The ANALYST

The Journal of the Society for Analytical Chemistry

A monthly International Publication
dealing with all branches of
Analytical Chemistry

Published by the
SOCIETY FOR ANALYTICAL CHEMISTRY

Volume 96
No. 1145, Pages 537-608 **August, 1971**

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

OFFICES OF THE SOCIETY: 9/10 SAVILE ROW, LONDON, WIX IAF

Telephone: 01-734 9864

Advertisement Agent: J. Arthur Cook, 9 Lloyd Square, London, WC1 9BA
Telephone: 01-837 6315

Published by The Society for Analytical Chemistry
Distributed by The Chemical Society, Publications Sales Office,
Blackhorse Road, Letchworth, Herts., SG6 1HN

Volume 96, No. 1145

August, 1971

THE ANALYST

Summaries of Papers in this Issue

Observations on the Theory of Action of Visual Indicators

Earlier treatments of visual indicator theory have made the tacit assumption that the molar absorptivities of the two forms of the indicator are equal, so equating the conditional indicator constant with the transition point and hence causing some confusion in certain instances. A more exact treatment of oxidation - reduction and ion-combination indicator parameters, conditional constant, transition point, transition range and transition interval, including the effects of molar absorptivities, indicator concentration and stoicheiometry, is outlined.

E. BISHOP

Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.

Analyst, 1971, **96**, 537–549.

An Automatic Capillary Viscometer
Part II. Automatic Apparatus for Viscometric Titrations

The basic principles of viscometric titrations are considered and examples of applications to a variety of analytical and other determinations are suggested.

An addition to the automatic capillary viscometer described in Part I provides for the introduction of successive measured volume increments of a solvent or solution, admixture with the solution already present in a suspended-level viscometer and the electronic measurement of the flow time including printing-out the results.

By using the new apparatus it is possible expeditiously to determine the B-coefficients of the Jones - Dole equation for the viscosity of electrolytes and the intrinsic viscosity coefficients for solutions of polymers, and to perform a wide variety of acid - base titrations. Practical examples of these determinations are given in illustration.

R. B. SIMPSON, J. S. SMITH and H. M. N. H. IRVING

Department of Inorganic and Structural Chemistry, The University, Leeds 2.

Analyst, 1971, **96**, 550–561.

An Inert Dilution Method for the X-ray Fluorescence Analysis of Niobate - Tantalate Mineral Concentrates

An X-ray fluorescence method, in which iron(III) oxide is used as inert diluent, is described for the determination of niobium, tantalum, tin and titanium in concentrates of polymineral composition. No time-consuming fusion procedures or tedious calculations are involved. The simplicity and rapidity of the method merit its use in routine analysis. Good agreement with chemical analysis is obtained.

Y. C. WONG and S. SEEVARATNAM

Geological Survey of Malaysia, Perak, Malaysia.

Analyst, 1971, **96**, 562–564.

Determination of Ammonium in Soil Extracts by an Automated Indophenol Method

An automated method is described for the determination of ammonium in 2 N potassium chloride soil extracts. The determination is based on the indophenol blue method following a dialysing step. As little as 0·03 mg l^{-1} of ammonium-nitrogen can be determined. The recoveries have been investigated for a number of different soil types and satisfactory results were obtained. Determinations can be carried out at the rate of thirty samples per hour.

A. R. SELMER-OLSEN

Agricultural College of Norway, Vollebekk, Norway.

Analyst, 1971, **96**, 565–568.

THE ANALYST

Observations on the Theory of Action of Visual Indicators

By E. BISHOP

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

Earlier treatments of visual indicator theory have made the tacit assumption that the molar absorptivities of the two forms of the indicator are equal, so equating the conditional indicator constant with the transition point and hence causing some confusion in certain instances. A more exact treatment of oxidation - reduction and ion-combination indicator parameters, conditional constant, transition point, transition range and transition interval, including the effects of molar absorptivities, indicator concentration and stoicheiometry, is outlined.

Visual indicators, with few exceptions, share the nature of the titrimetric reaction to which they are applied. Basically, there are only two types of reaction: oxidation - reduction, in which electrons constitute the common factor, and ion-combination, in which main and indicator reactions share a common ion. To conduct visual indicator titrations intelligently, knowledge is required of the equivalence point, pB, or potential, and the quality, Q,[1] of the titration, and the conditional constant, transition point, transition range and transition interval of the indicator. Earlier accounts of indicator theory[2,3] have neglected the possibility that the molar absorptivities of the two forms of the indicator may be different, and so have equated indicator constant and transition point. The approximation is often adequate in practice, but has led to confusion when the disparity in molar absorptivities is large, for example, in the case of tris(1,10-phenanthroline)iron(II)/(III),[4] where the ratio of molar absorptivities is 20:1, and while the formal potential in 1·0 M sulphuric acid is 1·06 V, the transition point is 1·14 V. The influence of indicator concentration for unsymmetrical stoicheiometries is also demonstrated, and some further points on choice of indicators are made. Unsymmetrical stoicheiometries are rare among oxidation - reduction indicators, but not uncommon among ion-combination indicators; the unsymmetrical case is, however, generally treated first and the solution then simplified to the more common symmetrical case, in accordance with current physicochemical practice. Derivations of equations are given in the Appendix.

Oxidation - reduction indicators

The indicator reaction can be represented as

$$a\ Ind_{ox} + n_{ind}\ e \rightleftharpoons b\ Ind_{red} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

and the few that are properly reversible show Nernstian potentials—

$$E_{ind} = E'_{oind} + \frac{2{\cdot}3\,RT}{n_{ind}\,F} \log_{10} \frac{[Ind_{ox}]^a}{[Ind_{red}]^b} \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The two forms, Ind_{ox} and Ind_{red}, display different signals of colour, fluorescence, etc. When both forms are present at unit concentration or, if a = b, at equal concentration, then the logarithmic term becomes zero and $E_{ind} = E'_{oind}$, where E'_{oind} is the *conditional potential*, the *indicator constant* for this class of indicator. The conditions implied are those of the titration to which the indicator is to be applied, and the measurement of E'_{oind} made under those conditions, and the value of E'_{oind} applies to those precise conditions alone and will change if the conditions are changed.

Two-colour indicators—

Transition point—For a two-colour indicator the transition point is the potential at which the two colours have equal intensity. If the oxidised and reduced forms of the indicator have molar absorptivities of ϵ_{ox} and ϵ_{red}, respectively, then from Beer's law the two colours are of equal intensity when

$$\epsilon_{ox}\,[Ind_{ox}]_{trans} = \epsilon_{red}\,[Ind_{red}]_{trans} \quad .. \quad .. \quad .. \quad (3)$$

$$\therefore \frac{[\mathrm{Ind_{ox}}]_{\mathrm{trans}}}{[\mathrm{Ind_{red}}]_{\mathrm{trans}}} = \frac{\epsilon_{\mathrm{red}}}{\epsilon_{\mathrm{ox}}} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

The transition point potential will therefore be, when a = b,

$$E_{\mathrm{trans}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{[\mathrm{Ind_{ox}}]_{\mathrm{trans}}}{[\mathrm{Ind_{red}}]_{\mathrm{trans}}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon_{\mathrm{red}}}{\epsilon_{\mathrm{ox}}} \quad .. \quad (5)$$

Hence the indicator constant and transition potential are equal only when $\epsilon_{\mathrm{ox}} = \epsilon_{\mathrm{red}}$.

When a ≠ b, and reaction (1) is unsymmetrical because of a change in molecularity, then the system becomes dependent on concentration and also on the values of the stoicheiometric coefficients. To minimise the complexity of the expressions, let the total concentration of the indicator at the appropriate point in the titration (here the transition point) be expressed in terms of the form in which the indicator is added (here the reduced form, c_{indred}). This concentration is calculated from the amount of indicator added and the total volume of the solution at the appropriate point in the titration. Thus, if v_{ind} ml of $\mathrm{Ind_{red}}$ of concentration c_{ind} mol l^{-1} are used, the sample volume is v_{d} ml and the titrant volume is v_{trans} ml, then (total volume) $= v_{\mathrm{ind}} + v_{\mathrm{d}} + v_{\mathrm{trans}}$ and $c_{\mathrm{indred}} = c_{\mathrm{ind}}\, v_{\mathrm{ind}}$/(total volume). The transition point potential is

$$E_{\mathrm{trans}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon^{\mathrm{a}}_{\mathrm{red}}}{\epsilon^{\mathrm{b}}_{\mathrm{ox}}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \left(\frac{\mathrm{a}\, c_{\mathrm{indred}}}{\mathrm{a}\, \epsilon_{\mathrm{ox}} + \mathrm{b}\, \epsilon_{\mathrm{red}}} \right)^{(\mathrm{a}-\mathrm{b})} \quad .. \quad (6)$$

If the indicator is added in the oxidised form to give a total concentration of c_{indox}, substitution of this value and the coefficient, b, in the numerator of the final logarithmic term in equation (6) gives the transition potential

$$E_{\mathrm{trans}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon^{\mathrm{a}}_{\mathrm{red}}}{\epsilon^{\mathrm{b}}_{\mathrm{ox}}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \left(\frac{\mathrm{b}\, c_{\mathrm{indox}}}{\mathrm{a}\, \epsilon_{\mathrm{ox}} + \mathrm{b}\, \epsilon_{\mathrm{red}}} \right)^{(\mathrm{a}-\mathrm{b})} \quad .. \quad (7)$$

The *transition range* of a two-colour indicator is subjective in that the human eye does not perceive all tints equally and the visual response varies among individuals. Properly, therefore, the transition range should be determined experimentally by the individual, but the traditional convention that when colour 1 has ten times the intensity of colour 2 the indicator appears to be completely of colour 1 can be applied to assess the transition range. Thus, when $\epsilon_{\mathrm{ox}}\,[\mathrm{Ind_{ox}}] = 10\,\epsilon_{\mathrm{red}}\,[\mathrm{Ind_{red}}]$ the indicator appears to the eye to be completely oxidised, and when $10\,\epsilon_{\mathrm{ox}}\,[\mathrm{Ind_{ox}}] = \epsilon_{\mathrm{red}}\,[\mathrm{Ind_{red}}]$ the indicator appears to be completely reduced. With this substitution made in equation (2) for the case where a = b, the indicator changes colour over the range of potentials

$$E_{\mathrm{ind}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon_{\mathrm{red}}}{\epsilon_{\mathrm{ox}}} \pm \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} 10 = E_{\mathrm{trans}} \pm \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \quad .. \quad (8)$$

When a ≠ b, the transition range, from E_{low} to E_{high}, is dependent on the indicator concentration, the stoicheiometry and further on the molar absorptivities—

$$E_{\mathrm{low}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon^{\mathrm{a}}_{\mathrm{red}}}{\epsilon^{\mathrm{b}}_{\mathrm{ox}}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \left(\frac{\mathrm{b}\, c_{\mathrm{indox}}}{10\,\mathrm{a}\, \epsilon_{\mathrm{ox}} + \mathrm{b}\, \epsilon_{\mathrm{red}}} \right)^{(\mathrm{a}-\mathrm{b})} - \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} 10^{\mathrm{b}}$$

$$E_{\mathrm{high}} = E'_{\mathrm{oind}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \frac{\epsilon^{\mathrm{a}}_{\mathrm{red}}}{\epsilon^{\mathrm{b}}_{\mathrm{ox}}} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} \left(\frac{\mathrm{b}\, c_{\mathrm{indox}}}{\mathrm{a}\, \epsilon_{\mathrm{ox}} + 10\,\mathrm{b}\, \epsilon_{\mathrm{red}}} \right)^{(\mathrm{a}-\mathrm{b})} + \frac{2{\cdot}3\,RT}{n_{\mathrm{ind}}\,F} \log_{10} 10^{\mathrm{a}} \quad .. \quad (9)$$

Rigorously, c_{indox} is different at E_{low} and E_{high} because of the additional volume of titrant consumed in traversing from one point to the other. The difference is small in practice, and it is sufficient in a subjective appraisal of this kind to use the equivalence point volume of titrant in calculating c_{indox} when the indicator is a valid choice for the titration. If the indicator is added in the reduced form, substitution of ($\mathrm{a}\, c_{\mathrm{indred}}$) for ($\mathrm{b}\, c_{\mathrm{indox}}$) in the third term of E_{low} and of E_{high} gives the corresponding values. An equation of the form of equation (8) cannot therefore be written, because the third terms in equation (9) differ from

the third terms in equation (6) or (7). The transition range is not symmetrically disposed around the transition potential.

The *transition interval*, which defines the sharpness of the colour change, is the difference between the upper and lower potentials of the transition range. For symmetrical indicator reactions (a = b) this is independent of concentration and molar absorptivities, but depends primarily on n_{ind}, and to a very small degree on temperature. By expressing the interval as ΔE V,

$$\Delta E = 2 \times \frac{2{\cdot}3\,RT}{n_{ind}F} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

or, roughly, $120/n_{ind}$ mV.

For unsymmetrical reactions, a $\neq$ b, the interval is a function of the stoicheiometric coefficients and the molar absorptivities as well as of n_{ind}—

$$\Delta E = \frac{2{\cdot}3\,RT}{n_{ind}\,F}\left[\log_{10}\left(\frac{10\,a\,\epsilon_{ox} + b\,\epsilon_{red}}{a\,\epsilon_{ox} + 10\,b\,\epsilon_{red}}\right)^{(a-b)} + \log_{10}10^{(a+b)}\right] \quad .. \quad .. \quad (11)$$

and the transition interval is not symmetrically disposed around the transition potential.

ONE-COLOUR INDICATORS—

When one form absorbs entirely outside the visible range, it appears colourless to the eye. Conventionally the transition point is taken as the point when half the colour has developed, and therefore for symmetrical indicator reactions (a = b) the *indicator constant*, $E_0'_{ind}$, and the *transition potential*, E_{trans}, are identical. For unsymmetrical reactions, the transition potential is independent of indicator concentration and of which form is coloured, but dependent on the stoicheiometry—

$$E_{trans} = E'_{0ind} + \frac{2{\cdot}3\,RT}{n_{ind}\,F}\log_{10}\frac{a}{b} \quad .. \quad .. \quad .. \quad .. \quad (12)$$

It is more difficult to define the *transition range* of a one-colour indicator. The full colour end, that is, the point at which the colour appears fully developed when the colourless form of the indicator is used or at which the first perceptible fading occurs when the coloured form is used, may be subjectively assigned to the condition when the colour is 10/11-ths developed, that is, 10/11-ths of the colourless form has been consumed. This point again depends on stoicheiometry and indicator concentration but is independent of molar absorptivity. When Ind_{ox} is the coloured form, the upper limit of the transition range is defined as

$$E_{upper} = E'_{0ind} + \frac{2{\cdot}3\,RT}{n_{ind}\,F}\left[(a-b)\log_{10}\frac{c_{indred}}{1{\cdot}1} + a\log_{10}\frac{a}{b} + b\log_{10}10\right] \quad .. \quad (13)$$

When Ind_{red} is the coloured form, it is now the lower limit of the transition range that is defined as

$$E_{lower} = E'_{0ind} + \frac{2{\cdot}3\,RT}{n_{ind}\,F}\left[(a-b)\log_{10}\frac{c_{indox}}{1{\cdot}1} + b\log_{10}\frac{a}{b} - a\log_{10}10\right] \quad .. \quad (14)$$

The other limit of the transition range is the point at which the first perceptible colour appears, and this depends on the molar absorptivity of the coloured form, the concentration of the indicator in the solution, the depth of solution (l cm) through which the colour is viewed, the minimum absorbance (A) that the individual is able to detect at the particular wavelength, and the stoicheiometry. If Ind_{ox} is the coloured form, and the indicator is added as the colourless reduced form to give a concentration at the end-point of c_{indred}, then the first perceptible colour will appear at the lower end of the indicator transition range

$$E_{lower} = E'_{0ind} + \frac{2{\cdot}3\,RT}{n_{ind}\,F}\log_{10}\frac{a^b\,A^a\,(l\,\epsilon_{ox})^{(b-a)}}{(a\,l\,\epsilon_{ox}\,c_{indred} - b\,A)^b} \quad .. \quad .. \quad (15)$$

If Ind_{red} is the coloured form, and the indicator is added as the colourless oxidised form to give a resultant concentration at the end-point of c_{indox}, then the first perceptible colour

will appear at the upper end of the transition range

$$E_{\text{upper}} = E'_{0\text{Ind}} + \frac{2{\cdot}3\,RT}{n_{\text{Ind}}\,F}\log_{10}\frac{(b\,l\,\epsilon_{\text{red}}\,c_{\text{Indox}} - a\,A)^a}{b^a\,A^b\,(l\,\epsilon_{\text{red}})^{(a-b)}} \quad .. \quad .. \quad .. \quad (16)$$

When Ind_{ox} is coloured, the *transition range* is from E_{lower} defined by equation (15) to E_{upper} defined by equation (13) and the *transition interval* is

$$\Delta E = \frac{2{\cdot}3\,RT}{n_{\text{Ind}}\,F}\log_{10}\left[\frac{(a\,l\,\epsilon_{\text{ox}}\,c_{\text{Indred}} - b\,A)^b}{(a\,l\,\epsilon_{\text{ox}}\,c_{\text{Indred}}/1{\cdot}1)^{(b-a)}}\cdot\frac{10^b}{(b\,A)^a}\right] \quad .. \quad .. \quad .. \quad (17)$$

When Ind_{red} is coloured the *transition range* is from E_{lower} defined by equation (14) to E_{upper} defined by equation (16) and the *transition interval* is

$$\Delta E = \frac{2{\cdot}3\,RT}{n_{\text{Ind}}\,F}\log_{10}\left[\frac{(b\,l\,\epsilon_{\text{red}}\,c_{\text{Indox}} - a\,A)^a}{(b\,l\,\epsilon_{\text{red}}\,c_{\text{Indox}}/1{\cdot}1)^{(a-b)}}\cdot\frac{10^a}{(a\,A)^b}\right] \quad .. \quad .. \quad (18)$$

and when $a = b = 1$ the *transition interval* is, in both cases,

$$\Delta E = \frac{2{\cdot}3\,RT}{n_{\text{Ind}}\,F}\log_{10}\frac{l\,\epsilon_{\text{ox}}\,c_{\text{Ind}} - A}{A} + \frac{2{\cdot}3\,RT}{n_{\text{Ind}}\,F} \quad .. \quad .. \quad .. \quad (19)$$

Ion-combination indicators

For a titrimetric reaction of the type $B + A \rightleftharpoons BA$ (neglecting charges), with a conditional formation constant $K = [BA]/([B][A])$, the indicators participate in similar equilibria of two kinds, depending on whether Ind replaces B or A. If Ind replaces B, it is an indicator base or anionic indicator having an equilibrium and conditional formation constant as in equation (20), where A can be hydroxyl ion,

$$b\,\text{Ind} + a\,A \rightleftharpoons \text{Ind}_b\,A_a;\quad K_{\text{Ind}} = \frac{[\text{Ind}_b\,A_a]}{[\text{Ind}]^b[A]^a} \quad .. \quad .. \quad .. \quad (20)$$

Replacement of A gives an indicator acid or cationic (metallochromic) indicator having an equilibrium and conditional formation constant as in equation (21), where B can be hydrogen ion,

$$b\,B + a\,\text{Ind} \rightleftharpoons B_b\,\text{Ind}_a;\quad K_{\text{Ind}} = \frac{[B_b\,\text{Ind}_a]}{[B]^b\,[\text{Ind}]^a} \quad .. \quad .. \quad .. \quad (21)$$

Practically all ion-combination indicators are weak acids or bases or salts thereof, and when used for purposes other than hydrogen-ion indication, the true equilibria involve hydrogen ion(s). However, by buffering, the hydrogen-ion concentration can be held constant and its effect absorbed into the conditional constant, K_{Ind}. Ringbom has made extensive use of such conditional constants.[5] For this class of indicator the *indicator constant* is the K_{Ind} in equations (20) or (21) and is *conditional*.

