrodes. It was found that various metal halide complexes do not interfere with the behaviour of halide-selective electrodes.[31] However, the problem is not so simple for halide-based cyanide electrodes, because if a silver iodide based cyanide electrode is used then complexes less stable than $Ag(CN)_2$ still give an exchange reaction on the membrane surface. It therefore means that the cyanide complex behaves as if the bound cyanide would partly be free and only a slight shielding effect of the metal can be observed when the e.m.f. *versus* mole ratio of metal ion to cyanide is measured. On the other hand, complexes more stable than $Ag(CN)_2$ seriously influence the cyanide determination. These two limiting cases are presented in Figs. 6 and 7, with cadmium and nickel complexes.

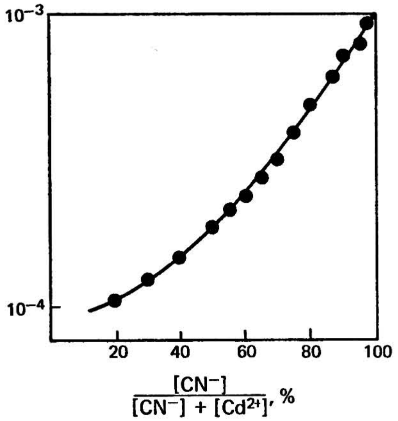

Fig. 6. Effect of Cd^{2+} on direct CN^- measurements. Indicator electrode CN^- selective electrode; reference electrode S.C.E. with KNO_3 salt bridge

The fluoride electrode can be used to determine the presence of some metal fluoride complexes as indicated by Srinivasan and Rechnitz,[35] who investigated the kinetics of the complex formation of FeF^{2+} and AlF^{2+}. The electrode did not measure the fluoride bound in these complexes, so it can be used for studying the formation kinetics of these complexes.

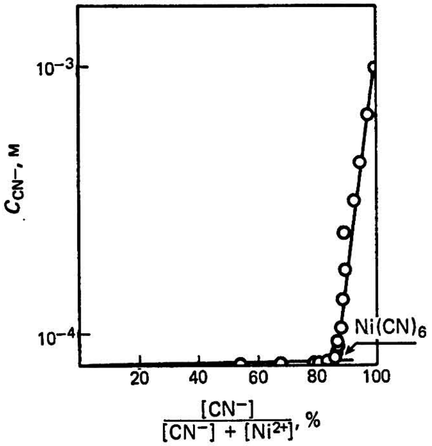

Fig. 7. The effect of Ni^{2+} on direct CN^- measurements. Indicator electrode CN^- selective electrode; reference electrode S.C.E. with KNO_3 salt bridge

A special problem arose when the anions of weak acids were measured as it was found experimentally that the component measured was always the dissociated anion and not the

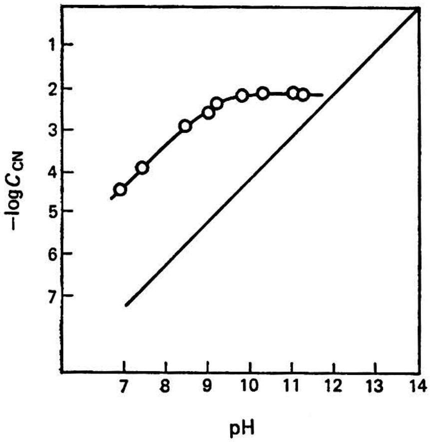

Fig. 8. The effect of pH on the CN^- measurement. Indicator electrode CN^- selective electrode; reference electrode S.C.E. with KNO_3 salt bridge

protonised anion. To demonstrate this, hydrocyanic acid is used as an example. Fig. 8 shows pa_{CN} *versus* pH function; the points represent the experimental results and the solid line indicates the theoretical values calculated according to the equation—

$$-\log a_{CN} = pK - \log c_t + \log (a_H + K)$$

where K is the dissociation constant of HCN,
c_t is the total cyanide concentration of the solutions, *i.e.*, (CN^-) + (HCN), and
a_H is the hydrogen-ion activity.

This applies to sulphide membrane electrodes and the second dissociation constant, calculated[36] from the results shown in Fig. 9, gave pK_2 equal to 12·65, which was in agreement with the result obtained by Hseu and Rechnitz.[37]

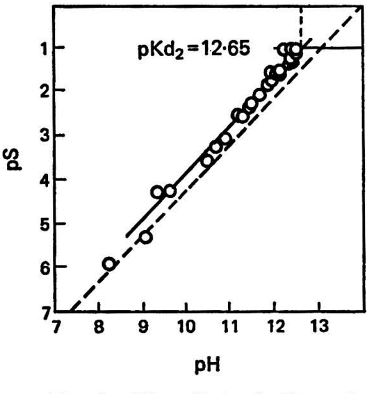

Fig. 9. The effect of pH on the direct S^{2-} measurement. Indicator electrode S^{2-} selective electrode; reference electrode S.C.E. with KNO_3 salt bridge

Hydrofluoric acid was also studied by means of a fluoride-selective electrode. Vanderborgh[38] and Srinivasan and Rechnitz[39] independently published results on the determination of the dissociation constant of hydrofluoric acid, which are in good agreement with those obtained by other methods. Srinivasan and Rechnitz also investigated the sensitivity of the electrode to HF_2^- and concluded that the electrode does not respond to this type of ion, or to such a slight extent that its effect is negligible.

SPECIAL ION-EXCHANGE ELECTRODES—

The behaviour of special ion-exchanger based ion-selective electrodes was studied by Stefanac and Simon,[40] Ross[41] and Walker and Eisenman.[42] In a detailed study of solid and liquid ion exchangers[43] the differences and similarities between solid and liquid ion exchangers are discussed on the basis of the ion exchanger and diffusion phenomena. Eisenman points out that liquid ion exchangers have advantages over solid ion exchangers because in the liquid system the ion-exchange sites can move, so the undissociated ion pairs contribute to the movement of the counter ion in the liquid phase.

Liquid ion exchanger based calcium, copper, perchlorate and nitrate, and so on, selective electrodes were worked out, the selectivity of which can change with time as was shown at the Vienna Conference.[44]

Although a complete theoretical description of the behaviour of liquid ion-exchanger electrodes is not yet possible, this does not detract from the practical value of the electrodes. A simplified theoretical treatment of this type of electrode was deduced for calcium-selective electrodes by Rechnitz and Lin and it was used successfully for the kinetic study of the replacement reaction of magnesium complexone with calcium.[45]

Rechnitz and Lin[46] reported on the application of the copper liquid ion-exchange electrode for the determination of the formation constants of various copper complexes.

TRANSIENT PHENOMENA OF ION-SELECTIVE ELECTRODES—

The examination of equilibrium conditions of ion-selective electrodes discussed so far does not give information on electrode processes. Study of the electrode kinetics is extremely important as the further development of ion-selective electrodes is considered. Furthermore, automatic analysers and continuous measuring cells require sensors with rapid response.

Only a few papers have so far appeared in the literature on the transient phenomena of ion-selective electrodes including glass electrodes. The transient phenomena of glass electrodes[47 to 54] is not discussed in this paper, but it is noticed that the theory of the transient phenomena is not entirely satisfactory.

Studies have been made of the transient phenomena of ion-selective electrodes other than glass electrodes and results have been published.[31,32,33,37,45,55,56] Unfortunately, research into the transient phenomena has not been carried out under the best conditions as the instruments generally used for the measurement of the e.m.f. *versus* time curve have a relatively high time constant, so the data determined cannot be used completely for kinetic studies. The results can also be misleading in that instead of the electrode response, the response time (the time taken for the electrode potential to attain a constant value) of the measuring cell, involving one or more liquid junction potentials, is measured. The liquid - liquid junction potentials can also be time dependent, so they may disturb the evaluation of the results. This relates both to our earlier results and to those of Rechnitz. The response time was found to vary from a few seconds to a few minutes and Rechnitz has shown that the response time increases with the increase in the width of the membrane layer.

The transient phenomena can be measured in two different ways: by the immersion method, in which the electrode is immersed in the solution at $t = 0$ time instant, and the injection method, in which a solution of given concentration is injected into the flowing system with constant speed. A variation of the former method was carried out in our Institute,[56] and it was found that two different concentrations of the appropriate ion had interchanged round the electrode within 1 millisecond, and the change in the electrode potential was recorded with an oscilloscope. The results were as follows: the e.m.f. *versus* time reached a constant value within a few hundred milliseconds; and the transient phenomena of the electrode can be described with one exponential equation; the response time of the electrode is independent of the thickness of the membrane layer and depends on the concentration level of the appropriate ion and on the concentration jump only to a small extent and also depends on the direction of the concentration jump; a great excess of other ions generally decreases the electrode response; the response time of the cyanide electrode is the same as that of a halide electrode, which also shows that the mechanism of the response of a halide-based electrode to complexing agent is the same as that of the electrode to precipitate-forming ions.

EXPERIMENTAL

The ion-selective electrodes are widely used either directly on the analogy of pH glass electrodes or as an indicator electrode in potentiometric titrations. In the former instance, the evaluation of the results is carried out with a calibration graph. The *E versus* —log a_X calibration graph (X is the ion to which the electrode is reversible) is linear in a certain activity range but it differs from it below a given activity value, which can be calculated for every electrode from equation (5). From this it follows that the lowest detection limit of an electrode lies at that activity value at which the slope of its calibration graph reaches zero. The electrode can be used for analytical purposes under restricted conditions in that activity range also, in which the slope of the calibration graph varies, but here the measurements must be repeated to reduce the mean error of the method.

The concentration of a component can be determined from its activity in various ways, the simplest of which is to work with dilute solutions, where the mean activity coefficient is about one. Another method of avoiding the effect of the activity coefficient is to use a solution maintained at a constant ionic strength. Naturally, the test solution should have the same ionic strength as the standard. Salts, to which the selectivity constant of the electrode is very low, can be used as "neutral" salts to maintain the constant ionic strength. The ratio of the activity of the ion tested to the activity of the "neutral" salt should be about 100 times higher than that allowed for by the selectivity constant of the electrode. On the other hand, the use of an indifferent salt in the measurements is accompanied by a rapid electrode response as discussed in the theoretical part. Other methods such as the calculation or the measurement of the mean activity coefficient are more tedious.

The application of ion-selective electrodes in potentiometric titrations as indicator electrodes is analogous to that of any other potentiometric electrode and needs no further comment.

The measurements with ion-selective electrodes can be carried out in cells with or without transference. The performance of the latter cell is not so simple because it requires a reversible electrode dipped in the test solution containing, in addition to the ion to be measured, a constant or known concentration of its appropriate ion. Such a non-transference cell was prepared by Pungor and Papp[57] and involved a perchlorate reference electrode and perchlorate ions in a relatively high concentration (0·1 to 1 M).

If the measurements are carried out in transference cells then the liquid - liquid junction potential may cause some trouble, which is especially marked when this cell is used continuously in flowing systems. Experiments show that the electrolyte around the reference electrode must also flow.

Some commercially available ion-selective electrodes and their properties are shown in Table III, only those electrodes with which we have had personal experience being listed. Besides these, Beckman, Corning Glass, etc., have also been advertising ion-selective electrodes.

CHLORIDE-SELECTIVE ELECTRODE—

The applications of a chloride-selective electrode have been discussed generally.[32, 8, 59]

Two methods were devised by Havas, Papp and Pungor[59] for the determination of chloride with a chloride-selective electrode in the presence of bromide and iodide ions. In one method partial oxidation of iodide was carried out with potassium permanganate in acidic medium and the iodide released was extracted with carbon tetrachloride, while the excess of potassium permanganate was eliminated with hydrogen peroxide. The chloride remaining in the solution was measured directly with a chloride-selective electrode. In the other method the separation of halides was carried out on a column containing a strong base ion-exchange resin in nitrate form. A solution of 0·5 N sodium nitrate was used for the elution of the resin. Van Loon used chromic acid instead of potassium permanganate [60] and determined the insoluble halides after fusion.

The chloride content of soils and tap water can also be determined directly by means of a chloride-selective electrode[61] and some results are shown in Table IV.

The difficulties involved in the micro determination of chloride might be solved by the use of a chloride electrode. A method was developed[59] for determining the chloride content of analytical-reagent grade potassium hydroxide. The potassium ions were converted into hydrogen ions on a column containing a cation-exchange resin, and the effluent was readily determined with a chloride membrane electrode. The chloride can be determined in potassium hydroxide by this method, at a concentration as low as 10^{-3} per cent. (see Table V).

TABLE III

CHARACTERISTICS OF SOME COMMERCIALLY AVAILABLE ION-SPECIFIC ELECTRODES

	Pungor *et al.* type electrodes, Radelkis, Hungary*					Orion type electrodes, U.S.A.†		
Electrode	Type No.	Selectivity		Suggested pre-treatment	Reference No.	Type No.	Selectivity	
Bromide	OP–Br–711	CN	1	1 to 2 hours in 10^{-3} M KBr	66, 68	94–35 (solid state)	S^{2-} must be absent	
		$S_2O_3^{2-}$	1				CN^-	$1{\cdot}2 \times 10^4$
		SCN^-	$1{\cdot}95 \times 10^{-1}$				I^-	5×10^3
		Cl^-	6×10^{-3}				NH_3	$0{\cdot}5$
		AsO_4^{3-}	$1{\cdot}6 \times 10^{-6}$				Cl^-	$2{\cdot}5 \times 10^{-3}$
		PO_4^{3-}	$3{\cdot}1 \times 10^{-7}$				OH^-	3×10^{-5}
		CrO_4^{2-}	$1{\cdot}15 \times 10^{-7}$					
		CO_3^{2-}	1×10^{-7}					
		SO_4^{2-}	$<10^{-7}$					
		NO_3^-	$<10^{-7}$					
Calcium	—	—		—	45, 97–110	92–20 (liquid ion exchange)	Zn^{2+}	$3{\cdot}2$
							Ca^{2+}	1
							Fe^{2+}	$0{\cdot}8$
							Pb^{2+}	$0{\cdot}63$
							Cu^{2+}	$0{\cdot}27$
							Ni^{2+}	$0{\cdot}08$
							Sr^{2+}	$0{\cdot}17$
							Mg^{2+}	$0{\cdot}14$
							Ba^{2+}	$0{\cdot}01$
Carbon	OP–C–711	—		1 hour in distilled water	—	—	—	
Chloride	OP–Cl–711	CN^-	1	1 to 2 hours in 10^{-3} M KCl	32, 58–67	94–17 (solid state)	CN^-	5×10^6
		$S_2O_3^{2-}$	1				I^-	2×10^6
		SO_3^{2-}	2×10^{-1}				Br^-	3×10^2
		AsO_4^{3-}	2×10^{-4}				$S_2O_3^{2-}$	10^2
		PO_4^{3-}	$4{\cdot}8 \times 10^{-5}$				NH_3	8
		CO_3^{2-}	$4{\cdot}6 \times 10^{-5}$				OH^-	$1{\cdot}2 \times 10^{-2}$
		$C_2O_4^{2-}$	$4{\cdot}5 \times 10^{-5}$				S^{2-} must be absent	
		SO_4^{2-}	$<10^{-6}$				No interference from NO_3^-, F^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}	
	—	—		—	—	92–17 (liquid ion exchange)	ClO_4^-	32
							I^-	17
							NO_3^-	$4{\cdot}2$
							Br^-	$1{\cdot}6$
							OH^-	1
							OAc^-	$0{\cdot}32$
							HCO_3^-	$0{\cdot}19$
							SO_4^{2-}	$0{\cdot}14$
							F^-	$0{\cdot}10$
Copper(II)	—	—		—	46	92–29 (liquid ion exchange)	H^+	7×10^3
							Fe^{2+}	1
							Ni^{2+}	5×10^{-3}
							Zn^{2+}	1×10^{-3}
							Na^+ less than 10^{-3}	
							K^+ less than 10^{-3}	
							Ca^{2+}	5×10^{-4}
							Sr^{2+}	2×10^{-4}
							Ba^{2+}	2×10^{-4}
							Mg^{2+} less than 10^{-4}	
Cyanide	OP–CN–711	Same as that with the iodide-selective electrode		6 hours in 10^{-2} M NaOH	72	94–06 (solid state)	No interference from common anions such as F^-, NO_3^-, CO_3^{2-}	
							S^{2-} must be absent	
							Cl^-	10^{-6}
							I^-	10
							Br^-	2×10^{-3}

TABLE III—*continued*

	Pungor *et al.* type electrodes, Radelkis, Hungary*				Orion type electrodes, U.S.A.†	
Electrode	Type No.	Selectivity	Suggested pre-treatment	Reference No.	Type No.	Selectivity
Bivalent cation	—	—	—	—	92–32 (liquid ion exchange)	at pH 6 Zn^{2+} 3·5 Fe^{2+} 3·5 Cu^{2+} 3·1 Ni^{2+} 1·35 Ca^{2+} 1 Mg^{2+} 1 Ba^{2+} 0·94 Sr^{2+} 0·54 Na^+ $\sim 10^{-2}$ K^+ $\sim 10^{-2}$
Fluoride	—	—	—	38, 39, 76–96	94–09	No interference from hydroxide if ten times less than F^-
Iodide	OP–I–711	CN^- 1 Br^- $1\cdot8 \times 10^{-4}$ SCN^- 3×10^{-5} $[Fe(CN_6)]^{4-}$ $3\cdot5 \times 10^{-6}$ SO_3^{2-} $5\cdot5 \times 10^{-7}$ Cl^- $3\cdot7 \times 10^{-7}$ SO_4^{2-} 1×10^{-7} OH^- $9\cdot1 \times 10^{-9}$ AsO_4^{3-} $2\cdot6 \times 10^{-10}$ CrO_4^{2-} $6\cdot6 \times 10^{-11}$ PO_4^{3-} $2\cdot5 \times 10^{-11}$ NO_3^- $<10^{-8}$	1 to 2 hours in 10^{-3} M KI	17, 18, 68–71	95–53 (solid state)	S^{2-}, $S_2O_3^{2-}$, CN^- interfere
Nitrate	—	—	—	—	92–07	ClO_4^- 10^3 I^- 20 ClO_3^- 2 Br^- 0·9 S^{2-} 0·57 NO_2^- 6×10^{-2} CN^- 2×10^{-2} HCO_3^- 2×10^{-2} Cl^- 6×10^{-3} OAc^- 6×10^{-3} CO_3^{2-} 6×10^{-3}
Perchlorate	OP–ClO_4–711	I^- 9×10^{-1} NO_3^- 5×10^{-1} Br^- $4\cdot9 \times 10^{-1}$ Cl^- $2\cdot7 \times 10^{-1}$ SO_4^{2-} $2\cdot6 \times 10^{-1}$ HPO_4^{2-} $1\cdot5 \times 10^{-1}$ OAc^- $9\cdot7 \times 10^{-2}$	1 hour in 10^{-1} M $KClO_4$	111	108 92–81 (liquid ion exchange)	OH^- 1·0 I^- $1\cdot2 \times 10^{-2}$ NO_3^- $1\cdot5 \times 10^{-3}$ Br^- $5\cdot6 \times 10^{-4}$ OAc^- $5\cdot1 \times 10^{-4}$ HCO_3^- $3\cdot5 \times 10^{-4}$ F^- $2\cdot5 \times 10^{-4}$ Cl^- $2\cdot2 \times 10^{-4}$ SO_4^{2-} $1\cdot6 \times 10^{-4}$
Sulphide	OP–S–711	No interference from I^-, Br^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}	1 to 2 hours in 10^{-3} M $AgNO_3$	18, 36, 37, 73–75	94–16 (solid state)	No interference from F^-, Cl^-, SO_4^{2-}, CO_3^{2-}, OH^-, PO_4^{3-}

* Data are being published.

† Information derived from Orion catalogues.

The chloride-selective electrode has also been used in biochemistry by Dahms, Rock and Seligson,[62] who reported the determination of chloride activity in human serum with a chloride electrode. They pointed out the effect of the protein on the activity coefficient, which should be taken into account during these determinations.

TABLE IV

DETERMINATION OF CHLORIDE IN TAP WATER

Method	Chloride content, pCl
Direct	3·97
Titration	3·903
Mohr	3·903

TABLE V

DIRECT DETERMINATION OF Cl^- IMPURITIES IN POTASSIUM HYDROXIDE

$[Cl^-]$, M			
Calculated	Found	Cl^- content, per cent.	Error, per cent.
$1{\cdot}00 \times 10^{-4}$	$1{\cdot}02 \times 10^{-4}$	$7{\cdot}24 \times 10^{-3}$	2
$1{\cdot}00 \times 10^{-4}$	$1{\cdot}04 \times 10^{-4}$	$7{\cdot}38 \times 10^{-3}$	4
$1{\cdot}00 \times 10^{-4}$	$1{\cdot}05 \times 10^{-4}$	$7{\cdot}45 \times 10^{-3}$	5

TABLE VI

DETERMINATION OF CHLORIDE IN URINE AND HORSE-BLOOD SERUM

	pCl determination by—			
		Membrane electrode		
Sample	Ag electrode (titration)	(titration)	(direct method)	Mohr method (titration)
Urine	0·77, 0·78	0·78, 0·78, 0·78	0·77, 0·78, 0·79	0·754
Horse-blood serum	0·85, 0·84	0·86, 0·85	0·86, 0·84, 0·84	0·824

Papp and Pungor[63] devised a method for the determination of the chloride content of horse-blood serum and human serum. The results are summarised in Table VI, where a comparison is made between various methods used for determining chloride. The results obtained by different methods are in good agreement with each other. The membrane electrode methods have the advantage that they do not need to be centrifuged to free them from proteins before measurement. The results were the same with the direct and titration methods.

Hansen, Buechele, Koroshec and Warwick[64] reported on the determination of the chloride in sweat in new-born infants with a chloride electrode, by using heat stimulation. The procedure is adequate with the standard technique.

The chloride-selective electrode is used in the pharmaceutical industry to determine pharmaceutical products by their ionisable or bonded chloride content, as shown by Papp and Pungor[65] and Dessouky, Tóth and Pungor.[66] Dessouky used the Schöniger method for liberating the bound chloride.

Chloride-selective electrodes have been used in food chemistry by Holsinger, Posati and Pallansch,[67] who developed a method for the rapid determination of the chloride content of cheese by using a chloride membrane electrode. The method gives good results and is suitable for the rapid qualitative determination of cheese.

TABLE VII

DETERMINATION OF CHLORIDE IN COW'S MILK

	Chloride content of natural milk, pCl	
Concentration, per cent. v/v	Direct method	Titration method
Natural milk	1·460	1·468
50 per cent. milk	1·468	1·468
20 per cent. milk	1·471	1·468

The chloride content of natural cow milk can also be measured directly with a chloride-selective electrode.[61] The amounts of chloride calculated from natural and diluted samples are the same, which means that there are no dissociation problems. Some results are given in Table VII.

BROMIDE-SELECTIVE ELECTRODE—

For the determination of bromide ions in serum a bromide-selective membrane electrode can successfully be used as shown by Carter.[68] He suggests the membrane electrode method as a useful screening procedure in psychiatric admissions.

The determination of the bromide content of pharmaceutical products is similar to that of the chloride.[66]

IODIDE-SELECTIVE ELECTRODE—

The iodide-selective electrode, produced in 1961, was the first highly selective anion-specific electrode.[17] Most theoretical studies were carried out with this electrode, but besides the fundamental theoretical importance of the electrode, it has practical advantages also.

The high selectivity of the iodide-selective electrode to iodide makes the direct determination of iodide in mineral waters possible. The results of the rapid, direct determination in some mineral waters occurring in Hungary have been compared with those obtained by the volumetric Winkler method,[18] and show good agreement.

An iodide-selective electrode was used for measuring components that release iodide in a chemical reaction. Such measurements were carried out for determining sulphur dioxide.[18] The gas containing sulphur dioxide was bubbled through an iodine solution and, after extracting the excess of iodine with carbon tetrachloride, the iodide produced was measured directly or volumetrically by using the iodide-selective electrode as an indicator electrode.

An extremely interesting application of the iodide-selective electrode was worked out by Arino and Kramer[69] for the determination of the iodine-131 and iodine-125 content of highly radioactive solutions. The specific activity of the iodine solution could be calculated from the radioactive determinations. The discovery that the 20-Ci radiation field of iodine-131 and iodine-125 has no effect on the behaviour of the electrode is most valuable.

Carter[68] suggested the use of the iodide electrode for determining the iodide content of serum in special cases.

The iodide electrode was used as an indicator electrode in the potentiometric titration of iodide in concentrations down to 10^{-4} and 10^{-5} M[18] and for the titration of a mixture of chloride, bromide and iodide.[70] The end-point of the titration of the mixture of halides for an individual halide is not correct and the deviation is caused by the adsorption of the halides on the precipitate surface. This can be overcome by using a large excess of potassium nitrate as shown by Küttel, Szabadka, Csákváry, Mészáros, Havas and Pungor.[71] Lower concentrations of barium nitrate could also be used.

CYANIDE-SELECTIVE ELECTRODE—

Theoretically, every halide membrane electrode can be converted into a cyanide electrode, but in practice the silver iodide based cyanide electrode is most suitable for the determination of cyanide because of its high selectivity. Before measurement, the cyanide electrode must be pre-treated by soaking it in 10^{-2} M sodium hydroxide solution overnight. It is carefully washed with distilled water before use.

The direct determination of cyanide can be carried out with a calibration graph, an example of which is shown in Fig. 10. The e.m.f. values were measured in solutions, the ionic strengths of which were maintained constant at 0·1 by the addition of potassium nitrate. Because the cyanide electrode measures only the dissociated cyanide, the pH of the standardising solutions was kept higher than 10·5 if the total cyanide content was to be measured ($pK + 1 = 10{\cdot}5$, where K is the dissociation constant of hydrocyanic acid). Some results obtained by direct cyanide measurement are collected in Table VIII, where the reproducibility of the results is given as pCN ($-\log C_{CN}$). It can be seen from this table that the reproducibility of the cyanide electrode is satisfactory.

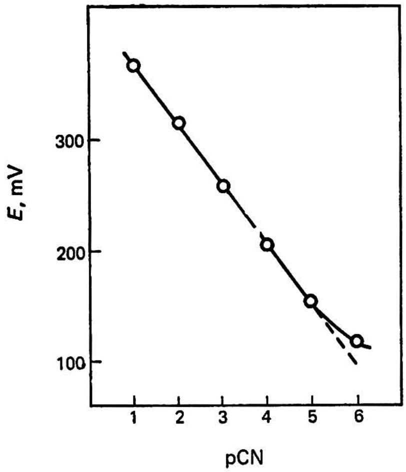

Fig. 10. Calibration graph for CN^-. Reference electrode S.C.E. with KNO_3 salt bridge

TABLE VIII

REPRODUCIBILITY OF THE CYANIDE ELECTRODE AT 25° C

CN^-, M	E_{mean}, mV	Reproducibility, pCN
10^{-1}	357	±0·02
10^{-2}	300	±0·04
10^{-3}	242	±0·02
10^{-4}	187	±0·02
10^{-5}	130	±0·05
10^{-6}	100	±0·4

Potential measured *versus* Ag - AgCl (0·1) with KNO_3 salt bridge.

Besides direct measurement, the cyanide electrode can also be used as an indicator electrode in the titrimetric determination of cyanide. The shape of the titration curve obtained when silver nitrate is used as titrant is shown in Fig. 11. Either inflection point can be used for calculating the cyanide concentration.