Two-colour indicators—

When cationic indicators are used for the illustration, the *transition point* of a two-colour indicator occurs when

$$\epsilon_{B_b\text{Ind}_a}\,[B_b\,\text{Ind}_a] = \epsilon_{\text{Ind}}\,[\text{Ind}] \quad .. \quad .. \quad .. \quad .. \quad (22)$$

For symmetrical indicators ($a = b$) substitution from equation (22) into equation (21) gives

$$[B] = \frac{\epsilon_{\text{Ind}}}{\epsilon_{\text{BInd}}}\cdot\frac{1}{K_{\text{Ind}}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (23)$$

and the transition point is therefore, in ion exponent form

$$pB_{\text{trans}} = \log_{10} K_{\text{Ind}} + \log_{10}\frac{\epsilon_{\text{BInd}}}{\epsilon_{\text{Ind}}} \quad .. \quad .. \quad .. \quad .. \quad (24)$$

When $a \neq b$, the transition point becomes dependent on indicator concentration and the

stoicheiometry. In addition to equations (21) and (22), the total concentration, c_{Ind}, of the indicator at the end-point is required and is given by equation (25)—

$$c_{Ind} = [Ind] + a\,[B_b\,Ind_a] \quad .. \quad .. \quad .. \quad .. \quad (25)$$

The transition point can then be derived, and is

$$pB_{trans} = \frac{1}{b}[\log_{10} K_{Ind} + (a - 1)\log_{10} c_{Ind} + a\log_{10} \epsilon_{B_bInd_a} - \log_{10} \epsilon_{Ind} + (1 - a)\log_{10}(a\,\epsilon_{Ind} + \epsilon_{B_bInd_a})] \quad .. \quad .. \quad .. \quad (26)$$

The *transition range* can be appraised on the basis of the 10/1 and 1/10 convention. The indicator appears to be completely in the free form when

$$\epsilon_{Ind}[Ind] = 10\,\epsilon_{B_bInd_a}\,[B_b\,Ind_a] \quad .. \quad .. \quad .. \quad (27)$$

and to be completely in the complex form when

$$10\,\epsilon_{Ind}\,[Ind] = \epsilon_{B_bInd_a}\,[B_b\,Ind_a] \quad .. \quad .. \quad .. \quad (28)$$

For a symmetrical indicator reaction (a = b) the *transition range* is given by the limits

$$pB = \log_{10} K_{Ind} + \log_{10}\frac{\epsilon_{BInd}}{\epsilon_{Ind}} \pm 1 = pB_{trans} \pm 1 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (29)$$

When $a \neq b$ the *transition range* is from

$$pB_{free\ ind} = \frac{1}{b}[\log_{10} K_{Ind} + (a - 1)\log_{10} c_{Ind} + a\log_{10} \epsilon_{B_bInd_a} - \log_{10} \epsilon_{Ind} + (1 - a)\log_{10}(a\,\epsilon_{Ind} + 10\,\epsilon_{B_bInd_a}) + a\log_{10} 10] \quad .. \quad (30)$$

to

$$pB_{complex} = \frac{1}{b}[\log_{10} K_{Ind} + (a - 1)\log_{10} c_{Ind} + a\log_{10} \epsilon_{B_bInd_a} - \log_{10} \epsilon_{Ind} + (1 - a)\log_{10}(10\,a\,\epsilon_{Ind} + \epsilon_{B_bInd_a}) - \log_{10} 10] \quad .. \quad .. \quad (31)$$

Although the first four terms are common to equations (26), (30) and (31), the difference in the fifth term prevents writing the transition range in terms of the transition point as in equation (29).

The *transition interval* is given by the difference between $pB_{free\ ind}$ of equation (30) and $pB_{complex}$ of equation (31) and is

$$\Delta pB = \frac{1}{b}\left[(1 - a)\log_{10}\frac{a\,\epsilon_{Ind} + 10\,\epsilon_{B_bInd_a}}{10a\epsilon_{Ind} + \epsilon_{B_bInd_a}} + (a + 1)\right] \quad .. \quad .. \quad (32)$$

This interval is not symmetrically spread around the transition point. When a = b = 1 the transition range simplifies to 2 pB units and is symmetrically disposed around the transition point.

Analogous expressions are readily derived for anionic indicators.

ONE-COLOUR INDICATORS—

For one-colour indicators the *indicator constant* is K_{Ind} and when a = b the *transition point* is necessarily $pB_{trans} = \log_{10} K_{Ind}$. When $a \neq b$ the colour is half developed when $[B_bInd_a] = c_{Ind}/(2a)$ and $[Ind] = c_{Ind}/2$, no matter which is the coloured form. Substitution of these values into

$$\frac{1}{[B]_{trans}} = \left(\frac{K_{Ind}\,[Ind]^a}{[B_bInd_a]}\right)^{\frac{1}{b}}$$

gives

$$\frac{1}{[B]_{trans}} = \left(\frac{K_{Ind}\,c_{Ind}^{(a-1)}\,a}{2^{(a-1)}}\right)^{\frac{1}{b}}$$

Taking logarithms gives the transition point—

$$pB_{trans} = \frac{1}{b}[\log_{10} K_{Ind} + (a - 1) \log_{10} (c_{Ind}/2) + \log_{10} a]$$

To illustrate the *transition range*, consider the case of a cationic indicator for which the coloured form is the complex. The point at which the colour appears to be completely developed, or at which the first perceptible fading occurs, when the total indicator concentration at the end-point is c_{Ind}, will be defined by

$$a [B_b Ind_a] = 10 [Ind] \quad .. \quad .. \quad .. \quad .. \quad (33)$$

from which, with the aid of equations (21) and (25), the lower ion exponent of the transition range can be derived as

$$pB_{lower} = \frac{1}{b}\left[\log_{10} K_{Ind} + (a - 1) \log_{10} \frac{c_{Ind}}{1 \cdot 1} + \log_{10} a - a \log_{10} 10\right] \quad .. \quad (34)$$

The upper limit at which the first perceptible colour appears depends on the absorbance, A, detectable by the eye of the individual at the particular wavelength and the depth of solution viewed, l cm, and is

$$pB_{upper} = \frac{1}{b}[\log_{10} K_{Ind} + (1 - a) \log_{10} l \epsilon_{B_bInd_a} + a \log_{10} (c_{Ind} \epsilon_{B_bInd_a} l - a A) - \log_{10} A] \quad (35)$$

For symmetrical indicator reactions, a = b, the limits simplify to

$$pB_{lower} = \log_{10} K_{Ind} + 1 \quad .. \quad .. \quad .. \quad .. \quad (36)$$

$$pB_{upper} = \log_{10} K_{Ind} + \log_{10} (l c_{Ind} \epsilon_{B_bInd_a} - A) - \log_{10} A \quad .. \quad .. \quad (37)$$

Analogous expressions can be derived for the other three cases: cationic indicator - coloured indicator, anionic indicator - coloured complex and anionic indicator - coloured indicator. For one-colour indicators, all the limits and ranges are concentration dependent except for the case of one limit for symmetrical indicator reactions as exemplified by equation (36).

USE OF ANIONIC INDICATORS FOR CATION INDICATION—

By using the simplest possible case as an illustration, that is, an indicator for which a = b and a titrimetric reaction B + A $\rightleftharpoons$ BA, and by making the substitution of

$$[A] = \frac{[BA]}{K_{BA} [B]}$$

in equation (20), the transformed indicator constant becomes

$$K_{Ind} = \frac{[IndA]}{[Ind]} \cdot \frac{[B] K_{BA}}{[BA]} \quad .. \quad .. \quad .. \quad .. \quad (38)$$

and the *transition point* is then, in contrast with equation (24),

$$pB_{trans} = \log_{10} \frac{K_{BA}}{K_{Ind}} + \log_{10} \frac{\epsilon_{Ind}}{\epsilon_{IndA}} - \log_{10} [BA] \quad .. \quad .. \quad .. \quad (39)$$

This expression now involves both the formation constant, K_{BA}, and the concentration, [BA], of the product of the titrimetric reaction, so that the transition point and the transition range will shift with a change in concentration of the reactants in the titration. The convention of using $\log_{10} K_{BA}/K_{Ind}$ as the indicator constant is strongly to be discouraged because it conceals the significance of the term $\log_{10} [BA]$. Furthermore, although K_{Ind} may have a small temperature coefficient, K_{BA} may have a large one; this is particularly relevant to the use of anionic indicators in acid - base titrations.

TITRATION CONDITIONS AND CHOICE OF INDICATOR—

The quality of a titration has been quantitatively assessed by means of Q functions.[1,6,7] For a volume, v_d ml, of sample of concentration c_d mol l^{-1}, titrated with a reagent of concentration c_t mol l^{-1} and requiring v_t ml of titrant to reach the equivalence point, let the

smallest increment it is required to distinguish in locating the end-point be Δv ml. The precision of the titration is $\Delta v/v_t$ and the percentage precision is $100\ \Delta v/v_t$. The quality, Q, of the titration is then the change in ion exponent or potential on adding this increment, Δv, symmetrically disposed around the equivalence point.

$$Q = \Delta E = \mid E_{\text{at } v = v_t - 0{\cdot}5\,\Delta v} - E_{\text{at } v = v_t + 0{\cdot}5\,\Delta v} \mid$$

$$Q = \Delta \text{pB} = \mid \text{pB}_{\text{at } v = v_t - 0{\cdot}5\,\Delta v} - \text{pB}_{\text{at } v = v_t + 0{\cdot}5\,\Delta v} \mid \quad .. \quad .. \quad (40)$$

For a satisfactory visual indicator titration, the indicator should change, that is, the end-point should occur, within the required increment, Δv, of the equivalence point, v_t. If Q is less than the transition interval of the indicator, then the required precision is not directly accessible, and some other method, such as photometric titration, must be used, or the titration conditions adjusted to increase Q. Furthermore, the indicator must be so chosen that its transition point lies within the required interval around the equivalence point, $\text{pB}_{\text{eq pt}}$ or $E_{\text{eq pt}}$, of the titration.

$$\text{pB}_{\text{trans}} = \text{pB}_{\text{eq pt}} \pm (Q - \text{transition interval})/2$$

$$E_{\text{trans}} = E_{\text{eq pt}} \pm (Q - \text{transition interval})/2 \quad .. \quad .. \quad (41)$$

where, for a reaction $\text{m B} + \text{n A} \rightleftharpoons \text{B}_\text{m}\,\text{A}_\text{n}$,

$$\text{pB}_{\text{eq pt}} = \frac{1}{\text{m} + \text{n}} \log_{10} \frac{\text{n}^{\text{n}+1}}{\text{m}^\text{n}} \cdot \frac{(v_\text{d} + v_t)}{c_\text{d}\, c_t} \cdot K_{\text{B}_\text{m}\text{A}_\text{n}} \quad .. \quad .. \quad .. \quad (42)$$

and for titration of a reductant $\text{Ox}_2 + \text{n}_2\,\text{e} \rightleftharpoons \text{Red}_2$ of conditional potential E'_{02} with an oxidant $\text{Ox}_1 + \text{n}_1\,\text{e} \rightleftharpoons \text{Red}_1$, of conditional potential E'_{01}

$$E_{\text{eq pt}} = \frac{\text{n}_1 E'_{01} + \text{n}_2 E'_{02}}{\text{n}_1 + \text{n}_2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (43)$$

It is unlikely that, in a real titration, the volume, v, added just before the last split drop will be exactly $v_t - 0{\cdot}5\ \Delta v$. Were it so, the indicator would change colour completely on adding the final increment. If the volume added before the final split drop exceeds $v_t - 1{\cdot}5\ \Delta v$, a perceptible colour change will occur and the volume will be within $\pm 0{\cdot}5\ \Delta v$ of v_t and so within the required precision.

The main titration is, of course, interrupted while the indicator is being titrated, and consumption of titrant by the indicator will constitute an error. For v_{ind} ml of indicator of concentration c_{ind}, the error will be negligible if $c_t\, v_t \gg c_{\text{ind}}\, v_{\text{ind}}$, and this can be assured if the indicator is chosen so that

$$\epsilon_{\text{ind}} \geqq \frac{A\ (v_\text{d} + v_t)}{l\, c_t\, \Delta v} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (44)$$

This is not often satisfied: either the indicator has too low a molar absorptivity, or too much of it is used. The pernicious habit of stating indicator concentrations in per cent. w/v is to blame for concealing this. If "two drops" of a 0·1 per cent. solution of an indicator of molar mass 200 are used, $c_{\text{ind}} = 0{\cdot}005$ M and $v_{\text{ind}} = 0{\cdot}1$ ml, and the error is up to 0·2 per cent. on a 25-ml titration with a 0·01 M reagent.

The author thanks Mr. P. L. Bailey and Dr. J. M. Ottaway for checking the arithmetic and for helpful criticism of the text.

Appendix

DERIVATION OF EQUATIONS—

Equation (6)—From equation (1) the mass balance equation is

$$c_{\text{Indred}} = [\text{Ind}_{\text{red}}] + \frac{\text{b}}{\text{a}} [\text{Ind}_{\text{ox}}] \quad .. \quad .. \quad .. \quad .. \quad (6a)$$

Substitution of $[\text{Ind}_{\text{red}}]$ from equation (6a) into equation (3) gives

$$\epsilon_{\text{ox}} [\text{Ind}_{\text{ox}}] = \epsilon_{\text{red}} \left(c_{\text{Indred}} - \frac{\text{b}}{\text{a}} [\text{Ind}_{\text{ox}}] \right) \quad .. \quad .. \quad .. \quad (6b)$$

whence

$$[\mathrm{Ind_{ox}}]_{\mathrm{trans}} = \frac{\epsilon_{\mathrm{red}}\, c_{\mathrm{indred}}}{\epsilon_{\mathrm{ox}} + \frac{b}{a}\epsilon_{\mathrm{red}}} \quad .. \quad .. \quad .. \quad .. \quad (6c)$$

Substitution of $[\mathrm{Ind_{ox}}]$ from equation (6a) into equation (3) gives

$$\epsilon_{\mathrm{ox}}\frac{a}{b}(c_{\mathrm{indred}} - [\mathrm{Ind_{red}}]) = \epsilon_{\mathrm{red}}\,[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad (6d)$$

whence

$$[\mathrm{Ind_{red}}]_{\mathrm{trans}} = \frac{\frac{a}{b}\epsilon_{\mathrm{ox}}\, c_{\mathrm{indred}}}{\epsilon_{\mathrm{red}} + \frac{a}{b}\epsilon_{\mathrm{ox}}} \quad .. \quad .. \quad .. \quad .. \quad (6e)$$

$$\therefore \quad \frac{[\mathrm{Ind_{ox}}]^{a}_{\mathrm{trans}}}{[\mathrm{Ind_{red}}]^{b}_{\mathrm{trans}}} = \left(\frac{\epsilon_{\mathrm{red}}\, c_{\mathrm{indred}}}{\epsilon_{\mathrm{ox}} + \frac{b}{a}\epsilon_{\mathrm{red}}}\right)^{a} \cdot \left(\frac{\epsilon_{\mathrm{red}} + \frac{a}{b}\epsilon_{\mathrm{ox}}}{\frac{a}{b}\epsilon_{\mathrm{ox}}\, c_{\mathrm{indred}}}\right)^{b} \quad .. \quad .. \quad (6f)$$

which simplifies to

$$\frac{\epsilon_{\mathrm{red}}{}^{a}}{\epsilon_{\mathrm{ox}}{}^{b}}\left(\frac{a\, c_{\mathrm{indred}}}{a\,\epsilon_{\mathrm{ox}} + b\,\epsilon_{\mathrm{red}}}\right)^{(a-b)} \quad .. \quad .. \quad .. \quad .. \quad (6g)$$

Substitution of equation (6g) into equation (2) then gives equation (6).

Equation (7)—Following the same steps as for equation (6) the mass balance equation from equation (1) is

$$c_{\mathrm{indox}} = [\mathrm{Ind_{ox}}] + \frac{a}{b}[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad .. \quad (7a)$$

Substitution of $[\mathrm{Ind_{red}}]$ from equation (7a) into equation (3) gives

$$\epsilon_{\mathrm{ox}}\,[\mathrm{Ind_{ox}}] = \epsilon_{\mathrm{red}}\frac{b}{a}(c_{\mathrm{indox}} - [\mathrm{Ind_{ox}}]) \quad .. \quad .. \quad .. \quad (7b)$$

whence

$$[\mathrm{Ind_{ox}}]_{\mathrm{trans}} = \frac{\epsilon_{\mathrm{red}}\frac{b}{a}\, c_{\mathrm{indox}}}{\epsilon_{\mathrm{ox}} + \epsilon_{\mathrm{red}}\frac{b}{a}} \quad .. \quad .. \quad .. \quad .. \quad (7c)$$

Substitution of $[\mathrm{Ind_{ox}}]$ from equation (7a) into equation (3) gives

$$\epsilon_{\mathrm{ox}}\,(c_{\mathrm{indox}} - \frac{a}{b}[\mathrm{Ind_{red}}]) = \epsilon_{\mathrm{red}}\,[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad (7d)$$

whence

$$[\mathrm{Ind_{red}}]_{\mathrm{trans}} = \frac{\epsilon_{\mathrm{ox}}\, c_{\mathrm{indox}}}{\epsilon_{\mathrm{red}} + \frac{a}{b}\epsilon_{\mathrm{ox}}} \quad .. \quad .. \quad .. \quad .. \quad (7e)$$

$$\therefore \quad \frac{[\mathrm{Ind_{ox}}]^{a}_{\mathrm{trans}}}{[\mathrm{Ind_{red}}]^{b}_{\mathrm{trans}}} = \left(\frac{\frac{b}{a}\epsilon_{\mathrm{red}}\, c_{\mathrm{indox}}}{\epsilon_{\mathrm{ox}} + \frac{b}{a}\epsilon_{\mathrm{red}}}\right)^{a} \cdot \left(\frac{\epsilon_{\mathrm{red}} + \frac{a}{b}\epsilon_{\mathrm{ox}}}{\epsilon_{\mathrm{ox}}\, c_{\mathrm{indox}}}\right)^{b} \quad .. \quad .. \quad (7f)$$

which simplifies to

$$\frac{\epsilon_{\mathrm{red}}{}^{a}}{\epsilon_{\mathrm{ox}}{}^{b}}\left(\frac{b\, c_{\mathrm{indox}}}{a\,\epsilon_{\mathrm{ox}} + b\,\epsilon_{\mathrm{red}}}\right)^{(a-b)} \quad .. \quad .. \quad .. \quad .. \quad (7g)$$

Substitution of equation (7g) into equation (2) then gives equation (7).

Equation (9)—E_{low}, with indicator added in the oxidised form. The mass balance equation is (7a), and the absorbance relationship is

$$10\,[\mathrm{Ind_{ox}}]\,\epsilon_{ox} = [\mathrm{Ind_{red}}]\,\epsilon_{red} \quad .. \quad .. \quad .. \quad .. \quad (9a)$$

Substitution of $[\mathrm{Ind_{red}}]$ from equation (7a) into equation (9a) gives

$$10\,[\mathrm{Ind_{ox}}]\,\epsilon_{ox} = \epsilon_{red}\frac{b}{a}(c_{1ndox} - [\mathrm{Ind_{ox}}]) \quad .. \quad .. \quad .. \quad (9b)$$

whence

$$[\mathrm{Ind_{ox}}]_{low} = \frac{\frac{b}{a}\epsilon_{red}\,c_{1ndox}}{(10\,\epsilon_{ox} + \frac{b}{a}\epsilon_{red})} \quad .. \quad .. \quad .. \quad .. \quad (9c$$

Substitution of $[\mathrm{Ind_{ox}}]$ from equation (7a) into equation (9a) gives

$$10\,\epsilon_{ox}\left(c_{1ndox} - \frac{a}{b}[\mathrm{Ind_{red}}]\right) = \epsilon_{red}\,[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad (9d)$$

whence

$$[\mathrm{Ind_{red}}]_{low} = \frac{10\,\epsilon_{ox}\,c_{1ndox}}{(\epsilon_{red} + 10\frac{a}{b}\epsilon_{ox})} \quad .. \quad .. \quad .. \quad .. \quad (9e)$$

$$\therefore \quad \frac{[\mathrm{Ind_{ox}}]^a_{low}}{[\mathrm{Ind_{red}}]^b_{low}} = \left(\frac{\frac{b}{a}\epsilon_{red}\,c_{1ndox}}{10\,\epsilon_{ox} + \frac{b}{a}\epsilon_{red}}\right)^a \cdot \left(\frac{\epsilon_{red} + 10\frac{a}{b}\epsilon_{ox}}{10\,\epsilon_{ox}\,c_{1ndox}}\right)^b \quad .. \quad .. \quad (9f)$$

which simplifies to

$$= \frac{\epsilon_{red}{}^a}{\epsilon_{ox}{}^b} \cdot \frac{1}{10^b}\left(\frac{b\,c_{1ndox}}{10\,a\,\epsilon_{ox} + b\,\epsilon_{red}}\right)^{(a-b)} \quad .. \quad .. \quad .. \quad (9g)$$

Substitution of equation (9g) into equation (2) gives E_{low}.

For E_{high}, with indicator added in the oxidised form, the mass balance equation is (7a) and the absorbance relationship is

$$[\mathrm{Ind_{ox}}]\,\epsilon_{ox} = 10\,[\mathrm{Ind_{red}}]\,\epsilon_{red} \quad .. \quad .. \quad .. \quad .. \quad (9h)$$

Substitution of the value of $[\mathrm{Ind_{red}}]$ obtained from equation (7a) into equation (9h) gives

$$[\mathrm{Ind_{ox}}]\,\epsilon_{ox} = \epsilon_{red}\,10\frac{b}{a}(c_{1ndox} - [\mathrm{Ind_{ox}}]) \quad .. \quad .. \quad .. \quad (9i)$$

whence

$$[\mathrm{Ind_{ox}}]_{high} = \frac{10\frac{b}{a}\epsilon_{red}\,c_{1ndox}}{\epsilon_{ox} + 10\frac{b}{a}\epsilon_{red}} \quad .. \quad .. \quad .. \quad .. \quad (9j)$$

Substitution of $[\mathrm{Ind_{ox}}]$ obtained from equation (7a) into equation (9h) gives

$$\epsilon_{ox}\left(c_{1ndox} - \frac{a}{b}[\mathrm{Ind_{red}}]\right) = 10\,\epsilon_{red}\,[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad (9k)$$

whence

$$[\mathrm{Ind_{red}}]_{high} = \frac{\epsilon_{ox}\,c_{1ndox}}{10\,\epsilon_{red} + \frac{a}{b}\epsilon_{ox}} \quad .. \quad .. \quad .. \quad .. \quad (9l)$$

$$\therefore \frac{[\mathrm{Ind_{ox}}]^{a}_{high}}{[\mathrm{Ind_{red}}]^{b}_{high}} = \left(\frac{10\frac{b}{a}\epsilon_{red}\, c_{indox}}{\epsilon_{ox} + 10\frac{b}{a}\epsilon_{red}}\right)^{a} \cdot \left(\frac{10\,\epsilon_{red} + \frac{a}{b}\epsilon_{ox}}{\epsilon_{ox}\, c_{indox}}\right)^{b} \quad .. \quad .. \quad (9m)$$

which simplifies to

$$\frac{\epsilon_{red}{}^{a}}{\epsilon_{ox}{}^{b}}\, 10^{a} \left(\frac{b\, c_{indox}}{a\,\epsilon_{ox} + 10\, b\,\epsilon_{red}}\right)^{(a-b)} \quad .. \quad .. \quad .. \quad (9n)$$

Substitution of equation (9n) into equation (2) gives E_{high}. A similar derivation based upon the mass balance equation (6a) for the indicator added in the reduced form and the absorbance equations (9a) and (9h) will give the results noted in the text following equation (9).

Equation (11) is obtained by subtracting E_{low} from E_{high} in equations (9) and simplifying.

Equation (12)—If the coloured form is $\mathrm{Ind_{ox}}$ and the reduced form is added to give a total finishing concentration of c_{indred} mol l^{-1}, then at the transition point, from equation (1)

$$[\mathrm{Ind_{ox}}] = 0{\cdot}5\frac{a}{b}c_{indred}; \quad [\mathrm{Ind_{red}}] = 0{\cdot}5\, c_{indred}$$

Substitution in equation (2) gives

$$E_{trans} = E'_{oind} + \frac{2{\cdot}3\, RT}{n_{ind}\, F}\log_{10}\frac{0{\cdot}5\frac{a}{b}c_{indred}}{0{\cdot}5\, c_{indred}}$$

which simplifies to equation (12). If the coloured form is $\mathrm{Ind_{red}}$ and the indicator is added in the oxidised form to give a finishing concentration of c_{indox} mol l^{-1}, then at the transition point, from equation (1),

$$[\mathrm{Ind_{red}}] = 0{\cdot}5\frac{b}{a}c_{indox}; \quad [\mathrm{Ind_{ox}}] = 0{\cdot}5\, c_{indox}$$

Substitution in equation (2) gives

$$E_{trans} = E'_{oind} + \frac{2{\cdot}3\, RT}{n_{ind}\, F}\log_{10}\frac{0{\cdot}5\, c_{indox}}{0{\cdot}5\frac{b}{a}c_{indox}}$$

which also simplifies to equation (12).

Equation (13)—$\mathrm{Ind_{ox}}$ is the coloured form and the indicator is added in the reduced form to give a finishing concentration as in the mass balance equation (6a). The optical condition is

$$[\mathrm{Ind_{ox}}] = 10\frac{a}{b}[\mathrm{Ind_{red}}] \quad .. \quad .. \quad .. \quad .. \quad (13a)$$

From equations (13a) and (6a)

$$[\mathrm{Ind_{ox}}] = 10\frac{a}{b}\left(c_{indred} - \frac{b}{a}[\mathrm{Ind_{ox}}]\right) = \frac{a}{b}\frac{c_{indred}}{1{\cdot}1} \quad .. \quad .. \quad (13b)$$

$$[\mathrm{Ind_{red}}] = c_{indred} - \frac{a}{b}10\frac{b}{a}[\mathrm{Ind_{red}}] = \frac{c_{indred}}{11} \quad .. \quad .. \quad .. \quad (13c)$$

$$\therefore \frac{[\mathrm{Ind_{ox}}]^{a}_{upper}}{[\mathrm{Ind_{red}}]^{b}_{upper}} = \left(\frac{a\, c_{indred}}{b \times 1{\cdot}1}\right)^{a} \cdot \left(\frac{11}{c_{indred}}\right)^{b}$$

$$= \left(\frac{a}{b}\right)^{a}\left(\frac{c_{indred}}{1{\cdot}1}\right)^{(a-b)} 10^{b} \quad .. \quad .. \quad .. \quad (13d)$$

which, when substituted into equation (2), gives equation (13).

Equation (14)—Ind_{red} is the coloured form, and the indicator is added in the oxidised form to give a finishing concentration as in the mass balance equation (7a). The optical condition is now

$$[Ind_{red}] = 10\frac{b}{a}[Ind_{ox}] \quad .. \quad .. \quad .. \quad .. \quad (14a)$$

From the simultaneous equations (7a) and (14a),

$$[Ind_{ox}] = c_{Indox} - \frac{a}{b}10\frac{b}{a}[Ind_{ox}] = \frac{c_{Indox}}{11} \quad .. \quad .. \quad .. \quad (14b)$$

$$[Ind_{red}] = \frac{b}{a}\left(c_{Indox} - [Ind_{red}]\frac{a}{b}\frac{1}{10}\right) = \frac{b}{a}\frac{c_{Indox}}{1{\cdot}1} \quad .. \quad .. \quad (14c)$$

From equations (14b) and (14c),

$$\frac{[Ind_{ox}]^a_{lower}}{[Ind_{red}]^b_{lower}} = \left(\frac{c_{Indox}}{11}\right)^a \cdot \left(\frac{1{\cdot}1\ a}{b\ c_{Indox}}\right)^b$$

$$= \left(\frac{a}{b}\right)^b \left(\frac{c_{Indox}}{1{\cdot}1}\right)^{(a-b)} \frac{1}{10^a} \quad .. \quad .. \quad .. \quad (14d)$$

which, when substituted into equation (2), gives equation (14).

Equation (15)—Ind_{ox} is the coloured form, the indicator is added in the reduced form to give a finishing concentration as shown in the mass balance equation (6a), and from Beer's law the first perceptible colour of Ind_{ox} appears when

$$[Ind_{ox}] = \frac{A}{l\,\epsilon_{ox}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (15a)$$

where A is the minimum absorbance detected by the eye when viewing through l cm of solution. From equations (15a) and (6a),

$$[Ind_{red}] = c_{Indred} - \frac{b}{a}\cdot\frac{A}{l\,\epsilon_{ox}} \quad .. \quad .. \quad .. \quad .. \quad (15b)$$

$$\therefore \frac{[Ind_{ox}]^a_{low}}{[Ind_{red}]^b_{low}} = \left(\frac{A}{l\,\epsilon_{ox}}\right)^a \cdot \left(\frac{a\,l\,\epsilon_{ox}}{a\,l\,\epsilon_{ox}\,c_{Indred} - b\,A}\right)^b \quad .. \quad (15c)$$

Re-arrangement of equation (15c) and substitution into equation (2) gives equation (15).

Equation (16)—Ind_{red} is the coloured form, the indicator is added in the oxidised form as in the mass balance equation (7a), and from Beer's law the first perceptible colour of Ind_{red} appears when

$$[Ind_{red}] = \frac{A}{l\,\epsilon_{red}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16a)$$

From equations (7a) and (16a),

$$[Ind_{ox}] = c_{Indox} - \frac{a}{b}\frac{A}{l\,\epsilon_{red}} \quad .. \quad .. \quad .. \quad .. \quad (16b)$$

$$\therefore \frac{[Ind_{ox}]^a_{high}}{[Ind_{red}]^b_{high}} = \left(\frac{b\,l\,\epsilon_{red}\,c_{Indox} - a\,A}{b\,l\,\epsilon_{red}}\right)^a \cdot \left(\frac{l\,\epsilon_{red}}{A}\right)^b \quad .. \quad (16c)$$

Re-arrangement of equation (16c) and substitution into equation (2) gives equation (16).

Equations (17) *and* (18)—These are obtained by subtracting equation (15) from equation (13) and equation (14) from equation (16), respectively, and simplifying.

Equation (26)—Concentrations of free indicator, [Ind], and of the complex, $[B_bInd_a]$, are obtained by solving the optical equation (22) and the mass balance equation (25).

$$\epsilon_{Ind}\,(c_{Ind} - a\,[B_bInd_a]) = \epsilon_{B_bInd_a}\,[B_bInd_a] \quad .. \quad .. \quad (26a)$$

whence

$$[B_bInd_a] = \frac{\epsilon_{Ind}\,c_{Ind}}{\epsilon_{B_bInd_a} + a\,\epsilon_{Ind}} \quad .. \quad .. \quad .. \quad .. \quad (26b)$$

Making the converse substitution,

$$\epsilon_{Ind}\,[Ind] = \epsilon_{B_bInd_a}\,(c_{Ind} - [Ind])/a \quad .. \quad .. \quad .. \quad (26c)$$

whence

$$[Ind] = \frac{c_{Ind}\,\epsilon_{B_bInd_a}}{a\,\epsilon_{Ind} + \epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad .. \quad (26d)$$

From the formation constant in equation (21),

$$\frac{1}{[B]} = \left(\frac{[Ind]^a\,K_{Ind}}{[B_bInd_a]}\right)^{\frac{1}{b}} \quad .. \quad .. \quad .. \quad .. \quad (26e)$$

Substitution of the transition point concentrations from equations (26b) and (26d) gives

$$\frac{1}{[B]_{trans}} = \left[\left(\frac{c_{Ind}\,\epsilon_{B_bInd_a}}{a\,\epsilon_{Ind} + \epsilon_{B_bInd_a}}\right)^a \cdot \frac{(\epsilon_{B_bInd_a} + a\,\epsilon_{Ind})}{\epsilon_{Ind}\,c_{Ind}}\,K_{Ind}\right]^{\frac{1}{b}} \quad .. \quad .. \quad (26f)$$

Taking logarithms to base 10 of both sides of equation (26f) gives pB_{trans} in equation (26).

Equation (30)—The mass balance equation is equation (25) and the optical condition is equation (27). Substitution for the concentration of the complex gives

$$\epsilon_{Ind}\,[Ind] = 10\,\epsilon_{B_bInd_a}\,(c_{Ind} - [Ind])/a \quad .. \quad .. \quad .. \quad (30a)$$

whence

$$[Ind] = \frac{10\,\epsilon_{B_bInd_a}\,c_{Ind}}{a\,\epsilon_{Ind} + 10\,\epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad .. \quad (30b)$$

The converse substitution gives

$$\epsilon_{Ind}\,(c_{Ind} - a\,[B_bInd_a]) = 10\,\epsilon_{B_bInd_a}\,[B_bInd_a] \quad .. \quad .. \quad .. \quad (30c)$$

whence

$$[B_bInd_a] = \frac{\epsilon_{Ind}\,c_{Ind}}{10\,\epsilon_{B_bInd_a} + a\,\epsilon_{Ind}} \quad .. \quad .. \quad .. \quad .. \quad (30d)$$

Substitution into equation (26e) gives

$$\frac{1}{[B]_{free\ ind}} = \left[K_{Ind}\left(\frac{10\,\epsilon_{B_bInd_a}\,c_{Ind}}{a\,\epsilon_{Ind} + 10\,\epsilon_{B_bInd_a}}\right)^a \cdot \frac{10\,\epsilon_{B_bInd_a} + a\,\epsilon_{Ind}}{\epsilon_{Ind}\,c_{Ind}}\right]^{\frac{1}{b}} \quad .. \quad .. \quad (30e)$$

and conversion into logarithms to base 10 gives equation (30).

Equation (31)—The mass balance equation is (25) and the optical condition is now equation (28). Substitution of the value of $[B_bInd_a]$ from equation (25) into equation (28) gives

$$10\,\epsilon_{Ind}\,[Ind] = \epsilon_{B_bInd_a}\,(c_{Ind} - [Ind])/a \quad .. \quad .. \quad .. \quad (31a)$$

$$\therefore\ [Ind] = \frac{\epsilon_{B_bInd_a}\,c_{Ind}}{10\,a\,\epsilon_{Ind} + \epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad (31b)$$

The converse substitution gives

$$10\,\epsilon_{Ind}\,(c_{Ind} - a\,[B_bInd_a]) = \epsilon_{B_bInd_a}\,[B_bInd_a] \quad .. \quad .. \quad .. \quad (31c)$$

$$\therefore\ [B_bInd_a] = \frac{10\,\epsilon_{Ind}\,c_{Ind}}{\epsilon_{B_bInd_a} + 10\,a\,\epsilon_{Ind}} \quad .. \quad .. \quad .. \quad (31d)$$

Substitution into equation (26e) gives

$$\frac{1}{[B]_{complex}} = \left[K_{Ind}\left(\frac{\epsilon_{B_bInd_a}\, c_{Ind}}{10\ a\ \epsilon_{Ind} + \epsilon_{B_bInd_a}}\right)^a \cdot \frac{\epsilon_{B_bInd_a} + 10\ a\ \epsilon_{Ind}}{10\ \epsilon_{Ind}\, c_{Ind}}\right]^{\frac{1}{b}} \quad .. \quad (31e)$$

Conversion into decadic logarithms gives equation (31).

Equation (34)—From equations (33) and (25),

$$[Ind] = \frac{c_{Ind}}{11};\ [B_bInd_a] = \frac{10\ c_{Ind}}{11\ a} \quad .. \quad .. \quad .. \quad (34a,b)$$

Substitution into equation (26e) gives

$$\frac{1}{[B]_{lower}} = \left[\left(\frac{c_{Ind}}{11}\right)^a \frac{11\ a}{10\ c_{Ind}}\ K_{Ind}\right]^{\frac{1}{b}}$$

$$= \left[\left(\frac{c_{Ind}}{1{\cdot}1}\right)^{(a-1)}\ a\ 10^{-a}\ K_{Ind}\right]^{\frac{1}{b}}$$

Conversion into decadic logarithms gives equation (34).

Equation (35)—The first perceptible colour of the complex appears when

$$[B_bInd_a] = \frac{A}{l\ \epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad .. \quad (35a)$$

Substitution into equation (25) gives

$$c_{Ind} = [Ind] + \frac{a\ A}{l\ \epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad .. \quad (35b)$$

whence

$$[Ind] = \frac{c_{Ind}\ l\ \epsilon_{B_bInd_a} - a\ A}{l\ \epsilon_{B_bInd_a}} \quad .. \quad .. \quad .. \quad .. \quad (35c)$$

Substitution into equation (26e) then gives

$$\frac{1}{[B]_{upper}} = \left[\left(\frac{l\ \epsilon_{B_bInd_a}\, c_{Ind} - a\ A}{l\ \epsilon_{B_bInd_a}}\right)^a \cdot \frac{l\ \epsilon_{B_bInd_a}}{A}\ K_{Ind}\right]^{\frac{1}{b}} \quad .. \quad .. \quad .. \quad (35d)$$

$$= \left[\frac{K_{Ind}}{A} \cdot \frac{(l\ \epsilon_{B_bInd_a}\, c_{Ind} - a\ A)^a}{(l\ \epsilon_{B_bInd_a})^{(a-1)}}\right]^{\frac{1}{b}}$$

Conversion into logarithms to base 10 gives equation (35).