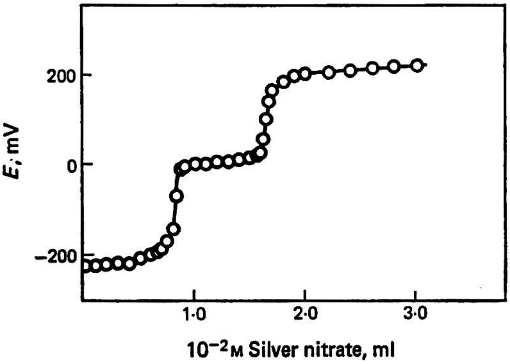

Fig. 11. Potentiometric titration curve of CN^- with $AgNO_3$. Reference electrode S.C.E. with KNO_3 salt bridge

Table IX shows a comparison between the results obtained by direct and titration methods. The cyanide content of the sample was checked by the volumetric Liebig-Deniges method, the limit of determination of which is of the order of milligrams. By using the membrane electrode method, the cyanide can be determined even in a concentration ten times lower, *i.e.*, about 100 µg, with the same accuracy.

TABLE IX

DETERMINATION OF CYANIDE BY VARIOUS METHODS

	Cyanide content, mg Method		
Sample	Liebig-Deniges	Direct	Titration
1	4·441	4·293	4·139
2	0·444	0·494	0·409
3	0·044	0·050	0·043

The direct determination of cyanide is essentially important for determining cyanide in industrial waste water, an example of which is shown in Table X. The results calculated for the cyanide content of sewage from the e.m.f. values measured in diluted samples were in good agreement with each other.

TABLE X

DETERMINATION OF CYANIDE IN SEWAGE

Sample	Dilution	Cyanide content of sewage, p.p.m., by direct method
1	1+1	13·1
	1+5	14·6
	1+10	13·1
2	—	24·7
	1+1	23·4

To summarise the cyanide determination in industrial waste water it can be said that all free cyanide and a part of cyanide complexes with a lower stability constant than silver(II) cyanide are measured by the cyanide membrane electrode. The potential of the cyanide electrode can be used as a transducer in automatic process control for the elimination of cyanide with hypochlorite. However, stronger cyanide complexes that are not measured by the electrode produce an error in such control. This can be overcome by using a potential much lower than the potential measured under the same conditions in 10^{-6} to 10^{-7} M cyanide solutions. If the potential caused by the cyanide concentration produced by the dissociation of metal - cyanide complexes is higher in the system than the potential used for the process control, the oxidation of metal - cyanide complexes with hypochlorite can also be controlled. The products of oxidation, such as Cl–CN, are not measured by the cyanide electrode.

The cyanide membrane electrode has found application in both agricultural chemistry and plant biochemistry. Cyanoglycosides are common in many cultivated plants. The glycoside itself, in which the cyanide is bonded, is not toxic to either human or animal organism, but hydrolysis produces hydrogen cyanide of high toxicity. The hydrolysis is catalysed by a glycoside splitting enzyme. Some raw materials, such as sudan grass, sorghum, almond and the distilled products of certain fruits, contain traces of cyanoglycosides, and the determination of cyanide must be carried out on these materials.[72]

The determination of cyanide was studied in various plants and brandies by means of a cyanide membrane electrode.[73] As an example of a glycoside, amygdalin was used. After the hydrolysis of amygdalin, both direct cyanide determination and argentometric titration were carried out in twenty different almond distillates. Table XI shows that the determination of cyanide is more accurate with a cyanide membrane electrode than with argentometric titration in the given concentration range.

Experiments performed to show the effect of ethanol on the direct cyanide determination indicate that the effect of ethanol is negligible, *i.e.*, it does not exceed an error of pCN = 0·15. The method is, therefore, entirely suitable for the determination of the cyanide content of fruit brandies without isolating the cyanide from the alcohol.

TABLE XI

COMPARISON BETWEEN THE CN^- CONTENT OF VARIOUS ALMOND DISTILLATES DETERMINED BY ARGENTOMETRIC TITRATION AND THE MEMBRANE ELECTRODE METHOD

	HCN content, p.p.m.	
No.	Argentometric titration	Measurement by the pCN electrode
1	265	275
2	280	272
3	243	284
4	267	288
5	271	270
6	248	290
7	246	274
8	263	283
9	277	280
10	255	282
11	244	277
12	280	280
13	280	284
14	281	272
15	249	278
16	241	288
17	255	280
18	240	276
19	244	281
20	271	286
	s = 15·38 p.p.m.	s = 5·75 p.p.m.

SULPHIDE-SELECTIVE ELECTRODE—

General studies on sulphide-selective electrodes have been made.[36,37,73] Bock and Puff[74] used a sulphide-selective electrode for the determination of sulphide in the presence of ascorbic acid at pH 13. They found that sulphide ions can be measured in low concentrations (10^{-5} to 10^{-6} M) only if the oxidation of sulphide is negligible, and for this de-aeration is not sufficient, while the addition of ascorbic acid is sufficient.

The sulphide membrane electrode is an excellent indicator for the potentiometric titration of sulphide and halides in aqueous solutions.[18] It is noteworthy that sulphide does not interfere in the determination of halides. This is especially important in the photographic industry, where halide-specific electrodes cannot be used because of poisoning by sulphide released from gelatin.

SILVER SALT CONTAINING ELECTRODES FOR MEASURING CATION ACTIVITIES—

All electrodes containing slightly soluble silver salts can be used to determine silver-ion activities. On this basis, the silver iodide based iodide-selective electrode can be used to determine the local silver-ion activities in the electrochemical corrosion of silver (personal communication from Dévay and Lengyel). Naturally, similar applications for this type of electrode can be found.

More interesting is the response of the silver sulphide based sulphide electrode to mercury(II) ion activities. In the potentiometric method of Papp and Havas,[75] four types of sulphur compounds can be determined in the presence of each other by successive titrations. In the titrations a sulphide indicator electrode and mercury(II) chloride titrant were used. The titration of sulphide and the sulphide content of polysulphides was carried out in 0·1 M sodium hydroxide solution (pH = 13) and, after adjusting the pH of the same solution to between 6·5 and 7, the total amount of $S_2O_3^{2-}$ and SO_3^{2-} was determined. In another aliquot of the sample the total sulphide content was determined again at pH 13, after which excess of formaldehyde was added to the sample. Formaldehyde converts the sodium sulphite into an inert hydrogen sulphide, which is not determined, thus in a further titration of the sample at pH 7, the thiosulphate content could be determined. Before the third titration a large excess of sulphite was added to an aliquot of the original sample and the solution was maintained at 50° C for 15 to 20 minutes. In this way from the polysulphide sulphur an equivalent amount of thiosulphate was formed, which could be titrated with mercury(II) chloride with a sulphide-selective electrode. From the results of the titrations the amounts of the four sulphur compounds were calculated.

FLUORIDE-SELECTIVE ELECTRODE—

Fluoride-selective electrodes are either made from a doped LaF_3 single crystal[76] or from slightly soluble fluoride salts embedded in silicone rubber.[77] The single-crystal fluoride electrode can be used for direct fluoride determinations over the range of 10^{-1} to 10^{-6} M fluoride-ion activity. Because of the weak acidic properties of hydrogen fluoride the pH of fluoride solutions must be controlled as stated.[38,39] For the determination of fluoride in water Frant and Ross[78] suggest a buffer containing acetic acid, sodium chloride and sodium citrate, the pH of which is adjusted to between 5·0 and 5·5 with 5 M sodium hydroxide solution. In industrial waste water the standard deviation between the method with a fluoride-selective electrode and a standard method was 0·06 p.p.m. at 0·3 p.p.m. fluoride concentration. When the buffer was not used then the standard deviation between the two methods is higher in the same fluoride concentration range.

Lingane[79] investigated thorium, lanthanum and calcium salts as titrants in the potentiometric titration of fluoride with a fluoride-selective electrode. He found that lanthanum nitrate is the best titrant and the experimental error is least if the titration is carried out in a neutral, unbuffered solution. Later, Lingane[80] studied the direct and indirect determination of fluoride with a fluoride electrode in ethanolic media and he found that the fluoride electrode obeyed the expected theoretical relationship up to about the same pF value in the presence of 60 per cent. v/v ethanol as in aqueous medium. Further, he studied the effect of acids and stirring on the fluoride determination and observed that the upper pF limit of the theoretical response is greater in acidic media than in neutral media. The stirring had no effect in fluoride concentrations greater than 10^{-3} M, but in lower concentrations it extended the limit of the theoretical response. Lingane determined the solubility products of lanthanum fluoride and europium fluoride. They are $1{\cdot}2 \times 10^{-18}$ and $2{\cdot}2 \times 10^{-17}$ moles l^{-1}, respectively, at an ionic strength of 0·03 M in aqueous medium at 25° C.

Anfält, Dyrssen and Jagner[81] determined fluoride from Lingane's experimental technique[79] and compared the experimental and calculated data. The calculation was carried out by means of the computer program, Haltafall, written by Ingri, Kakolowicz, Sillén and Warnquist.[82] It was concluded that the fluoride titration with lanthanum nitrate in unbuffered solution should give an accurate end-point if the titration graph is analysed with a computer.

The fluoride determination was examined by Bock and Strecker[83] in the presence of various other components. They found that non-ionic compounds, such as glucose, carbamide and hydrogen peroxide, cause only a slight shift in the calibration graph, while sodium chloride and magnesium sulphate cause a greater shift. Further, iron, borate and silicate had no marked effect on the potential of the fluoride electrode, while aluminium, beryllium, zirconium and titanium did. An addition technique was introduced for the evaluation of fluoride.

Mesmer[84] used the fluoride-selective electrode in a molar chloride medium, and concluded that the fluoride electrode can be used for measuring fluoride impurities of less than 1 p.p.m. in chloride salts.

Van Loon[85] analysed various fluoride minerals with a fluoride-selective electrode. The fluoride results differ from those calculated by up to about 5 per cent.

A method was worked out by Raby and Sunderland[86] for determining fluoride in tungsten.

Baumann[87] used a fluoride-selective electrode to determine fluoride in the range of 10^{-4} to 10^{-5} M, evaluating the result with the standard addition method. The work was extended to solutions of sodium chloride, sodium nitrate, acidified sodium silicate, sodium hydroxide, lithium chloride and phosphoric acid. The effect of metal ions (*e.g.*, Al^{3+}, UO_2^{2+}, Fe^{3+} and Th^{4+}) can be suppressed by pre-complexing them with phosphoric acid.

Durst and Taylor[88] elaborated on an apparatus for the micro determination of fluoride, which permits measurements on volumes as small as 1 drop. By using linear null-point potentiometry[89] down to 0·38 ng of fluoride in 10 μl was determined.

The determination of fluoride with a fluoride electrode in air and stock gas samples is described by Elfers and Decker.[90] The air, containing about 1 p.p.m. of fluoride, was filtered through cellulose acetate membrane filters impregnated with sodium formate. The fluoride retained by the filter was liberated by washing the filter with 0·1 M sodium citrate. Down to 0·25 part per 10^9 of fluoride in air could be measured in this way. Stock gas samples containing gaseous fluorides are allowed to react with a hot glass probe to form gaseous silicon tetrafluoride, which hydrolyses in water to form soluble fluorosilicic acid. In both instances, the adsorbed fluoride is determined by a direct potentiometric method in a citrate buffer. The use of the fluoride specific-ion electrode has been shown to be rapid and convenient.

The fluoride-selective electrode has also been used in biochemistry. Singer and Armstrong[91] determined fluoride successfully with a fluoride-selective electrode in bone ashes. They prefer to use this method for normal and pathological classifications of materials such as kidney stones.

The fluoride content of human parotid saliva was determined by Groen, McCann and Brudevold.[92] The best results were obtained when the pH of saliva was adjusted to between 4·7 and 4·8 before the measurements. The other components of saliva did not interfere in the fluoride determination. Fluoride determination on enamel, dentine or bone has also been reported by McCann.[93] An aliquot of the sample was dissolved in 0·5 M perchloric acid, and diluted with 0·5 M trisodium citrate. The fluoride determination was carried out with a fluoride-selective electrode, which was influenced only by aluminium. Brudevold, McCann and Groen[94] studied the determination of fluoride in human teeth.

Light and Mannion[95] gave a method for the micro determination of fluorine in organic compounds by potentiometric titration with a fluoride electrode.

Besides the common potentiometric applications, Muto and Nozaki[96] recommended the use of a fluoride electrode as an indicator electrode in the coulometric titration of fluoride.

CALCIUM-SELECTIVE ELECTRODE—

Ross[97] found that the calcium salt of didecylphosphoric acid dissolved in di-octylphenyl phosphonate was suitable for the determination of calcium-ion activities. This calcium-selective electrode was used by Thompson and Ross[98] for measuring the calcium content of sea water.

Shatkay[99] investigated the suitability of paraffin membranes, solid polymeric membranes and Orion liquid ion-exchange electrodes for the measurement of calcium activity. It was concluded that the polymeric and Orion electrodes are equally selective to calcium ions. On this subject a polemic has started between Rechnitz[100] and Shatkay.[101] This was followed by the paper by Frant,[102] who disputes the validity of an assumption made by Shatkay,[99] that the calcium single-ion activity is directly proportional to the mean activity of calcium in 1 to 10^{-5} M calcium chloride solutions. This is answered by Shatkay.[103]

Bloch, Shatkay and Saroff[104] have reported on new calcium membrane electrodes made from an inert poly(vinyl chloride) matrix impregnated with tributylphosphate or a mixture of tributylphosphate and thenoyltrifluoroacetone. Both types of electrodes were tested for calcium selectivity and were found highly specific for calcium in the presence of sodium, barium and magnesium ions.

A calcium-selective electrode was evaluated for use in the routine measurement of serum calcium by Arnold, Stansell and Malvin.[105] The electrode permits the direct assay of calcium in fresh serum with an error of 0·2 to 0·3 mg per 100 ml.

A calcium-selective electrode has been used[106] as an indicator electrode in complexometric titrations, and the results used for chemical-complex studies.

The calcium-selective electrode was also used for physico-chemical studies. Rechnitz and Lin[45] used the calcium ion-specific electrode for a kinetic study of the calcium and magnesium - EDTA exchange reaction. The formation constants for Ca - EDTA and Ca - NTA were successfully evaluated and the kinetics of the above reaction were elucidated within the limits imposed by the properties of the calcium electrode.

Nakayama and Rasnick[107] used a calcium-selective electrode for investigating the dissociation and solubility of calcium sulphate dihydrate.

The determination of calcium at concentrations above 1·0 M in the presence of sodium was studied by Huston and Butler.[108] Reproducible measurements were made with up to 5·5 M calcium(II). From the examination of the Nernst response of the electrode, it was concluded that the most accurate measure of calcium activity in a given solution can be obtained if the internal solution is of similar concentration to the test solution. From the selectivity measurement, it is obvious that the selectivity of the electrode for calcium over sodium decreases at high chloride concentrations.

A calcium-selective electrode made from a solution of the calcium salt of a dialkylphosphoric acid in collodion has been reported.[109]

Rechnitz and Hseu[110] used the calcium-selective solid ion-exchange electrode elaborated by Schulz *et al.*[109] for measuring calcium-ion activity and for studying the complex formations between Ca^{2+} and various complexing agents.

OTHER ION-SELECTIVE ELECTRODES—

Light[111] gives a summary on such liquid selective electrodes as bivalent copper chloride, perchlorate and nitrate. The properties of these electrodes are shown in Table XII, according to Light.[111]

TABLE XII

CHARACTERISTICS OF COMMERCIALLY AVAILABLE LIQUID ION-EXCHANGE ELECTRODES[111]

Electrode designated for	Manufacturer's characteristics	
	Range	Interferences, selectivity constants
Calcium	pCa 0 to 5 pH 5·5 to 11	Zn^{2+} 3·2, Fe^{2+} 0·8, Pb^{2+} 0·6, Mg^{2+} 0·01, Ba^{2+} 0·01, Na^+ 0·0003
Bivalent metals (water hardness) ..	pM 0 to 8 pH 5·5 to 11	Zn^{2+} 3·5, Fe^{2+} 3·5, Cu^{2+} 3·1, Ni^{2+} 1·4, Ba^{2+} 0·9, Na^+ 0·02
Copper(II)	pCu 1 to 5 pH 4 to 7	Fe^{2+} 1·0, Ni^{2+} 0·005, Zn^{2+} 0·001, Ca^{2+} 0·0005, Na^+, K^+ 0·0001
Chloride	pCl 1 to 5 pH 2 to 11	I^- 17, NO_3^- 4·2, Br^- 1·6, HCO_3^- 0·19, SO_4^{2-} 0·14, F^- 0·10
Perchlorate	$pClO_4$ 1 to 5 pH 4 to 11	I^- 0·012, NO_3^- 0·002, Br^- 0·0006, F^- 0·0003, Cl^- 0·0002
Nitrate	pNO_3 1 to 5 pH 2 to 12	I^- 20, Br^- 0·9, NO_2^- 0·06, CO_3^{2-} 0·006, SO_4^{2-} 0·0006, F^- 0·0009

FURTHER DEVELOPMENT OF ION-SELECTIVE ELECTRODES—

The great development of ion-selective electrodes has opened a new vista in both analytical chemistry and process control. The further development of the application of ion-selective electrodes is in progress,[112,113] and they will be used on a large scale in industry as sensors in process control. However, future progress depends on whether or not more ion-selective electrodes can be developed.

The assumption that no more will be developed may well be disproved in future work. We therefore think that some directions relating to the development of ion-selective electrodes should be made. Research must be directed to matrixes, on the surface of which the appropriate ion gives a faster exchange reaction than any of the other ions, and across which the ionic-electrical transfer is assured. The electrodes on which the electron transfer is fast are good redox electrodes.

Finally, the large amount of work that needs to be carried out both in the practical and theoretical aspects should be emphasised.

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The Determination of Aliphatic Ketones by Polarography of their Girard T Hydrazone Derivatives

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A method is described for the determination of a range of aliphatic ketones by polarography of their Girard T derivatives. The compound is formed *in situ* in a 75 per cent. ethanolic - acetate buffer (apparent pH 4·00) solution 0·1 M with respect to the Girard T reagent.

It has been shown that a wide range of carbonyl compounds can be determined polarographically via their azomethine derivatives,[1,2,3,4,5] the advantage of this particular method being that it obviates the need for isolation of the derivatives as the reagent itself is electro-inactive. A survey of the mechanism of reduction of this class of compound has been carried out by Lund.[6]

In general, the polarographic reduction of aldehyde and ketone azomethine derivatives of structure R′R″C=N–N–R occurs by a 4-electron process. Fleet and Zuman[7] confirmed this for a range of semicarbazones and, subsequently, a method for the determination of a range of aldehydes was developed.[8] The waves for the lower aliphatic aldehydes and ketones, however, are not well defined and some degree of hydrolysis is encountered with some of the latter compounds. A comparison of several nucleophilic reagents[9] showed that the Girard T (trimethylammonium acetylhydrazide chloride) hydrazones of aliphatic aldehydes give better defined waves than the corresponding semicarbazone derivatives.

Preliminary observations indicated that the Girard T reagent was also superior for the determination of aliphatic ketones. The aim of this work, therefore, was to establish the optimum conditions for the determination of a range of aliphatic ketones.

EXPERIMENTAL

APPARATUS—

The polarographic waves were recorded on a Radelkis polarograph, Type OH-102 (Metrimpex, Hungary). A Kalousek vessel with a separated saturated calomel reference electrode was used. Capillary constants measured at the potential of the S.C.E. in 0·1 M potassium chloride solution were $t = 4{\cdot}1$ s and $m = 2{\cdot}04$ mg s^{-1} at $h = 61$ cm. Separate values of m and t were calculated for the calculation of diffusion current constants.

MATERIALS—

The ketones studied are listed in Table I. Standard solutions (10^{-2} M) of the carbonyl compounds in absolute ethanol were prepared. Buffer solutions were prepared from analytical-reagent grade reagents: sulphuric acid (pH 1 to 2); sodium acetate - acetic acid (pH 4 to 6); and sodium dihydrogen phosphate - sodium hydroxide (pH 6 to 8). Girard T reagent was recrystallised from ethanol - water and a 0·5 M stock solution in ethanol prepared.

TABLE I

DIFFUSION CURRENT CONSTANTS OF GIRARD T DERIVATIVES OF ALIPHATIC KETONES

Carbonyl compound	Diffusion current constant, $I = i_{\mathrm{lim}}/cm^{2/3}t^{1/6}$
Acetone	2·55
Ethyl methyl ketone	1·90
Isopropyl methyl ketone	2·71
Isobutyl methyl ketone	1·93
Methyl pentyl ketone	2·31
Hexyl methyl ketone	2·22

RECOMMENDED PROCEDURE—

An aliquot of a solution of the carbonyl compound in ethanol is placed in a 10-ml calibrated flask containing 2·0 ml of 0·5 M Girard T reagent in ethanol, 2·5 ml of aqueous buffer solution (0·4 M sodium acetate - 4·0 M acetic acid) and 0·5 ml of 0·5 M tetrabutylammonium perchlorate in ethanol. The solution is then diluted to volume with ethanol. Polarograms are recorded from —1·0 to —1·8 V *versus* S.C.E.

RESULTS AND DISCUSSION

A comparison of several nucleophilic reagents showed that the best defined waves were obtained for the Girard T derivatives. This reagent was superior to semicarbazide, hydroxylamine and Girard P reagent (pyridinium acetylhydrazide chloride). The effect of solvent composition was next studied by using ethanol as the organic co-solvent. It was found that the optimum conditions were obtained when 75 per cent. v/v ethanol was used (Fig. 1).

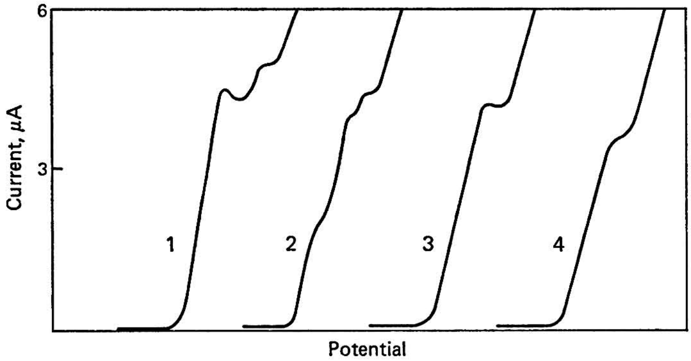

Fig. 1. Effect of solvent composition on the polarographic waves of 5 × 10^{-4} M acetone Girard T hydrazone in 0·4 M sodium acetate - 4 M acetic acid buffer. Ethanol, per cent. v/v: 1, 40; 2, 50; 3, 75; and 4, 90

Detailed studies of pH dependences were made on representative members of the series of carbonyl compounds studied, *viz.*, acetone and isopropyl methyl and hexyl methyl ketones. The behaviour in all instances was essentially similar to that observed earlier for azomethine derivatives of aliphatic carbonyl compounds.[8,9] At low pH values two waves were observed, both decreasing fairly rapidly with time because of hydrolysis. At pH values greater than 2

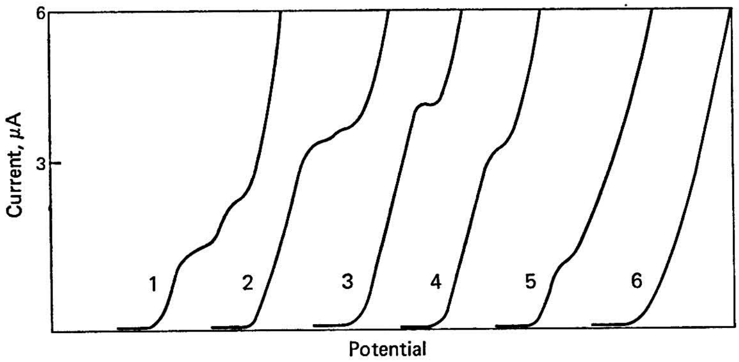

Fig. 2. pH dependence of waves of 5 × 10^{-4} M acetone Girard T hydrazone in 75 per cent. ethanol. pH: 1, 1·01; 2, 2·04; 3, 4·00; 4, 5·30; 5, 6·40; and 6, 8·35. $E_{\frac{1}{2}}$, V *versus* S.C.E.: 1, —0·85, —1·0; 2, —0·95; 3, —1·18; 4, —1·28; 5, —1·37; and 6, no wave

the two waves coalesced and a single, well defined wave was observed. Above pH 5 the wave decreased in the normal manner in the form of a dissociation curve (Fig. 2). This behaviour is typical of electroactive species which are reduced in the protonated form. As in the earlier studies, the optimum pH region for the determination of this class of compound was found to be 4 to 5.

The effect of the nature of the cation of the supporting electrolyte was investigated. No improvement in wave shape was observed when sodium ions were replaced by 0·1 M potassium, ammonium, magnesium or lithium ions. However, it was found that the addition of tetra-alkylammonium ions, particularly the tetrabutyl salts, improved the definition of the waves of the isopropyl and isobutyl methyl derivatives. This effect is almost certainly due to the surface-active properties of the tetra-alkylammonium ions.

TABLE II

CONCENTRATION DEPENDENCE OF ACETONE GIRARD T HYDRAZONE AT pH 4·0 (0·1 M SODIUM ACETATE - 1 M ACETIC ACID BUFFER) IN 75 PER CENT. ETHANOL - 0·1 M TETRABUTYLAMMONIUM PERCHLORATE

Concentration, M	1×10^{-4}	2×10^{-4}	4×10^{-4}	6×10^{-4}	8×10^{-4}	1×10^{-3}
Current, μA	0·90	1·50	3·00	4·62	6·10	7·72

The diffusion-controlled nature of the wave for the Girard T derivatives at pH 4·0 was confirmed by the rectilinear dependence of the wave height on the square root of corrected mercury pressure. A linear dependence of wave height on concentration was observed over the range 10^{-4} to 10^{-3} M (Table II). The values of the diffusion current constant, I, for the range of ketones studied are shown in Table I. A much wider variation in these values is observed than in the corresponding homologous series of alkanals, and is presumably caused by the effect of the branched chain on the diffusion coefficient.

No attempt was made to elucidate the nature of the electrode process as, from the general polarographic behaviour (wave shape, $n = 4$, etc.), it was apparent that the reduction of this class of compound followed the general pattern of azomethine derivatives.

We thank the Science Research Council for the award of a studentship to one of us (M.D.B.).

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Automatic Titration by Stepwise Addition of Equal Volumes of Titrant

Part II.* An Automatic Titration System

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A fully automatic titration system is described. The system carries out transfer of the sample by pipette, and dilution, titration and washing of electrodes and titration vessels. Titrations are performed by adding titrant stepwise in equal volumes to the sample, with recording of potential after each addition. These results are used to calculate equivalence points. The system has a loading capacity of 200 samples, and an analysis rate of up to 30 samples per hour.

THE first paper in this series[1] describes a method of titration in which the titrant is added stepwise in equal volumes to the sample solution with measurement of potential after each addition. This paper describes a fully automatic system for this method of titration.

The system carries out all necessary titration operations. It delivers measured volumes of sample solution and diluent, titrates until a pre-set potential has been passed and finally washes the titration vessel and the electrode. These operations are performed at different positions in the instrument, thus facilitating high analysis rates (up to 30 samples per hour). The system has a loading capacity of 200 samples.

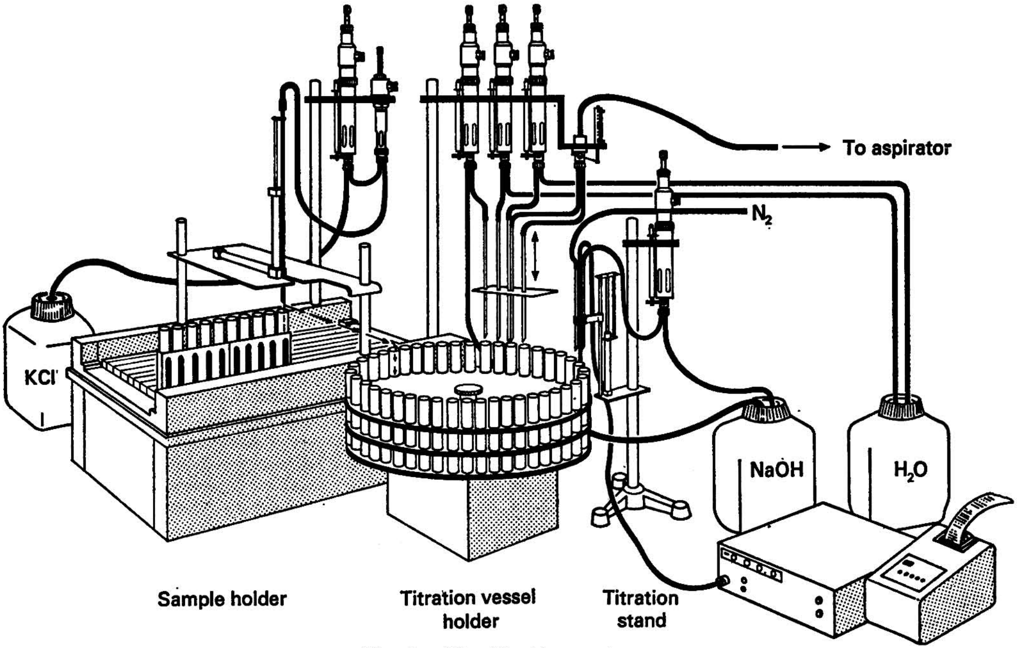

Fig. 1. The titration system

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* For details of Part I of this series, see reference list, p. 656.

SYSTEM COMPONENTS—

The system is shown in Fig. 1 and schematically in Fig. 2. It consists of units for solution handling, measurement of potential and operation control. The solution handling unit has been constructed by using five automatic pipettes, two automatic fraction collectors and pneumatic lifts. The plunger-type automatic pipettes (AGA automatic pipettes, AGA AB, Lidingö, Sweden) are driven by compressed air, controlled by magnetically operated valves (Miniatur-Ventile, 44.201–1, M. Kuhnke Elektrotechnische Fabrik GmbH, 2427 Malente/Holstein, West Germany). Two types of pipettes were used: (*i*) reagent pipettes, fitted with two-way valves to permit the reagent to be sucked up from a stock solution container through one tube and pumped via another tube into the reaction vessel; and (*ii*) sample pipettes, which do not require a valve as the sample is sucked up from the sample container and introduced into the titration vessel through the same tube; 0 to 0·7-ml sample pipettes and 0 to 5-ml reagent pipettes were used. Pipette volumes may be continuously altered by adjusting a stop on the plunger. These pipettes are shown schematically in Fig. 2. Reagent pipette B is used only for the titration of weak acids. The delivery volume precision of these pipettes was determined by collecting and weighing thirty consecutive aliquots. Results are shown in Table I.

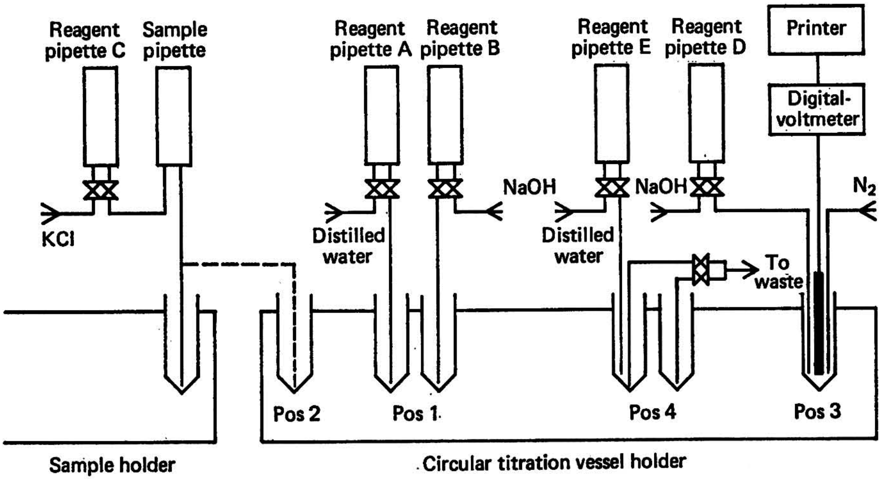

Fig. 2. Diagram of the titration system

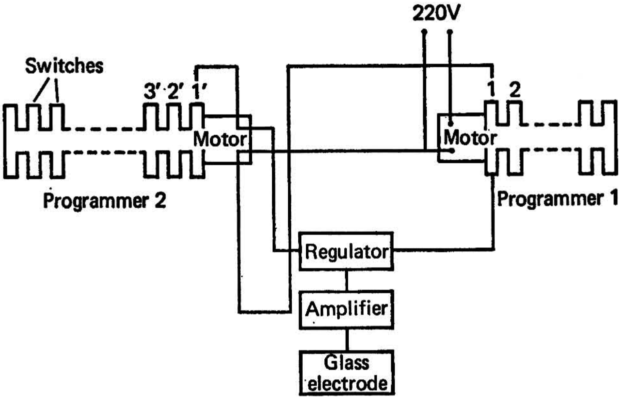

Fig. 3. Diagram of the control unit

TABLE I

PRECISION OF AUTOMATIC PIPETTES

Pipette	Mean volume, ml	Standard deviation of volume, ml
Sample pipette	0·5560	0·0005
Reagent pipette B	1·9255	0·0007
Reagent pipette C	4·2345	0·0005
Reagent pipette D (titration pipette)	0·5067	0·0004

An Ultro Rac fraction collector (Model 7000, LKB Produkter AB, Bromma 1, Sweden) is used as a sample feeder. It has a capacity of 200 samples and is the component that limits sample loading capacity. A conventional circular fraction collector is used as a titration vessel holder. Pneumatic lifts are used to facilitate solution transfer, firstly to raise and lower the glass electrode, the outlet tube for nitrogen and the outlet tubes for pipettes A, B, D and E and, secondly, to raise, move across and lower the inlet tube of the sample pipette (see Figs. 1 and 2). Lift movements are carried out by compressed-air driven pistons (Miniatur-Zylinder, 38.263, M. Kuhnke Elektrotechnische Fabrik GmbH, 2427 Malente/Holstein, West Germany). The unit for measurement of potential consists of a micro glass - calomel electrode (HA-401 M5, Dr. Ing. chem. W. Ingold, 8006 Zürich, Switzerland), a digital voltmeter (Model 801, Orion Research Incorporated, 11 Blackstone Street, Cambridge, Massachusetts, U.S.A.) and a printer (Digital Printer D4, Kienzle Apparate GmbH, 7730 Villingen/Schwarzwald, West Germany).

The control unit (see Fig. 3) consists of an amplifier, a regulator and two programmers and is used to control system operation from measured pH values. The potential at the glass electrode is monitored by using a high input impedance amplifier (PR 9405, Philips; $5 \times 10^{11}\ \Omega$), which does not disturb the potential measurement process. The amplifier output is fed to a regulator, where it closes a gate when a pre-set pH is attained. This pH value is chosen by setting a dial control on the regulator (GOAB 44, Philips). Two motor-driven switching units are used as programmers. Programmer 1 (P6 MR-ZT, Sandblom & Stohne, Lindhagensgatan 122, Stockholm, Sweden) has a pre-selectable cycle time of 12 to 120 s. It operates continuously and has three switches to control the operation of the components used during titration. These are the titration pipette, digital voltmeter and printer. A further switch (switch 1, Fig. 3) closes for a short fraction of time during each cycle and is used with the regulator to start the operation cycle of the second programmer. Programmer 2 (P24M, Sandblom & Stohne) operates intermittently. It has a fixed cycle time of 40 s and is used to control all remaining system functions.

Sample change-over procedures—These are carried out as follows.

When the pH of the titrated solution attains the pre-set value, the regulator gate closes. Switch 1, programmer 1, is closed for a small part of its cycle, and mains current can then flow through this switch and regulator gate to the motor that drives programmer 2. This programmer starts, carries out all sample change-over procedures and is then stopped by switch 1′, programmer 2. Programmer 1 begins the next titration while these procedures are being carried out.

SYSTEM OPERATION—

The regulator is set to the pH at which it is decided to cease titration. Programmer 1 is set to give the desired cycle time, which determines the time between successive additions of titrant, and samples are placed in the Ultro Rac fraction collector.

When the system is working, the following operations are carried out (see Fig. 2).

Addition of distilled water (position 1)—Reagent pipette A fills every second titration vessel with distilled water.

Addition of sample and dilution of sample (position 2)—The sample is sucked up into the sample pipette, the inlet tube of which is briefly dipped into a titration vessel containing distilled water to remove excess of sample on the outside of the tube (see Note 1), and then the sample is introduced into the next titration vessel.

A 4-ml aliquot of potassium chloride solution (see Note 2) is then pipetted by reagent pipette C through the sample pipette into the titration vessel while the plunger is at its lowest position. This rinses the sample delivery system, thus minimising carry-over.

NOTES—

1. A small amount of sample adheres to the outside of the Teflon sample inlet tube. As this amount is not constant from sample to sample, the inlet tube is dipped into distilled water to replace adhered sample with water. The improvement in precision resulting from this modification was determined as follows. Thirty aliquots of copper sulphate solution were transferred, by using the sample pipette, into titration vessels and diluted with distilled water from reagent pipette C. The volume of copper sulphate solution transferred, with and without rinsing of the outside of the inlet tube, was determined spectrophotometrically. Mean volume transferred without rinsing was 0·5642 ± 0·0040 ml. Mean volume transferred with rinsing was 0·5540 ± 0·0004 ml, giving an improvement in precision of one order of magnitude.

2. The volumes of the sample and titrant are similar and the ionic strength of the titration mixture may change appreciably during the titration if there is a large difference in their ionic strengths. To obtain the best titration results it is therefore essential to maintain a constant ionic strength during the titration, and this can be achieved by maintaining the diluted sample solution at 1 M with respect to potassium chloride. The titrant should be 1 M with respect to potassium chloride, and the salt solution delivered by reagent pipette C should have a concentration of $\frac{V_s + V}{V}$ M potassium chloride where V_s = volume of sample pipette and V = volume of reagent pipette C.

Titration—Titration is carried out at position 3 with nitrogen bubbling through the solution to ensure thorough mixing. The titrant is added stepwise from pipette D. The potential is measured after every addition, and the printer is programmed to print out this value, together with sample number. From these results, equivalence points are calculated by using the methods given by Johansson.[1]

When the titration is stopped, the electrode and the inlet tubes for nitrogen and titrant are rinsed in distilled water in the following vessel before they are transferred to the next titration vessel.

Rinsing of titration vessels (position 4)—Two suction tubes are lowered into the vessels (see Figs. 1 and 2) to suck off the titrated mixture and the rinsing water. The vessel that contained the titrated mixture is then rinsed with 10 ml of distilled water from pipette E.

RESULTS

The system has been used to titrate a strong acid (hydrochloric acid), a weak acid (acetic acid) and a mixture of a strong acid (hydrochloric acid) and a weak acid (acetic acid) with sodium hydroxide solution.

TITRATION OF A STRONG ACID (HYDROCHLORIC ACID) WITH SODIUM HYDROXIDE SOLUTION—

Thirty samples containing 0·05389 M hydrochloric acid were analysed.

Titrant	0·01103 M sodium hydroxide
Number of titrant additions	5
Analysis rate, samples per hour	30
Mean value for hydrochloric acid concentration	0·05375 M
Standard deviation	0·00017 M
Coefficient of variation	0·3 per cent.

TITRATION OF A WEAK ACID (ACETIC ACID)—

When calculating equivalence points for titrations of weak acids, it is preferable to use results obtained after the equivalence point.[1] As it is not necessary to obtain results before the equivalence point, pipette B is added to the system to deliver a volume of sodium hydroxide approximately equivalent to the sample, before measurement of potential is begun.

Twenty samples containing 0·04051 M acetic acid were analysed.

Titrant	0·01103 M sodium hydroxide
Number of titrant additions	4
Analysis rate, samples per hour	30
Mean value for acetic acid concentration	0·04030 M
Standard deviation	0·0014 M
Coefficient of variation	0·4 per cent.

The total acidity of a mixture of a weak and a strong acid may also be determined in this way by using results obtained after the second equivalence point.

TITRATION OF A MIXTURE OF A STRONG ACID (HYDROCHLORIC ACID) AND A WEAK ACID (ACETIC ACID)—

Twenty samples, 0·03354 M with respect to hydrochloric acid and 0·02293 M with respect to acetic acid, were analysed.

Titrant	0·01106 M sodium hydroxide
Number of titrant additions	8
Analysis rate, samples per hour	10
Mean value for hydrochloric acid concentration	0·03370 M
Standard deviation	0·00007 M
Coefficient of variation	0·2 per cent.
Mean value for acetic acid concentration	0·02276 M
Standard deviation	0·00021 M
Coefficient of variation	0·9 per cent.

DETERMINATION OF CARRY-OVER ERRORS—

Carry-over is a major source of error with all automated sample handling systems. In this system it may arise because of the following.

Incomplete rinsing of sample pipette and sample pipette inlet tube—This carry-over was measured by sequentially loading the sample holder with two samples of a sodium chloride solution followed by two samples of distilled water. Samples were then automatically transferred by pipette into the titration vessels and diluted with distilled water from reagent pipette C. Sodium concentrations in the titration vessels were then determined. If these concentrations are denoted by C_1, C_2, C_3 and C_4, respectively, the percentage carry-over is given by—

$$\text{Percentage carry-over} = \frac{C_3 - C_4}{C_2 - C_4} \times 100 \text{ or } \frac{C_1 - C_2}{C_2 - C_4} \times 100 \quad .. \quad .. \quad (1).$$

The mean carry-over for thirty such cycles was found to be 0·3 per cent.

Incomplete rinsing of the electrode and of the inlet tubes for titrant and nitrogen—This carry-over was measured by filling every second titration vessel with distilled water from reagent pipette A. The remaining titration vessels were sequentially filled with two 6·5-ml samples of sodium chloride solution and two 6·5-ml samples of distilled water. The titration vessel holder was rotated through one complete revolution, with the electrode and the tubes automatically dipping into each vessel. Carry-over for each cycle was determined from equation (1), giving a mean carry-over for thirty such cycles of less than 0·1 per cent.

Incomplete rinsing of titration vessels—The carry-over from this source was measured by filling a titration vessel with 6·5 ml of sodium chloride solution, rinsing it automatically, filling the vessel with 6·5 ml of distilled water, mixing and measuring its sodium concentration. The mean carry-over for thirty such determinations was less than 0·1 per cent.

Adhering sample solution on the sample pipette inlet tube—This source of carry-over is minimised as described in Note 1. Systematic error from this source is eliminated by determining the actual volume of sample delivered to the titration vessels, as described in Note 1, and using this value in equivalence point calculations.

DISCUSSION

A major advantage of the system described in this paper is the high analysis rate, although this is partly counteracted by the need to calculate equivalence points. These calculations have been carried out by feeding the electrode potential results, as recorded by the printer, into a computer. Data handling would be facilitated by replacing the printer with a tape punching machine. Punched tape could then be fed directly into the computer. Alternatively, the digital voltmeter could be coupled directly to the computer.

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Reference 1 is to Part I of this series.

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The Use of Enthalpimetric Titration to Study the Reaction of Thiourea and its *N*-substituted Derivatives with Cerium (IV)

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The oxidation of thiourea and its symmetrically *N*-substituted derivatives has been examined by enthalpimetric titrimetry. The initial reaction is considered to cause the formation of a disulphide and slower secondary oxidations of these products have been detected. Reaction rates are acid dependent and studies have been carried out in hydrochloric and sulphuric acids. In hydrochloric acid, thiourea and ethylenethiourea can be titrated to within ±0·3 per cent. of the theoretical value for the first reaction step over the acid range 0·3 to 0·2 M, while in sulphuric acid (0·3 to 0·6 M) the values for *N*,*N*′-diethylthiourea are within ±0·4 per cent. of the theoretical. Comparison is made with the titration method for the determination of thiourea by cerium(IV), which has been shown to be satisfactory within certain acidity ranges in sulphuric acid.

In a recent publication[1] we demonstrated the use of enthalpimetric titrimetry in investigating the oxidation of organic sulphur-containing substrates by cerium(IV) ions. These reactions which, in general, involve large heat changes are particularly amenable to study in this way and are of use in investigating correlations between thermodynamic and kinetic parameters[2,3] involved in metal-ion oxidations. In the present paper we report the results of studies on thiourea and its nitrogen-substituted derivatives. The oxidation of thiourea by cerium(IV) ions was first examined by Cuthill and Atkins,[4] who refluxed for 30 minutes a thiourea - cerium(IV) sulphate solution containing an excess of cerium(IV) ions. The over-all reaction corresponds to

$$CS(NH_2)_2 + 4[O] + H_2O \rightarrow CO(NH_2)_2 + H_2SO_4.$$

A method for titrating thiourea at room temperature was developed by Agarwal and Ghosh,[5] who found that the acidity was the controlling factor in the efficacy of the procedure. At concentrations of sulphuric acid less than 1·5 M the ratio of cerium(IV) ions to thiourea was greater than 1 : 1, and above 3·2 M the ratio was less than 1 : 1. Within this acidity range, however, the method gave satisfactory results if duplicate titrations were carried out under conditions in which the over-all time of the titration was maintained constant. By using the enthalpimetric titration procedure we have examined this variation in reactivity, and have extended the study to examine the oxidation of the nitrogen-substituted derivatives, *N*,*N*′-dimethyl-, *N*,*N*′-diethyl- and ethylenethiourea (imidazolidinethione).

Experimental

All materials used were of analytical-reagent grade. The stock ammonium sulphatocerate(IV) solutions were standardised by using ammonium iron(II) sulphate, with ferroin as indicator. Thiourea and thiosemicarbazide (B.D.H.) and ethylenethiourea (Aldrich Chemical Co.) were recrystallised from 50 per cent. ethanol, diethylthiourea (Fluka A.G.) from 50 per cent. methanol and dimethylthiourea (Aldrich Chemical Co.) from dioxan. Analysis of these compounds showed them to be more than 99·5 per cent. pure.

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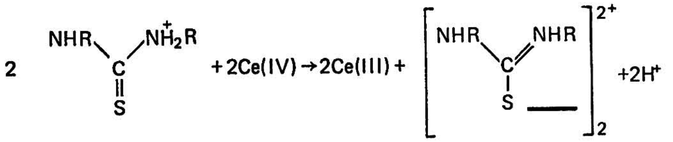
Reaction products were shown to be disulphides,[2] which had also been prepared by oxidation[6] of the substrates with hydrogen peroxide. Infrared spectra showed the products from both methods to be identical.

The titration assembly was of conventional design and has been described previously.[1] Experiments were carried out at various hydrogen-ion concentrations in both sulphuric and hydrochloric acids media. The thiourea was placed in the reaction cell, diluted to 50 ml with oxygen-free water and titrated with the oxidant, which was generally 100 times more concentrated than the substrate solution. In this way volume changes were small, being generally less than 2 per cent.

RESULTS AND DISCUSSION

The initial steps in these oxidations have been shown to take place rapidly[2] and, by direct titration with ferroin as indicator, it was found that 1 mole of thiourea or substituted thiourea reacted with 8 moles of cerium(IV) at room temperature. The rates of reaction varied markedly with acidity and temperature and in all instances (except thiosemicarbazide, *N*-aminothiourea) the initial step occurred at a much faster rate than the subsequent reactions. Thiourea and its derivatives are mono-protonated in 0·5 M sulphuric acid,[7] and the first step corresponding to the reaction—



was found to take place within about 30 s under these acidity conditions, whereas for the complete 1:8 reaction the time required varied between 8 hours and several days.

Enthalpimetric titrations gave good curves, with no indication of the side reactions detected with the α-mercapto acids.[1] By allowing for the heat effects involved in the secondary reactions it was also possible to derive the over-all heat changes for the first reaction.

THIOUREA—

In 0·5 M sulphuric acid the enthalpigrams exhibited curvature after about 10 per cent. of the reaction had occurred, which was attributed to the slow rate of reaction and not to any side reaction. In hydrochloric acid, however, the rate was increased and, in the acidity range 0·5 to 2·0 M, traces were found to be linear for the titration up to about 95 per cent. of the reaction. On extrapolation of the base and excess of reagent lines it was found that the volume of cerium(IV) ion solution consumed corresponded to ±0·3 per cent. of the theoretical for a 1:1 reaction (see Table I).

In the derivation of heats of reaction, the oxidation of the disulphide in 0·3 to 1·0 M sulphuric acid was sufficiently slow to enable values to be derived, but in 0·3 to 2·0 M hydrochloric acid the heat of the secondary reaction had to be corrected for[1] to obtain a value for ΔH. The heat of reaction is insensitive to the acid used, being $-26·4 \pm 0·4$ kcal. mole^{-1} in sulphuric acid and $-25·9 \pm 0·3$ kcal. mole^{-1} in hydrochloric acid.

DIETHYLTHIOUREA—

The symmetrically substituted species reacted more rapidly in both hydrochloric and sulphuric acids. In 0·3 to 0·6 M sulphuric acid, good linearity was observed in the enthalpigrams over 90 per cent. of the reaction, the values for cerium(IV) consumption being ±0·4 per cent. of the theoretical for 1:1 reaction. In 0·5 to 1·0 M hydrochloric acid, however, the values are about 4 per cent. high, suggesting that further oxidation of the disulphide occurred at a measurable rate before the diethylthiourea had completely reacted. Confirmation of this was given by a visual titration of the substrate in 1 M hydrochloric acid, in which it was found that 1 mole of the thiourea reacted with 2 moles of cerium(IV) within 2 minutes.

The ΔH value for the reaction (Table I) in sulphuric acid was evaluated as $-25·2 \pm 0·5$ kcal. mole^{-1} and that in hydrochloric acid (corrected for the secondary step) as $-27·3 \pm 0·6$ kcal. mole^{-1}.

TABLE I

REACTIONS OF THIOUREA AND ITS DERIVATIVES WITH CERIUM(IV)

Heats of reaction, T = 20° ± 2° C

Acid	Concentration, M	$-\Delta H$, kcal. mole^{-1}	Volume deviation, per cent.	
Moles of thiourea reacted, 1·331 × 10^{-4}—				
Sulphuric acid	0·5	26·8	—*	
	0·5	26·6	—*	
	0·3	26·4	—*	
	0·5	26·0	—*	
	1·0	26·2	—*	
Hydrochloric acid	0·3	26·2	+0·2	±0·3
	0·5	26·2	−0·3	
	0·5	25·5	−0·3	
	1·0	25·8	−0·1	
	2·0	25·7	+0·3	
Moles of diethylthiourea reacted, 1·420 × 10^{-4}—				
Sulphuric acid	0·3	25·1	+0·6	±0·4
	0·5	25·8	+0·2	
	0·5	24·8	−0·1	
	0·5	24·9	+0·3	
	0·6	25·3	−0·8	
Hydrochloric acid	0·5	27·1	+4·4	
	0·5	27·4	+3·8	
	0·5	26·8	+3·4	
	0·5	27·1	+4·1	
	1·0	28·1	+5·2	
Moles of ethylenethiourea reacted, 1·618 × 10^{-4}—				
Sulphuric acid	0·5	22·1	—*	
	0·3	22·2	—*	
	0·5	21·8	—*	
	0·5	22·8	—*	
	1·0	22·5	—*	
Hydrochloric acid	0·3	17·7	+0·2	±0·3
	0·5	17·7	+0·3	
	0·5	17·4	−0·3	
	1·0	17·9	−0·1	
	2·0	18·2	−0·3	
Moles of dimethylthiourea reacted, 1·328 × 10^{-4}; 1·614 × 10^{-4}—				
Hydrochloric acid	0·2	19·1	12·4	
	0·5	20·3	11·2	
	0·5	19·4	10·6	
	1·0	19·5	10·8	
	2·0	19·1	11·4	

* Curvature precluded identification of end-point.

ETHYLENETHIOUREA—

The rates of reaction were comparable with those of thiourea itself and the results were similar. The marked curvature of the enthalpigram in 0·3 to 1·0 M sulphuric acid precluded the derivation of a precise end-point, whereas in 0·3 to 2·0 M hydrochloric acid the volume deviation was ±0·2 per cent. of the theoretical value. In 0·3 to 1·0 M sulphuric acid, $\Delta H = -22{\cdot}3 \pm 0{\cdot}5$ kcal. mole^{-1} and in 0·3 to 2·0 M hydrochloric acid (corrected for the second step) $\Delta H = -17{\cdot}8 \pm 0{\cdot}4$ kcal. mole^{-1}.

DIMETHYLTHIOUREA—

Visual titration showed the reaction rates to be similar to those for thiourea, the traces in 0·3 to 1·0 M sulphuric acid showing curvature. Although the traces in 0·2 to 2·0 M hydrochloric acid showed good linearity, the volume of cerium(IV) solution consumed was 11 per cent. low. It was considered that this might be caused by reactions involving the radical produced prior to dimerisation, but in the presence of methyl acrylate the results were identical with those obtained previously.

Except in the case of dimethylthiourea, enthalpimetric titrimetry provides an accessible method for the determination of thiourea by cerium(IV). The method of Agarwal and Ghosh[5] is unsatisfactory as the oxidations proceed beyond the 1:1 ratio predicted by the equation.

At lower acidities they indicated that it was necessary to add less than the calculated amount of thiourea, because the product of the oxidation (the disulphide) is itself oxidised at a measurable rate. At higher acidities, when the reactions are slower, it is difficult to characterise where the first reaction ceases and the second begins. In the enthalpimetric titration, however, accurate reproducible results are given over a range of hydrochloric acid concentrations in which secondary effects can be eliminated.

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Spectrophotometric Study of the Reaction of Uranium(VI) with a New Salicylazochromotropic Acid Derivative*

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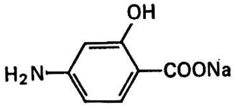
On the basis of a study of substituted salicylic acid groups as functional analytical groups in the determination of uranium(VI), a new bissalicylazochromotropic derivative has been synthesised, *i.e.*, the 3,6-bis(4-carboxy-3-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid, as the tetrasodium salt. The reagent thus obtained gives a sensitive reaction with uranium(VI), which enables between 0·5 and 16 μg ml^{-1} of uranium to be determined. Uranium(VI) combines with the reagent in the ratio 1 : 2, and the instability constant of the compound is $1{\cdot}2 \times 10^{-9}$.

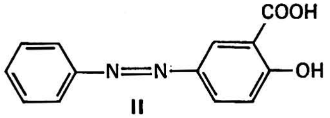
EARLY investigations have shown that uranium(VI) reacts mainly with organic reagents containing analytical functional groups able to form U–O linkages.

As the reaction of uranium(VI) with salicylic acid[1] and sulphosalicylic acid[2] is not very sensitive, previous investigations carried out by us were devoted to the study of the chromogenic properties of several salicylazo derivatives such as 4-aminosalicylic acid (sodium salt) (**I**), benzeneazosalicylic acid (**II**), *p*-nitrophenylazosalicylic acid (sodium salt) (**III**), *m*-nitrophenylazosalicylic acid (sodium salt)[3] (**IV**), 5(4-nitro-3-sulphophenylazo)salicylic acid (disodium salt)[4] (**V**), 3-methyl-1-phenyl-4(3-carboxy-4-hydroxyphenylazo)pyrazol-5-one(sodium salt)[5] (**VI**) and 3(4-carboxy-3-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid (**VII**) (Baiulescu, Gh., Greff, C., and Bărbulescu, T., unpublished results).