References

1. Bishop, E., Proceedings of the SAC Conference, Nottingham 1965, Society for Analytical Chemistry, London, 1965, p. 291.
2. Kolthoff, I. M., and Stenger, V. A., "Volumetric Analysis," Volume I, Interscience Publishers Inc., New York, 1942.
3. Bishop, E., *in* Wilson, C. L., and Wilson, D. W., *Editors*, "Comprehensive Analytical Chemistry," Volume IB, Elsevier, Amsterdam and London, 1960.
4. Walden, G. M., Hammett, L. P., and Chapman, R. P., *J. Amer. Chem. Soc.*, 1931, **53**, 3908.
5. Ringbom, A., "Complexation in Analytical Chemistry," Interscience Publishers Inc., New York, 1963.
6. Bishop, E., "Indicators," Pergamon Press, Oxford, 1971, Chapters 2 and 8b.
7. ——, "Coulometric Analysis," *in* Wilson, C. L., and Wilson, D. W., *Editors*, "Comprehensive Analytical Chemistry," Volume IIB, Elsevier, Amsterdam and London, in the press.

Received *December 29th*, 1970
Accepted *March 16th*, 1971

Analyst, August, 1971, Vol. 96, *pp.* 550–561

An Automatic Capillary Viscometer

Part II.* Automatic Apparatus for Viscometric Titrations

BY R. B. SIMPSON, J. S. SMITH† AND H. M. N. H. IRVING‡

(Department of Inorganic and Structural Chemistry, The University, Leeds 2)

The basic principles of viscometric titrations are considered and examples of applications to a variety of analytical and other determinations are suggested.

An addition to the automatic capillary viscometer described in Part I provides for the introduction of successive measured volume increments of a solvent or solution, admixture with the solution already present in a suspended-level viscometer and the electronic measurement of the flow time including printing-out the results.

By using the new apparatus it is possible expeditiously to determine the B-coefficients of the Jones - Dole equation for the viscosity of electrolytes and the intrinsic viscosity coefficients for solutions of polymers, and to perform a wide variety of acid - base titrations. Practical examples of these determinations are given in illustration.

TITRIMETRIC procedures for carrying out the reaction between one material, S (the sample), and another material, T (the titrant), can form the basis of quantitative measurements provided that the end-point can be detected by suitable means and various other obvious conditions are fulfilled.

$$S + T \rightarrow \text{products (P)} \qquad (1)$$

A titration graph is constructed with some linear function of the concentration of T along the abscissa and some function of the concentration of S (or of P) along the ordinate. The end-point of the titration (which may or may not coincide with the stoicheiometric end-point) is then indicated by the value or values of [T] at which there is an extremum or inflection.

Although measurements, for example, of optical absorption, optical rotation, conductivity, electrode potentials, diffusion currents, radioactivity and thermal and magnetic effects are among the many physical properties that have been made use of, there would seem to be no previous reference to the measurement of viscosity as the basis of a titration procedure. This is scarcely surprising if the process is envisaged as one in which samples of the titration mixture are removed after successive additions of titrant for measurements of their viscosity in one or other of the conventional instruments. Practical considerations, such as loss of material, problems of cleaning the viscometer between successive samples and possible changes in calibration, problems of temperature control and the excessive time required, have clearly discouraged analysts from considering viscometric titration as a useful experimental technique.

In Part I[1] we described an instrument by use of which the process of determining the viscosity of a liquid can be carried out automatically as often as required and with high precision, the flow time being measured electronically to the nearest millisecond. Provision for printing out the results has since been added.

We have now extended the usefulness of this equipment by combining it with an automatic burette (Radiometer ABU12b) that is capable of adding aliquots of the titrant, T, in precisely pre-determined volumes, to the sample solution, S, contained in the reservoir of a suspended-level viscometer maintained at a constant temperature. By using a combination of logic units controlling a source of compressed gas through a series of valves, it is possible to program a sequence of operations in which the sample solution receives an aliquot portion

* For particulars of Part I of this series, see reference list, p. 561.

† Present address: Department of Chemical Sciences, The Hatfield Polytechnic, Hatfield, Hertfordshire.

‡ Requests for reprints should be sent to Professor Irving.

of titrant, the whole is then well mixed, its viscosity is measured as previously described[1] and finally the flow time is printed out. The whole sample is then returned to the reservoir and a further addition of titrant is made, the cycles being repeated automatically to give a series of flow times which, when plotted against the volume of titrant, constitute the viscometric titration curve. Changes in flow time can then be used to reveal changes in the viscosity of the mixture and thus changes in its composition. Where sudden changes in the slope of the graph (break-points) coincide with changes in the stoicheiometry of the reaction the results can readily be used for the quantitative determination of the sample. We shall show later that in certain acid - alkali determinations the changes in viscosity may actually be more informative than changes in, for example, pH. Under strictly reproducible conditions break-points can be used for quantitative measurements even when the process is non-stoicheiometric.

POSSIBLE APPLICATIONS OF THE METHOD—

Viscometric titrations could be used, in principle, for any systems that remain homogeneous throughout. They need not be restricted to purely aqueous solutions and they may well be applicable to systems for which conventional methods of following changes in the concentration of a sample (or products) fail. The essential new feature is that there must be a sufficient difference between the effects of the sample S, the titrant T and admixtures with the reaction products P on the viscosity of the solvent, so that in the course of a titration, changes in the relative concentrations of these species can be indicated by changes in flow time. For example, the sudden change in hydrogen-ion concentration at the end-point of an acid - alkali titration is reflected in the sudden change of slope in a graph of flow time against volume of titrant.

Quite apart from the possibility of its use to discover viscometric titrations of analytical interest, the present apparatus is particularly suitable for studying the viscosity of mixtures; we give below examples of its use for deriving the constants A and B of the Jones - Dole equation (2) for a solution of an electrolyte—

$$\eta_{rel.} = 1 + A\sqrt{c} + Bc \quad .. \quad .. \quad .. \quad .. \quad (2)$$

and to obtain the constants k and $[\eta]$ for the equation—

$$\eta_{rel.} = 1 + [\eta]c + kc^2 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

which is extensively used in the characterisation of polymers.

We would certainly anticipate differences between the effect of a base and its conjugate acid on the viscosity of the solvent, although the magnitude of this difference will depend on the nature of the species involved. Indeed, any reaction in which the products are of a significantly different size, or charge, or both, and which could interact with the solvent to give aggregates of different viscosity, should be suitable for viscometric titration. The interactions between cations and EDTA and between borates and *cis*-diols are obvious fields for study and many complexation and adduction reactions that proceed only in non-aqueous solvents are open to investigation. We have found measurable differences between the viscosities of certain *cis* and *trans* isomers of co-ordination compounds and this opens up the possibility of investigating the kinetics of isomerisation when other methods fail. The kinetics of other reactions, such as polymerisations, condensations, depolymerisations, hydrolyses and substitutions can be conveniently studied in the automatic apparatus now described. While many preliminary studies will be necessary to explore the field and to develop new procedures it is not premature to recognise that when sufficiently large changes in viscosity are found to occur they could (with appropriate apparatus) be used to monitor a reaction and to control plant.

DESCRIPTION OF THE AUTOMATIC VISCOMETER—

The fill - empty cycle of the viscometer, as defined and described previously,[1] remains unmodified in the present extended sequence, which may be described as a fill - empty - add - mix cycle. The start and stop-level detector circuits are essentially the same as before, the main differences being the addition of a line from the output of the start-level timer unit, and the introduction of the operations-mode circuit.

The output from the decade counter used, as described in Part I, to pre-determine the number of measurements on the single sample, is now used both to inhibit the fill process

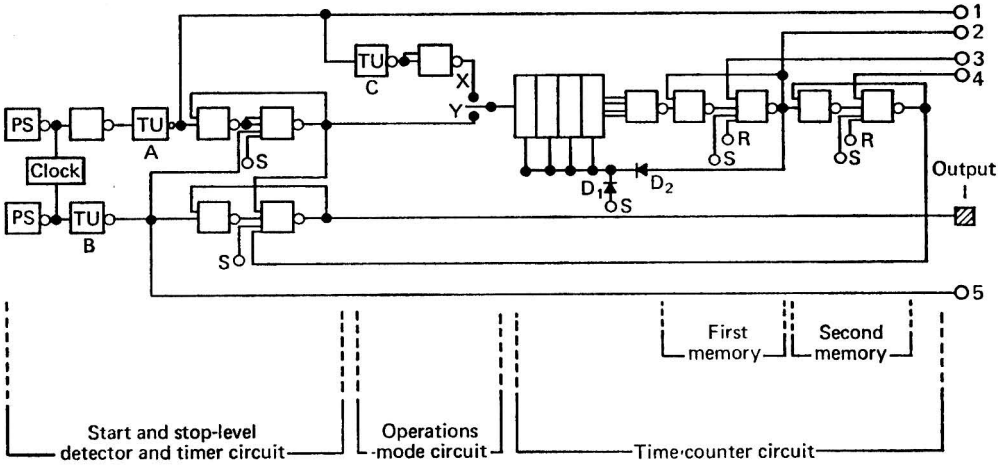


Fig. 1 (*a*). Start-level and stop-level detector circuits, operations-mode circuit and time-counter circuit

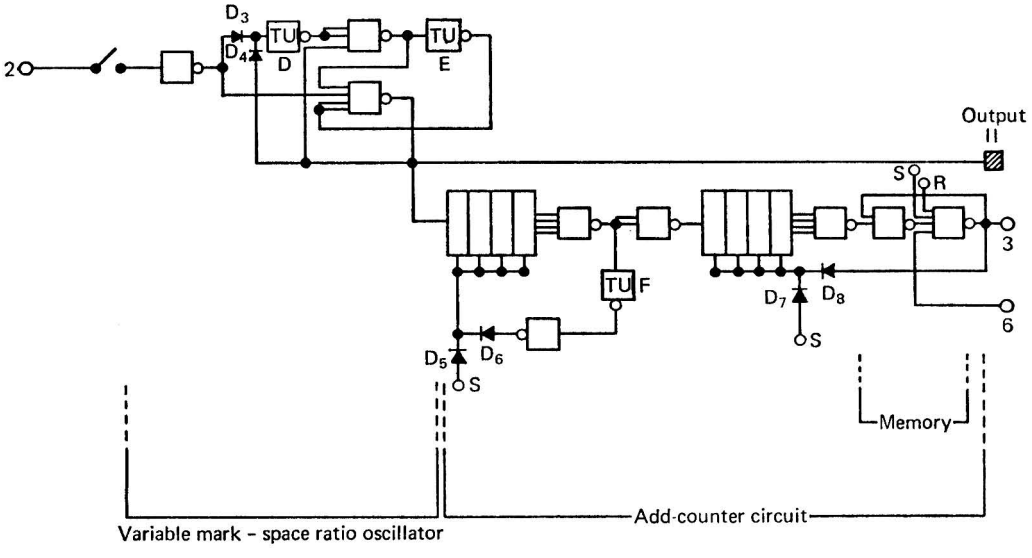


Fig. 1 (*b*). Variable mark - space ratio oscillator and add-counter circuit

(via an extra memory unit) and to energise a variable mark - space ratio oscillator. The output of this oscillator is used to cause increments of the titrant to be added to the viscometer from the automatic burette, the number of increments being counted on another decade counter (the add-counter circuit). When a pre-determined number of increments has been added this counter output goes to a 1 level (as previously defined[1]) and the oscillator is de-energised. This same counter output is also used to close the solenoid valves in a sequence that causes mixing by a brief passage of inert gas through the viscometer. After mixing has been completed, the output of the memory unit inhibiting the fill - empty cycle is returned to the 0 level and the complete cycle is recommenced. The start and stop-level detector circuits are shown in Fig. 1 (*a*), the oscillator and add-counter circuit in Fig. 1 (*b*) and the mix circuit in Fig. 1 (*c*). We now describe in detail the two new aspects of the process, namely the addition and the mixing of liquid.

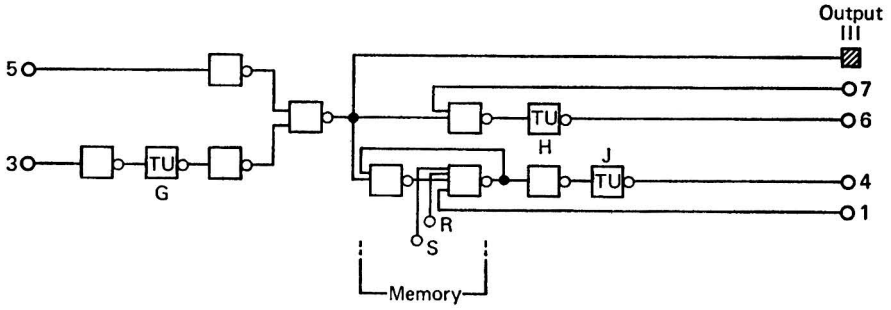


Fig. 1 (*c*). Mix circuit

ADDITION OF LIQUID TO THE VISCOMETER—

Provision is made for two possible modes of addition by introducing between the basic start-level output and the time-counter circuit a simple circuit [Fig. 1 (*a*)], which we term the operations-mode circuit. With the counter connected to Y the addition of an increment of titrant takes place after the flow time of the existing mixture has been determined. However, with the switch in position X, the addition of titrant to the reservoir commences a short time after the measurement of flow time begins and while the previous mixture is still flowing down the capillary. This addition of fresh titrant cannot affect the composition of the liquid of which the viscosity is being measured, but there can be a substantial saving of over-all time as the addition can be made to take place during the period required to measure the flow time.

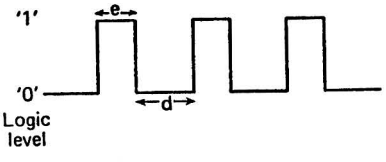


Fig. 2. Oscillator output wave form

Let us suppose that an initial charge of liquid, sample S, has been placed in the viscometer, and that the required number of flow time measurements has been taken (in the manner described in detail in Part I[1]). The number of flow time measurements required is pre-set on the time-counter switch. The output of this counter goes to 1 and is remembered by both first and second memory units [Fig. 1 (*a*)]. The output of the second memory unit returns to the stop-level circuit to inhibit the fill process and the output of the first memory unit goes to the variable mark - space ratio oscillator via terminal 2 [Fig. 1 (*b*)]. The output of this oscillator goes between 0 and 1 in square-wave form as shown in Fig. 2. The length of pulse, e, (Fig. 2) and the separation of the pulses, d, (Fig. 2) depend on the values of the capacitors and resistors used with the two timer units (Fig. 3, D and E). The output of the oscillator is used in the present equipment to drive a Radiometer Autoburette ABU12b, each pulse causing one increment of titrant, T, to be delivered. This instrument can be supplied with a range of burette assemblies, but in each case one increment is 0·04 per cent. of the total burette volume. The delivery of an increment is triggered by energising the ABU12b internal relay with approximately 70 V d.c. and the output of the oscillator [output II, Fig. 1 (*b*)] is used to effect this operation via a low power, thyristor trigger, output unit (YL6023/01), as shown in Fig. 4. (In a modified version of the apparatus constructed by one of us (J.S.S.) in London, the output from the low power amplifier 21A60 is used to drive a 600-Ω miniature relay. The input socket 2 on the back of ABU12 is taken to the contacts of this relay so that the ABU12 delivers one increment each time they close.)

When it is required to add large amounts of titrant, the switch at the input of the oscillator is opened and the autoburette is operated manually. The Radiometer Autoburette has a gearbox that provides a choice of delivery rates. As it is necessary for the increment to be completely delivered before the start of the next command pulse, the values of the parameters d and e must depend on the delivery rate chosen. Further, it is a characteristic of this instrument that the command pulse must be held for 60 per cent. of the time taken to deliver one increment. Both these factors make it imperative to choose carefully the values of the capacitors and resistors associated with the two timer units in the oscillator. It has been found that 10-μF fixed capacitors, used in conjunction with resistor chains connected to a pair of ganged rotary switches, provide the most convenient way of matching the oscillator to the requirements of the autoburette at its various delivery rates (see Fig. 3).

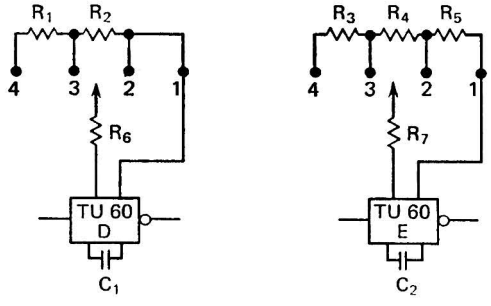


Fig. 3. Adjustable oscillator settings (d and e) compatible with autoburette delivery rate

Switch position	Autoburette delivery rate (percentage of total burette volume minute^{-1})	Space (d)/s	Pulse (e)/s
1	20	2·7	1·0
2	10	2·7	2·0
3	5	5·4	3·0
4	2·5	6·4	5·7

The number of pulses generated by the oscillator and hence the number of increments added by the autoburette is counted by what we have called the add-counter circuit. This comprises two decade counters in series so that the total number of increments added is the product of the numbers on each counter; this produces a wider range of additions than with one counter alone. In early experiments with this sytem it was found that one of the four flip-flops in the first decade was not re-setting during the time required for its output to be transferred to the second decade. This weakness was overcome by introducing the time delay, F, of approximately 1 second's duration.

When the pre-set number of increments have been delivered the output of the second counter goes to 1 and immediately re-sets the first memory unit of the time-counter circuit via terminal 3, thus de-energising the oscillator and ending the process of addition. The output is also taken to that part of the circuit controlling the mixing process [Fig. 1 (*c*)], which we now describe.