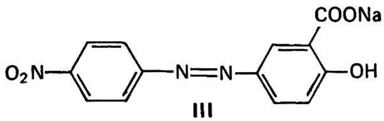
I

$\epsilon^{436} = 569$



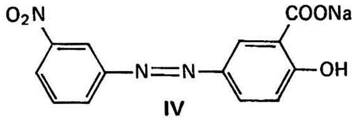
II

$\epsilon^{469} = 1897$



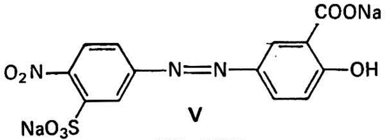
III

$\epsilon^{533} = 1897$



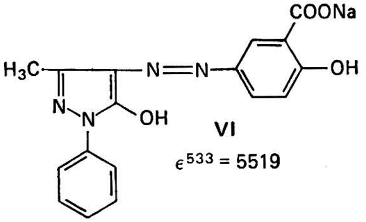
IV

$\epsilon^{469} = 1854$



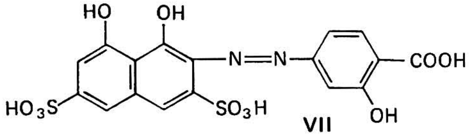
V

$\epsilon^{496} = 2816$



VI

$\epsilon^{533} = 5519$



VII

$\epsilon^{570} = 4906$

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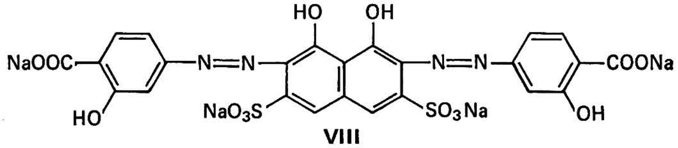
* Paper presented at the International Symposium on Analytical Chemistry, 1969, Birmingham.

An examination of the molar absorptivities of the uranium(VI) complex compounds of these monoazoic derivatives of aminosalicylic acid shows that they are more sensitive than the aminosalicylic acid itself.

As a result of the above examination, we decided to synthesise a chromotropic acid derivative containing two symmetrical salicylic groups within its molecule, namely the tetrasodium salt of 3,6-bis(4-carboxy-3-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid (**VIII**).



VIII

$\epsilon^{580} = 14,280$

SYNTHESIS OF THE REAGENT

Dissolve 40 mmole of 4-aminosalicylic acid in 20 ml of 5 M sodium hydroxide solution containing 5·6 g of sodium nitrite. At the same time, cool 10 ml of concentrated hydrochloric acid and 10 g of ice in an ice-bath until the mixture reaches a temperature of 0° to 5° C.

Add the first solution dropwise, while stirring, so that the temperature does not rise above 5° C. Leave the solution of diazonium salt thus obtained for 5 to 10 minutes at this low temperature.

Prepare also a solution containing 10 mmole of chromotropic acid (disodium salt) and 1·2 g (30 mmole) of sodium hydroxide in 25 ml of water and cool it to 0° C.

To this solution, slowly with constant stirring, add the solution of the diazonium salt previously prepared, the temperature being kept between 0° and 5° C.

The mixture thus obtained is maintained in the ice-bath for 1 hour with intermittent stirring, and left in the refrigerator overnight.

The product is filtered off by suction, purified by recrystallisation from ethanol - water, and then air dried. The dye obtained is reddish brown in colour, the yield being 40 per cent. The purity of the reagent is checked by elemental and chromatographic analyses.

METHOD

REAGENTS—

Uranyl nitrate solution, aqueous—Prepare a solution of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, containing 100 μg ml^{-1} of uranium and determine the concentration gravimetrically with 8-hydroxyquinoline.

Reagent solution, 0·1 per cent., aqueous—This solution is stable for at least 1 month.

Hexamethylenetetramine (hexamine) buffer solution—Ten per cent. aqueous solution, pH 6·5 to 7.

PROCEDURE—

Ligand spectra—The solutions for optical measurements were prepared by diluting 4 ml of reagent solution and 3 ml of buffer solution (hexamine) in 25-ml graduated flasks with distilled water.

The absorption spectra were recorded by using a Beckman spectrophotometer, Model D.B (Fig. 1), with reference to a water - hexamine blank.

Complex spectra—Amounts of uranyl nitrate solution containing 200 μg of uranium (2 ml) are introduced into 25-ml graduated flasks, and 4 ml of reagent solution (0·1 per cent.) and 3 ml of hexamine buffer solution are added. The volume is made up to 25 ml with distilled water.

Determinations are performed at room temperature by using blanks, prepared in the same way, but excluding the metal ion. The results are shown in Fig. 1. Colour development is instantaneous and is stable for at least 24 hours.

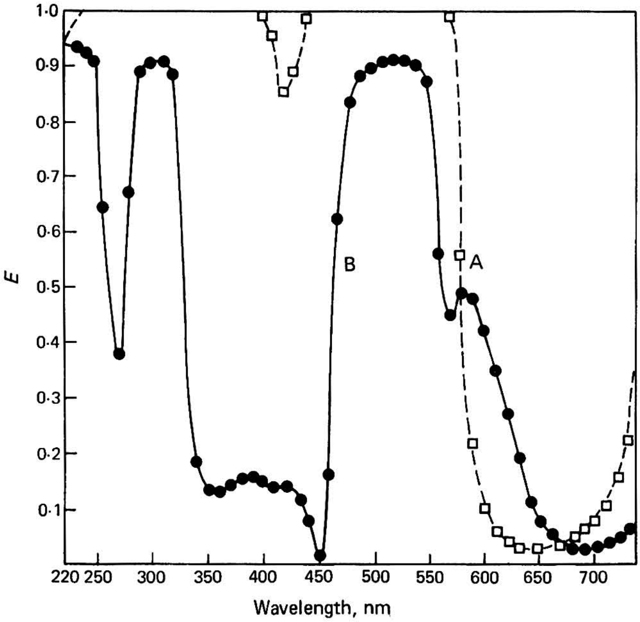


Fig. 1. Absorption spectra of: curve A, reagent; curve B, uranium(VI) compound

If the solution is heated to about 80° C the complex is destroyed, and it does not re-appear on cooling it to room temperature.

An examination of ligand and complex spectra shows that the optimum wavelength is 580 nm, which has been used throughout the present work.

STUDY OF EXTINCTION VARIATION FUNCTION OF URANIUM(VI) CONCENTRATION

The red-violet complex compound obeys the Lambert-Beer law between 0·5 and 16 μg ml^{-1} of uranium(VI). Measurements are made analogous to those performed for the complex spectra, but with various amounts of uranyl ion.

Determinations are performed at 580 nm by using a Zeiss-Jena VSU-1 spectrophotometer. The results are shown in Fig. 2.

NOTE.—The order of addition is uranium, reagent, buffer solutions.

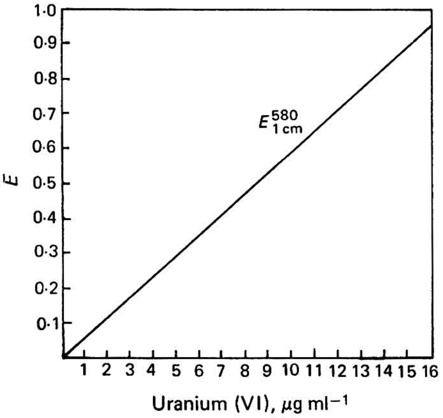


Fig. 2. Extinction depending on uranium(VI) concentration

Fig. 2 shows that the method enables uranium(VI) to be determined at concentrations between 0·5 and 16 μg ml^{-1} of uranium(VI) and therefore surpasses in sensitivity most of those involving other reagents ($\epsilon = 1{\cdot}43 \times 10^4$).

STUDY OF EXTINCTION VARIATION FUNCTION OF pH

The greater part of the buffer media being strong complexing agents for the uranyl ion, the study of the influence of pH on the formation of the complex was made in non-buffered solution, with instrumental control of pH by using a MV 11S pH meter.

It has been determined that the formation of the complex is possible for pH values higher than 4, the hydrogen-ion concentration having a direct influence only on the ligand absorbance.

A study was made on the influence of pH on the ligand alone, by using samples of 0·3 ml of dye diluted to 25 ml with standard buffers.

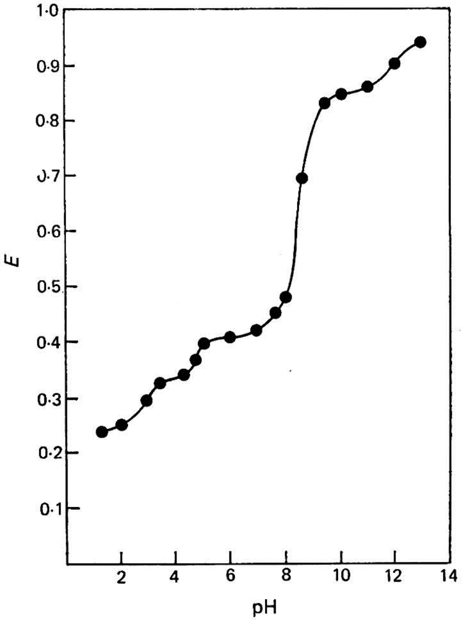


Fig. 3. Radiation extinction dependency on pH

The measurements made at a wavelength of 580 nm are shown in Fig. 3. It shows that with a pH value higher than 8, the ligand absorption is considerably increased. That is why a 10 per cent. solution of hexamine was used as a buffer agent between pH 6·5 and 7.

DETERMINATION OF COMBINATION RATIO AND OF THE INSTABILITY CONSTANT OF THE URANIUM(VI) - REAGENT COMPOUND

By using Job's method of continuous variation, the ratio of uranium(VI) to reagent in the compound was found to be 1:2. With the use of the non-isomolar series, the average value for the instability constant was found to be equivalent to $1{\cdot}2 \times 10^{-9}$, which shows good stability.

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Determination of Sulphate Ion by Replacement of Iodate in Iodine-131 Labelled Barium Iodate

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Between 2 and 100 μmoles of sulphate (60 to 3200 μg of sulphur) can be determined in aqueous solution, by passing the solution through a column of iodine-131 labelled barium iodate and counting the filtrate. The blank can be reduced by using 20 per cent. methanol. Each determination takes only a few minutes, and the precision is ±2·5 per cent. The apparatus required is simple and inexpensive, apart from the counting equipment. The method has been tested with standard kale, and has been applied to the determination of sulphur in fruticose lichens.

THE determination of micromolar amounts of sulphate ion is a matter of some difficulty. The precipitation of barium sulphate from solutions containing sulphate ions in amounts of less than 30 mg l^{-1} is slow, so gravimetric methods are slow and titrimetric methods unsuitable at these concentrations. According to Canals and Charra,[1] 0·5 to 5 μmoles of sulphate can be determined by nephelometry. Errors in methods based on the precipitation of barium sulphate have been demonstrated by radiochemical work.[2] The displacement of the chloranilate ion from its barium salt by sulphate has been used for spectrophotometric analysis by Bertolacini and Barney.[3] In this work the displacement of the iodine-131 labelled iodate ion from its barium salt by sulphate ions has been used as a radiometric method. The method has so far been applied to aqueous solutions and vegetable materials, but need not be restricted to these samples.

EXPERIMENTAL

REAGENTS—

Nitrate mixture—Mix 45·7 per cent. of sodium nitrate and 54·3 per cent. of potassium nitrate w/w.[4]

Iodine-131 *labelled barium iodate*—Transfer 2 mCi of iodine-131 labelled sodium iodide into a 250-ml round-bottomed flask with 1 drop of a 5 per cent. sodium iodide carrier and a little water. Fit a reflux condenser. Liberate iodine-131 labelled iodine by adding 2 drops of chlorine water, and then synthesise barium iodate by the method of Lamb, Bray and Geldard.[5] Add 5 g of solid iodine and 6·4 g of barium chlorate, $Ba(ClO_3)_2.H_2O$, to the flask, and warm to 85° C for 1½ hours. Filter, wash and dry the product which gives a quantitative yield of barium iodate, $Ba(IO_3)_2.H_2O$.

Sulphate standards—Prepare by diluting a stock solution of potassium sulphate containing 0·1 mole l^{-1}.

PROCEDURE—

Ash vegetable samples by using the molten nitrate mixture at 390° C, which has been shown by radiochemical tests to retain at least 96 per cent. of the sulphur in labelled leaves.[4] Neutralise them with 2 M nitric acid and make up to volume with water or 20 per cent. v/v methanol.

Transfer 5 g of labelled barium iodate to a filtration tube, 15 cm long × 1 cm internal diameter, where it forms a column about 2·5 cm high resting on a sintered-glass disc. Apply 5-ml aliquots of sulphate-containing solutions to the upper end of this column and, with a filter pump, suck them through it in approximately 4 minutes. Transfer the filtered solutions to tared counting vials, and weigh and count them by using a well-type sodium iodide crystal focused on the 0·36-MeV γ-ray from iodine-131. The counts, after correcting for weight losses, are compared with those obtained from a suitably diluted portion of the original barium iodate dissolved in dilute acid.

It was found convenient to pass a large number of samples and standards through the column during a day's run. About four replicates of each solution tested were passed successively through the column, and it was found that it was not necessary to wash the column between samples, provided that the first 5 ml of filtrate from each new solution were rejected.

RESULTS

Preliminary work with inactive barium iodate showed that the method was feasible. The solubilities of barium sulphate and barium iodate at 25° C have been given[6] as 2·23 and 280 mg kg^{-1} of solution, respectively, although more recent work[7,8] gives figures for barium iodate of 330 mg l^{-1} and 395 mg l^{-1}, respectively. When solutions of potassium sulphate are passed through a column of barium iodate, displaced iodate ions appear in the filtrate and can be measured by their absorbance at 218 nm with an ultraviolet spectrophotometer. Unfortunately, many other ions (and organic substances) absorb in this region, notably nitrate ions, which it was intended to use in the ashing process.

When aqueous solutions of potassium sulphate were passed through a column of iodine-131 labelled barium iodate, the liberated iodate ions were readily detected in the filtrates by their radioactivity. The blank for water at 22° C was 2·837 μmoles of barium iodate per 5 ml of sample, or 276·4 ± 15·7 mg l^{-1}, indicating that the water became fully saturated with barium iodate on passing through the column. When the amount of sulphate added was plotted against the amount of iodate displaced, a calibration graph was obtained, which was linear between 5 and 100 μmoles of sulphate (Fig. 1). When the experiment was repeated in 20 per cent. v/v methanol, the blank was reduced, but the calibration graph became non-linear above 40 μmoles of sulphate. Further work was carried out with sulphate standards made up in solutions containing 80 g l^{-1} of nitrate mixture, which involved blanks of about 8 μmole of barium iodate per 5 ml of sample. This blank could be reduced to about 5 μmole of barium iodate per sample by making up standards in 20 per cent. v/v methanol instead of water. Although relatively high, these blanks remained constant to within ±2·5 per cent. during a run.

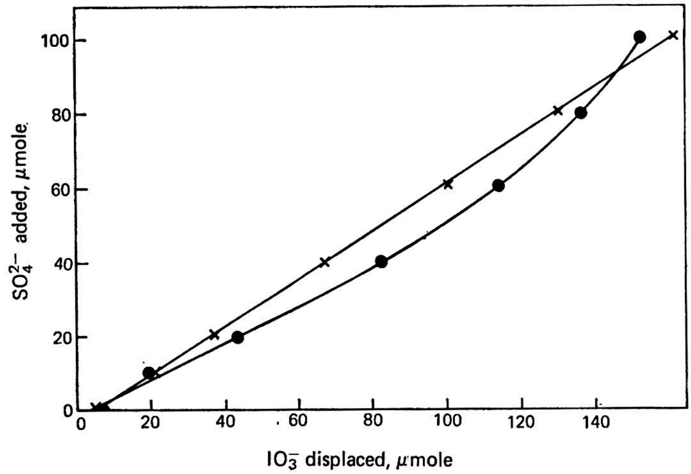

Fig. 1. Calibration curve for the displacement of ^{131}I-labelled iodate from a barium iodate column by solutions of potassium sulphate in (×), water; (●), 20 per cent. v/v methanol

The technique was first checked by the analysis of kale powder that had been previously analysed for sulphur.[9] Nine replicate determinations from a 0·4-g sample of kale powder gave a mean of 16·92 mg of sulphur per g of dry kale, compared with a literature mean value of 16·0 mg g^{-1}. The standard deviation was ±2·9 per cent.

An attempt was made to measure the sulphur contents of fruticose lichens, as these are believed to concentrate sulphur dioxide from polluted atmospheres. At least 0·5 g of lichen was needed to obtain four replicate determinations, and the results obtained are shown in Table I. The low results are much less precise than the high results because of the high blank mentioned above.

TABLE I

SULPHUR CONTENTS OF FRUTICOSE LICHENS

Species	Where collected	Sulphur, mg per g of dry lichen
Usnea subfloridana	Jerbourg, Guernsey	0·061
Usnea subfloridana	Weymouth, Dorset	0·653
Usnea subfloridana	Thame, Oxon	0·654
Usnea subfloridana	Taynton, Oxon	0·328
Usnea subfloridana	Aberystwyth, Cardigan	0·351
Usnea subfloridana	Inveraray, Argyll	0·088
Cetraria glauca	Loch Shiel, Inverness	0·131

Despite the poverty of the results, it appears that fruticose lichens contain much less sulphur than do vascular plants, and that lichens growing in essentially unpolluted areas (West Scotland and Channel Isles) contain very small amounts of sulphur.

So far, possible interferences in the method have not been investigated. From published solubility data, one would expect carbonate, oxalate, chromate and selenate anions to interfere. In this work oxalates were destroyed by the ashing procedure and carbonates by neutralising with acid after ashing. Chromium and selenium occur in negligible amounts in plant material compared with sulphur. There is no obvious reason why common cations should interfere. The effects of excess of sodium and potassium nitrates have been mentioned. In this work the addition of these salts probably swamped any interference from other ions in the plant ash. The solubility of calcium iodate is 3070 mg l^{-1}, so solutions containing large amounts of calcium might require special treatment.

The method has the advantages of simplicity, speed and reasonable precision ($\pm 2{\cdot}5$ per cent.). These must be set against the disadvantages of the expense of counting equipment needed, the 8-day half-life of iodine-131 and the blank caused by the solubility of barium iodate in aqueous solutions.

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Comparison of Low Temperature Radiofrequency Ashing with Other Methods of Organic Sample Oxidation for the Determination of Sodium in an Acrylic Fibre

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Acrylic fibre samples can be prepared for sodium determination by low temperature radiofrequency ashing, by ignition in air and by wet oxidation with a mixture of sulphuric and nitric acids or sulphuric acid and hydrogen peroxide. The sodium is determined by flame photometry. A minimum of eleven determinations by each technique allows a statistical examination of the results. It is demonstrated that low temperature radiofrequency ashing offers advantages in both precision of analysis and simplicity of sample handling.

Before the introduction of the low temperature radiofrequency asher, samples of organic material were prepared for metal-content determination either by ignition in a free air supply, or by various wet-oxidation methods. The latter methods demand some manipulative skill by the analyst to avoid losses, and also require the determination of a reagent blank correction. Ignition in air, although not needing the same care as the wet methods, requires the analyst's attention, certainly during the earlier stages. The determination of alkali-metal contents with accuracy, in particular sodium, is difficult because contamination can easily occur.

The work reported was initially done by the three earlier methods: ignition in air in a platinum crucible; wet oxidation with a sulphuric acid - nitric acid mixture; wet oxidation with sulphuric acid - hydrogen peroxide. A radiofrequency asher was used in later work and the results compared with those obtained with the other methods. All the samples were of an acrylic fibre.

Final sodium determination was by flame-emission photometry, scanning the 589 nm doublet. The precision of the final determination was established by repetitive analysis of samples of a solution of analytical-reagent grade sodium chloride containing the same average amount of sodium as the fibre samples.

EXPERIMENTAL

APPARATUS—

Flame spectrophotometer—A Unicam SP900A emission atomic-absorption spectrophotometer was used in the emission mode.

Radiofrequency asher—Tracerlab L.T.A.-600L.

REAGENTS—

Analytical-reagent grade sulphuric and nitric acids and sodium chloride were used.

Hydrogen peroxide, 50 per cent.—Analytical-reagent grade, Laporte Chemicals Ltd.

Water—Distilled water was treated with a cation-exchange resin, Amberlite IR120(H), analytical grade, to reduce the sodium content to less than 0·01 p.p.m.

SAMPLE PREPARATION—

Ignition in air—Samples, in a platinum Lawrence-Smith crucible, were charred over a micro burner to a small residue, which was subsequently strongly ignited with a Meker burner. The final residue was taken up with 5 ml of 2 N sulphuric acid, heated almost to boiling-point and cooled. It was then decanted and diluted to 100 ml with water.

Oxidation with sulphuric acid - nitric acid mixture—Samples were digested with 1 ml of concentrated sulphuric acid and 4 drops of concentrated nitric acid in Pyrex or silica tubes until a clear solution was obtained. This was cooled, decanted and diluted to 100 ml with water.

Oxidation with sulphuric acid - hydrogen peroxide—Samples were charred for 10 minutes with 1 ml of concentrated sulphuric acid in Pyrex or silica tubes, and then 50 per cent. hydrogen peroxide was added dropwise until the solution cleared. After cooling and decanting the solution was diluted to 100 ml with water.

Low temperature radiofrequency ashing—Fibre samples were weighed into shallow silica dishes about 50 mm in diameter, which had been checked for freedom from sodium by washing with 100 ml of water and determining the sodium content of the wash solution. The normal procedure applicable to massive samples of powdering or shredding the material to present the maximum surface area for oxidation was not necessary with fibrous samples.

An oxygen flow of 70 ml minute^{-1} was used for ashing. Under leakless conditions the reaction chamber pressure was about 1 mm of mercury. Although the maximum power available was 300 W, it was only possible to use 50 to 75 W for the acrylic fibre. Higher powers produced yellow flashes in the ionisation chambers and caused scattering of the sample residues. Ashing times at the lower power were 2½ to 3 hours for 20-mg samples.

The residues were washed into sodium-free silica bowls with water, decanted into 100-ml flasks and diluted to volume with water.

Sample weights—Initially these were governed by the capacity of the Lawrence-Smith crucible, which could only accommodate about 10 mg of the bulky fibre, and by the amount, also about 10 mg, which could be speedily wet oxidised. The radiofrequency asher could take much larger samples and about 20 mg was a convenient amount for the total sodium content to lie within the calibrated range 0·1 to 1·0 p.p.m. of the flame-emission determination.

RESULTS

The results are expressed in Table I for ease of comparison. Those for the two wet-oxidation methods have been corrected for "sodium blanks" for the reagents.

TABLE I

SUMMARY OF RESULTS

	Method of oxidation			
	Ignition in air	Sulphuric - nitric acids	Sulphuric acid - hydrogen peroxide	Radio-frequency ashing
Mean sample weight, mg	9·95	10·91	9·17	23·02
Mean sodium content, per cent.	0·36	0·34	0·32	0·36
95 per cent. confidence limits for the mean ..	±0·05	±0·03	±0·02	±0·01
Standard deviation	0·088	0·071	0·028	0·013
Number of results	13	18	12	11

DISCUSSION

The true sodium content of this fibre is not known, but it is reasonable to assume that it cannot be less than 0·36 per cent. as found by ignition in air and low temperature ashing. The two wet methods could be subject to undetected spray losses or to over-estimation of the reagent blank, and must be considered to be less reliable than the dry methods. The cause of the larger scatter for ignition in air could be air turbulence created by the Meker burner over the crucible, leading to both abstraction of particles and introduction of airborne sodium salts. It is clear from the results that low temperature radiofrequency ashing provides more precise analyses than the other methods. The time required to prepare a sample for final determination is longer than that needed to destroy the organic material by the older methods, but this is offset by the ability to ash several samples simultaneously without the constant attention and skill demanded for, in particular, a wet oxidation. The ashing time is a function of the nature of the organic material, the sample size and the electrical power that can be used. Low power was demanded by the nature of this fibre to prevent scattering of the residue. However, 30 to 40-mg samples of carbon char have been ashed in about three quarters of an hour at 225 W. A further point in favour of radiofrequency ashing is the wider range of sample size that can be easily oxidised.

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The Extraction and Determination of Copper, Chromium and Arsenic in Preserved Softwoods

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A method is described for the rapid extraction and determination of copper, chromium and arsenic in preservative-treated softwoods. A saw cut is made through the cross-section of the sample and the preserving compounds are leached quantitatively from the sawdust with a mixture of dilute sulphuric acid solution and hydrogen peroxide solution. Copper, chromium and arsenic in aliquots of the leach solution are allowed to react with zinc dibenzyldithiocarbamate, diphenylcarbazide and ammonium molybdate - hydrazine reagent, respectively, and the determinations are completed by the spectrophotometric measurement of the coloured complexes formed.

The procedure has been used to determine copper, chromium and arsenic in the cross-sections of preserved Baltic redwood, Douglas fir, lodgepole pine and silver fir.

SOLUTIONS containing copper sulphate, potassium or sodium dichromate and arsenic pentoxide are used in some commercial preservative formulations for preserving timber. The usual form of treatment is carried out by impregnating seasoned wood with an aqueous solution of the preservative by the full-cell, vacuum and pressure-impregnation process[1] or the Lowry empty-cell, pressure-impregnation process.[1] After impregnation, the chemical components of the preserving solution react with each other, and with the wood, and become fixed, *i.e.*, copper, chromium and arsenic compounds are formed that are insoluble in water. Copper remains in the bivalent state and arsenic in the quinquivalent state, but the dichromate is reduced to tervalent chromium.[2]

Current specifications for the pressure treatment with copper, chromium and arsenic salts require different average loadings, for the whole charge, for different service conditions, although they do not call for analysis of the treated timber. For particular purposes, however, it is often necessary to check whether the average loading has been achieved in individual samples and a rapid and accurate method of analysis is required. Chemical methods[1,3,4,5] are available for the determination of copper, chromium and arsenic in preserved timber, but they involve lengthy ashing or acid-digestion techniques followed by slow and tedious procedures to complete the analysis. Although these methods have the required accuracy, they are not practicable when large batches of specimens need to be examined. Modern instrumental techniques such as X-ray fluorescence spectrometry, atomic-absorption spectrophotometry and optical spectrophotometry allow rapid finishes to determinations, but this advantage is offset when sample preparation and dissolution of the wood or extraction of the preservative from the matrix is time consuming.[6,7] The problem posed requires for its solution, first, a rapid sampling technique, secondly, a simple and fast quantitative method for separating the preservative from the matrix and, thirdly, an accurate procedure for determining the copper, chromium and arsenic.

Recent work at the Forest Products Research Laboratory has shown that fixed and unfixed preservative chemicals can be quantitatively and rapidly leached from thin sections of wood and from sawdust.[8,9] Previously, three separate samples were used for the determination of copper, chromium and arsenic, but in the present work the determinations were made on the leach solution from one sample. It was found that the fixed copper, chromium and arsenic compounds were all soluble in 5 N sulphuric acid solution. Both the copper and arsenic were completely soluble, but approximately 20 per cent. of the chromium salt was found to be insoluble; the addition of hydrogen peroxide solution made the chromium salt completely soluble in the leach solution. The copper in the leach solution was allowed to react with zinc dibenzyldithiocarbamate,[10] the chromium was oxidised to the sexavalent state and allowed to react with diphenylcarbazide,[11] arsenic was allowed to react with ammonium molybdate - hydrazine solution,[12] and the determinations were finished by the spectrophotometric measurement of the coloured complexes formed.

The proposed method of chemical analysis was compared with that involving the recovery of copper, chromium and arsenic from solutions after digestion of treated wood with sulphuric acid and nitric acid (Table I).

EXPERIMENTAL

Copper, chromium and arsenic preservative is rarely evenly distributed throughout the cross-section of treated timber. Not only do concentration gradients occur, but there is often a great difference in the permeability of sap and heartwood, which results in variations in the penetration of preservative solution during impregnation. Converted timber usually contains both sap and heartwood. It has been shown in previous work[9] that an accurate saw cut, made with a saw machine, produces a sawdust sample containing an amount of preservative representing that in the cross-section of the wood. This rapid sampling technique was used to prepare samples for this investigation. The sawdust was collected in a tared weighing bottle and dried to constant weight at 100° to 105° C.