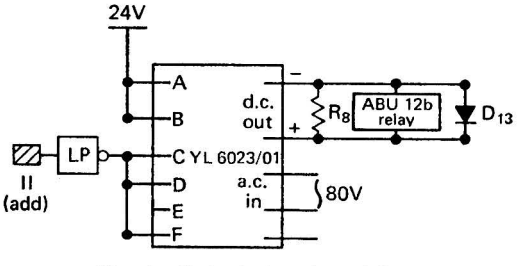


Fig. 4. Output stage to autoburette

MIXING OF LIQUID IN THE VISCOMETER—

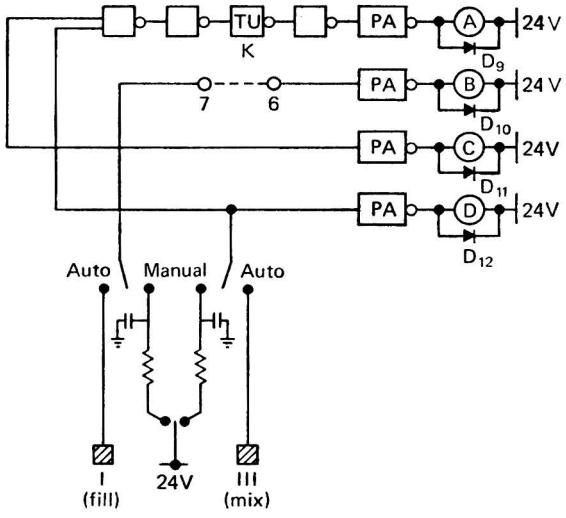


Fig. 5. Output stage to solenoid valves

The mix circuit [Fig. 1 (*c*)] is so designed that, 5 s after the add process has been completed, output III goes to the 1 level (provided that the measurement of flow time has been completed and the subsequent stop-level time delay, B, has elapsed). This output is held at the 1 level for a period of from 1 to 10 s, as controlled by a potentiometer at the time unit, H, and is then cancelled by breaking the add-counter memory circuit via terminal 6. Output III is taken to the output stage and valve circuit (Figs. 5 and 6), thus causing the mix process. It is also taken to the mix memory circuit, which remembers the 1 level at output III after it has fallen back to 0 level. After a fixed period of 20 s in this case, the output of timer unit J goes to 1 level and cancels the time count second memory unit via terminal 4, thus allowing the fill - empty cycle to recommence. The mix memory circuit is cancelled immediately after the next filling has been completed.

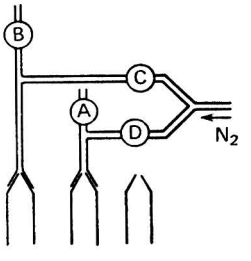


Fig. 6. Solenoid valve assembly. Valves A and B are normally open and valves C and D are normally closed

OUTPUT STAGE AND VALVES—

The solenoid valve output stage is shown in Fig. 5 and the associated assembly of solenoid valves in Fig. 6. It will be noted that this is a modification of the circuit described in Part I of this paper and that it is now necessary to use four valves in order to carry out the filling and mixing operations. The valves are again those manufactured by Skinner Precision Industries. Valves A and B are of the normally open type (specifically V51 DA 2125

24/DC), whereas valves C and D are normally closed (B2 DA 1400 24/DC). These valves receive power, as before, from a separate supply in order to avoid large voltage swings on the logic supply.

Outputs I and III are taken to the output stage via a pair of switches, which may be used to operate the valves manually. With these switches in the "auto" position, the valves will operate as directed by the process control unit in the manner described above, but when these switches are at the manual setting the valves can be operated by placing the "centre-off" switch, which is connected to the 24-V supply, in the appropriate position.

One difficulty that occurred in initial trials was the gradual build-up of pressure behind the solenoid valve C between successive flow time measurements. Sometimes this led to the formation of gas bubbles and in any case to less reproducible conditions for precise measurement of flow times. The problem was solved by introducing a short delay in energising valve B on the command to fill. This was effected without additional logic units by making use of the mix timer unit, H, as shown in Figs. 1 (*c*) and 5.

Experimental

In all applications up to the present time the viscometer used in conjunction with the automatic control system has been of the suspended-level type with a capillary bore of 0·6 mm. All measurements of flow time were made at a constant temperature of 25° ± 0·005 °C. In preliminary trials with pure water as the test material, thirty consecutive measurements of flow time over a period of approximately 2 hours produced a standard deviation of only 2 ms in a flow time of approximately 2·5 minutes.

Standard solutions of hydrochloric acid, sodium hydroxide, ammonia and sulphuric acid were prepared; except where otherwise stated, all analytical chemicals used in this work were of reagent grade and were used without further purification. The results of some typical applications will now be described to illustrate the potentialities of the apparatus.

Table I

Determination of the Jones - Dole equation for hydrochloric acid at 25 °C

Additions of titrant (N HCl)/ ml	Flow time (t)/s	Relative density ($d_{rel.}$)	Concentration (c)/ mole l^{-1}	η_{rel}
0	156·270	1·000 00	0·000 00	1·000 00
0·020	156·302	1·000 01	0·000 89	1·000 22
0·050	156·310	1·000 04	0·002 22	1·000 30
0·100	156·328	1·000 08	0·004 42	1·000 46
0·150	156·346	1·000 12	0·006 62	1·000 61
0·200	156·360	1·000 16	0·008 81	1·000 74
0·250	156·377	1·000 20	0·010 99	1·000 89
0·300	156·391	1·000 24	0·013 16	1·001 02
0·400	156·432	1·000 32	0·017 47	1·001 36
0·500	156·459	1·000 39	0·021 74	1·001 61
0·750	156·543	1·000 58	0·032 26	1·002 33
1·000	156·626	1·000 77	0·042 55	1·003 06
1·250	156·704	1·000 95	0·052 63	1·003 74
1·500	156·777	1·001 16	0·062 50	1·004 41
1·750	156·846	1·001 31	0·072 16	1·005 01
2·000	156·915	1·001 48	0·081 63	1·005 62
2·250	156·987	1·001 64	0·090 91	1·006 24
2·500	157·060	1·001 81	0·100 00	1·006 88

Determination of the A and B coefficients of the Jones - Dole equation (2) for hydrochloric acid at 25·0° ± 0·005 °C—

Pure water (22·50 ml) was placed in the viscometer reservoir initially and increments of M hydrochloric acid were added. The final acid concentration of 0·1 M was achieved by a total addition of 2·50 ml of acid. Flow time readings for each solution are shown in Table I.

Relative densities, $d_{rel.}$, were calculated from the equation—

$$d_{rel.} = 1 + 0{\cdot}0181\, c \qquad (4)$$

based on data by Hückel and Schaaf[2] and valid for the range $c = 0{\cdot}0008$ to 0·15, where c is

the concentration in mole l^{-1}; these are shown in the third column of Table I. From the calculated concentrations (column 4) the relative viscosities (column 5) were determined by using equation (5)—

$$\eta_{rel.} = \frac{t_{solution}}{t_{solvent}} \times d_{rel.} \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where t is the flow time in seconds. The coefficients A and B of the Jones - Dole equation (2) were then calculated from equations (6) and (7)—

$$B = \frac{(\eta_{rel.} - 1)c^{1/2}\Sigma c^{1/2} - (\eta_{rel.} - 1)\Sigma c}{\Sigma c^{3/2}\Sigma c^{1/2} - (\Sigma c)^2} = 0{\cdot}0601^5 \quad .. \quad .. \quad .. \quad (6)$$

$$A = \frac{\Sigma\,(\eta_{rel.} - 1) - B\Sigma c}{\Sigma c^{1/2}} = 0{\cdot}0025 \quad .. \quad .. \quad .. \quad (7)$$

whence

$$\eta_{rel.} = 1 + 0{\cdot}0025\sqrt{c} + 0{\cdot}0601^5 c \quad .. \quad .. \quad .. \quad .. \quad (8)$$

when c is in the range 0·00089 to 0·10000 mole l^{-1}. The standard deviation of $\eta_{rel.}$ ($\sigma_{\eta_{rel.}} = \pm 0{\cdot}004$ per cent.) lies well within the estimated experimental error for such results. The present results are also in reasonably good agreement with those given by Hückel and Schaaf[2] for hydrochloric acid at 25 °C. Their results are summarised in equation (9)—

$$\eta_{rel.} = 1 + 0{\cdot}0021\sqrt{c} + 0{\cdot}0648c \quad .. \quad .. \quad .. \quad (9)$$

where

$$\sigma_{\eta_{rel.}} = 0{\cdot}015 \text{ per cent.}$$

CHARACTERISATION OF POLYMERS BY SOLUTION VISCOSITY—

The usefulness of solution viscosity as a technique for measuring the molecular weights of polymers is well established,[3] and the new apparatus provides for complete polymer characterisation by a rapid and accurate process. The results of measurements on solutions of polymers are generally fitted to an equation of the form—

$$\eta_{rel.} = 1 + [\eta]c + kc^2 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where c is the concentration of the polymer in grams per 100 ml; $[\eta]$ and k are constants for the sample of polymer under investigation.

Both $[\eta]$ and k depend upon the average molecular weight of the sample and, if the form of this dependence is known for a particular polymer, the values of $[\eta]$ and k obtained by experiment can be used to find the molecular weight of the sample.

The subject chosen to demonstrate this characterisation of polymers was a sample of poly(vinyl alcohol), supplied by B.D.H., with a molecular weight of approximately 14 000. An initial charge of 22·5 ml of pure water was placed in the viscometer and a total of 2·00 ml of a stock solution of poly(vinyl alcohol) was added from the autoburette in 0·250-ml aliquots. Values of flow time (t s) and concentration (c g per 100 ml) are shown for each solution in Table II.

TABLE II

DETERMINATION OF THE INTRINSIC VISCOSITY OF POLY(VINYL ALCOHOL) (PVA) IN WATER AT 25 °C

Additions of titrant, PVA stock solution*/ml	Flow time (t)/s	Concentration (c), g per 100 ml	$(t-t_0)/t_0c$
0	156·150(t_0)	0	0
0·250	159·517	0·0552	0·3904
0·500	162·783	0·1092	0·3890
0·750	165·731	0·1621	0·3790†
1·000	169·151	0·2138	0·3894
1·250	172·196	0·2644	0·3887
1·500	175·194	0·3140	0·3884
1·750	178·219	0·3626	0·3898
2·000	180·972	0·4102	0·3875

* Concentration of stock solution was 5·0244 g per 100 ml.
† This point was omitted from the final analysis.

Now,

$$\eta_{rel.} - 1 = [\eta]c + kc^2 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$\therefore \frac{(\eta_{rel.} - 1)}{c} = [\eta] + kc$$

or

$$\frac{(t - t_o)}{t_o c} = [\eta] + kc \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

Values of $(t - t_o)/t_o c$ are also tabulated in Table II. Equation (10) was subjected to a least squares analysis to find $[\eta]$, the intrinsic viscosity and k, whence

$$[\eta] = 0{\cdot}390$$

and

$$k = -0{\cdot}005$$

i.e.,

$$\frac{(t - t_o)}{t_o c} = 0{\cdot}390 - 0{\cdot}005c$$

where

$$\frac{\sigma_{(t-t_o)}}{t_o c} < 0{\cdot}002$$

Difficulty was experienced in achieving complete mixing with these viscous solutions without introducing persistent air bubbles that would invalidate measurements of flow time. Clearly, in its present form the viscometer itself is not suited to this type of measurement and a viscometer should be chosen that is specially designed for work with solutions of high viscosity.

TITRATION OF BASES WITH A STRONG ACID—

The previous two applications, the production of Jones - Dole graphs and the characterisation of polymers, merely demonstrate the automation of well established experimental techniques, but the technique of being able to make and follow changes of species in a solution by a continuous monitoring of solution viscosity is, we believe, a novel use of such measurements.

Viscometric titrations show many similarities with conductimetric titrations both in the shapes of the resultant graphs and in the fundamental theory. As each ion has its own conductivity, so is it possible to assign to it an ionic viscosity derived from the B-coefficients of the Jones - Dole equation for different electrolytes.[4]

For example, B values for salt pairs with the same anion but different cations have constant differences and therefore additivity is adduced to the separate ions. Just as the isoelectronic K^+ and Cl^- ions are assigned the same ionic radius so they are considered to contribute equally to the total viscosity of a solution of potassium chloride. Reference 4 lists the B-coefficients for such a solution up to 0·1 M at 25 °C as −0·014. It is therefore apparent that the assigned ionic viscosity for both K^+ and Cl^- is −0·007. In a similar manner, by using this principle of additivity, the ionic viscosities of the other ions can be determined. Table III lists some of these values that are particularly relevant to the present work.

TABLE III

IONIC VISCOSITIES IN WATER AT 25 °C
Concentrations normally <0·1 M

Ion	K^+	Cl^-	H^+	Na^+	OH^-
Viscosity (B-coefficient)	−0·007	−0·007	+0·067	+0·086	+0·119

It can be predicted from the values given in Table III that the viscosity changes during a titration of sodium hydroxide solution with hydrochloric acid at the temperature and concentration stated will consist of a relatively sharp decrease in viscosity (and flow time) up to the end-point as hydroxide ions (large B-coefficient) are replaced by chloride ions (smaller B-coefficient), followed by a more steady increase beyond the end-point as hydrochloric acid is added to the solution of sodium chloride that results at the end-point, so

increasing the total concentration of ions. Such a titration was performed, a single flow time being recorded after each addition of acid. The results are expressed graphically as the titration "curve" in Fig. 7. Similar acid-to-base titrations were carried out by using hydrochloric acid and a variety of bases including ammonia solution, pyridine and ethylenediamine. In each instance graphs similar in general appearance to that in Fig. 7 were obtained, all with clearly discernible break-points coincident with the stoicheiometric end-points. In the case of ethylenediamine two such break-points were evident. Also, as expected, no significant changes were observed when the titrations were repeated in solutions of high, constant ionic strength (*e.g.*, in a molar solution of sodium nitrate).

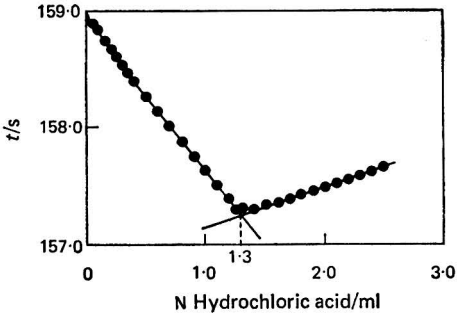


Fig. 7. Viscometric titration of 0·1 N sodium hydroxide solution (13 ml) with N hydrochloric acid

TITRATIONS OF ACIDS WITH A STRONG BASE—

A large number of acids have been titrated viscometrically to date with sodium hydroxide solution as the base and titrant. Fig. 8 shows two typical graphs recorded for the strong acid, hydrochloric acid, and for phenol ($pK_a = 10{\cdot}00$ at 25 °C). The difference in acid strength appears to have little or no effect on the significance or validity of the end-points.

Polybasic acids have also been successfully titrated with the capillary-flow titrimeter. These include sulphuric, oxalic, tartaric, citric and orthophosphoric acids. With the last, distinct breaks were produced for all three end-points, including that for the removal of a proton from HPO_4^{2-} ($pK_a = 12{\cdot}30$), which is not readily detectable by other analytical techniques.

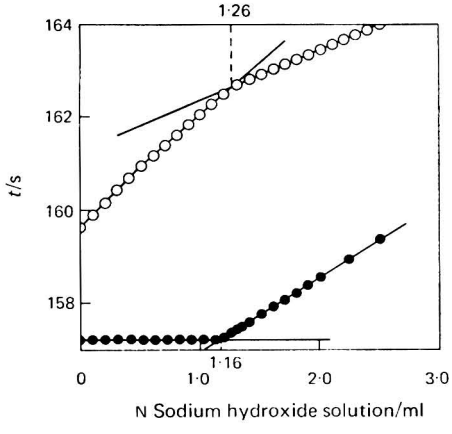


Fig. 8. Viscometric titration of 0·1 N hydrochloric acid (12 ml) and 0·1 N phenol (13 ml) with N sodium hydroxide solution: ○, hydrochloric acid; and ●, phenol

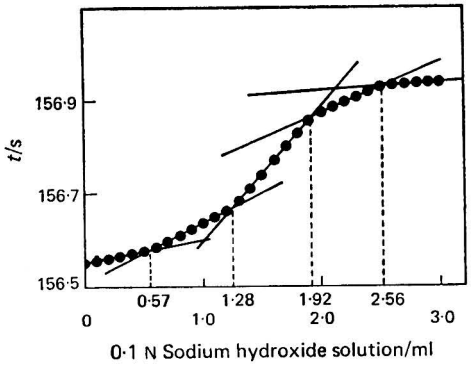


Fig. 9. Viscometric titration of 0·01 N EDTA solution (25 ml) with 0·1 N sodium hydroxide solution

However, an excellent example of the potential of viscometric titrimetry is the neutralisation of ethylenediaminetetraacetic acid (EDTA; H_4Y) with sodium hydroxide. This titration was carried out by adding aliquots of 0·1 N sodium hydroxide solution to a solution of 0·01 N EDTA initially contained in the viscometer reservoir. Fig. 9 depicts the viscometric titration graph for the pure acid (EDTA), break-points attributable to all four end-points being clearly visible. In order to show clearly the association between these break-points and changes of species in solution, the distribution of the species H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-} in solution during the course of the titration was calculated and is shown together with the calculated pH titration curve in Fig. 10. In this case it is evident that the new technique of titration by viscosity monitoring provides much more information than does pH measurement about the basic changes occurring during the titration and the relationship of these changes to the stoicheiometry of the neutralisations. Although only simple acid - base neutralisations have been discussed in this report on applications of our capillary-flow titrimeter, it is probable that the instrument and technique will lend themselves to the study of innumerable analytically important systems. Further, the electronic logic circuitry has been designed so that additional or alternative circuits to extend the versatility of the automatic operation can be incorporated as the need arises and with the least possible disturbance of existing circuitry.

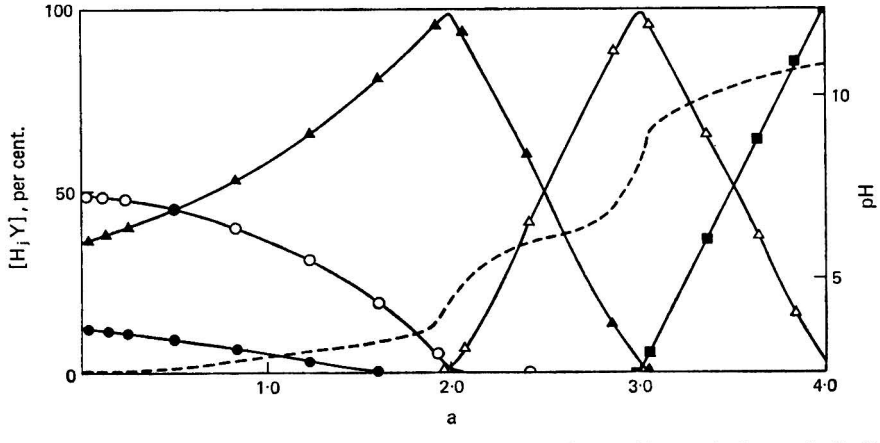


Fig. 10. Graphs of percentage $[H_iY]$ for EDTA against a (the equivalents of alkali added per mole of EDTA). The graphs relate directly to the viscometric titration shown in Fig. 9. Also shown is the pH titration curve for the neutralisation of EDTA. ●, H_4Y; ○, H_3Y^-; ▲, H_2Y^{2-}; △, HY^{3-}; ■, Y^{4-}; and – – –, pH

One of us (J.S.S.) thanks the Royal Society and the Chemical Society for grants towards the cost of his equipment and another (R.B.S.) is grateful to the Science Research Council for a Research Studentship.