Initially, sawdust samples were leached with 5 N sulphuric acid solution at a temperature of 75° C, but approximately 20 per cent. of the chromium compound remained in the wood. It was found that the preservative was completely soluble in a mixture of 5 N sulphuric acid solution and 100-volume hydrogen peroxide solution. In this solution, the wood darkened in colour but this did not cause any interference during the final stages of the procedure. The leach solution was filtered before aliquots were taken for the determination of copper, chromium and arsenic. Small particles of wood would have interfered with the oxidation of tervalent chromium to the sexavalent state, and with the formation of the molybdoarsenate-blue reduction complex during the determination of arsenic with ammonium molybdate - hydrazine reagent. The aliquots of filtrate for chromium and arsenic determinations were gently evaporated to small volumes to remove hydrogen peroxide, which would also have caused interference. It is known that there is negligible inter-elemental interference between copper, chromium and arsenic in the ratios used in commercial formulations, during the final stages of the determinations.[8] Phosphates react with ammonium molybdate - hydrazine reagent to give a blue reduction complex; the procedure is therefore not suitable for arsenic in the presence of phosphates. Only minute amounts of phosphates occur naturally in wood.

The recovery of copper, chromium and arsenic compounds leached from sawdust was compared with the results obtained by digestion of adjacent sawdust samples with sulphuric acid and nitric acid. The sawdust samples for comparison were cut at a distance of 5 mm along the timber from where the samples for leaching were taken. After digestion of the wood, the solution was evaporated to remove excess of nitric acid, and any residual nitric acid was decomposed with hydrogen peroxide solution. The solution was evaporated to remove the excess of hydrogen peroxide. The sulphuric acid solution containing copper, chromium and arsenic was carefully diluted, cooled, and made up to 250 ml with water. Aliquots of solution were taken for the determination of copper, chromium and arsenic and analysed as described in the proposed procedure.

In the proposed procedure the leach solution containing sawdust was diluted to 250 ml. The volume displacement caused by sawdust, which reduces the actual volume of the solution in the graduated flask, was determined and taken into account when calculating the results. The volume displacement for 1 g of oven-dry sawdust was 0·6 ml of solution.

RESULTS

The proposed procedure and acid-digestion method were applied to sawdust samples cut from the cross-sections of specimens of commercially treated Baltic redwood, Douglas fir, lodgepole pine and silver fir. Adjacent samples, within 5 mm of each other, were analysed by the different techniques to reduce the effect of any variations in the structure of the wood.

The method was sufficiently rapid and the results, based on oven-dry wood, given in Table I, are in good agreement and show that the proposed procedure is quantitative and precise.

TABLE I

RESULTS OBTAINED BY LEACHING AND ACID DIGESTION

Specimen		Copper, per cent.		Chromium, per cent.		Arsenic, per cent.	
		Leach	Digest	Leach	Digest	Leach	Digest
Baltic redwood	1	0·13	0·13	0·17	0·17	0·17	0·17
	2	0·19	0·19	0·24	0·25	0·29	0·29
	3	0·083	0·081	0·11	0·12	0·15	0·15
	4	0·073	0·072	0·10	0·10	0·12	0·11
	5	0·069	0·072	0·13	0·13	0·12	0·12
Douglas fir		0·096	0·092	0·14	0·14	0·18	0·17
Lodgepole pine	1	0·13	0·12	0·25	0·25	0·21	0·21
	2	0·42	0·42	0·73	0·74	0·63	0·62
Silver fir	1	0·30	0·29	0·44	0·44	0·45	0·44
	2	0·096	0·092	0·14	0·14	0·18	0·17

The method was found to be suitable for the determination of copper, chromium and arsenic in the range 0·01 per cent. upwards. Standard deviations, each based on seven determinations, were ±0·0013 per cent. for copper at the 0·20 per cent. level, ±0·0010 per cent. for chromium at the 0·24 per cent. level and ±0·0012 per cent. for arsenic at the 0·30 per cent. level.

METHODS

LEACHING

REAGENTS—

Use analytical-grade reagents when possible.

Sulphuric acid, 5 N—Cautiously add, with stirring, 140 ml of concentrated sulphuric acid to 800 ml of water, cool, and dilute to 1 litre with water.

Hydrogen peroxide, 100 *volume.*

PROCEDURE—

Dry the sawdust sample at 100° to 105° C. Transfer the weighed sample to a 250-ml graduated flask, add 50 ml of 5 N sulphuric acid solution and 10 ml of 100-volume hydrogen peroxide solution, and heat in a water-bath at 70° to 75° C for 20 minutes, with occasional swirling to mix the contents of the flask. Remove the flask from the water-bath, add 150 ml of water, swirl to mix, cool to room temperature, dilute to the mark with water and mix. Mix twice more at 5-minute intervals and then allow the solids to settle for 10 minutes. Filter 10 ml of the leach solution through a dry 7·0-cm Whatman No. 44 filter-paper, discarding the first 5 ml of filtrate. Continue as described below.

COPPER

REAGENTS—

Use analytical-grade reagents when possible.

Sulphuric acid, N—Cautiously add, with stirring, 28 ml of concentrated sulphuric acid to 900 ml of water, cool, and dilute to 1 litre with water.

Zinc dibenzyldithiocarbamate solution—Dissolve 0·5 g of zinc dibenzyldithiocarbamate in 500 ml of carbon tetrachloride.

PROCEDURE—

Transfer a 1-ml aliquot of the filtrate to a 150-ml separating funnel, dilute to 100 ml with N sulphuric acid solution and swirl to mix. Add, with a pipette, 10 ml of zinc dibenzyldithiocarbamate solution and shake the separating funnel for 90 s. Allow the phases to separate, run off the carbon tetrachloride layer through a dry 7·0-cm Whatman No. 1 filter-paper into a 10-mm cell, discarding the first runnings. Measure the optical density of the yellow complex against a reagent blank, prepared in a similar way, at a wavelength of 435 nm on a Unicam SP600 spectrophotometer. To determine the copper content of the test solution, compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Standard solution A—Dissolve 3·9689 g of analytical-reagent grade copper sulphate, $CuSO_4.5H_2O$, in water. Transfer the solution to a 500-ml graduated flask, add 10 ml of 5 N sulphuric acid solution, dilute to the mark with water and mix.

1 ml of standard solution A ≡ 2000 μg of copper.

Standard solution B—Transfer, by pipette, 10 ml of standard solution A into a 1-litre graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B ≡ 20 μg of copper.

Standard solution C—Transfer, by pipette, 10 ml of standard solution B into a 100-ml graduated flask, add 20 ml of 5 N sulphuric acid solution, dilute to the mark with water and mix.

1 ml of standard solution C ≡ 2 μg of copper.

Preparation of calibration graph—Transfer aliquots of 2, 5, 10, 15 and 20 ml of standard solution C to 150-ml separating funnels. Dilute to 100 ml with N sulphuric acid solution. The aliquots contain 4, 10, 20, 30 and 40 μg of copper, respectively. Continue as described under Procedure. Plot a calibration graph of optical densities against micrograms of copper.

CHROMIUM

REAGENTS—

Use analytical-grade reagents when possible.

Potassium permanganate solution, 0·1 N—Dissolve 0·32 g of potassium permanganate in water and dilute to 100 ml with water.

Sodium azide solution, 5 per cent. w/v—Dissolve 5 g of sodium azide in water and dilute to 100 ml with water. Caution—Sodium azide liberates poisonous fumes in contact with water or acids.

1,5-*Diphenylcarbazide solution*—Dissolve 0·5 g of 1,5-diphenylcarbazide in 40 ml of acetone containing 3 drops of 5 N sulphuric acid solution and dilute to 50 ml with acetone. This solution must be freshly prepared.

PROCEDURE—

Transfer a 1-ml aliquot of the filtrate to a 25-ml beaker and gently evaporate to a small volume, but do not evaporate off the sulphuric acid. Allow the solution to cool and add 6 ml of water, 4 ml of N sulphuric acid solution and 0·5 ml of 0·1 N potassium permanganate solution. Heat on a steam-bath for 20 minutes and add potassium permanganate solution dropwise to maintain a slight excess. Add sodium azide solution to the hot solution at the rate of about 1 drop every 10 s, swirl after each addition, and continue until the solution is clear. It is important to avoid an excess of sodium azide solution. Remove the beaker immediately from the steam-bath and cool it to room temperature. Transfer the solution to a 100-ml graduated flask containing 15 ml of N sulphuric acid solution and 60 ml of water and swirl to mix. Add 2 ml of 1,5-diphenylcarbazide solution, dilute to the mark with water and mix again. Measure the optical density of the violet - red chromium - diphenylcarbazide complex against a reagent blank, prepared in a similar way, in 10-mm cells at a wavelength of 540 nm on a Unicam SP600 spectrophotometer. To determine the chromium content of the test solution, compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Standard solution A—Dissolve 0·2828 g of analytical-reagent grade potassium dichromate, $K_2Cr_2O_7$, in water. Transfer the solution to a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution A ≡ 1000 μg of chromium.

Standard solution B—Transfer, by pipette, 10 ml of standard solution A into a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B ≡ 100 μg of chromium.

Preparation of calibration graph—Transfer aliquots of 0·1, 0·2, 0·4, 0·6, 0·8, 1·0, 1·2 and 1·3 ml of standard solution B to covered 25-ml beakers and dilute to 5 ml with water in each instance. Add 5 ml of N sulphuric acid and continue as described under Procedure. The aliquots taken contain 10, 20, 40, 60, 80, 100, 120 and 130 μg of chromium, respectively. Plot a calibration graph of optical densities against micrograms of chromium.

ARSENIC

REAGENTS—

Use analytical-grade reagents when possible.

Ammonium molybdate solution—Dissolve 1 g of ammonium molybdate in 80 ml of water containing 12·9 ml of concentrated sulphuric acid, and dilute to 100 ml with water.

Hydrazinium sulphate solution—Dissolve 0·15 g of hydrazinium sulphate in water and dilute to 100 ml with water.

Ammonium molybdate - hydrazine reagent solution—Just before use mix 10 ml of ammonium molybdate solution and 10 ml of hydrazinium sulphate solution, and dilute to 100 ml with water.

PROCEDURE—

Transfer a 1-ml aliquot of the filtrate to a 25-ml beaker and gently evaporate to a small volume, but do not evaporate off the sulphuric acid. Add 20 ml of the molybdate - hydrazine solution, warm on a steam-bath until the blue reduction complex appears, and continue heating for 15 minutes. Cool the solution, wash it into a 25-ml graduated flask and dilute to the mark with reagent solution and mix. Measure the optical density of the molybdenum-blue complex against a reagent blank, prepared in a similar way, in 10-mm cells at a wavelength of 840 nm on a Unicam SP600 spectrophotometer. To determine the arsenic content of the test solution, compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Standard solution A—Dissolve 1·3203 g of analytical-reagent grade arsenic trioxide, As_2O_3, in a minimum volume of N sodium hydroxide solution. Transfer the solution to a 1-litre graduated flask, dilute to the mark with water and mix.

1 ml of standard solution A ≡ 1000 μg of arsenic.

Standard solution B—Transfer, by pipette, with suitable precautions, 10 ml of standard solution B into a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B ≡ 100 μg of arsenic.

Preparation of calibration graph—Transfer aliquots of 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7 and 0·8 ml of standard solution B to 25-ml beakers. The aliquots taken contain 10, 20, 30, 40, 50, 60, 70 and 80 μg of arsenic, respectively. To each beaker, add 2 ml of concentrated nitric acid and evaporate the solution just to dryness. Add 1 ml of concentrated nitric acid, evaporate the solution to dryness and heat the residue for 30 minutes at a temperature not exceeding 130° C. Cool the residue and add 1 ml of N sulphuric acid and 1 drop of 50-volume hydrogen peroxide solution. Continue as described under Procedure. Plot a calibration graph of optical densities against micrograms of arsenic.

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Gas-chromatographic Determination of Chlorcholine Chloride Residues in Natural Tomato Juice

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A method is presented for the gas-chromatographic determination of chlorcholine chloride at residue levels. The technique is based on prior reaction with sodium benzenethiolate. When this procedure is extended to plant extracts, some pre-purification and concentration must be carried out before the reaction with the benzenethiolate salt.

CHLORCHOLINE chloride (2-chloroethyltrimethylammonium chloride, CCC, Cycocel) and related compounds have marked growth-inhibitory effects when applied to many plants.[1,2,3] Because of the widespread use of CCC in agriculture it has been necessary to devise a sensitive and specific analytical procedure for determining residues in vegetable foods.

Linser, Kuehn and Bohring[4] reported on the ultraviolet determination of CCC in a soil extract as a periodide complex. This method would not differentiate CCC from other choline-containing compounds occurring naturally in plant tissues.

Jung and Henjes[5] determined CCC residues in plant material. The CCC was isolated from alcoholic extract by cation-exchange resin chromatography and subsequently by thin-layer chromatography. Chromatograms made visible with a modified Dragendorff reagent allowed the semi-quantitative determination of CCC by visual comparison of the spots with standards similarly treated.

Bier and Faust[6] precipitated the CCC in the cation-exchange resin column eluate as the Reinecke salt and found the amount of CCC by determining the nitrogen by the Kjeldahl procedure.

These methods lacked either the specificity or the quantitative sensitivity required by a residue procedure.

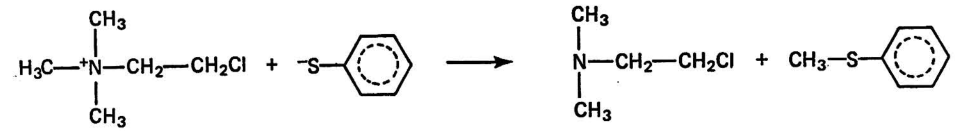
Mooney and Pasarela[7] determined CCC residues in green foliage, grain and wheat straw. The CCC was isolated from methanolic plant extract by a two-column adsorption chromatographic system on alumina. This method gave low recoveries of CCC when applied to strawberries, tomatoes and grapes, because the residue from the first-column eluate is syrupy and CCC is probably incompletely dissolved when transferred to the second column. This difficulty has been overcome by a method[8,9] based on the chromatographic separation of CCC from vegetable aqueous extracts by a two-column chromatographic system, by using in the first column a cation-exchange resin and in the second, aluminium oxide.

In both of these last methods CCC was measured colorimetrically as dipicrylamine - CCC complex at 415 nm.

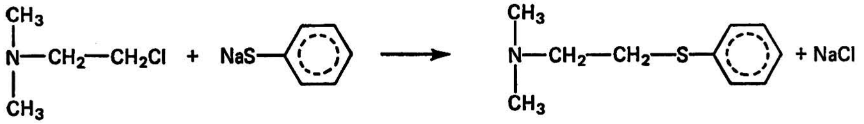
Gas chromatography cannot be applied to CCC directly because this compound has a very low degree of volatility. Jenden, Hanin and Lamb[10] have described a gas-chromatographic procedure for the micro determination of acetylcholine and related compounds. The purpose of the present study was to show that CCC, after quantitative conversion into a volatile compound, can also be determined by gas chromatography.

PRINCIPLE OF THE METHOD

Conversion of CCC into a volatile compound is based on *N*-demethylation with sodium benzenethiolate and on the subsequent reaction of the compound obtained (2-chloro-*NN*-dimethylethylamine) with excess of benzenethiolate.



2-Chloro-*NN*-dimethyl-
ethylamine



NN-Dimethyl-2-(thiophenyl)-
ethylamine

he reaction is carried out in anhydrous butan-2-one at 80° C.

Experimental and results

Reagents—

Sodium benzenethiolate[10]—Add 20 g of sodium hydroxide to 83 g of thiophenol in 100 ml of anhydrous ethanol, swirling and warming the mixture until dissolved. Add 700 ml of toluene and slowly distil the mixture. While sodium benzenethiolate crystallises out as the ethanol and water distil, add successively six 100-ml portions of toluene to maintain the volume of the distilling mixture at 500 ml. Filter the contents of the flask, under dry nitrogen, through a coarse fritted-glass filter (G1), and wash the benzenethiolate salt with boiling toluene.

Dissolve the salt in 200 ml of anhydrous ethanol and 5 ml of ethyl acetate under dry nitrogen and allow it to stand for 60 hours. Filter and distil again as described above. After filtering and washing the salt with boiling toluene, transfer it to a vented desiccator over phosphorus pentoxide, together with 200 g of dry ice and some freshly cut shavings of paraffin wax for absorbing toluene, and leave for 65 hours. Quickly transfer the benzenethiolate salt to individually sealed phials for storage.

Chlorcholine chloride (*Cycocel*)—Available from American Cyanamid Co. Prepare two standard solutions in methanol, containing 0·1 mg ml^{-1} and 1 mg ml^{-1} of CCC.

Butan-2-one—Purify by distillation.

Chloroform—Purify by shaking it with an equal volume of 2 N ammonia solution and leave it to stand for 3 hours. Wash it twice with 2 N sulphuric acid and three times with distilled water, and then store it with 1 per cent. of absolute ethanol in a dark bottle.

Pentane—Treat as for chloroform and store in pure form.

Apparatus—

A Perkin-Elmer, Model 880, gas chromatograph with dual column, equipped with a flame ionisation detector and a Leeds & Northrup 1-mV Speedomax recorder was used in this work. Stainless-steel packed columns (6 feet × $\frac{1}{8}$ inch) containing 80 to 100-mesh Chromosorb W, coated with 15 per cent. w/w succinate polyester of 1,4-butanediol, were used.

Injections were made with a Hamilton 1-µl syringe. The column temperature was maintained at 200° C. Injection port and flame detector temperatures were 235° and 230° C, respectively. Nitrogen was used as carrier gas, at a rate of 25 ml minute^{-1}.

Separating funnels of 10 and 5-ml capacity, and glass-stoppered test-tubes were used.

ANALYTICAL PROCEDURE—

Transfer, by pipette, aliquots of the standard solutions containing 0·1, 0·3, 0·5, 0·8, 1·0 1·5 and 2·0 mg of CCC to test-tubes and evaporate them to dryness with a stream of dry nitrogen. Add 2 ml of sodium benzenethiolate reagent (6 mg ml^{-1} in butan-2-one) and displace air from the rest of the tube with a gentle stream of nitrogen.

The sodium benzenethiolate reagent must be freshly prepared each day and stored under nitrogen until used.

Stopper the tubes and place in a thermostatically controlled water-bath at 80° C for 30 minutes, shaking them every 5 minutes. When the tubes are cool, filter and inject into the gas chromatograph 0·5 to 1 µl of the butan-2-one solutions.

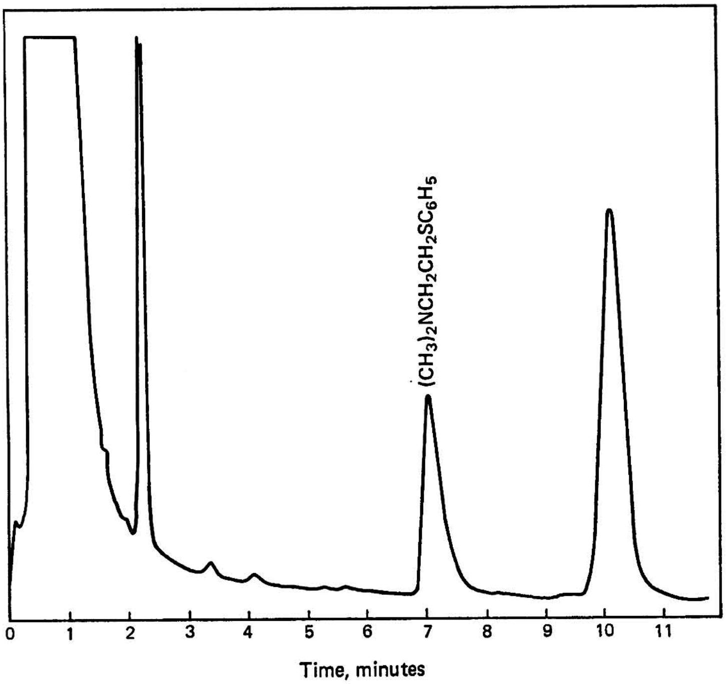


Fig. 1. Chromatogram obtained by products of the reaction between 0·48 mg of CCC and sodium benzenethiolate in 2 ml of anhydrous butan-2-one. Injection of 1 µl corresponds to 0·24 µg. Attenuation × 5

Fig. 1 shows a typical chromatogram obtained by products of reaction between 0·48 mg of CCC and sodium benzenethiolate in anhydrous butan-2-one.

Quantitative determinations can readily be made by peak area measurements. Calibration curves, micrograms of CCC (0·05 to 1) *versus* peak areas, can be plotted on linear graph paper.

The following extraction procedure, a slightly modified version of the one by Jenden *et al.*,[10] was applied to concentrate the *NN*-dimethyl-2-(thiophenyl)ethylamine; after completion of the reaction, pour the content of the tubes into 10-ml separating funnels. Rinse successively the contents of the tubes into the funnels with two 0·5-ml portions of anhydrous butan-2-one and with 2 ml of pentane. Add 0·5 ml of 0·5 M aqueous citric acid. Stopper the funnels and shake them vigorously. Allow the layers to separate, and collect the lower aqueous layers in 5-ml separating funnels. Remove the remaining traces of pentane with a gentle stream of dry nitrogen. Add 0·5 ml of 2 M potassium citrate - 2 M potassium hydroxide and 0·5 ml of chloroform and shake the funnels vigorously. Allow the layers to separate out and inject 0·5 to 1 µl of the chloroform phase into the gas chromatograph.

Fig. 2 shows a typical chromatogram obtained by the injection of *NN*-dimethyl-2-(thiophenyl)ethylamine as the product of reaction between 0·48 mg of CCC and benzenethiolate in chloroform solutions.

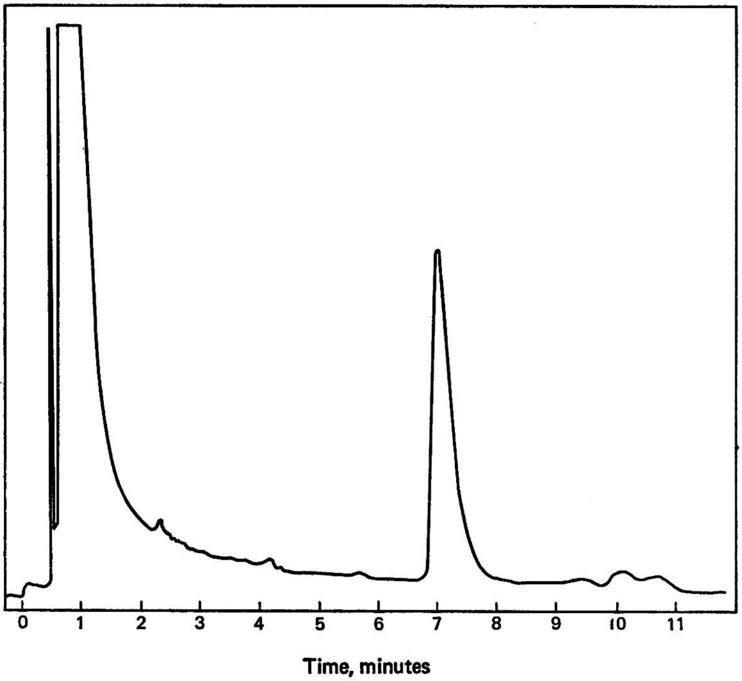


Fig. 2. Chromatogram of *NN*-dimethyl-2-(thiophenyl)ethylamine, the product of reaction between 0·48 mg of CCC and benzenethiolate, isolated from the butan-2-one mixture as described in the text. Final volume of chloroform solution, 0·5 ml. Injection of 0·5 µl corresponds to 0·48 µg. Attenuation × 5

The extraction procedure described provides about 85 per cent. recovery of the *NN*-dimethyl-2-(thiophenyl)ethylamine that was present in butan-2-one solutions. A new solution curve is plotted.

Care must be taken with the injection technique to ensure reproducible results.

The above studies have been carried out with pure CCC and it is clear that when this method is extended to plant extracts, some pre-purification and concentration must be carried out before the reaction with benzenethiolate.

The gas-chromatographic procedure has been tested by using natural tomato juice to which known amounts of CCC have been added.

GAS-CHROMATOGRAPHIC MICRO DETERMINATION OF CCC IN NATURAL TOMATO JUICE—

Preliminary purification of the vegetable extract is by a method essentially the same as that used for the colorimetric determination of CCC residues in strawberries.[8] The only differences are that the effluent from the cation-exchange resin column is collected in a 100-ml calibrated flask and is made up to volume with distilled water; and the eluate from the second aluminium oxide column is evaporated in a beaker to near dryness on a steam-bath. The residue is cooled and transferred from the beaker to a test-tube by using five 1-ml portions of (1 + 1) methanol - acetone.

The methanol and the acetone are removed by a stream of dry nitrogen, and 2 ml of sodium benzenethiolate reagent are added. The analysis is continued as under the Analytical procedure.

Average recoveries of CCC are about 80 per cent., as shown in Table I.

TABLE I

RECOVERY OF CCC FROM 250 g OF NATURAL TOMATO JUICE

Added, p.p.m.	Found,* p.p.m.	Average recovery, per cent.
0·0	<0·005	—
0·1	0·080	80
0·2	0·158	79
0·5	0·405	81
1·0	0·780	78

* Mean of three determinations.

CONCLUSION

These results suggest that it is now possible to use gas chromatography to detect minute residues of chlorcholine chloride in vegetable foods.

By using gas chromatography, as little as 10 ng of CCC in pure solution can be determined.

While average plant blank values are about 0·05 p.p.m. by the colorimetric method,[8] blank values of <0·005 p.p.m. are obtained with the gas-chromatographic method.

Naturally occurring quaternary ammonium compounds, such as choline and betaine, do not interfere chromatographically.

The method evaluated for reproducibility and accuracy has given good results.

The technique at its present level of development is not rapid. However, the time required for the analysis of other vegetable materials may be shortened if the purification steps required for tomatoes could be reduced or simplified, as may be likely.

Although considerable amounts of plant extractives can be injected into the gas chromatograph, it is desirable to keep them to a minimum so as to ensure a longer column life. It is particularly desirable to avoid injecting large amounts of oils, fats and waxes because excessive accumulation of these materials results in the distortion of elution peaks.[11]

The method can also be extended to the determination of CCC in formulations, and further experiments will be performed to this end.

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The Determination of Cyclohexylamine by Electron-capture Gas Chromatography

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Cyclohexylamine is allowed to react with 1-fluoro-2,4-dinitrobenzene and the 2,4-dinitrophenyl derivative is measured by electron-capture gas chromatography. Procedures are described for the determination of cyclohexylamine in cyclamates and in soft drinks down to levels of 1 p.p.m. and 0·1 p.p.m., respectively; the technique could also be of value when the content of cyclohexylamine in urine is required.

CYCLAMATE sweetening agents, although recently banned in the United Kingdom pending toxicological re-assessment in the light of further investigation, have attracted much analytical attention in recent years, particularly in regard to their cyclohexylamine content. Trace amounts of cyclohexylamine occur in commercial cyclamates for which regulations prescribe a limit of 100 p.p.m.,[1] and cyclohexylamine can also occur as a metabolite after the ingestion of cyclamates.[2] A study of the published procedures for the determination of cyclohexylamine shows that both the colorimetric[3] and the gas-chromatographic[3,4] methods indicate the need for a sensitive and specific method free from the difficulties encountered in the concentration of cyclohexylamine extracts. These are avoided in the method described. 1-Fluoro-2,4-dinitrobenzene reacts with primary aromatic amines to yield derivatives with strong electron-capturing properties, which can be separated by gas chromatography.[5] Primary alicyclic amines also follow this reaction, which is applied to the determination of trace amounts of cyclohexylamine described in this paper.

EXPERIMENTAL

APPARATUS—

An isothermal gas chromatograph fitted with an an electron-capture detector was used.[6] The column was of glass, 140 cm long, with an internal diameter of 1·5 mm, and was packed with silanised Chromosorb G, acid washed, 60 to 80 mesh, coated with 1·0 per cent. GE-XE-60 silicone and 0·1 per cent. Epikote 1001. The column temperature was 215° C, and the carrier gas was nitrogen at a flow-rate of 180 ml minute^{-1}.

REAGENTS—

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

Antifoam "S"—Supplied by Thompson & Capper Ltd.

Buffer solution—A 2·5 per cent. w/v solution of sodium tetraborate, $Na_2B_4O_7.10H_2O$, in water.

1-Fluoro-2,4-dinitrobenzene reagent—A 4 per cent. w/v solution in dioxan.

Hydrochloric acid, 6 N.

Sodium hydroxide solution, 6 N.

Sodium hydroxide pellets.

Sodium sulphate, granular, anhydrous.

Sodium sulphate solution—A 10 per cent. w/v solution of anhydrous sodium sulphate in water.

Toluene.

Cyclohexylamine, stock solution—Dissolve 1 g of cyclohexylamine in acetone and make up to 100 ml.

Cyclohexylamine, standard solution—Dilute 10 ml of cyclohexylamine stock solution to 100 ml with acetone.

PROCEDURE—

(*a*) *Cyclohexylamine in cyclamates*—Dissolve 10 g of cyclamate in buffer solution and make up to 100 ml with buffer solution. Transfer an aliquot estimated to contain between 1 and 10 μg of cyclohexylamine to a stoppered test-tube and make up to a volume of 10 ml with buffer solution. Add 0·5 ml of 1-fluoro-2,4-dinitrobenzene reagent, stopper the tube and shake it to mix. Prepare a series of standards containing 1 to 10 μg of cyclohexylamine and make them up to 10 ml with buffer solution. Add 0·5 ml of 1-fluoro-2,4-dinitrobenzene reagent to each tube, stopper and mix as before. Immerse the tubes containing the sample aliquots and those containing the standards in a water-bath, maintained at 60° C, for 20 minutes. Remove the tubes and leave them to cool. Wash the contents of each tube into a 50-ml separator with not more than 20 ml of water. Extract the aqueous layer with 5 ml of hexane and transfer the hexane to a dry, stoppered tube containing about 0·5 g of granular anhydrous sodium sulphate. Stopper the tube, shake it and allow the contents to settle. Take 5-μl aliquots from each tube for injection into the gas chromatograph.

(*b*) *Cyclohexylamine in soft drinks*—To 100 ml of soft drink in a 500-ml flask, add boiling chips, antifoam preparation and 10 g of sodium hydroxide pellets. Connect to an all-glass distillation apparatus. Collect about 40 ml of distillate in a 100-ml calibrated flask containing 2 ml of concentrated hydrochloric acid and 10 ml of sodium sulphate solution. Neutralise the distillate with ammonia solution and add 10 ml of sodium hydroxide solution. Make the volume up to 100 ml. Transfer the alkaline distillate to a separator and extract with 20 ml of toluene. Discard the aqueous phase. Wash the toluene extract with 5 ml of sodium sulphate solution and discard the aqueous washings. Extract the toluene with two 10-ml portions of 6 N hydrochloric acid and pass each portion through a moistened filter-paper into a 100-ml graduated flask. Wash the filter-paper with water and neutralise the combined portions with sodium hydroxide solution, with phenolphthalein as the indicator. Make up to 100 ml with buffer solution. Proceed as described under (*a*), from "Transfer an aliquot estimated to contain between 1 and 10 μg of cyclohexylamine to a stoppered test-tube. . . ." Standards must be passed through the toluene extraction procedure described above.

DISCUSSION

The 2,4-dinitrophenyl derivative of cyclohexylamine was found to give rise to a chromatographic peak with a retention time of 4·2 minutes under the conditions described. (The retention time of the aniline derivative is 3·6 minutes.) The peak height response of a standard series was linear over the range 1 to 10 $\mu g\ ml^{-1}$ of cyclohexylamine and the detection limit of the derivative was about 0·25 ng. Dicyclohexylamine, if present in the reaction mixture, did not interfere. The recovery of cyclohexylamine added to sodium cyclamate at the level of 5 p.p.m. ranged from 92 to 100 per cent., with a mean value of 97 per cent.

The content of cyclohexylamine found in thirty-five samples of sodium cyclamate is given in Table I. The level of cyclohexylamine in soft drinks, as purchased, ranges from 0 to 0·4 p.p.m.

TABLE I

CYCLOHEXYLAMINE CONTENT OF COMMERCIAL SODIUM CYCLAMATE

Range of cyclohexylamine, p.p.m. ..	1 to 10	11 to 20	21 to 50	51 to 100	100
Number of samples in range	12	8	9	4	2
Percentage of samples in range	34	23	26	11	6

The combined distillation and extraction procedure is necessary to isolate cyclohexylamine from soft drinks. Even so, ammonia liberated from the juice in the distillation process forms 2,4-dinitroaniline with the reagent (gas-chromatographic retention time of 2·0 minutes). Although this reaction would afford a basis for a sensitive ammonia determination, it interferes with the formation of the cyclohexylamine derivative by altering the reagent concentration. The ammonia and cyclohexylamine collected in the distillate are effectively separated by the extraction with toluene and re-extraction with hydrochloric acid. As the recovery of cyclohexylamine is incomplete in this extraction procedure, it is essential that standards are treated in the same way. Aniline was found to be present in the distillate obtained from some samples of soft drinks; this was believed to arise from the reduction of certain azo dyes (*e.g.*, orange RN) by sugars under the alkaline conditions of the distillation. Aniline, if present in the distillate, can be selectively removed by the addition of bromine water to the acidic distillate. The brominated aniline formed does not give rise to a gas-chromatographic peak under the conditions described.

The two methods described here make it possible to determine cyclohexylamine in cyclamates down to 1 p.p.m. and in soft drinks down to 0·1 p.p.m. At low levels of detection, the gas-chromatographic injection trace may slope, because of the presence of co-extracted reagent in the hexane phase. This can be removed by the addition of 0·5 ml of 6 N sodium hydroxide solution to the reaction mixture after the initial 20-minute period, and by further heating at 60° C for 20 minutes. By this treatment excess of reagent is effectively hydrolysed.

Gunner and O'Brien[7] have recently described the detection and quantitative determination of cyclohexylamine by gas - liquid chromatography with an electron-capture detector. In their paper, which appeared after the submission of this paper, the trinitrophenyl derivative is used for the fixation and measurement of the amine.

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A Simple Field Test for the Determination of Acetone Vapour in Air

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A field method is described for the determination of acetone vapour in air in concentrations up to 2000 p.p.m. v/v. The vapour is collected in a solution containing sodium nitroprusside and ammonium acetate. On the addition of ammonia solution, a coloured complex is formed, which is compared visually with standards after 10 minutes. Two series of standards are used, the choice of which depends upon the temperature at which colour development is carried out. Both apparatus and method are simple and a complete determination can be carried out in about 15 minutes.

ACETONE is widely used industrially as a solvent and chemical intermediate. Although not normally considered toxic, its vapour has a strong irritant and narcotic effect on man and can form flammable and explosive mixtures with air. The current threshold limit value for acetone in the United Kingdom[1] is 1000 p.p.m. v/v (2400 mg m^{-3}), and a simple field test is needed to determine its concentration in air at about this level.

Most of the reagents reported in the literature for the colorimetric determination of ketones involve reactions of the carbonyl group and hence are not specific. Direct production of stains on chemically impregnated papers by acetone vapour proved unsuccessful. Positive results were obtained when the vapour was passed through solutions of the reagents and when necessary treated with a suitable colour developing agent. Of the many reagents that were investigated, including vanillin, salicylaldehyde, furfuraldehyde, 2,4-dinitrophenylhydrazine, *o*-nitrobenzaldehyde and sodium nitroprusside, it seemed that, with suitable adjustment of reaction conditions, the last might be made effectively specific for acetone.

Since von Bitto's[2] early systematic investigation of the reaction of sodium nitroprusside with certain aldehydes and ketones, many modifications of the test have been described. These have included the formation of the coloured complex at a liquid - liquid interface[3] and the use of powdered mixtures of the reagents,[4] both of which are unsuitable for a field test, which needs to be simple, reliable and capable of being carried out by relatively unskilled persons. The basic requirements for the test appeared to be the addition of ketone to a freshly prepared solution of sodium nitroprusside, together with one or more ammonium salt and, in some cases, acetic acid. The colour was then developed by the addition of alkali, usually ammonia solution. Preliminary experiments with aqueous solutions of the reagents and of acetone (at a concentration of about 900 μg ml^{-1}) showed the test to be adaptable for field work.

EXPERIMENTAL

PREPARATION AND CALIBRATION OF STANDARD ATMOSPHERES—

Atmospheres containing known concentrations of acetone were required to assess the efficiency of the sampling technique and for use in the development of the field test.

Preparation—Dynamic atmospheres of acetone were prepared by an injection - atomisation technique. Acetone was supplied to an all-glass atomiser[5] through a syringe driven at a steady, known rate by a slow-injection apparatus and was diluted with a metered stream of air. By variation of the injection and dilution rates, atmospheres of various concentrations were obtained. A suitable volume of the atmosphere was further diluted with air and fed to a flame-ionisation detector, the output from which was connected to an amplifier and recorder system so that the generator output could be monitored.

Calibration—Several methods are available for the determination of acetone, but a spectrophotometric procedure proposed by Lappin and Clark[6] seemed most suitable for our purpose as it could also be used to determine other ketones in which we were interested. The experimental parameters of the method were not precisely defined, and an investigation of these was carried out. Our findings confirmed those of Mendelowitz and Riley[7] as regards the effect of acid concentration, heating at high temperatures and the high reagent blank at the proposed wavelength for measurement. It was also found that the black precipitate formed on the addition of the alkali took time to re-dissolve, depending upon the amount of ketone present in the original solution, with consequent variations in optical density readings. Consistent results were obtained, however, if at least 8 minutes elapsed before measurement.

The modified method finally adopted was found to give reproducible results and is as follows.

To 1 ml of the ketone solution add 1 ml of 2,4-dinitrophenylhydrazine reagent [0·1 g of 2,4-dinitrophenylhydrazine (recrystallised) *plus* 0·4 ml of concentrated hydrochloric acid in 100 ml of carbonyl-free methanol[6]] and heat the mixture for 30 minutes at 50° C in loosely stoppered tubes. Cool, add 5 ml of potassium hydroxide solution (10 per cent. in methanol) and read the optical density after 10 minutes in 10-mm cells at 530 nm against the reagent blank. Obtain the ketone content by reference to a calibration graph prepared by using ketone solutions of known concentration. For acetone this was found to be linear over the range 0 to 50 μg ml^{-1}.

For calibration of the generated acetone atmosphere, samples were collected quantitatively at the rate of 100 ml minute^{-1} for 5 minutes in two all-glass impingers in series, each containing 10 ml of water. The contents of the impingers were combined and diluted to a suitable volume with water, *e.g.*, to 50 ml for an atmosphere containing 2400 mg m^{-3}, and the concentration of the acetone atmosphere was calculated with the aid of the prepared calibration graph.

COLORIMETRIC DETERMINATION OF ACETONE—

It appeared that the main essentials for a field test would be the production of a reasonably intense colour for an acetone concentration at half its threshold limit value (currently 500 p.p.m. v/v), a good colour differentiation between those given by concentrations at the 0·5, 1 and 2 threshold limit values, and the test should be capable of completion in reasonable time. From the preliminary experiments mentioned previously it was evident that compromises in experimental conditions would be necessary. Too high a concentration of sodium nitroprusside (greater than 2 per cent. w/v) produced murky colours; a 1 per cent. w/v solution was consequently chosen. The presence of an ammonium salt (ammonium acetate was chosen) was required for optimum colour production, acetic acid producing less intense colours. Whereas the intensity of the colour produced was proportional to the ammonium salt concentration, it was found at the higher concentrations that this intensity was sensitive to small variations in the ammonium salt concentration. The use of a 25 per cent. w/v ammonium acetate solution minimised this disadvantage and yet produced adequate coloration. Ammonia produced a more intense purple colour than either sodium carbonate or hydroxide, and it was noted that, although the colour intensity and the rate of colour development were proportional to the concentration of ammonia added, high concentrations reduced the stability of the colour produced. A 50 per cent. v/v ammonia solution proved to be a suitable compromise. A 250-ml sample of an atmosphere containing 500 p.p.m. v/v of acetone vapour, trapped in 3 ml of a collecting reagent (1 per cent. w/v with respect to sodium nitroprusside and 25 per cent. w/v with respect to ammonium acetate), was found to provide a suitable colour after the addition of 1 ml of 50 per cent. v/v ammonia solution.

COLOUR STABILITY—

Some quantitative measure of colour stability was necessary as it was obvious from visual observation that the colour developed slowly for about 20 minutes, after which there was a gradual deterioration. By using aqueous acetone solutions, small aliquots (about 0·1 ml), equivalent to 250 ml of atmospheres containing 0, 500, 1000 and 2000 p.p.m. v/v, were added to 3 ml of the nitroprusside reagent, and 1 ml of the ammonia solution added. Graphs were plotted of optical density against time, measured from the addition of alkali

(Fig. 1). Maximum intensity of colour was achieved after 20 minutes, but this was considered too long for field work and 10 minutes was chosen as a convenient time; at this point the rate of change should be fairly slow. It was later found that good colour matches with prepared standards were possible 10 ± 0·5 minutes after the addition of alkali.

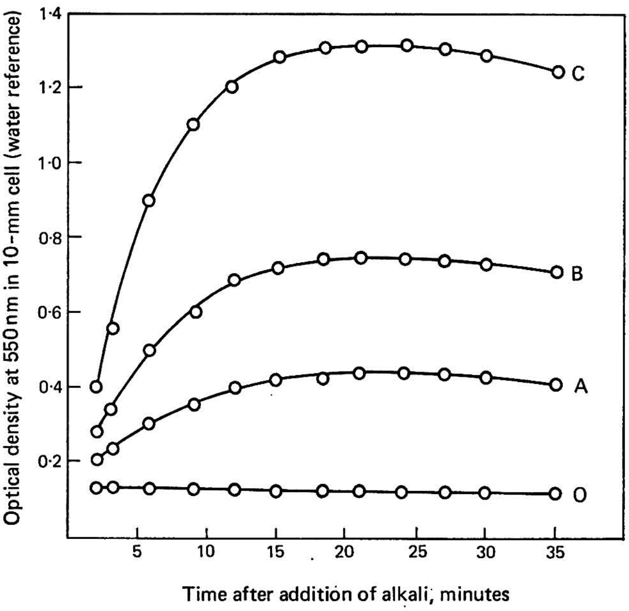
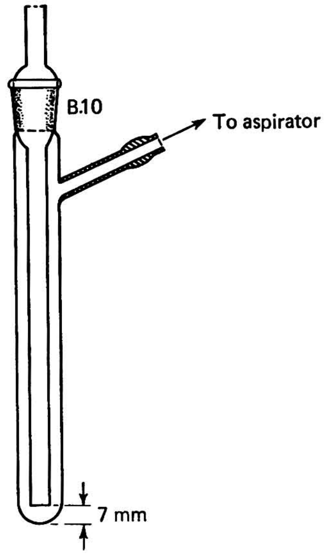


Fig. 1. Relationship between the optical density of the sodium nitroprusside - acetone complex and development time. Curve O, reagent blank; curve A, 500 p.p.m. of acetone; curve B, 1000 p.p.m. of acetone; curve C, 2000 p.p.m. of acetone

STABILITY OF THE SODIUM NITROPRUSSIDE SOLUTION—

The proposed field test was checked at various levels by using the acetone generator, the samples being drawn through the collecting solution contained in an all-glass absorber (Fig. 2) by means of an aspirator bulb. The colour was developed at a constant temperature of 20° C by adding ammonia solution; the optical density was measured at 550 nm after 20 minutes and plotted against the actual acetone concentration determined, on samples taken in parallel, by the 2,4-dinitrophenylhydrazine method. The points fell on a smooth curve. Using different sodium nitroprusside, ammonium acetate and ammonia solutions prepared from the same batches of reagents, similar curves were obtained but with different gradients, which could represent differences in estimated acetone concentration of about ±15 per cent. of a mean value. This variation was much greater than would be expected from minor differences possible in the preparation of the reagents. However, it was noted that a freshly prepared sodium nitroprusside reagent gave higher optical densities than one that had been stored for some hours before use. An investigation of the ageing properties of the reagent showed that, when stored in the dark, erratic results could be obtained during the first few hours after preparation, the optical density then remaining constant for a further period of about 24 hours, after which it slowly fell. If the reagent was stored in the light, the optical density slowly decreased for a period of about 12 hours and then became constant at a level much lower than that of solutions stored in the dark. The results are summarised in Table I.

The effect of storage temperature was also investigated over a period of 48 hours, and it was found that temperatures between about 5° and 27° C had no significant effect on the results obtained. At higher temperatures, visible signs of deterioration of the reagent were noticed after about 16 hours and the colours obtained in the test were murky and tended to be orange - brown rather than red - purple.



Over-all length of absorption tube, 155 mm
External diameter, 15 mm
Internal diameter, 13 mm

Over-all length of inlet tube, about 185 mm
External diameter, 6 mm
Internal diameter, 4·5 mm

Fig. 2. All-glass absorber

As a result of these findings, and from the practical considerations necessary for field work, it was decided to store the nitroprusside reagent in the dark at temperatures below 27° C and to use it between 16 and 24 hours after preparation. When this modification was incorporated, the method was found to give reproducible results.

TABLE I

EFFECT ON STORAGE OF SODIUM NITROPRUSSIDE REAGENT ON THE OPTICAL DENSITY OF FINAL SOLUTION

	Optical density*	
Time	Storage in dark	Storage in light
3 minutes	0·724	—
5 minutes	0·740	—
10 minutes	0·820	0·820
35 minutes	0·872	0·824
65 minutes	0·818	0·800
2½ hours	0·818	0·730
3½ hours	0·820	0·628
4½ hours	0·818	0·610
18½ hours	0·782	0·570
23 hours	0·785	0·570
28½ hours	0·788	0·570
46 hours	0·738	0·575
73 hours	0·720	—

* Measured at 550 nm in 10-mm cells against water reference.

PREPARATION OF COLOUR STANDARDS—

Colour standards equivalent to 0, 500, 1000 and 2000 p.p.m. v/v of acetone vapour in air were prepared by matching mixtures of inorganic salt solutions against samples taken from the generator by the field test method, the colour being developed at 20° C.

EFFECT OF TEMPERATURE ON SAMPLE COLLECTION AND COLOUR DEVELOPMENT—When the colours produced in the field method were compared with the prepared colour standards after 10 ± 0·5 minutes, occasional low results were obtained. Further study showed that these were apparently coincidental with periods of high ambient temperature. Consequently an investigation was made of the effect of the temperature of collection on the colour stability.

TABLE II

EFFECT OF COLLECTING A STANDARD ACETONE ATMOSPHERE OF CONCENTRATION 2040 mg m^{-3} AT VARIOUS TEMPERATURES

Temperature of collecting solution, °C	7	8·5	22·6	23·0	37·8	42·0
Acetone concentration found, mg m^{-3}	2190	2120	1900	1920	1750	1660

With the absorber and contents maintained at various temperatures by a controlled water-bath, samples were taken from the generator and the colour developed at 20° C. After 20 minutes the optical density was measured and the concentration determined from the previously prepared calibration graph. Over the range measured, 7° to 42° C, the optical density was inversely proportional to temperature; but the over-all error was within the tolerance permissible for field work (±0·25 of the threshold limit value). Hence for practical purposes the effect of collection temperature, which could be expected to be well within this extreme range, could be ignored. A selection of the results obtained is given in Table II.

TABLE III

EFFECT OF COLOUR DEVELOPMENT TEMPERATURE ON OPTICAL DENSITY OF SODIUM NITROPRUSSIDE - ACETONE COMPLEX

Development temperature, °C	10	15	20	25	30
Optical density*	0·755	0·855	0·830	0·680	0·465
Acetone concentration found, mg m^{-3}†	2200	2540	2460	1940	1180

* Measured at 550 nm in 10-mm cells against water reference.

† Based on a calibration graph prepared at a development temperature of 20° C.

To determine the effect of development temperature on the colour obtained, samples of acetone atmosphere (nominally 2400 mg m^{-3}) were taken and colour development carried out at different, controlled temperatures between 10° and 30° C, the optical density being measured after 20 minutes. The results, shown in Table III, indicated that the temperature at which the development of colour takes place has a significant effect on the result obtained. For example, the change in optical density between 20° and 25° C, which can be regarded as average room temperature conditions, represents an indicated concentration of about 500 mg m^{-3}, based on a calibration graph prepared at 20° C. The position was further confused by the fact that, whereas optical density was used as a convenient parameter for comparison, visually the final colour of the solution was also markedly different; at low temperatures it was distinctly purple whereas at high temperatures it was orange. Ideally a different set of colour standards would be required for each development temperature.

TABLE IV

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

	Acetone concentration found, p.p.m. v/v									
By 2,4-dinitrophenylhydrazine method	220	270	450	650	730	920	1030	1360	1980	2940
By field test with appropriate colour standard	0 to 500	0 to 500	500−*	500+*	500 to 1000	1000−	1000	1000 to 2000	2000−	≫2000

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

This would obviously be impracticable, and it was found that for field work sufficiently accurate results could be obtained by using two sets of standards prepared at 20° C and 25° C, the former set being used in the range 19° to 22° C and the latter in the range 22° to 26° C. Details of the preparation of these colour standards are given in Table V. If some means of temperature control is available then either temperature can be used for colour development. It was found that, except in extreme conditions, a large beaker of water would maintain a sufficiently constant temperature within the required range during the 10 minutes required for colour development. A selection of the results obtained when acetone atmospheres of known concentrations were sampled by the proposed field test, and the levels assessed by the colour standards, is given in Table IV.

TABLE V

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

Acetone standard, p.p.m.		0	500	1000	2000
Standard A*	Yellow component, ml	9·2	5·6	4·0	—
	Blue component, ml	—	7·2	16·0	27·2
	Red component, ml	2·4	8·4	20·0	58·0
Standard B*	Yellow component, ml	9·2	6·3	5·6	2·0
	Blue component, ml	—	7·3	16·8	20·0
	Red component, ml	2·4	9·4	20·4	40·0

* Standard A for colour development temperatures between 19° and 22° C.
Standard B for colour development temperatures between 22° and 26° C.

RELIABILITY OF FIELD TEST REAGENTS—

A comparison was made of ammonium acetate and sodium nitroprusside from various manufacturers, and of different batches from the same manufacturer. Negligible differences were noted for ammonium acetate. With sodium nitroprusside slight differences were noted, but the variations were always well within the acceptable field test limit.

An investigation of the effect of ammonia concentration on the test showed that the indicated level of acetone was proportional to the ammonia concentration. A 10 per cent. v/v increase resulted in an indicated extra 250 p.p.m. of acetone. It was concluded that, provided the ammonia solution used was 50 ± 5 per cent. v/v (as NH_4OH sp.gr. 0·88), no serious errors should occur in the field test. This represents a concentration of approximately 16 ± 2 per cent. w/v (as ammonia), a condition satisfied by all the commercially available ammonia solutions of sp.gr. 0·88 that were compared, provided they had not been stored for long periods in partially full bottles. In this connection it was found that unstoppered bottles of the ammonia reagent tended to lose ammonia, and over a period of about 6 hours the fall in the indicated acetone level could be about 250 p.p.m. This emphasised the need for keeping the reagent bottle tightly stoppered when not in use.

It was observed that reagents and wet apparatus must be kept well away from contaminated atmospheres when not in use. Wet, unstoppered bottles stored in an acetone atmosphere of about 2000 p.p.m. were found to absorb the equivalent of about 5 $\mu g\ ml^{-1}$ of acetone in 3 hours. In a similar atmosphere, an unstoppered bottle of the sodium nitroprusside reagent absorbed about 250 p.p.m. of acetone in 5 hours as indicated by the field test method, whereas a stoppered bottle showed no significant absorption. Ammonia reagent in stoppered bottles showed no tendency to absorb acetone.

INTERFERENCES—

The effect of possible interference with the proposed field test by substances likely either to be used with acetone or to react in a similar way was checked by sampling their near-saturated vapours. A representative selection of aldehydes, ketones, alcohols, hydrocarbons and halogenated hydrocarbons has been checked in this way, and only those mentioned below were found to give colours different from the blank.

Formaldehyde was found to give a faint red colour after about 5 minutes, but this had completely disappeared after 10 minutes when a colour comparison was carried out. Ethyl methyl ketone, isobutyl methyl ketone and diacetone alcohol gave strong purple colours and obviously required further investigation. Atmospheres of the former two ketones were generated by using the permeation technique devised in this laboratory.[8] Samples taken by the proposed method gave positive results at levels greater than 1000 p.p.m. v/v for ethyl methyl ketone and 500 p.p.m. v/v for isobutyl methyl ketone (current threshold limit values 200 and 100 p.p.m. v/v, respectively[1]). The colours produced would indicate levels of between 0 and 500 p.p.m. v/v of acetone. At levels below 400 and 200 p.p.m. there was negligible indication. Because of its low permeation rate, diacetone alcohol atmospheres could not be prepared by this technique. By using solutions of the ketone, small aliquots of about 0·1 ml, equivalent to 250 ml of the ketone atmosphere at various levels, were added to 3 ml of the sodium nitroprusside reagent and the colour developed with ammonia solution. At levels below 100 p.p.m. (current threshold limit value[1] 50 p.p.m. v/v) the coloration was negligible, but at higher levels a definite pink colour was obtained, becoming distinctly purple at about 500 p.p.m. Atmospheres with humidities within the range normally experienced in this country were found to have no apparent effect on the method.

PROPOSED FIELD METHOD FOR THE DETERMINATION OF ACETONE VAPOUR IN AIR

APPARATUS—

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

Aspirator—A rubber-bulb hand aspirator, obtainable from Siebe Gorman and Co. Ltd., Chessington, Surrey, was adjusted to sample at the rate of 125 ml minute^{-1}.

REAGENTS—

All reagents should be of analytical grade and the solutions prepared in distilled or de-ionised water.

Sodium nitroprusside reagent—Dissolve 1·00 g of sodium nitroprusside and 25·0 g of ammonium acetate in water and dilute to 100 ml. Store in the dark, below 27° C, and use between 16 and 24 hours after preparation.

Ammonia solution—Dilute 25 ml of concentrated ammonia solution (sp.gr. 0·88) to 50 ml with water (Note 1). Store in well stoppered bottles and prepare fresh daily.

All solutions should be stored in an acetone-free atmosphere and kept tightly stoppered.

PROCEDURE—

In an uncontaminated atmosphere, well away from the suspected source of acetone vapour, transfer with a pipette 3 ml of the sodium nitroprusside reagent into the absorption tube. Insert the inlet tube and connect the aspirator to the assembly. Transfer the apparatus to the sampling site and collect 250 ml of the atmosphere by two aspirations of the bulb, ensuring that bubbling has ceased before the second aspiration is made. Remove the apparatus to an uncontaminated atmosphere; disconnect the aspirator, remove the inlet tube and, with a pipette, transfer 1 ml of the ammonia solution into the absorption tube. Stopper the tube and mix the contents well by inverting the tube several times, ensuring that no liquid is lost through the side-arm. Note the air temperature (see Note 2). After 10 ± 0·5 minutes, compare the colour of the solution with the appropriate liquid colour standards, contained in similar tubes, by viewing through the solutions in daylight.