References

1. Smith, J. S., Irving, H. M. N. H., and Simpson, R. B., *Analyst*, 1970, **95**, 743.
2. Hückel, E., and Schaaf, H., *Z. Phys. Chem.*, 1959, **21**, 326.
3. Billmeyer, F. W., jun., "Textbook of Polymer Chemistry," Interscience Publishers Inc., New York, 1957, pp. 80–87.
4. Stokes, R. H., and Mills, R., "Viscosity of Electrolytes and Related Properties," Pergamon Press, Oxford, 1965.

NOTE—Reference 1 constitutes Part I of this series.

Received *December 11th*, 1970
Accepted *March 16th*, 1971

Appendix

List of components

Resistors—

R_1, R_4, R_5, R_7	= 100-kΩ, ¼-W
R_2, R_3, R_6	= 270-kΩ, ¼-W
R_8	= 1·5-kΩ, 6-W

Capacitors—

C_1, C_2	= 10-μF low-leakage polycarbonate type

Diodes—

D_1, D_2, D_5, D_6, D_7, D_8	= BAX 16
D_3, D_4	= BAX 13
D_9, D_{10}, D_{11}, D_{12}	= BYX 22/200
D_{13}	= BYX 22/400

Norbit 2 components—

Quantity	Symbol lettering	Description
2	PS	Pulse shaper PS90
9	TU*	Timer unit TU60
1	LP	Low power amplifier LPA60
4	PA	Medium power amplifier PA60
16	—	Twin 4 input Norbits 2NOR60
1	YL6023/01	Low power thyristor trigger output unit
or 1	24 V	Miniature relay (see text)

* Timer units—

Letter	Time delay/s	
A	1 to 11	Variable
B	1 to 11	Variable
C	5	Fixed
D	Oscillator (see Fig. 3)	
E		
F	1	Fixed
G	5	Fixed
H	1 to 11	Variable
J	20	Fixed
K	1 to 3	Variable

Terminal inputs—

Letter	Description
R	Manual re-set input
S	Switch-on re-set input

For a more detailed explanation of components and design, including decade counters, used in the circuitry of this paper consult "A design guide for Norbit 2" and associated literature obtainable from Industrial Electronic Controls (Mullard) Ltd.

Analyst, August, 1971, Vol. 96, *pp.* 562–564

An Inert Dilution Method for the X-ray Fluorescence Analysis of Niobate - Tantalate Mineral Concentrates

BY Y. C. WONG AND S. SEEVARATNAM

(Geological Survey of Malaysia, Perak, Malaysia)

An X-ray fluorescence method, in which iron(III) oxide is used as inert diluent, is described for the determination of niobium, tantalum, tin and titanium in concentrates of polymineral composition. No time-consuming fusion procedures or tedious calculations are involved. The simplicity and rapidity of the method merit its use in routine analysis. Good agreement with chemical analysis is obtained.

THE mineral concentrates submitted to the Geological Survey of Malaysia for the determination of niobium and tantalum are usually high grade columbite or tantalite - columbite containing various proportions of ilmenite, rutile, cassiterite, monazite, xenotime, wolframite and zircon; the latter concentrate is particularly difficult and tedious to analyse by conventional chemical methods. Rose and Brown[1] have described an X-ray fluorescence method in which matrix effects are minimised by fusing the sample with a mixture of lithium borate and lanthanum oxide. The present investigation was undertaken to find a more rapid and cheaper method of determining niobium, tantalum, tin and titanium in concentrates of polymineral composition. Such a method would be of direct benefit to the mining industry in instances when quick and accurate results are required, as with beneficiation processes and the evaluation of mineral dumps.

According to Sherman[2] and Vera Mège,[3] if a sample can be mixed with a definite proportion of an arbitrary diluent, it is possible to derive simple inert dilution equations containing measurable quantities only. With this technique, X-ray fluorescence measurements are made directly on a portion of the original sample, and on another portion after it has been mixed with a definite proportion of an inert diluent. By solving the intensity equations of these samples, an expression is obtained which is independent of the absorption coefficient of the original sample. This inert dilution equation may be written as $X = K.D(X).R(I)$, where the concentration, X, is dependent only on the intensity relation, $R(I)$. $D(X)$ is the dilution factor. The constant K for each analytical line, diluent, tube voltage and reference sample is determined from the inert dilution equation by using a standard sample. This value of K can be used with any sample provided the latter is prepared and measured under conditions similar to those used with the standard. The same two sample portions, the original and the diluted, are used for the determination of niobium, tantalum, tin and titanium. Equipment variables are almost completely eliminated by using a reference sample. The inexpensive calcined iron(III) oxide (supplied by British Drug Houses Ltd.) is used as inert diluent. Iron(III) oxide was chosen because it has been found to mix homogeneously with heavy mineral concentrates that pass a 300-mesh sieve.[4]

Among the major elements normally encountered in the tantalite - columbite concentrates, yttrium and zirconium can interfere in the determination of niobium. To ascertain how these interferences could be overcome, five spiked samples containing various proportions of xenotime and zircon were prepared. The concentration of yttrium oxide (Y_2O_3) and zirconium dioxide (ZrO_2) in the spiked samples ranged from 5 to 30 per cent. Five concentrate samples were also analysed by the inert dilution method to determine niobium and tantalum pentoxides, tin dioxide and titanium dioxide, and the results obtained were compared with those determined chemically.

Experimental

Sample preparation—

All samples were ground to less than 300 mesh in a Siebtechnik vibratory disc-type mill. The mixing of sample and diluent was also carried out in this mill.

The diluted sample was prepared by mixing 0·5000 g of sample and 1·5000 g of iron(III) oxide in the mill for 5 minutes. It was then made into a boric acid backed and edged button under a pressure of 10 tons inch^{-2}. The original sample was prepared by pressing 2 g of the powdered concentrate into a button under the same pressure as for the diluted sample.

Instrumentation—

A fully stabilised all-vacuum Philips X-ray spectrograph, Model PW1540, with a pulse-height analyser attachment and a tungsten-target X-ray tube was used in this investigation. Measurements of X-ray intensities were made in air with the aid of a lithium fluoride crystal (2d = 0·4208 nm). Other relevant instrumental conditions are summarised in Table I.

Table I

Operating conditions for X-ray analysis

Element	Line	Voltage/ kV	Current/ mA	Pulse-height analyser		Detector
				L level/V	Window/V	
Niobium	$K\beta_1$	30	10	0·650	1·225	Scintillation
Tantalum	$L\alpha_1$	32	20	0·850	1·700	Scintillation
Tin	$K\alpha$	40	20	0·635	0·925	Scintillation
Titanium	$K\alpha$	32	22	0·650	1·300	Flow-proportional

For niobium, tantalum and tin the net counts of each element were obtained by subtracting the average value of the background counts from that taken at the analytical line. There was no need to correct for background in the determination of titanium. Table II lists the line and background angles (2θ) for the various elements.

Table II

Settings for line and background angles

Element	Line/°	Background/°
Niobium	18·97	18·00; 19·90 (low Zr), 19·50 (high Zr)
Tantalum	44·40	43·70
Tin	13·97	13·00; 15·00

Analysis time—

The analysis time for one sample analysed in duplicate was about 2 hours, which included preparation of samples, measurement of X-ray fluorescence intensities and calculations. Depending on the concentration of the element under analysis, the counting times on the line and background of the concentrate sample and diluted sample vary from 10 to 100 s.

Calculation—

The inert dilution equation for calculating the percentage of metal oxide is

$$\text{Metal oxide, per cent.} = \frac{\mathrm{K}.D(X).I_\mathrm{c}.I_\mathrm{d}}{I_\mathrm{r}\,(I_\mathrm{c} - I_\mathrm{d})}$$

where K and $D(X)$ are constants, and I_c, I_d and I_r refer to the net counts of the concentrate, the diluted sample and reference sample, respectively.

Results and discussion

Analysis of the spiked samples showed that it was necessary to correct for background when the niobium $K\beta_1$ line was used because of the proximity of the zirconium $K\beta_1$ line. It can be seen in Table III that when background correction was not made the positive error became particularly large at low concentrations of niobium pentoxide. If the sample does not contain yttrium the use of the niobium $K\alpha$ line is preferred because it gives better sensitivity. In the determination of tantalum, the second-order reflection of niobium $K\alpha$ is

almost completely removed by pulse-height analysis while the scattered tungsten $L\alpha_1$ is well resolved by the lithium fluoride crystal with the aid of fine collimation. Results presented in Table III show that niobium and tantalum can be determined accurately in the presence of yttrium and zirconium.

Table III

Effect of background on the analysis of niobium and tantalum pentoxides

	Nb_2O_5, per cent.			Ta_2O_5, per cent.		
Sample	Calculated	Found	Found*	Calculated	Found	Found*
S1	53·7	53·4	54·5	10·9	11·1	11·3
S2	46·1	46·6	48·8	9·30	9·48	9·80
S3	30·7	30·4	33·6	6·20	6·40	7·15
S4	15·4	15·1	18·4	3·10	3·18	4·16
S5	7·70	7·75	10·7	1·55	1·46	2·62

* These results have not been corrected for background.

A comparison of results obtained by X-ray and chemical analysis is presented in Table IV. Results obtained by the inert dilution method are within ± 5 per cent. of those determined chemically.

Table IV

Comparison of results obtained by X-ray and chemical analysis

	Nb_2O_5, per cent.		Ta_2O_5, per cent.		SnO_2, per cent.		TiO_2, per cent.	
Sample	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical
A	59·4	58·4	14·4	15·1	1·50	1·57	2·24	2·22
B	58·5	58·3	10·8	10·2	1·79	1·88	3·87	3·72
C	57·6	56·8	16·9	17·7	2·24	2·29	1·49	1·43
D	21·8	22·3	38·7	39·2	5·14	5·28	1·62	1·66
E	19·9	20·5	45·3	45·8	8·00	7·97	3·98	4·24

Precision—

Ten samples of B were prepared and analysed four times. The calculated coefficients of variation corresponded to 0·30 per cent. for niobium pentoxide, 0·28 per cent. for tantalum pentoxide, 0·12 per cent. for tin dioxide and 0·08 per cent. for titanium dioxide.

Conclusion

The results presented here demonstrate that the powder X-ray fluorescence method, with iron(III) oxide as inert diluent, can be used to provide rapid and accurate determinations of niobium, tantalum, tin and titanium in concentrates of different mineralogical composition. The simplicity of this method merits its use in routine analytical work.

This paper is published with the permission of the Director, Geological Survey of Malaysia. We thank Dr. T. R. Sweatman for valuable discussion, Mr. E. H. Yin and Mr. A. G. Darling for their comments and suggestions in the presentation of this paper, Mr. Y. L. Tong (Senior Chemist) and his assistants, Mr. M. H. Yap and Mr. F. C. Thong, for carrying out the chemical analyses, Mr. S. H. Ow for his able experimental assistance and Mrs. Y. C. Wong for her encouragement.

References

1. Rose, H. J., jun., and Brown, R., *Adv. X-ray Analysis*, **1963**, **7**, 598.
2. Sherman, J., *Ibid.*, **1957**, **1**, 231.
3. Vera Mège, R., *Analyt. Chem.*, **1969**, **41**, 42.
4. Sweatman, T. R., Wong, Y. C., and Toong, K. S., *Trans. Instn Min. Metall.*, **1967**, **76**, B149.

Received *October 19th*, **1970**
Accepted *December 2nd*, **1970**

Analyst, August, 1971, Vol. 96, *pp.* 565–568

Determination of Ammonium in Soil Extracts by an Automated Indophenol Method

By A. R. SELMER-OLSEN

(Agricultural College of Norway, Vollebekk, Norway)

An automated method is described for the determination of ammonium in 2 N potassium chloride soil extracts. The determination is based on the indophenol blue method following a dialysing step. As little as 0·03 mg l^{-1} of ammonium-nitrogen can be determined. The recoveries have been investigated for a number of different soil types and satisfactory results were obtained. Determinations can be carried out at the rate of thirty samples per hour.

Inorganic nitrogen in soils may exist as ammonium, nitrate or nitrite. An automated method for determining nitrite and nitrate has previously been reported.[1] Ammonium determinations, however, are mostly carried out by distillation with magnesium oxide, followed by titration or spectrophotometric determination.[2] Hanawalt and Steckel[3] and Keay and Menage[4,5] have automated the distillation procedure. A disadvantage of their technique, however, is that a special distillation apparatus is required.

This paper describes an automated indophenol method, in which 2 N potassium chloride extracts of soils are analysed to determine exchangeable ammonium[2] or ammonia formed by anaerobic incubation, which involves the use of a dialyser unit.

Method

Apparatus—

A Technicon AutoAnalyzer with a manifold construction, as shown in Fig. 1, was used.

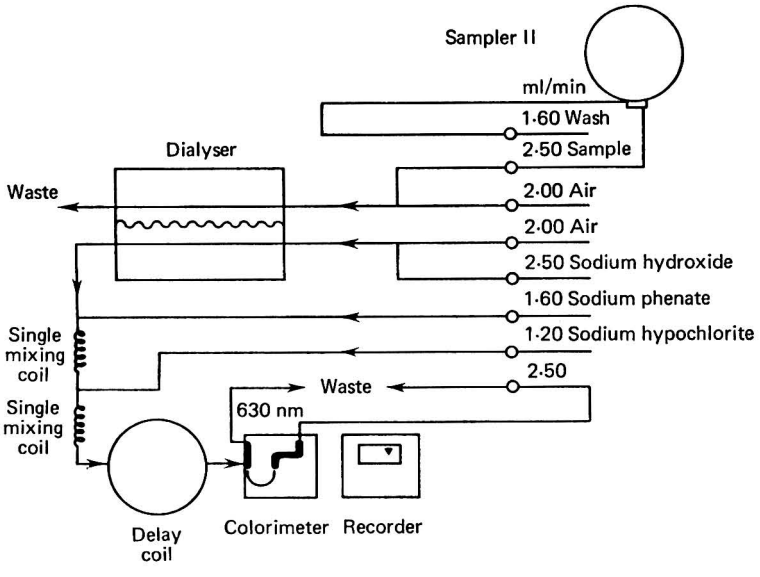


Fig. 1. Flow diagram of apparatus used in automatic method for determining ammonium in soil extracts

REAGENTS—

Potassium chloride, 2 N.

Sodium hydroxide - sodium tartrate solution—Dissolve 1 g of sodium hydroxide and 5 g of potassium sodium tartrate in water and make the volume up to 1 litre.

Alkaline phenol solution—Dissolve 62·4 g of phenol in 100 ml of 27 per cent. sodium hydroxide solution, cool, add 20 ml of acetone, and make the volume up to 1 litre with water.

Sodium hypochlorite solution—Dilute 50 ml of commercial sodium hypochlorite solution (containing about 12 per cent. of available chlorine) with water to 1 litre.

PROCEDURE—

Shake 5-g samples of soil for 1 hour with 25 to 100 ml of 2 N potassium chloride, depending on the ammonium content, and filter the extracts through Schleicher and Schüll No. 589 white ribbon filters.

In determining ammonium after anaerobic incubation, the solution was diluted with an equal volume of 4 N potassium chloride so as to obtain a solution 2 N with respect to potassium chloride. The filtered extracts seemed to remain stable for several hours at room temperature. For longer storage, however, they should be placed in a refrigerator.

Because the soil extracts can be coloured or contain particles the samples are dialysed in the AutoAnalyzer into a sodium hydroxide solution containing tartrate (to prevent precipitation of hydroxides). The ammonium present produces a blue colour with the alkaline phenol and hypochlorite. If the laboratory temperature is not constant it is advisable to place the delay coil in a heating bath at 22 °C.[6]

EFFECT OF pH—

Interference will occur if the concentration of acids in the extracts is too high, because the amounts of alkaline reagents used in the system will not then neutralise the acids. On the other hand, if the extracts are alkaline there will be some loss of ammonia. Soils with pH values in the range 3·5 to 7·6 were extracted with 2 N potassium chloride. Known amounts of ammonium were added to aliquots of the extracts, and the ammonium contents were determined. Table I shows recoveries of 97 to 102 per cent.

TABLE I

RECOVERY OF AMMONIUM ADDED TO EXTRACTS FROM SOILS WITH DIFFERENT pH VALUES

Soil	pH	Ammonium-nitrogen/mg l^{-1}		
		Found in extracts without addition	Found in extracts with addition of 3·43 mg l^{-1} of ammonium-nitrogen	Recovered
Peat	3·5	0·71	4·10	3·39
Sand (large organic matter content)	4·1	0·71	4·05	3·34
	4·3	0·46	3·80	3·34
	4·5	0·21	3·60	3·39
Coarse sand	5·2	2·15	5·60	3·45
Sand	5·3	0·67	4·10	3·43
	5·4	0·54	4·00	3·46
Sandy clay	6·4	0·53	3·93	3·40
Clay	6·6	1·69	5·20	3·51
Sandy peat	6·8	1·83	5·30	3·47
Coarse sand	7·0	0·53	3·95	3·42
Sand	7·4	0·48	3·93	3·45
Coarse sand	7·4	0·42	3·90	3·48
Sand	7·6	0·18	3·62	3·44
	7·6	0·52	3·90	3·38

INTERFERENCES—

Known amounts of ammonium were quantitatively recovered from 2 N potassium chloride solutions containing at least 2 g l^{-1} of the following salts: sodium sulphate, sodium sulphite, potassium nitrate, potassium nitrite, dipotassium hydrogen orthophosphate, potassium bromate, copper sulphate, aluminium sulphate, zinc sulphate, iron(II) sulphate,

iron(III) chloride, calcium sulphate, magnesium chloride, urea and guanidine. Up to 0·5 g l^{-1} of asparagine, betaine, glucosamine, glutamine, galactosamine and diphenylamine did not cause noticeable interference; 10 per cent. of the nitrogen contained in hydroxylammonium chloride was determined as ammonium, probably because of the presence of ammonium in this chemical. More than 1 g l^{-1} of manganese sulphate interfered seriously because precipitation occurred. If present in amounts exceeding 0·1 g l^{-1}, methionine decreased the recovery of ammonium.

RECOVERY OF ADDED AMMONIUM—

Known amounts of ammonium chloride were added to 10-g samples of different soils prior to extraction with 50 ml of 2 N potassium chloride. The ammonium contents found are given in Table II, and the results indicate that the recovery of added ammonium was satisfactory for all of the soils investigated.

TABLE II

RECOVERY OF AMMONIUM ADDED TO DIFFERENT SOILS

Ammonium-nitrogen added per 100 g of soil/mg	0	4		8		20	
		Ammonium-nitrogen/mg					
Sample	Found	Found	Recovered	Found	Recovered	Found	Recovered
Clay	2·15	6·30	4·15	10·2	8·05	20·2	18·05
	3·50	7·40	3·90	11·6	8·10	23·3	19·8
	8·00	12·1	4·10	16·2	8·20	28·4	20·4
	2·80	6·90	4·10	11·2	8·40	22·4	19·6
Sand	4·10	8·00	3·90	12·2	8·10	24·0	19·9
	3·50	7·20	3·70	11·5	8·00	22·6	19·1
Peat	8·20	12·1	3·90	16·0	7·80	27·2	19·0
	12·1	16·2	4·10	20·3	8·20	31·6	19·5
	20·0	23·8	3·8	—	—	38·2	18·2
	22·0	25·9	3·9	—	—	40·2	18·2

SENSITIVITY AND PRECISION OF THE METHOD—

With the manifold shown in Fig. 1, ammonium in 2 N potassium chloride extracts could be determined within the range 0·1 to 20 mg l^{-1} of ammonium-nitrogen. If a small peak follows a very large peak some contamination may occur, in which event it would be advisable

TABLE III

AMOUNTS OF AMMONIUM FOUND IN 2 N POTASSIUM CHLORIDE EXTRACTS BY DISTILLATION AND BY AUTOANALYZER

Soil	Ammonium-nitrogen found in 100 g of soil/mg	
	By distillation	By AutoAnalyzer
Clay	5·1	4·82
	7·7	7·55
	5·2	4·83
	5·4	5·40
	3·9	3·57
	4·4	4·17
	7·2	6·58
	6·4	5·98
Sandy clay	4·6	4·73
	7·0	7·60
	5·4	5·23
Silty clay	5·9	5·88
Silt	2·4	2·40
Sand	1·9	1·97
Mud from sewage	29	25·0
	57	56·3

to carry out a wash between samples. If 5-g soil samples are extracted with 25 ml of 2 N potassium chloride, then 0·05 mg of ammonium-nitrogen per 100 g of soil can be determined. The sensitivity can be increased by using the range expander at $\times 2$, $\times 4$ or $\times 10$ expansion. With $\times 10$ expansion, the determination can be carried out in solutions containing 0·03 mg l^{-1} of ammonium-nitrogen.

On the basis of forty-one samples, the standard deviation of the method was found to be $\pm 0{\cdot}08$ mg l^{-1} of ammonium-nitrogen within the range 0·4 to 15 mg l^{-1} of nitrogen. On the basis of thirty-eight samples, with the range expander at $\times 10$ expansion, the standard deviation was found to be $\pm 0{\cdot}012$ mg l^{-1} of ammonium-nitrogen within the range 0·03 to 0·3 mg l^{-1} of nitrogen. The standard deviation given above is of the same order of magnitude as the errors in the reading of results from the calibration graph.

Comparison of methods

A series of soil extracts was prepared, and the ammonium contents were determined directly by the automated method and by steam distillation with magnesium oxide, according to Bremner.[2] The results shown in Table III indicate that the distillation method gave slightly higher results than those given by the AutoAnalyzer method, which is probably caused by interference from labile organonitrogen compounds destroyed by the steam distillation with magnesium oxide and determined as ammonium.

References

1. Henriksen, A., and Selmer-Olsen, A. R., *Analyst*, 1970, **95**, 514.
2. Bremner, J. M., "Inorganic Forms of Nitrogen in Methods of Soil Analysis," Part 2, Agronomy No. 9, American Society of Agronomy, 1965.
3. Hanawalt, R. B., and Steckel, J. E., "Automation in Analytical Chemistry, Technicon Symposium, New York," 1966, Volume 1, p. 133.
4. Keay, J., and Menage, P. M. A., *Analyst*, 1969, **94**, 895.
5. ——, ——, *Ibid.*, 1970, **95**, 379.
6. Davidson, J., Mathieson, J., and Boyne, A. W., *Ibid.*, 1970, **95**, 181.

Received *November 16th*, 1970
Accepted *April 5th*, 1971

Analyst, August, 1971, Vol. 96, *pp.* 569–578

A Field Method for the Determination of Zinc Oxide Fume in Air

BY B. S. MARSHALL, I. TELFORD AND R. WOOD

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

A method is described for the determination of zinc oxide fume in industrial atmospheres at concentrations up to 20 mg m^{-3} of zinc oxide. The fume is collected on a filter and dissolved in acid, and the zinc is determined spectrophotometrically or visually with 4-(2′-thiazolylazo)resorcinol reagent. The apparatus used is simple and the time required for a determination is about 20 minutes. A dynamic method for the generation of atmospheres of zinc oxide is also described.

THE main environmental health hazard from zinc, a metal widely and diversely used in industry, is from the inhalation of fume of freshly formed zinc oxide. It is well known that overexposure to this can cause metal-fume fever.[1] Two of the main industrial processes that produce zinc oxide fume are the casting of zinc-containing alloys and the welding of galvanised steel sheet. A relatively low threshold limit value for zinc oxide fume of 5 mg per cubic metre of air is recommended at present.[2]

No doubt the total zinc content of an industrial atmosphere could be determined by the use of a suitable physical technique such as atomic-absorption spectrophotometry. However, in view of the toxicity and widespread occurrence, often in the smaller industrial establishments, of zinc oxide fume, the need appeared for a field test that required no sophisticated equipment yet could be used to determine the total zinc content of an air sample quickly and reliably. It was envisaged that any such test developed would involve the collection of the zinc-containing fume and dust on a suitable filter, rapid dissolution of the sample in acid and finally the colorimetric determination of the total zinc. It was recognised that the results obtained from such tests might include some zinc not originally present in the air as the oxide, but any over-estimation in this way of the zinc oxide content would err on the side of safety.

PREPARATION AND CALIBRATION OF ATMOSPHERES OF ZINC OXIDE FUME

Atmospheres of zinc oxide fume were required for use in the development of the field test. A search of the literature revealed no simple way of generating atmospheres of zinc oxide fume and in view of this the assistance of the Chemical Defence Establishment, Porton, was sought. They suggested a system whereby suitable atmospheres were produced by the pyrolysis in a bunsen burner flame of a zinc acetate aerosol issuing from a Collinson atomiser.[3] A generator incorporating these basic principles was constructed. After several modifications had been made to the original generator to increase the yield of fume produced, the model shown in Fig. 1 was finally adopted as it provided the most consistent results.

PREPARATION—

Air at 15 p.s.i. ($1{\cdot}034 \times 10^5$ N m^{-2}) was passed through a Collinson atomiser, A (Fig. 1), containing initially 100 ml of an aqueous solution of zinc acetate, B. The resulting aerosol was fed into the burner chamber, C, where it was used as the air supply to the Meker burner, D, which had a ceramic grid 24 mm in diameter with 37 holes, each 2 mm in diameter. The burner had no gas adjustment and consumed about 4 l $minute^{-1}$ of town gas, the unwanted aerosol escaping through a vent for excess air. The burner chamber was fashioned from a tin can and the chimney, E, which was 0·72 m in height and 0·15 m in diameter, from tin plate.

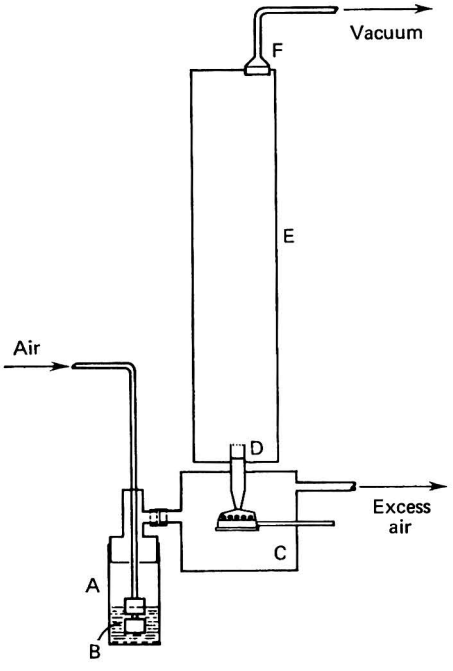


Fig. 1. Metal oxide aerosol generator: A, Collinson atomiser; B, zinc acetate solution; C, burner chamber; D, burner; E, chimney; and F, filter-paper holder

In the early experiments with the fume generator, the chimney was sited directly on top of the burner chamber. With this arrangement it was necessary to sample at a considerable height above the chimney to avoid distortion of the filters by heat; also, it was impossible to obtain reproducible results from duplicate samples taken simultaneously at the same site. The arrangement shown in Fig. 1, with a 12·5-mm gap between burner chamber and chimney, obviated these disadvantages and it was possible to sample with the filter-paper holder, F, just inside the top of the chimney. When compressed air, containing only 4 to 5 mg m^{-3} of water vapour, was used to atomise the zinc acetate solution, a progressive increase in the concentration of the fume generated was noted. This was attributed to a gradual evaporation of water from the solution by the flow of air. The use of compressed air that had been passed through a water saturator prior to the atomiser minimised this effect.

CALIBRATION—

Our normal practice in developing a field test for any particular contaminant is to generate a constant known atmosphere of this contaminant. Despite the modifications described above, the generator was not capable of producing constant atmospheres of zinc oxide fume. There was invariably a tendency for a progressive increase in the concentration of successive atmospheres generated from any one zinc acetate solution, although the use of 5 and 15 per cent. w/v solutions in the above generator initially gave aerosol atmospheres of 4·4 and 9·2 mg m^{-3} of zinc oxide fume, respectively. In view of this inability to produce a constant atmosphere, the required calibration was carried out on collected samples of zinc oxide fume, which were analysed by different techniques. A series of these samples, which were adjudged to be in the range 0 to 100 μg, was first examined by a non-destructive method of analysis, X-ray fluorescence spectrometry, and the relative responses were recorded. Each

sample was then dissolved in acid and the zinc content determined by the proposed spectrophotometric method and an atomic-absorption method for which calibration graphs had been prepared previously by using a standard zinc solution. A graph of the X-ray fluorescence response against the average zinc content found by use of the two standard methods gave a straight line. These results were further analysed by means of a suitable computer programme to obtain the best straight line (see Fig. 2), which was subsequently used as the zinc calibration curve in the various stages of the development of the field test.

Sampling and collecting total zinc

Choice of filter-paper—

Any sampling technique used in this work had to be capable of quantitatively collecting all particles with a diameter down to 10 nm, this being the lower limit of zinc oxide fume particle size.[4] As it had been shown previously[5] that the Millipore Filter, Type AA, is virtually 100 per cent. efficient for trapping particles with a diameter down to at least 8 nm, when collected at a face velocity of 0·4 m s^{-1}, this filter was considered suitable for the work in question. It has also been independently recommended for the collection of metal fume.[6]

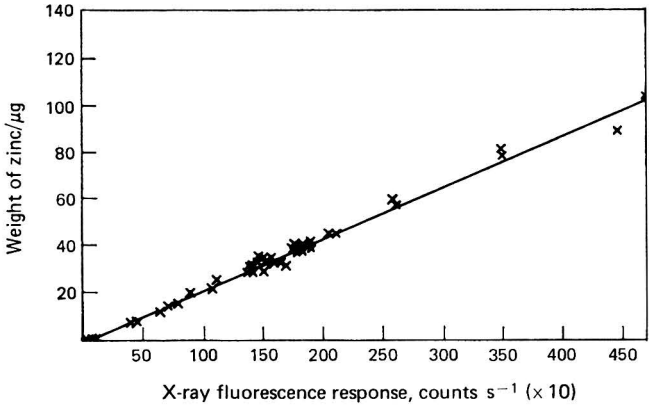


Fig. 2. Relationship between concentration and X-ray fluorescence response for the zinc content of collected zinc oxide fume samples

Removal of fume samples from filters—

The linearity of the graph in Fig. 2 suggested that a collected sample of zinc oxide fume could be dissolved easily and quantitatively from a Millipore filter with dilute acid. This was confirmed by X-ray fluorescence analysis when only trace amounts of zinc (less than 1 μg) were detected on a series of filters, from each of which the zinc oxide fume (in the range 0 to 130 μg) collected on it had been dissolved by soaking it in 2 ml of 5 M hydrochloric acid for a few minutes. The removal of mixed metal fumes from filters is described later (see Interferences).

Colorimetric determination of zinc

A comprehensive survey of the literature showed that zinc is one of the most difficult metals to determine specifically except by a physical technique. A number of reagents that give colorimetric reactions were evaluated, but most were found to be subject to interference by one or more of the metals that could occur with zinc in an industrial atmosphere, *e.g.*, lead, copper, tin and iron. Although zincon[7] and compounds of the thiazolylazophenol[8] type were considered worthy of further examination as reagents, the relatively rapid fading of the zinc - zincon coloured complex detracted from the usefulness of this reagent in a field method. Of the several thiazolylazophenols examined by Kawase[8] for the spectrophotometric determination of zinc, 4-(2′-thiazolylazo)resorcinol (TAR) was selected for the present work

because of its almost unique facility for forming a water-soluble zinc chelate and its commercial availability in the United Kingdom. Kawase[8] had determined most of the optimum reaction parameters but it was decided, in the light of our requirements for a field test, to re-investigate the formation of the red zinc - TAR complex when using a 0·002 M hydrochloric acid solution containing 12·5 μg ml^{-1} of zinc.

CONCENTRATION OF TAR REAGENT—

The original use[8] of the reagent whereby the final reaction mixture contained 1 μg ml^{-1} of TAR was found to give an adequate response for a spectrophotometric determination of zinc.

OPTIMUM pH AND CHOICE OF BUFFER—

By using a buffer solution of borax with sodium acetate, to which dilute hydrochloric acid was added to vary the pH, the previous worker[8] found that the absorbance of the zinc - TAR complex was constant over the pH range from 7·4 to at least 8·4 and selected 7·5 as the optimum value. We substantially confirmed this finding but preferred to use a solution having a higher buffer capacity and also capable of giving a pH nearer the middle of the constant range. On theoretical grounds, and also to accommodate the acid in the eluate from the column used to separate zinc from iron (see section on Separation of iron), a buffer solution of triethanolamine and sodium hydroxide was devised such that the presence of 10 ml of this in the final reaction mixture gave a solution of pH 8. The buffering capacity of this final reaction solution can be gauged from the fact that the addition of 2·5 ml of N sodium hydroxide solution increased the pH to only 9·1 and the addition of the same volume of N hydrochloric acid gave a pH of 7·6. In neither case was the optical density resulting from a known amount of zinc altered. In contrast, similar experiments with the borax - sodium acetate buffer revealed a much reduced buffering capacity, for example, the effect of adding 2 ml of N acid to this buffer was to reduce the pH from 9·1 to 5·8. Later, to minimise the number of reagents required, it was found possible to make up the TAR reagent in the triethanolamine - sodium hydroxide buffer solution. This mixture was stable for at least 14 days at temperatures up to 30 °C.

FORMATION AND STABILITY OF ZINC -TAR COMPLEX—

The formation of the zinc - TAR complex appeared to be rapid and complete within the time lapse (about 1 minute) before a spectrophotometric reading could be taken. The colour was then stable for at least 30 minutes. The slight observed drop (approximately 3 per cent.) in optical density over the next hour was due to an equivalent increase in that of the reagent blank against which all samples were measured; this was not investigated further. At ambient temperatures, 15° to 30 °C, the colour developed was independent of temperature.

PURITY OF TAR REAGENT—

It was intended to check the reliability of solid TAR reagent from various sources, but with material available from only one manufacturer in the United Kingdom, this was not possible. However, materials with identical batch numbers but received more than 1 year apart, and also a sample of the original material received (which had been re-crystallised from aqueous methanol after extraction of any impurities by using a sodium hydroxide solution - diethyl ether partition), were compared with respect to their spectrophotometric responses with standard amounts of zinc. Identical optical densities were obtained. Further confirmation of the purity of the reagent was obtained by thin-layer chromatography on a cellulose plate by using a 2-ethoxyethanol - methanol - water mixture (4 + 1 + 2 v/v) as the mobile phase. Each TAR sample gave a single spot of R_F 0·85.

SPECTROPHOTOMETRIC DETERMINATION OF ZINC—

It was established that 530 nm was the optimum wavelength for the measurement of the zinc - TAR complex with respect to the reagent blank. Also, a plot of the optical density against the weight of zinc was linear over the range 0 to 70 μg, 70 μg of zinc (equivalent to 87·14 μg of zinc oxide) giving an optical density of 0·75 in a 10-mm cell. To ensure that reproducible samples of the test atmosphere would be taken, a sampling rate of 1 l minute^{-1} for a period of 5 minutes was chosen. Thus, the above calibration curve enabled atmospheres

of zinc oxide fume to be determined at concentrations up to 17·4 mg m^{-3}, which is considerably more than twice the present threshold limit value.

The choice of the spectrophotometric procedure finally adopted for use was governed largely by one requirement, namely the necessity to accommodate in the procedure the aqueous acetone - hydrochloric acid eluate from the ion-exchange column used to remove iron contamination prior to the determination of the zinc (see Separation of iron). This eluate, 20 ml in volume, contained 12 ml of acetone and 8 ml of 1·25 M hydrochloric acid. Thus, for samples containing no iron (the presence or absence of iron in an atmosphere can normally be ascertained at the site of testing) the collected fume was dissolved in an equivalent amount of acid (2 ml of 5 M) and 12 ml of acetone were added. A uniform procedure was established thereafter whether or not the samples contained iron. With this procedure 10 ml of TAR reagent were added, the mixture was diluted to 50 ml with water and the resulting colour measured spectrophotometrically.

VISUAL DETERMINATION OF ZINC—

A visual method for the determination of zinc was devised, based on colour standards, by using the TAR reagent at a reduced concentration. Tests showed that the use of the reagent at three twentieths of the concentration of that used in the spectrophotometric method gave the best colour differentiation between standards representing 0, 12·5, 25 and 50 μg of zinc oxide. The colour differentiation was further improved by screening the yellow background colour of the TAR reagent by the addition of a Pontamine sky blue (C.I. 24410) dye solution. Later, it was found possible to add the dye to the dilute TAR reagent when the latter was being prepared. In this visual technique full colour development again occurred within 1 minute and the colour was stable for at least 20 minutes. However, the dilute TAR reagent was stable for only 24 hours.

With the co-operation of Tintometer Ltd., a set of standard discs was prepared representing the intensity of colours produced by collecting 5-litre samples of 0, 2·5, 5 and 10 mg m^{-3} atmospheres of zinc oxide. Colour matching was carried out by comparing a 50-mm depth of the sample solution with the standard discs. Although the visual method is not as precise as the spectrophotometric method, it permits the determination of the zinc oxide content of an atmosphere to at least 2·5 mg m^{-3} (*i.e.*, half of the present threshold limit value) when a 5-litre sample is taken over 5 minutes.