NOTES—

1. In the interest of safety, pipette fillers should be used to dispense the reagents used in this test.
2. The colour should preferably be developed at between 20° and 25° C. Except in extreme temperature conditions this range can normally be maintained by placing the tubes in water previously adjusted to the temperature required.

PREPARATION OF COLOUR STANDARDS—

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

Blue component—Dissolve 300 g of copper 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 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 V, diluting each to 100 ml with water and mixing thoroughly.

As an alternative to the above colour standards, a series of permanent glass standards on 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 acetone. However, under strictly controlled conditions, particularly in respect of colour development temperature and time, and by using a spectrophotometer it is probably capable of determining acetone concentrations fairly accurately. A suitable calibration graph can be prepared by using standard acetone solutions made up in the sodium nitroprusside reagent. For field work the best results will be obtained at a colour development temperature of either 20° or 25° C (the temperature at which the colour standards were prepared) and if apparatus is available to achieve these conditions it should be used.

Assessment of the proposed method has been carried out under field conditions at an industrial site where acetone is used in large amounts. Samples of the contaminated atmosphere were taken by the field method and were simultaneously collected in water for analysis by the 2,4-dinitrophenylhydrazine method. Good agreement was obtained between the results.

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A Simple Field Test for the Determination of Isophorone Vapour in Air

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A field method is described for determining isophorone vapour in air at concentrations of up to 280 mg m^{-3}. The vapour is collected in water and determined by its reduction of dodecamolybdophosphoric acid to molybdenum blue in the presence of perchloric acid. After removal of the yellow background colour of unreacted dodecamolybdophosphoric acid with sodium citrate solution, the isophorone concentration is determined by comparing the residual molybdenum-blue coloration with a series of colour standards. The apparatus used is simple and the time taken to complete an analysis is about 30 minutes.

ISOPHORONE (3,5,5-trimethylcyclohex-2-enone) is used in certain sections of the chemical industry as a solvent for lacquers based on phenol - formaldehyde resins, epoxy resins or co-polymers of vinyl chloride and vinyl acetate; it is also used in the processing of certain PVC goods. In view of these wide applications, and bearing in mind that the recommended threshold limit value for isophorone vapour in air[1] is currently 25 p.p.m. v/v (140 mg m^{-3}), there is a need for a simple rapid field test for its determination at about this level in industrial atmospheres.

A search of the literature revealed only one method[2] for the determination of isophorone vapour in air which might be capable of adaptation to a field test; that involving the reduction of molybdophosphoric acid reagent to molybdenum blue. The use in this test of glacial acetic acid, a corrosive and pungent material, as both the absorbent solution and the reagent solvent, and the need to heat for 45 minutes in a boiling water bath, appeared to limit its usefulness as a field test. Also, as the background colour of molybdophosphoric acid in acetic acid is yellow, the colour change appears as yellow to green, which is not a suitable change for easy visual colour differentiation between adjacent standards. However, the method was apparently sensitive enough for our requirements, thought at this stage to be up to 280 μg of isophorone, and was also stated[2] to be specific for isophorone in the presence of other industrially used ketones, *viz.*, acetone, butan-2-one and 4-methylpentan-2-one. This method was therefore examined with a view to making modifications that would enable it to be used as a field test.

EXPERIMENTAL

PREPARATION AND CALIBRATION OF STANDARD ATMOSPHERES OF ISOPHORONE—

Atmospheres containing known concentrations of isophorone were required, both to assess the efficiency of the sampling technique and for use in the development of the field test.

Preparation—The atmospheres were generated by using the permeation technique previously developed in this laboratory.[3] Isophorone was allowed to permeate through the walls of a sealed bag, made from 0·0635 mm thick polythene, suspended in a drying tower through which a metered stream of air was passed.

Calibration—The concentrations of the isophorone atmospheres produced were calculated from the rate of loss of weight of the bag and the flow-rate of the diluting air stream. They were then checked by an independent chemical method which was a general procedure for determining ketones, originally devised by Lappin and Clark[4] and recently modified in this laboratory.[5] Briefly, this method involves the quantitative trapping of the isophorone vapour in 10 ml of water contained in an all-glass impinger, by using sampling rates of 250 and 125 ml minute^{-1}. The isophorone 2,4-dinitrophenylhydrazone was then formed and the colour produced on treatment with an alkali was measured spectrophotometrically. The concentration of isophorone in the atmosphere was calculated by reference to a standard graph previously prepared with aliquots of solutions of isophorone in carbonyl-free aqueous methanol. All aliquots of the standard solutions were further diluted with water to ensure that the final solution before colour development did not contain more than 0·5 per cent. v/v of methanol, a level which was known not to interfere with the determination of the ketone.

COLORIMETRIC DETERMINATION OF ISOPHORONE—

Preliminary investigations were carried out with the standard isophorone solutions mentioned above and with the same limitations on the methanol concentration. Initially, the reduction of dodecamolybdophosphoric and dodecamolybdosilicic acids[6,7] by isophorone in sodium hydroxide solution was investigated. Although discernible blue colours were obtained at room temperature with 3 mg of isophorone, it was not sensitive enough for use as a field test when an appreciable blue colour from about 50 µg of the ketone would be required.

In an attempt to obviate the disadvantages of the original method of Kacy and Cope,[2] the reduction of dodecamolybdophosphoric acid in the presence of acids other than glacial acetic acid was investigated. In no case was colour development obtained at room temperature, so the solution was heated on a boiling water bath. No significant colour was produced from 200 µg of isophorone with a 5 per cent. w/v solution of dodecamolybdophosphoric acid in 50 per cent. v/v aqueous acetic acid, 20 per cent. w/v aqueous (+)-tartaric acid or 5 per cent. w/v aqueous oxalic acid. More encouraging results were obtained with inorganic acids. An aqueous 5 per cent. w/v solution of dodecamolybdophosphoric acid is bright yellow, but in concentrations of hydrochloric acid greater than 1·9 N almost colourless solutions are obtained. Thus, if the reduction could be carried out with such hydrochloric acid solutions, a colourless-to-blue reaction might be expected, and the disadvantage of a yellow-to-green colour change overcome. In practice very little reduction of dodecamolybdophosphoric acid by isophorone occurred under these conditions. When hydrochloric acid concentrations of less than 1·9 N, and 15 minutes' heating times, were used, sufficient reduction occurred, although considerable interference was apparent, under these conditions, from solutions with concentrations equivalent to 1-l samples of atmospheres of 200 mg m^{-3} of cyclohexanone and 460 mg m^{-3} of 3-methylcyclohexanone (the present threshold limit values[1] of these ketones). In view of this lack of specificity for isophorone, reduction in hydrochloric acid was rejected, as was reduction in phosphoric and sulphuric acids. In nitric acid solution no reduction was observed.

TABLE I

RELATIONSHIP BETWEEN THE DEGREE OF REDUCTION OF DODECAMOLYBDOPHOSPHORIC ACID BY ISOPHORONE, CYCLOHEXANONE, 3-METHYLCYCLOHEXANONE AND THE CONCENTRATIONS OF PERCHLORIC ACID ADDED

		Relative reponse, per cent. of	
Concentration of perchloric acid (2 ml) added to reaction mixture, M	Optical density at 720 nm for isophorone (140 µg)*	cyclohexanone (200 µg)*	3-methyl-cyclohexanone (460 µg)*
1·9	0·268	52	85
3·8	0·360	36	61
5·8	0·440	27	46
7·7	0·495	22	38
9·2	0·523	19	34

* Equivalent to the ketone collected with 100 per cent. efficiency from a 500-ml sample of an atmosphere containing twice the present threshold limit value.

The most satisfactory results were obtained by using perchloric acid. Aqueous solutions, each 2 ml in volume, of isophorone, cyclohexanone and 3-methylcyclohexanone, the last two of which might interfere in the test, were heated for 15 minutes with 1 ml of a 25 per cent.w/v aqueous solution of dodecamolybdophosphoric acid and 2 ml of different concentrations of perchloric acid solution ranging from 1·9 to 9·2 M (the latter being 60 per cent. w/w perchloric acid). After cooling by immersion in cold water for a few minutes (the exact cooling conditions were not important), the optical densities were read at 720 nm with 10-mm cells and water as reference. From Table I it can be seen that the response of isophorone increased with increasing concentration of perchloric acid although the converse occurred with cyclohexanone and 3-methylcyclohexanone. Also, over the range of perchloric acid solutions from 7·7 to 9·2 M, the rate of increase of response for isophorone was not large. It was decided that 7·7 M perchloric acid (75 ml of 60 per cent. w/w perchloric acid diluted to 90 ml with water) should be used, this being a compromise between three factors: the isophorone response; the magnitude of the difference between the response of isophorone and the other two cyclic ketones; and the considerations of safety in the handling of perchloric acid. At the perchloric acid concentration chosen, the colour produced by 460 μg of 3-methylcyclohexanone (equivalent to a 500-ml sample of an atmosphere containing twice its present threshold limit value) was equal to that produced by 53 μg of isophorone, *i.e.*, the equivalent of a 500-ml sample of an atmosphere containing 0·75 times its present threshold limit value. On a similar basis the response of cyclohexanone was approximately one fifth of that of isophorone. These levels of interference were considered sufficiently acceptable to justify the investigation of methods for discharging the yellow background colour of the unused dodecamolybdophosphoric acid after reduction has taken place by this procedure.

RELIABILITY OF FIELD TEST REAGENTS—

Although reduction in perchloric acid gave reproducible results when dodecamolybdophosphoric acid solutions were prepared from the same batch of reagent, considerable variation in results was observed with samples from different sources of supply. This was not caused by the different amounts of partially reduced material which these samples of heteropoly acid contained; definite differences in response to isophorone were obtained. In the course of efforts to obviate these and so avoid the necessity of calibrating the method for each batch of reagent, it was found that the use of a solution of dodecamolybdophosphoric acid in sodium hydroxide in place of the aqueous solution eliminated these variations. The mechanism whereby this was achieved is not clear. Titration of aqueous solutions of 0·25 g of the various samples of heteropoly acid with sodium hydroxide showed that at a pH of 6·2 or 6·3 a yellow-to-colourless change occurred, or yellow to blue if some reduced material was present. Also, the amount of alkali required to reach a pH of 6·3 was found to vary from sample to sample. Further experiments showed that reproducible results were obtained if the pH of the heteropoly acid reagent lay between 5·8 (at which the solution was still slightly yellow) and 7·1, and so the concentration of sodium hydroxide could be under or over-estimated by 20 per cent. without incurring serious error. It was finally found most convenient to prepare the molybdophosphoric acid reagent by dissolving the material in 2 N sodium hydroxide to give a 25 per cent. w/v solution in the pH range 6·7 to 6·8.

The use of this modified dodecamolybdophosphoric acid reagent in a reaction mixture in conjunction with the addition of 2 ml of 7·7 M perchloric acid again gave the optimum reducing conditions and the interferences from cyclohexanone and 3-methylcyclohexanone were of the same magnitude as before.

The presence of reduced material (molybdenum blue) in the heteropoly acid reagent did not produce serious error in the field test provided that the intensity of the colour of the solution was not greater than that of the 140 mg m^{-3} isophorone colour standard when compared by the field test procedure. This ensured that the colour blank due to this reagent, which comprised one eighth of the volume of the final solution used for colour matching, would not be greater than the equivalent of 17·5 mg m^{-3} of isophorone from a 500-ml sample. No differences were noted in the results obtained when using perchloric and hydrochloric acids from different sources.

REMOVAL OF BACKGROUND COLOUR—

Discharge of the residual yellow colour of dodecamolybdophosphoric acid in hydrochloric acid solutions of 1·9 N and above showed two disadvantages, namely that small variations in the hydrochloric acid concentration produced considerable differences in the intensity of the residual molybdenum blue colours, and also strict temperature control was required before the addition of the acid. An immediate discharge of background colour was achieved by the addition of sodium hydroxide but, as the intensity of the residual blue colour again depended on cooling conditions, the use of this alkali was also rejected.

Of several organic acid salts used to discharge the background colour, trisodium citrate showed the most promise in preliminary experiments. All additions of 3-ml portions of trisodium citrate solutions with concentrations between 25 and 50 per cent. w/v to the reaction mixture at 20° C gave complete discharge of background colour within 5 minutes, and enhanced the blue colour. Cooling the reaction mixture prior to the addition of the citrate solution was desirable, otherwise the discharge of the colour took longer and variations occurred in the intensity of the final blue colour.

When the reaction mixtures were cooled in a water-bath for 5 minutes at temperatures between 2° and 27° C (a range wider than that of tap water) prior to the addition of citrate, complete discharge of colour occurred within 5 minutes, with no variation in the residual blue colours for citrate concentrations in the range 30 to 50 per cent. w/v; by using a 25 per cent. w/v citrate solution satisfactory results were obtained only down to a cooling temperature of 5° C. No difference in response was obtained between samples returned to the water-bath and those allowed to stand at ambient temperature after addition of the citrate solution.

By using the above technique for the discharge of background colour, it was found that a slow increase in intensity of the blue colour occurred with time, the rate increasing with increase of citrate concentration, a slight change in hue becoming just apparent. However, with 30 per cent. w/v citrate these effects were minimal. The change in colour occurring within 20 minutes of the addition of citrate in the temperature range studied was acceptable for field test purposes and consequently this concentration of citrate solution was selected.

The interferences from cyclohexanone and 3-methylcyclohexanone when the above colour discharge procedure was used were found to be less than those observed when the background colour was not discharged. The colours produced by atmospheres of twice the threshold limit value of 3-methylcyclohexanone (460 mg m^{-3}) and cyclohexanone (200 mg m^{-3}) were now equivalent to 0·49 and 0·27 times the threshold limit value of isophorone, respectively.

COLLECTION OF ISOPHORONE—

With standard isophorone solutions, a calibration graph over the range 0 to 162 μg was prepared, by using the colour development procedure of the proposed field test. The optical densities were measured at 720 nm in 10-mm cells on a spectrophotometer and an almost linear response between these figures and the concentrations from approximately 20 μg upwards was found. The calibration figures are given in Table II. A good gradation of colour over the range 0 to 140 μg was noted, the optical density for 140 μg of isophorone being 0·435. This suggested that a sample volume of 500 ml would allow adequate visual colour differentiation at the levels of 0, 70, 140 and 280 mg m^{-3} of isophorone.

TABLE II

CALIBRATION RESULTS FOR THE DETERMINATION OF ISOPHORONE BY THE PROPOSED FIELD TEST

Isophorone concentration, μg per 2 ml of water	0	9·1	18·3	30·5	42·7	61·0	91·5	103	122	143	162
Optical density* at 720 nm	0·027	0·073	0·114	0·155	0·185	0·230	0·313	0·351	0·398	0·439	0·483

* 10-mm cell, water as reference.

Standard atmospheres of isophorone over the range 36 to 336 mg m^{-3} were then set up and 500 ml of each collected in 2 ml of water contained in an all-glass absorber as previously described[5] and determined by the proposed field test. A collection efficiency of 88 to 92 per cent. was indicated over the ambient temperature limits of 18° to 24° C. As this was reproducible, a revised calibration graph based on this collection efficiency was prepared.

PREPARATION OF COLOUR STANDARDS—

The colours equivalent to 0, 70, 140 and 280 mg m^{-3} of isophorone, corrected for collection efficiency, were matched by using solutions of inorganic salts. Details of the preparation of these colour standards are given later. With these standards it was found possible to determine the isophorone content of a sample to an accuracy of at least ± 35 mg m^{-3} (*i.e.*, a quarter of the present threshold limit value) between 0 and 140 mg m^{-3} of isophorone and at least to the nearest 70 mg m^{-3} between 140 and 280 mg m^{-3} of isophorone. Atmospheres of isophorone were set up by the permeation method. Parallel 500-ml samples were collected and analysed by the 2,4-dinitrophenylhydrazine method and by the proposed field test, the levels in the latter case being assessed by using the colour standards. Table III compares the results obtained with those based on the permeation rate.

TABLE III

COMPARISON OF THE RESULTS OF THE ANALYSIS OF ISOPHORONE ATMOSPHERES BY THE PROPOSED FIELD TEST AND TWO OTHER METHODS

	Isophorone concentration found, mg m^{-3}		
Sample	By proposed field test	By 2,4-dinitrophenylhydrazine test	From permeation rate
1	~35	36	36
2	70	70	69
3	70	75	75
4	~105	112	111
5	140	162	158
6	~210	222	221
7	280	235	242
8	280	305	300
9	>280	353	358

INTERFERENCES—

Other organic solvents besides cyclohexanone and 3-methylcyclohexanone were examined for their effect on the field test. Stock aqueous solutions or, for water-insoluble materials, stock solutions in aqueous methanol, were diluted with water and 2-ml samples of the diluted solutions treated by the field test procedure. Methanol concentrations in diluted solutions did not exceed 0·5 per cent. v/v and no interference from this source was observed whether or not material previously treated to reduce the carbonyl content was used. Under field test conditions, the substances listed in Table IV, at least up to the level indicated, did not interfere in the test. Diacetone alcohol was observed to interfere to some extent; 600 µg (equivalent to a 500-ml sample of an atmosphere containing five times its present threshold limit value) gave a colour of an intensity approximately equal to that of 70 µg of isophorone.

TABLE IV

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

Class	Compound	Weight, mg	p.p.m.*
Ketones	Acetone	18·0	15,000
	Butan-2-one	4·42	3000
	4-Methylpentan-2-one	3·07	1500
	5-Methylheptan-3-one	0·65	250
Aromatic hydrocarbons	Benzene	0·60	375
	Toluene	5·62	3000
	o-Xylene	3·25	1500
	m-Xylene	3·25	1500
Aromatic hydrocarbons with unsaturated side chain	Styrene	1·05	500
	α-Methylstyrene	1·20	500
	Vinyltoluene	1·20	500
Alcohols	Methanol	8·0	12,300
	Ethanol	14·2	15,000
	Propanol	3·75	3000
	Pentanol	1·81	1000
	Butanol	2·25	1500
	Cyclohexanol	1·50	750
	3-Methylcyclohexanol	3·52	1500
Glycol ethers	2-Ethoxyethanol	5·55	3000
	2-Methoxyethanol	0·60	375

* Equivalent concentration of vapour in a 500-ml sample of atmosphere if 100 per cent. trapping is achieved.

Of the compounds found to interfere in the field test, 3-methylcyclohexanone and cyclohexanone are the most likely to be present with isophorone in an industrial atmosphere. Consequently, standard atmospheres of these ketones were sampled by the field test. The absorbent solution trapped 84 to 88 per cent. and 98 to 100 per cent. of 3-methylcyclohexanone and cyclohexanone, respectively, and the extent of their interference was similar to that observed during work on standard solutions. Mixed atmospheres of each of these ketones with isophorone were generated, and the optical densities obtained with the field test agreed with those calculated from the permeation rates.

FIELD TEST FOR THE DETERMINATION OF ISOPHORONE VAPOUR IN AIR

APPARATUS—

All-glass absorbers of the type previously described.[5]

Aspirator—A rubber-bulb hand aspirator (obtainable from Siebe Gorman and Co. Ltd., Davis Road, Chessington, Surrey) adjusted to deliver 125 ml minute^{-1} of sample.

REAGENTS—

All reagents should be of analytical-reagent quality whenever possible.

Dodecamolybdophosphoric acid reagent—Dissolve 4 g of sodium hydroxide and 12·5 g of dodecamolybdophosphoric acid in water and dilute to 50 ml. Use the solution within 3 days of its preparation. (If the colour of the solution is more intense than that of the 140 mg m^{-3} isophorone standard, discard the solution and prepare another with fresh reagents.)

Dilute perchloric acid solution—Dilute 75 ml of 60 per cent. w/w perchloric acid to 90 ml with water.

Trisodium citrate solution, 30 per cent.—Dissolve 30 g of trisodium citrate dihydrate in water and make up to 100 ml.

These solutions must be kept in well stoppered glass bottles when not in use and stored in an isophorone-free atmosphere.

PROCEDURE—

Pipette 2 ml of water into the absorption tube in an uncontaminated atmosphere away from the suspected source of isophorone vapour, insert the inlet tube and connect the aspirator to the assembly. At the sampling site draw a 500-ml sample (four aspirations) of the atmosphere through the water. Remove the apparatus to an uncontaminated atmosphere, disconnect the aspirator, remove the inlet tube and to the absorption tube add, by pipette, 1 ml of dodecamolybdophosphoric acid reagent and 2 ml of dilute perchloric acid solution. Stopper the tube and mix the contents well by inverting it several times, ensuring that no liquid is lost through the side-arm.

Heat the solution in a boiling water bath for 15 minutes with the absorption tube suspended vertically and not touching the bottom of the bath. Remove the tube from the bath and cool by immersion for 5 minutes in a water-bath whose temperature does not exceed 27° C. Add 3 ml of the citrate solution, remove from the bath and mix by inverting the tube. After 5 minutes compare the colour of the sample solution with that of the colour standards, contained in identical tubes, by viewing through 5 cm depths of the respective liquids against a white (paper) background.

For safety a pipette filler should be used for dispensing the reagents used in this test.

PREPARATION OF COLOUR STANDARDS—

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

Blue component—Dissolve 60 g of copper sulphate pentahydrate, $CuSO_4.5H_2O$, in water, add 5 ml of concentrated hydrochloric acid and dilute to 200 ml.

Red component—Dissolve 50 g of cobalt(II) sulphate heptahydrate, $CoSO_4.7H_2O$, in 425 ml of water.

Prepare the colour standards by mixing these solutions in the proportions shown in Table V, diluting each to 100 ml with water and mixing thoroughly.

TABLE V

VOLUMES OF STANDARD POTASSIUM DICHROMATE, COPPER SULPHATE AND COBALT SULPHATE SOLUTIONS PER 100 ml TO PRODUCE ISOPHORONE FIELD TEST COLOUR STANDARDS

Isophorone standard, mg m^{-3}	0	70	140	280
Yellow component, ml	0·1	0·7	2·0	5·0
Blue component, ml	0·4	8·4	17·4	36·0
Red component, ml	0	3·4	6·0	9·0

As an alternative to the above colour standards, a series of permanent glass standards on a comparator disc is available from Tintometer Ltd., Salisbury.

DISCUSSION AND APPLICATION OF METHOD

Although it has been found necessary to recommend the use of the relatively dangerous perchloric acid, the preparation of the reagent solution required for any test can, and should, be carried out previously in a laboratory conforming to normal safety regulations regarding the handling of concentrated acids. Once the 2-ml aliquot of perchloric acid reagent has been added to the absorption tube, no further transfer of liquid involving this acid is necessary in the field test and its concentration in the final solution for colour measurement is less than 2 M.

Initially, in the development of this method, an apparent drawback was the necessity for the application of heat to speed the reducing effect of isophorone on the dodecamolybdophosphoric acid. This criticism was not entirely valid as the heating ensured that the reduction was independent of any ambient temperature.

Although this method was specifically developed for field use with visual standards, it has been shown that by using a spectrophotometer and standard solutions, a calibration curve for isophorone can be prepared, and from measured optical densities of samples, a more precise determination of the isophorone content of an atmosphere can be made. In this case, there is no need to remove the background heteropoly acid colour, and optical density measurements at 720 nm can be made after the heating stage, without addition of sodium citrate solution, particularly if no interference from cyclohexanone or 3-methylcyclohexanone is expected.

An assessment of the proposed method was carried out under field conditions when isophorone was being used in the processing of PVC. Parallel 500-ml samples of atmosphere were taken and analysed by the field method and the 2,4-dinitrophenylhydrazine check test. Results obtained were in agreement although it was noted that reagents and wet apparatus, when not in use, had to be kept well away from contaminated atmospheres. Significant absorption of isophorone from atmospheric concentrations as low as 35 mg m^{-3} was obtained with water and reagents stored in open vessels and even in stoppered glass containers which were only opened intermittently for the withdrawal of contents.

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

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A Scheme of Qualitative Analysis for Twenty Common Cations

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A qualitative scheme has been devised for the separation and subsequent identification of twenty common cations in 1 drop of unknown mixture by the ring-oven technique. The solution containing the unknown mixture is spotted on to a circular filter-paper, and it is then separated into different small groups containing not more than four cations by washing the spot with appropriate organic solvents. The separated cations are collected in the form of thin rings, 22 mm in diameter, on separate filter-papers. The rings of the deposited cations are then cut into sectors depending on the number of the metal ions present in a particular ring and tested for individual ions with the specific chromogenic reagents.

THIS paper describes the separation of twenty common cations by using a combination of solvent-extraction and ring-oven techniques. The method described here has an advantage over an earlier method[1] in that separations are achieved on the ring oven itself and no prior separations are necessary. The procedure is also less time consuming.

The spot containing the metal ions is washed with the organic solvents: (*i*), acetylacetone; (*ii*), acetylacetone - chloroform[2]; (*iii*), chloroform - acetone[2]; (*iv*), butanol; (*v*), diethyl ether - ethanol; (*vi*), 80 per cent. aqueous ethanol; and (*vii*), aqueous pyridine. The organic precipitants used are sodium diethyldithiocarbamate and 8-hydroxyquinoline. The organic solvents are used both as extracting agents and as solvents. These solvents often form some soluble as well as insoluble compounds with the cations. Sometimes the compounds formed may dissolve or remain insoluble in the solvents. The soluble portion moves to the ring zone, while the insoluble portion is retained at the centre of the original spot.

EXPERIMENTAL

APPARATUS—

A Weisz ring oven (National Appliance Co., Portland, Oregon, U.S.A.) with its accessories was used as described earlier.[3] A self-filling pipette (about 1·5 μl) was used throughout for spotting.

METAL SOLUTIONS—

Molar solutions of the following analytical-reagent grade chemicals were prepared: nitrates of silver(I), lead(II), mercury(II), copper(II), bismuth(III), cadmium(II), iron(III), chromium(III), aluminium(III), nickel(II), cobalt(II), zinc(II), manganese(II), barium(II), strontium(II), calcium(II) and magnesium(II); and sodium arsenate, potassium antimony tartrate and tin(II) oxide oxidised in a concentrated nitric acid solution. Equal volumes of each of these solutions were mixed and the resulting mixture used for the separations.

REAGENTS—

Sodium diethyldithiocarbamate solution—Dissolve 1·0 g of sodium diethyldithiocarbamate (analytical-reagent grade) in 100 ml of water.

8-*Hydroxyquinoline solution*—Dissolve 2·0 g of 8-hydroxyquinoline in 6 ml of glacial acetic acid, add 10 ml of water and 6 ml of ammonia solution (sp.gr. 0·91) and make the volume up to 100 ml. The pH of the 8-hydroxyquinoline solution was 5·1.

Solvents for washing—The analytical-reagent grade solvents used were: (*i*), acetylacetone; (*ii*), 1 + 4 acetylacetone - chloroform; (*iii*), 5 + 2 chloroform - acetone; (*iv*), butanol; (*v*), 1 + 1 diethyl ether - ethanol; (*vi*), 80 per cent. aqueous ethanol; and (*vii*), 20 per cent. aqueous pyridine. All other chemicals used were of analytical-reagent grade.

DETECTING REAGENTS—

Aluminon—Prepare a solution containing 0·1 per cent. w/v of aluminon and 1 per cent. w/v of ammonium acetate in water.

Anthraquinone-1-*azo*-4-*dimethylaniline*—Prepare a 0·1 per cent. w/v solution of the reagent in 30 per cent. v/v ethanol with 2 ml of hydrochloric acid (sp.gr. 1·12).

Brucine citrate—A 50 per cent. w/v citric acid and 6 per cent. w/v brucine solution in water.

Cadion 2B, 0·1 *per cent. w/v in ethanol.*

Dimethylglyoxime, 1 *per cent. w/v in ethanol.*

4-*Dimethylaminobenzylidenerhodanine,* 0·05 *per cent. w/v in acetone.*

3,3′-*Dimethylnaphthidine*—Make a saturated solution in 0·1 N hydrochloric acid.

Diphenylcarbazide, 0·2 *per cent. w/v in ethanol.*

Dithizone, 0·05 *per cent. w/v in carbon tetrachloride.*

Magneson(II)—Prepare a 0·001 per cent. w/v solution of magneson(II) in N sodium hydroxide.

1-*Nitroso*-2-*naphthol,* 0·05 *per cent. w/v in ethanol.*

Potassium ferrocyanide, 0·5 *per cent. w/v in water.*

Rhodamine B, 0·01 *per cent. w/v in water.*

Rubeanic acid, 1 *per cent. w/v in ethanol.*

Sodium rhodizonate, 0·2 *per cent. w/v in water.*

Zirconium fluoride - alizarin—Prepare a solution of 0·1 per cent. w/v of alizarin S, 0·5 per cent. of zirconium oxychloride and 1 per cent. of sodium fluoride in water.

Filter-paper—Circles of Whatman No. 1 filter-paper for chromatography (55 mm diameter) were used.

PROCEDURE—

The solution of the mixture was spotted on to the marked centre of a circular filter-paper with a self-filling micro pipette and dried over the ring oven at 105° C. After drying, the spotted portion (disc) was punched out. This was placed on a filter-paper circle 2 and treated with 1 drop of N nitric acid. The moist disc was then washed ten times with 20 per cent. acetylacetone in chloroform. Mercury, copper, iron and tin moved to the ring zone (A) on paper 2. The disc containing the remaining sixteen cations was kept on paper 3, and was again treated with 1 drop of N nitric acid and washed six to eight times with pure acetylacetone. Thus, bismuth, arsenic and antimony were transferred to ring zone (B). The disc now contained thirteen cations, and was kept on paper 4, moistened with 1 drop of N nitric acid and washed with butanol; zinc was transported to ring zone (C). The disc, containing the remaining cations, was put in the disc holder supplied with the ring oven and fumed over concentrated ammonia solution. It was then treated with three drops of 1 per cent. sodium diethyldithiocarbamate, after which it was placed on paper 5 and washed about ten times with a (5 + 2) mixture of chloroform and acetone. Lead, manganese, nickel and cobalt ions moved to ring zone (D). The disc was again treated with three drops of 1 per cent. sodium diethyldithiocarbamate, dried, kept on paper 6 and washed ten times with 50 per cent. diethyl ether in ethanol. Calcium, cadmium and strontium ions moved to ring zone (E), leaving silver, aluminium, chromium, barium and magnesium ions on the disc. The disc was treated with four drops of 2 per cent. 8-hydroxyquinoline solution, dried, put on paper 7 and washed with 80 per cent. ethanol to move aluminium, magnesium and barium to ring zone (F). The disc was put on paper 8 and washed with 20 per cent. aqueous pyridine so that silver moved to ring zone (G) and only chromium remained on the disc. The disc was treated with hydrogen peroxide and ammonia solution and heated in the ring oven. It was then put on paper 9 and washed with 80 per cent. ethanol to take chromium(VI) into ring zone (H). The disc was then discarded. The procedure is represented schematically in the chart.

IDENTIFICATION—

The filter-papers containing the metal ions in the form of a ring were cut into sectors depending on the number of the metal ions present in a particular ring. Each sector was tested for the individual ions with the reagents described in Table I.

SCHEMATIC QUALITATIVE ANALYSIS OF TWENTY COMMON CATIONS

The mixture was spotted on a filter-paper circle, dried and a disc punched out. This disc was placed on paper 2, 1 drop of N nitric acid added and the moist disc was then washed with 20 per cent. acetylacetone in chloroform

Ring A (Paper 2)
Hg, Cu, Fe, Sn

Disc
Ag, Pb, Bi, Cd, As, Sb, Al, Cr, Zn, Ni, Co, Mn, Ca, Ba, Sr, Mg
Disc placed on paper 3, one drop of N HNO_3 added and moist disc washed with pure acetylacetone

Ring B (Paper 3)
Bi, As, Sb

Disc
Ag, Pb, Cd, Al, Cr, Zn, Ni, Co, Mn, Ba, Ca, Sr, Mg
Disc put on paper 4 and washed with butanol

Ring C (Paper 4)
Zn

Disc
Ag, Pb, Cd, Al, Cr, Ni, Co, Mn, Ba, Ca, Sr, Mg
Disc fumed over concentrated ammonia solution. Three drops of 1 per cent. sodium diethyldithiocarbamate were then added. The disc was put on paper 5 and washed with a (5 + 2) mixture of chloroform and acetone

Ring D (Paper 5)
Pb, Mn, Ni, Co

Disc
Ag, Cd, Al, Cr, Ba, Ca, Sr, Mg
Three drops of 1 per cent. sodium diethyldithiocarbamate were added to the disc, which was dried, placed on paper 6 and washed with 50 per cent. diethyl ether in ethanol

Ring E (Paper 6)
Cd, Ca, Sr

Disc
Ag, Al, Cr, Ba, Mg
Three drops of 2 per cent. 8-hydroxyquinoline solution were added to the disc, which was dried, placed on paper 7 and washed with 80 per cent. ethanol

Ring F (Paper 7)
Al, Mg, Ba

Disc
Ag, Cr
Disc placed on paper 8 and washed with 20 per cent. aqueous pyridine

Ring G (Paper 8)
Ag

Disc
Cr
Disc treated with H_2O_2 and NH_4OH, heated in the oven, placed on paper 9 and washed with 80 per cent. ethanol

Ring H (Paper 9)
Cr

Disc
(Discard)

TABLE I

REAGENTS FOR METAL IONS[3,4]

Metal ion	Pre-treatment	Reagent	Colour
		Ring A	
Hg(II)	Dilute HNO_3	4-Dimethylaminobenzylidene rhodanine in acetone	Violet
Cu(II)	—	Ethanolic rubeanic acid and fume over ammonia	Olive green
Fe(III)	—	$K_4Fe(CN)_6$ solution	Blue
Sn(IV)	—	Ethanolic anthraquinone-1-azo-4-dimethylaniline	Blue - violet
		Ring B	
Bi(III)	KI solution	Brucine citrate solution	Deep orange
As(V)	—	Gutzeit test	Yellow - black
Sb(III)	Treated with (1+1) HCl + a few crystals of $NaNO_2$	Aqueous rhodamine B	Violet
		Ring C	
Zn(II)	—	Dithizone in carbon tetrachloride	Purple - red
		Ring D	
Pb(II)	—	Aqueous sodium rhodizonate	Reddish violet
Mn(II)	Treated with 0·05 N NaOH solution and rinsed with water	3,3′-dimethylnaphthidine in 0·1 N HCl	Purple
Ni(II)	—	Dimethylglyoxime and fumed over ammonia	Red
Co(II)	—	Ethanolic 1-nitroso-2-naphthol	Brown - red
		Ring E	
Cd(II)	0·5 N NaOH solution	Ethanolic Cadion 2B	Pinkish red
Ca(II)	—	Zirconium fluoride - alizarin	Red - violet
Sr(II)	—	Aqueous sodium rhodizonate	Red
		Ring F	
Al(III)	—	Aqueous aluminon containing CH_3COONH_4	Bright red
Mg(II)	—	Magneson II in N NaOH	Deep blue
Ba(II)	—	Aqueous sodium rhodizonate	Red
		Ring G	
Ag(I)	—	H_2S water	Black
		Ring H	
Cr(III)	Treated with $H_2O_2 + NH_4OH$ and heated on the ring oven	Ethanolic diphenylcarbazide + dilute H_2SO_4	Violet

This procedure has been tried with a number of artificial mixtures and has been found to be satisfactory when the amount of a metal in 1 drop (1·5 μl) is between 2 and 10 μg. The total time required for the analysis is about 1 hour. For the analysis of an unknown mixture, a solution is prepared as usual with nitric acid. The interfering anions, *e.g.*, phosphate, fluoride, borate and oxalate, should be absent.

For spotting on the paper, 5 drops of the mixture are taken with the self-filling micro pipette (each drop being about 1·5 μl). To keep the diameter of the spot (10 mm) within reasonable limits, each drop should be dried before introducing a second. This is also necessary when more than 1 drop of the reagent is added.

The advantages of this scheme over previous ones[1,5,6] are that it is less time consuming; no prior separations are necessary; all the separations, in groups as well as of the individual cations, are done on the ring oven; the number of members separated in an individual group is small, and thus interferences of cations in a single ring are minimised; and, finally, only one disc is used throughout the entire separation.

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Communication

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

THEORETICAL ASSESSMENT OF THE NITROUS OXIDE - HYDROGEN FLAME IN SPECTROSCOPIC ANALYSIS

MANY apparent discrepancies are to be found in the literature because attempts have been made to compare results obtained in flame-spectroscopic analysis under varying experimental conditions. Frequently these differences arise, or the comparisons drawn are not conclusive, because a different optical arrangement has been used with flames of unknown or different gas composition with various burner designs and occasionally even with a different method of measurement (*i.e.*, emission or absorption). A recent example of this appears in the conflicting reports on the suitability of the nitrous oxide - hydrogen flame as an atom reservoir for analytical spectroscopic purposes.[1,2,3] We have undertaken a theoretical study to eliminate such differences and provide a more objective evaluation of several flames as atom reservoirs. This communication describes some of these results, which it is hoped will elucidate the value of the nitrous oxide - hydrogen flame in emission or absorption-spectroscopic analysis.

The method employed involves calculation of equilibrium concentrations of flame species by minimisation of free energy (Gibbs function) by using the basis of an established digital computer programme[4] over a range of temperatures and flame stoicheiometries. After some modification (J. E. Chester, R. M. Dagnall and M. R. G. Taylor, unpublished work), this programme (with an IBM 7094 computer) has been used for studying the composition of a variety of flames with and without the introduction of several elements in aqueous solution, which on comparison provide useful analytical data. Particular attention has been given to the nitrous oxide - acetylene and nitrous oxide - hydrogen flames and their use as atom reservoirs for elements that tend to form refractory oxides, *e.g.*, aluminium and silicon.

It is assumed in the application of the method that chemical equilibrium is attained and the gaseous species exhibit ideal gas behaviour. Also, air entrainment is not considered because no measurements of this are currently available. Thus, the results can be considered as approximating to the conditions existing in the interconal region of a flame shielded flame (K. M. Aldous, R. F. Browner, R. M. Dagnall and T. S. West, unpublished work). A range of flame temperatures has been investigated to account for temperature differences reported in the literature and heights of measurement in the flames.

TABLE I

PERCENTAGE ATOMISATION OF ALUMINIUM AND SILICON IN THE NITROUS OXIDE - ACETYLENE FLAME

Flame composition, C/O* ratio	Temperature, °K†	Volume, per cent.		Atomisation, per cent.	
		O	O_2	Al‡	Si‡
1·0§	2500	8×10^{-4}	$3{\cdot}1 \times 10^{-5}$	24·7	$1{\cdot}6 \times 10^{-3}$
	2900	$2{\cdot}4 \times 10^{-2}$	$9{\cdot}5 \times 10^{-4}$	86·8	$1{\cdot}2 \times 10^{-2}$
	3200	$1{\cdot}6 \times 10^{-1}$	$5{\cdot}8 \times 10^{-3}$	88·9	$4{\cdot}0 \times 10^{-2}$
1·25	2500	8×10^{-8}	3×10^{-13}	95·3	14·2
	2900	1×10^{-6}	$1{\cdot}5 \times 10^{-12}$	97·2	74·2
	3200	$5{\cdot}4 \times 10^{-6}$	$6{\cdot}5 \times 10^{-12}$	98·1	92·4

* Oxygen present in nitrous oxide.

† Maximum temperature of a conventional pre-mixed flame is about 3050° K.[5]

‡ 10^{-4} g atom of element per mole of feed (1 mole of feed = $2N_2O \times xC_2H_2 + 2yH_2O/(2 + x + 2y)$ where y is the number of moles of H_2O reaching the flame per mole of N_2O. Values used are typical of those measured in the authors' laboratories with conventional analytical pre-mixed flames, *e.g.*, an aqueous solution uptake rate of about 5 ml minute^{-1}, about 5 per cent. nebuliser efficiency and a total nebuliser gas flow-rate of about 5 l minute^{-1}).

§ Refers to $2N_2O + C_2H_2 \rightleftharpoons 2CO + H_2 + 2N_2$.

It is considered that the results obtained by this method show both qualitative and quantitative trends, and comparisons between these "ideal" flames are valuable in the context of analytical flame spectroscopy.

TABLE II

PERCENTAGE ATOMISATION OF ALUMINIUM AND SILICON IN THE NITROUS OXIDE - HYDROGEN FLAME

Flame composition, H_2/O* ratio	Temperature, °K†	Volume, per cent.		Atomisation, per cent.	
		O	O_2	Al‡	Si‡
1·0§	2500	$1{\cdot}7 \times 10^{-1}$	1·3	$5{\cdot}1 \times 10^{-3}$	$6{\cdot}3 \times 10^{-6}$
	2900	1·3	2·6	3·1	$2{\cdot}1 \times 10^{-4}$
	3200	4·0	3·4	27·9	$1{\cdot}6 \times 10^{-3}$
1·5	2500	$1{\cdot}9 \times 10^{-2}$	$1{\cdot}8 \times 10^{-2}$	$1{\cdot}3 \times 10^{-1}$	$6{\cdot}6 \times 10^{-5}$
	2900	$4{\cdot}9 \times 10^{-1}$	$3{\cdot}8 \times 10^{-1}$	12·5	$5{\cdot}6 \times 10^{-4}$
	3200	2·4	1·2	38·9	$2{\cdot}7 \times 10^{-3}$
2·0	2500	$9{\cdot}4 \times 10^{-3}$	$4{\cdot}3 \times 10^{-3}$	$3{\cdot}7 \times 10^{-1}$	$1{\cdot}4 \times 10^{-4}$
	2900	$2{\cdot}7 \times 10^{-1}$	$1{\cdot}1 \times 10^{-1}$	30·8	$1{\cdot}1 \times 10^{-3}$
	3200	1·6	$5{\cdot}3 \times 10^{-1}$	48·6	$4{\cdot}2 \times 10^{-3}$

* Oxygen present in nitrous oxide.

† Maximum temperature of a conventional pre-mixed flame is about 2920° K.[3]

‡ 10^{-4} g atom of element per mole of feed

(1 mole of feed = $N_2O + xH_2 + yH_2O/(1 + x + y)$ where y is the number of moles of H_2O reaching the flame per mole of N_2O. Values used are typical of those measured in the authors' laboratories with conventional analytical pre-mixed flames, *e.g.*, an aqueous solution uptake rate of about 5 ml minute^{-1}, about 5 per cent. nebuliser efficiency and total nebuliser gas flow-rate of about 5 l minute^{-1}).

§ Refers to $N_2O + H_2 \rightleftharpoons N_2 + H_2O$.

RESULTS AND CONCLUSIONS

The results in Tables I and II show clearly that the nitrous oxide - hydrogen flames examined are highly oxidising in nature compared with the nitrous oxide - acetylene flames and that the degree of atomisation of aluminium and silicon in the former flame type is sharply temperature dependent. For both flames the isothermal degree of atomisation is inversely related to the concentration of atomic and molecular oxygen. Calculations also show that the isothermal degree of atomisation of these elements in the nitrous oxide - acetylene flame is directly related to the concentrations of the HCN, CN and atomic carbon species [the concentration of HCN and CN being about two orders of magnitude greater than that of atomic carbon (J. E. Chester, R. M. Dagnall and M. R. G. Taylor, unpublished work)]. The apparent high degree of atomisation of aluminium in the "ideal" stoicheiometric nitrous oxide - acetylene flame results from the absence of the entrained air present in conventional analytical flames.

The high temperature, low background nitrous oxide - hydrogen flame can be considered to be satisfactory for thermal emission of elements that are readily atomised.[1] It may also be valuable for reducing some chemical interferences encountered in both emission and absorption-spectroscopic techniques without producing a high degree of ionisation.[2,3] However, its value for the determination of those elements that are prone to refractory oxide formation is questionable. In these instances the degree of atomisation depends largely on the flame temperature and hence burner design and flame characteristics. This observation may explain why Willis, Fassel and Fiorino[3] found less ionisation of calcium at low concentrations in a long path nitrous oxide - hydrogen flame than Dagnall, Thompson and West[1] with a circular flame.

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Book Reviews

ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGION. Edited by Dr. L. LANG. Collaborators DR. A. BARTECKI, DR. G. HORVATH, DR. J. SZOKE and DR. G. VARSANYI. VOLUME XI. Pp. 400. Budapest: Akademiai Kiado. 1969. Price 135s.

This volume adds 190 to the substances covered by the collection of data for nearly 3000 compounds published in Volumes I to X. There are data on phenylsilanes, a phenylgermane and phenyltins. Curves are included for natural steroid hormones and some related synthetic products. The spectra of numerous anilides are given.

The collection contains absorption data for many compounds that have not often been studied, but there was less need to include data on, *e.g.*, L-tryptophan and numerous simple di-substituted benzene derivatives for which there is already a wealth of accessible information. It must, however, be agreed that as the series of volumes lengthens, the cumulative value increases. R. A. MORTON

ELEMENTARY REACTION KINETICS. By J. L. LATHAM, B.Sc., Ph.D., F.R.I.C. Second Edition. Pp. xii + 175. London: Butterworth & Co. (Publishers) Ltd. 1969. Price 18s.

This book gives an excellent introduction to the subject of reaction kinetics and would be a suitable and inexpensive text to recommend to students taking introductory lectures on this subject in degree or Higher National Diploma courses. There are now available a number of texts covering a similar subject area, but perhaps the advantage of Dr. Latham's book lies in its readability. Too few of such books succeed in putting over to the new student either the practical reasons for carrying out kinetic studies of chemical reactions or the application of the results obtained, but this book manages to convey something of each. I particularly liked the inclusion of experimental data in the "worked examples," as new students frequently find difficulty in proceeding from their data to the final rate constant and reaction mechanism of the reaction. The author might consider including a few problems of a similar nature in future editions.

J. M. OTTAWAY

ELECTRONIC STRUCTURES IN SOLIDS. Lectures presented at the Second Chania Conference, held in Chania, Crete, June 30–July 14, 1968. Edited by E. D. HAIDEMANAKIS. Pp. xvi + 459. London: Heyden & Son Ltd. 1969. Price £11 15s.

This book provides a detailed record of the proceedings of an international conference on current research on the electronic structure of solids. It includes some thirty contributions which cover underlying theory and recent experimental results for a range of topics including energy-band theory, narrow-band semiconductors, transition-metal oxides, impurity states, tunnelling spectroscopy, neutron spectroscopy, superconductivity, magneto-optics, non-linear optics, light scattering, excitons, lasers, and the Gunn and accousto-electric effects. There is some discussion of the rôle of chemical impurities in semiconductor and electro-optic devices, but the book's main appeal will be for those concerned with detailed solid state physics and crystallographic studies of these materials. R. K. WEBSTER

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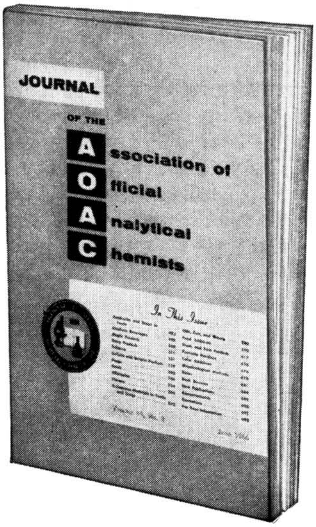
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The Extraction and Determination of Copper, Chromium and Arsenic in Preserved Softwoods

A method is described for the rapid extraction and determination of copper, chromium and arsenic in preservative-treated softwoods. A saw cut is made through the cross-section of the sample and the preserving compounds are leached quantitatively from the sawdust with a mixture of dilute sulphuric acid solution and hydrogen peroxide solution. Copper, chromium and arsenic in aliquots of the leach solution are allowed to react with zinc dibenzyldithiocarbamate, diphenylcarbazide and ammonium molybdate - hydrazine reagent, respectively, and the determinations are completed by the spectrophotometric measurement of the coloured complexes formed.

The procedure has been used to determine copper, chromium and arsenic in the cross-sections of preserved Baltic redwood, Douglas fir, lodgepole pine and silver fir.

A. I. WILLIAMS

Forest Products Research Laboratory, Princes Risborough, Aylesbury, Bucks.

Analyst, 1970, **95**, 670-674.

Gas-chromatographic Determination of Chlorcholine Chloride Residues in Natural Tomato Juice

A method is presented for the gas-chromatographic determination of chlorcholine chloride at residue levels. The technique is based on prior reaction with sodium benzenethiolate. When this procedure is extended to plant extracts, some pre-purification and concentration must be carried out before the reaction with the benzenethiolate salt.

F. TAFURI, M. BUSINELLI and P. L. GIUSQUIANI

Istituto di Chimica Agraria dell'Università di Perugia, Centro Chimica degli Antiparassitari del C.N.R., Italy.

Analyst, 1970, **95**, 675–679.

The Determination of Cyclohexylamine by Electron-capture Gas Chromatography

Cyclohexylamine is allowed to react with 1-fluoro-2,4-dinitrobenzene and the 2,4-dinitrophenyl derivative is measured by electron-capture gas chromatography. Procedures are described for the determination of cyclohexylamine in cyclamates and in soft drinks down to levels of 1 p.p.m. and 0·1 p.p.m., respectively; the technique could also be of value when the content of cyclohexylamine in urine is required.

R. E. WESTON and B. B. WHEALS

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

Analyst, 1970, **95**, 680–682.

A Simple Field Test for the Determination of Acetone Vapour in Air

A field method is described for the determination of acetone vapour in air in concentrations up to 2000 p.p.m. v/v. The vapour is collected in a solution containing sodium nitroprusside and ammonium acetate. On the addition of ammonia solution, a coloured complex is formed, which is compared visually with standards after 10 minutes. Two series of standards are used, the choice of which depends upon the temperature at which colour development is carried out. Both apparatus and method are simple and a complete determination can be carried out in about 15 minutes.

A. F. SMITH and R. WOOD

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

Analyst, 1970, **95**, 683–690.

REPORTS OF THE ANALYTICAL METHODS COMMITTEE
Reprinted from *The Analyst*

Additives in Animal Feeding Stuffs

The following thirteen Reports dealing with Additives in Animal Feeding Stuffs may be obtained direct from The Society for Analytical Chemistry, Book Department, 9/10 Savile Row, London, WIX IAF (not through Trade Agents), price 1s. 6d. each to members of the Society and 2s. 6d. each to non-members.

The Determination of Penicillin, Chlortetracycline and Oxytetracyline in Diet Supplements and Compound Feeding Stuffs.
The Determination of Stilboestrol and Hexoestrol in Compound Feeding Stuffs.
The Determination of Nitrofurazone in Compound Feeding Stuffs.
The Determination of Water-soluble Vitamins in Compound Feeding Stuffs.
The Determination of Fat-soluble Vitamins in Diet Supplements and Compound Feeding Stuffs.
The Determination of Amprolium in Animal Feeding Stuffs.
The Determination of Sulphaquinoxaline.
The Determination of Acinitrazole.
The Determination of Ethopabate in Feeds.
The Determination of Furazolidone in Feeds.
The Determination of Dimetridazole in Animal Feeds.
The Determination of Dinitolmide (Zoalene) in Animal Feeds.
The Determination of Amprolium, Sulphaquinoxaline and Ethopabate when Present together in Animal Feeds (*Gratis*).

A Simple Field Test for the Determination of Isophorone Vapour in Air

A field method is described for determining isophorone vapour in air at concentrations of up to 280 mg m^{-3}. The vapour is collected in water and determined by its reduction of dodecamolybdophosphoric acid to molybdenum blue in the presence of perchloric acid. After removal of the yellow background colour of unreacted dodecamolybdophosphoric acid with sodium citrate solution, the isophorone concentration is determined by comparing the residual molybdenum blue coloration with a series of colour standards. The apparatus used is simple and the time taken to complete an analysis is about 30 minutes.

P. ANDREW and R. WOOD

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

Analyst, 1970, **95**, 691–697.

A Scheme of Qualitative Analysis for Twenty Common Cations

A qualitative scheme has been devised for the separation and subsequent identification of twenty common cations in 1 drop of unknown mixture by the ring-oven technique. The solution containing the unknown mixture is spotted on to a circular filter-paper, and it is then separated into different small groups containing not more than four cations by washing the spot with appropriate organic solvents. The separated cations are collected in the form of thin rings, 22 mm in diameter, on separate filter-papers. The rings of the deposited cations are then cut into sectors depending on the number of the metal ions present in a particular ring and tested for individual ions with the specific chromogenic reagents.

ANIMESH K. GHOSE and ARUN K. DEY

Chemical Laboratories, University of Allahabad, Allahabad, India.

Analyst, 1970, **95**, 698–701.

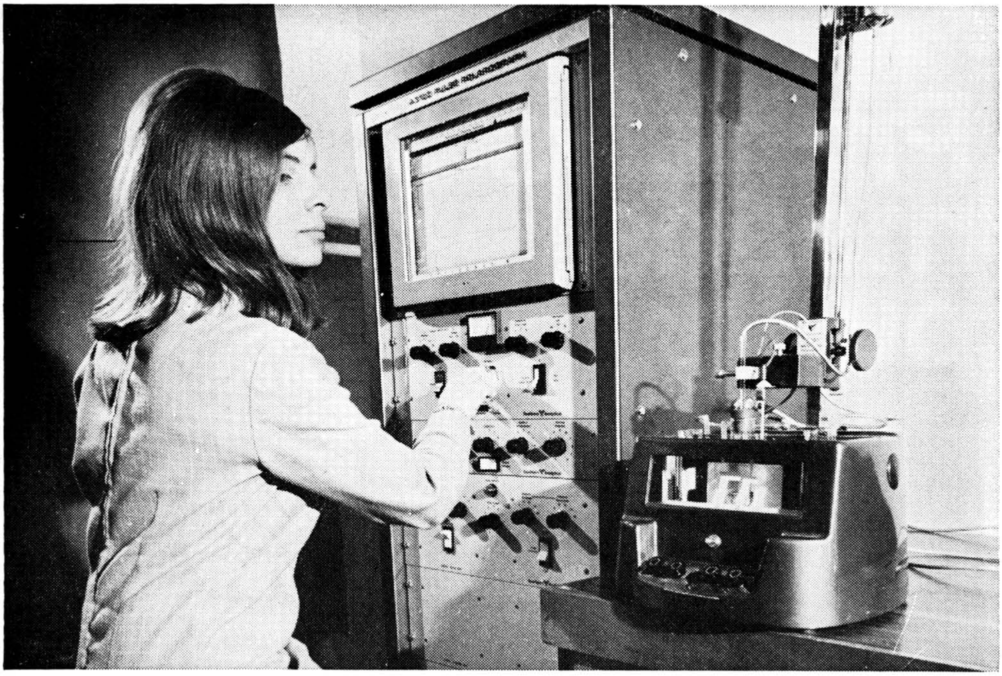
Theoretical Assessment of the Nitrous Oxide - Hydrogen Flame in Spectroscopic Analysis

Communication

J. E. CHESTER, R. M. DAGNALL and M. R. G. TAYLOR

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

Analyst, 1970, **95**, 702–703.



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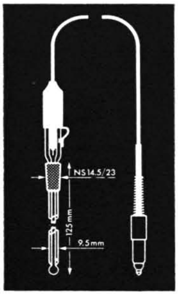

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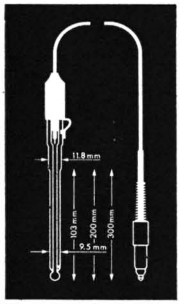

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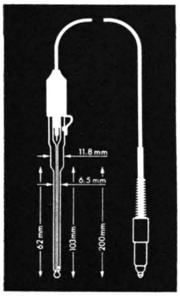

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