INTERFERENCES

It has already been mentioned that the two main industrial processes that produce zinc oxide fume in the atmosphere are the smelting of alloys containing zinc and the welding of galvanised steel plate. Obviously, fumes of other metals may occur in concentrations sufficient to interfere in the determination of zinc with the TAR reagent. Consequently, an investigation was carried out to establish the interference that might be caused by each of a selection of metals present in the ratio of twice the threshold limit value of interfering metal to one half of the threshold limit value of zinc. (This has been a normal criterion upon which to base interferences in other field tests developed in the past. If as much as twice the threshold limit value of an interfering substance occurs in an atmosphere it is a hazard

TABLE I

INTERFERENCES OF METALS PRESENT IN A 5-LITRE SAMPLE AT TWICE THEIR THRESHOLD LIMIT VALUES IN THE DETERMINATION OF 10 μg OF ZINC* BY THE PROPOSED METHOD

Metal	Amount of metal present/μg	Indicated zinc/μg	Interference, per cent.
Antimony	5	10·0	0
Arsenic	5	10·0	0
Cadmium	0·9†	10·2	2†
Calcium	35·8†	10·1	1†
Copper	1	10·4	4†
Iron	70†	16·5	65†
Lead	2	10·5	5†
Tin	20	10·1	1†

* Equivalent to 5 litres of an atmosphere of zinc oxide at half its threshold limit value.
† Derived from the threshold limit value of the metal oxide.

in its own right.) Solutions, each containing 10 μg of zinc (equivalent to 5 litres of an atmosphere of zinc oxide at one half of its threshold limit value) and an amount of each interfering species (equivalent to 5 litres of an atmosphere of the interfering species at twice its threshold limit value), were analysed by the proposed method for zinc. The results are shown in Table I. Considering the aforementioned criterion, these interference levels, apart from iron, were considered to be sufficiently low to be ignored in the proposed field methods for the determination of zinc, so that a further series of interference tests with 1 to 1 w/w ratio of zinc to interfering metal was carried out, this time leaving out iron. It was found that the percentage interference in the proposed test did not increase proportionately with the rise in concentration of interfering metal. Apart from copper, all interferences were less than 13 per cent. up to the 50-μg level. The interferences of copper were 60 and 55 per cent. at the 10 and 40-μg levels, respectively.

To test the effect of copper interference under conditions akin to those of field testing, mixed atmospheres of copper and zinc oxide fumes that were expected to correspond to a zinc-to-copper w/w ratio in the range from 10 to 1 to 120 to 1, were generated and sampled. (At ratios of less than 40 to 1 copper would be the greater hazard.) The zinc and copper content of each sample was first determined non-destructively by X-ray fluorescence, the sample was removed, apparently quantitatively, from the filter by using 2 ml of 5 M hydrochloric acid and the zinc content was then determined by the spectrophotometric version of the proposed field test. The results in Table II indicate that the presence of copper within the stated ranges in the collected mixed fume did not interfere either with the dissolution of the zinc fraction or in its determination by the proposed field method.

TABLE II

COMPARISON OF THE RESULTS OBTAINED BY ANALYSIS OF ZINC OXIDE FUME SAMPLES CONTAINING COPPER FUME BY THE PROPOSED FIELD TEST AND BY X-RAY FLUORESCENCE SPECTROMETRY

	Zinc/μg, found by		Copper/μg found by X-ray fluorescence spectrometry	Ratio of zinc to copper
Sample	Field test	X-ray fluorescence spectrometry		
1	187	195	13·3	14·7
2	194	185	12·5	14·8
3	177	183	13·6	13·5
4	285	294	2·6	113
5	361	357	11·7	30·5
6	391	396	26·7	14·8
7	582	575	4·8	120
8	695	684	11·7	58·5

SEPARATION OF IRON—

It was apparent in the treatment of samples taken when iron and zinc co-exist, *e.g.*, in certain welding processes, that the iron would have to be separated from the zinc prior to the determination of the latter. The use of ion-exchange columns was investigated. Anionic resins suffered from the disadvantage that the iron had to be removed from the column before the zinc. However, on the basis of previous work[9] it appeared that good separation of the two metals could be obtained by using a strong cationic resin in the acidic form and acetone - 0·5 M hydrochloric acid solution (3 + 2 v/v) as eluting agent, iron being retained on the column. Various parameters of the column procedure were examined in the light of our requirements. The use of prepared coarse Zeo-Karb 225 resin (1 g of 52 to 100 mesh) in a glass column (Fig. 3) was finally selected as it facilitates a rapid and efficient column procedure. This column was found to have an iron retaining capacity of 100 μg, *i.e.*, greater than the amount of iron present in a 5-litre sample of an atmosphere containing twice the threshold limit value of iron oxide. The fume samples requiring column treatment were dissolved in 1 ml of 50 per cent. v/v nitric acid and then diluted with aqueous acetone. This solution had no adverse effect on the functioning of the column. The use of nitric acid at this stage of the procedure was necessary to avoid the premature elution of the column under non-standard conditions, as would have occurred had hydrochloric acid been used.

The efficiency of the column was assessed by use of collected mixed fume samples of iron and zinc oxides that were expected to contain a zinc-to-iron ratio over the range from 1 to 1 to 1 to 8, w/w. Each sample was dissolved from its filter-paper as described above. The zinc content of an aliquot was determined by the atomic-absorption technique. Another aliquot was passed through the column and its zinc content determined by the spectrophotometric version of the field test. Iron was not detected in the column eluate. No attempt was made to determine accurately the iron content in the sample extract before its passage through the column because X-ray fluorescence examination of the filter-paper after its treatment with nitric acid revealed the presence of undissolved iron that comprised between 40 and 50 per cent. of the amount expected to have been collected. The amounts of zinc remaining on the various papers were minimal (less than 1 μg) and apparently independent of the total zinc collected, and were not considered to invalidate the proposed procedure for the dissolution of the mixed fume sample. The results in Table III indicate that the column procedure effected a separation of zinc from iron that allowed the determination of zinc by the proposed field test to proceed without interference.

TABLE III

EFFICIENCY OF COLUMN PROCEDURE FOR THE SEPARATION OF ZINC FROM SAMPLES OF MIXED FUMES OF ZINC OXIDE AND IRON OXIDE

		Zinc/μg found by	
Sample	Estimated* iron content/μg	Atomic absorption before column procedure	Proposed field test after column procedure
1	9	8·5	9·1
2	18	18·0	20·3
3	13	6·6	5·9
4	30	15·0	14·6
5	25	6·3	5·5
6	52	13·0	15·2
7	26	3·2	4·7
8	51	6·3	6·5

* Estimated on the basis of the output of the metal fume generator when atomising an iron solution of known concentration.

CONTAMINATION OF APPARATUS—

A number of spurious results were obtained, which were traced to the incomplete removal of the zinc - TAR complex from the various pieces of glassware used, *i.e.*, spectrophotometer cells, visual comparison tubes and the 50-ml flasks used for the development of the complex. Such contamination can be avoided by rinsing all such glassware with concentrated hydrochloric acid.

DETERMINATION OF ZINC OXIDE FUME IN AIR

APPARATUS—

Filter-paper holder—A holder suitable for Millipore AA filters (0·8 μm), 25 mm in diameter.

Sampling pump—A pump capable of drawing air through the filter-paper in the holder at a steady rate of about 1 l minute^{-1}. [This can be achieved either by using a critical orifice (such as Gelman Catalogue No. 7041) in conjunction with a pump capable of producing a pressure differential of at least 300 mm of mercury, or by the use of a pump such as the Dymax IIA (Chas. Austen Ltd.) with a variable eccentric that can be adjusted to give a specific flow-rate.]

Ion-exchange column holder—A glass tube of shape and dimensions as shown in Fig. 3.

Tubes for colour comparison—Flat-bottomed glass tubes, 10 mm in internal diameter and of a height that permits viewing vertically through a liquid depth of 50 mm. (Tintometer Ltd., Salisbury, supply pairs of tubes suitable for use in conjunction with the Lovibond "1000" comparator.)

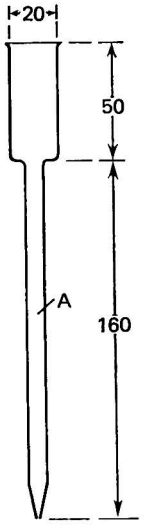


Fig. 3. Ion-exchange column holder (dimensions in mm): A, glass tube 7 mm i.d.

REAGENTS—

All reagents should be of recognised analytical quality when possible and all solutions should be made up with distilled or de-ionised water.

Hydrochloric acid, 5 M—Dilute 43·5 ml of concentrated hydrochloric acid (sp.gr. 1·19 at 20 °C) to 100 ml with water.

Triammonium citrate solution—A 10 per cent. w/v aqueous solution.

Nitric acid (1 + 1 *v*/*v*)—Dilute concentrated nitric acid with an equal volume of water.

Acetone solution, aqueous—Dilute 6 volumes of acetone with 4 volumes of water.

Acetone - hydrochloric acid solution—Add 10 ml of 5 M hydrochloric acid to 60 ml of acetone and dilute the mixture to 100 ml with water.

Preparation of ion-exchange resin—Place about 50 g of Zeo-Karb 225 ion-exchange resin (52 to 100 mesh, 8 per cent. divinylbenzene, sodium form) in a large glass column about 500 mm in length and 30 mm in internal diameter with a sintered-glass disc (porosity No. 1) fitted in the lower part and terminating in a tap. Back-wash the column with distilled water to remove the fines, then calculate the bed volume of the resin (height × cross-sectional area of the wet resin). Drain off the water and wash with four bed volumes of the triammonium citrate solution, followed by a similar volume of 5 M hydrochloric acid. Finally, wash the resin with water until it is free from chloride, as indicated by testing the eluate with silver nitrate solution. Remove the excess water with a filter-pump and allow the resin to dry in air. Store in a screw-topped bottle.

Preparation of ion-exchange column—Place a small plug of cotton-wool at the narrow end of the ion-exchange column holder and add a slurry of 1 g of the prepared resin in 20 ml of the acetone - hydrochloric acid solution. Allow nearly all of the liquid to pass through the resin and add a further 20 ml of the same solution to equilibrate the resin. Stopper the lower end of the column holder with a piece of plugged rubber tubing just as the meniscus enters the resin. Transport the prepared columns in the vertical position.

4-(2′-*Thiazolylazo*)*resorcinol (TAR) solution*—A 0·1 per cent. w/v solution in methanol.

TAR reagent (solution A)—Weigh 15 g of triethanolamine into a standard 100-ml flask, add 60 ml of N sodium hydroxide, 1·5 ml of TAR solution and, 1·5 ml of 0·168 per cent. w/v aqueous Pontamine sky blue (C.I. 24410) solution and dilute the mixture to 100 ml with

water. Store at temperatures below 30 °C and renew after 24 hours. (Solution A is for use with the visual method for determining zinc.)

TAR reagent (solution B)—Weigh 15 g of triethanolamine into a 100-ml flask, add 60 ml of N sodium hydroxide solution and 10 ml of TAR solution and dilute the mixture to 100 ml with water. Store below 30 °C and renew after 14 days. (Solution B is for use with the spectrophotometric method for determining zinc.)

Standard zinc oxide solution—Dissolve 125·0 mg of zinc oxide in 4 ml of 5 M hydrochloric acid and dilute to 1 litre with water. Dilute 25 ml of this solution to 250 ml to give a solution containing the equivalent of 12·5 μg ml^{-1} of zinc oxide.

All standard glassware must be washed with concentrated hydrochloric acid and rinsed well with water to remove traces of metal ions and any TAR complex adhering from previous determinations.

PROCEDURE—

Place a filter in the filter holder, attach the assembly to the pump and draw a 5-litre sample of the atmosphere through the paper at a constant rate of about 1 l minute^{-1}. Disconnect the holder from the pump, remove the filter and place it in a small beaker (diameter 25 to 30 mm).

Samples containing no iron—Add 2 ml of 5 M hydrochloric acid and, after 5 minutes, transfer the acidic solution with a few millilitres of water to a 50-ml standard flask. Add 12 ml of acetone to the flask and determine the zinc either visually or spectrophotometrically as described below.

Samples containing iron—Add 1 ml of nitric acid (1 + 1 v/v) and, after 5 minutes, add 8 ml of the aqueous acetone solution. Transfer the liquid on to the ion-exchange column, wash the beaker with 2 ml of aqueous acetone solution and add the washings to the column. Remove the stopper from the bottom of the column and allow the solution to pass through the resin until just before the meniscus reaches the top of the resin. Discard this eluate, add 20 ml of the acetone - hydrochloric acid solution and collect all the subsequent eluate from the column in a 50-ml standard flask. Determine the zinc either visually or spectrophotometrically as described below.

VISUAL DETERMINATION OF ZINC OXIDE—

Add 10 ml of TAR reagent solution A to the 50-ml flask, dilute to 50 ml with water and mix well. Fill a colour comparison tube to a depth of 50 mm with the solution and compare the colour in turn with each of the zinc oxide colour standards prepared at the same time and contained in similar tubes, viewing down the depths of the liquids against a white (paper) background. Alternatively, a comparator disc containing coloured glass standards for this test is available from Tintometer Ltd., Salisbury, and should be used with the Lovibond "1000" comparator.

Preparation of zinc oxide colour standards—To four 50-ml standard flasks add 0, 1, 2 and 4 ml of the standard zinc oxide solution (12·5 μg ml^{-1}), respectively. Then to each add 20 ml of the acetone - hydrochloric acid solution and 10 ml of the TAR reagent solution A, and dilute to volume with water. For a 5-litre air sample these standards represent, respectively, 0, 2·5, 5 and 10 mg of zinc oxide per cubic metre of air.

SPECTROPHOTOMETRIC DETERMINATION OF ZINC OXIDE—

Add 10 ml of TAR reagent solution B to the 50-ml flask, dilute to volume with water and measure the optical density of the solution at 530 nm in a 10-mm glass cell against a reference solution prepared at the same time from all of the reagents used. Determine the amount of equivalent zinc oxide in the solution by reference to the calibration graph. The concentration of zinc oxide present in the sample of air taken is given by $X/5$ mg m^{-3}, where X is the total amount of zinc oxide found in micrograms.

Preparation of calibration graph—To a series of 50-ml standard flasks add 0, 1, 2, 3, 4, 5 and 6 ml of the standard zinc oxide solution. Then, to each flask add 20 ml of the acetone - hydrochloric acid solution and 10 ml of the TAR reagent solution B, and dilute each mixture to 50 ml with water. Measure the optical densities of the solutions at 530 nm in a 10-mm cell with the solution containing no zinc oxide as reference. Plot a graph of the weight of zinc oxide in micrograms against the optical density.

Application and scope of the method

The procedures described above have been satisfactorily assessed with samples taken under field conditions at industrial establishments. Mixed atmospheric fumes of zinc oxide and copper were sampled in the vicinity of brass alloy casting. The mixed zinc oxide - iron fumes generated during the welding of galvanised steel sheet were also sampled. In the experiments, for the purpose of check testing and to obviate any possible errors caused by non-reproducibility of sampling, it was decided not to use the method of duplicate sampling whereby one sample would be examined by the proposed field test and the other by an independent method. Instead, the collected fume samples were returned to the laboratory where they were first examined non-destructively by X-ray fluorescence spectrometry and then by the appropriate field method.

The apparatus required for the test is portable and requires only an external electrical power supply to operate the pump. A determination can be completed in 20 minutes. Permanent glass standards are available that allow the determination of zinc oxide fume in air over the range 2·5 to 10 mg m^{-3} from a sample taken at a rate of 1 l $minute^{-1}$ for 5 minutes. More precise determinations are possible with the use of a spectrophotometer and a previously prepared calibration graph. Here, the sample volume need not be restricted to 5 litres taken at a rate of 1 l $minute^{-1}$, as when using visual permanent standards, and sample volumes ranging from 2·5 to 50 litres have been taken at sampling rates ranging from 0·5 to 5 l $minute^{-1}$, the zinc oxide contents being successfully determined. The use of a spectrophotometer and a calibration graph therefore allows for greater flexibility in sampling parameters.

This work was carried out on behalf of the Department of Employment Committee on Tests for Toxic Substances in Air. We thank the Government Chemist for permission to publish this paper, H.M. Factory Inspectorate for arranging the field tests, the Chemical Defence Establishment, Porton, for advice on the generation of zinc oxide fume atmospheres and Mr. D. M. Groffman for his technical assistance.

References

1. Browning, E., "Toxicology of Industrial Metals," Second Edition, Butterworths, London, 1969, p. 352.
2. "Threshold Limit Values 1969," Technical Data Note 2/69, Department of Employment and Productivity, London, 1969.
3. Green, H. L., and Lane, W. R., "Particulate Clouds: Dusts, Smokes and Mists," E. & F. N. Spon Ltd., London, 1957, p. 39.
4. "Characteristics of Particles and Particle Dispersoids," *SRI J.*, 1961, **5**, 95.
5. Megaw, W. J., and Wiffen, R. D., *Int. J. Air Wat. Pollut.*, 1963, **7**, 501.
6. Farrah, G. H., *J. Air Pollut. Control Ass.*, 1967, **17**, 738.
7. Rush, R. M., and Yoe, J. H., *Analyt. Chem.*, 1954, **26**, 1345.
8. Kawase, A., *Talanta*, 1965, **12**, 195.
9. Fritz, J. S., and Rettig, T. A., *Analyt. Chem.*, 1962, **34**, 1562.

Received *March* 10*th*, 1971
Accepted *March* 31*st*, 1971

Analyst, August, 1971, Vol. 96, *pp.* 579–583

Polarographic Determination of Uranium in Monazite Sands

BY R. W. MARTRES AND J. J. BURASTERO

(Administración Nacional de Combustibles, Alcohol y Portland, Centro de Investigaciones Tecnológicas, Pando, Uruguay)

A practical method is described for the extraction of uranium from monazite sands and its subsequent polarographic determination.

The sample is decomposed by fusion with potassium hydrogen difluoride followed by fusion with potassium pyrosulphate. Uranium is extracted from nitric acid solution with tributyl phosphate in 2,2,4-trimethylpentane, with aluminium nitrate as a salting-out agent, and back-extracted from the organic phase with water.

The final polarographic determination is carried out in 2 M acetic acid - 2 M ammonium acetate - 0·1 M ascorbic acid solution as supporting electrolyte. Neither a maximum suppressor nor removal of oxygen is needed.

The interference by lead and some factors influencing the extraction of uranium are studied.

The results are reproducible and agree with those obtained by other, more laborious, techniques. The proposed procedure is suitable for the determination of uranium in monazites and monazite sand concentrates containing not less than 0·005 per cent. of uranium oxide, and is superior in speed, reliability and convenience to other methods previously reported.

MANY methods involving the application of classical and instrumental analytical techniques have been developed in recent years for the determination of uranium.

However, only a few titrimetric, gravimetric, fluorimetric, spectrophotometric or polarographic procedures that are specifically applicable to the determination of uranium in monazite have been described. Many of them proved to be too time consuming, insufficiently sensitive or lacking in accuracy for this purpose.

The polarographic method has found considerable application in the determination of uranium, and its sensitivity is adequate for normal uranium contents in monazite sands. Moreover, rigorous preliminary purification is not required, provided a suitable supporting electrolyte is used.

However, the polarographic procedures described for the specific determination of uranium in monazite[1,2,3,4] are not reliable and are too time consuming because of the laborious purification steps needed. Further, they do not give good waves, and one of them in particular[4] gives very poorly defined waves.

By contrast, the proposed method is rapid and accurate. The preliminary separation of uranium is accomplished easily with a single solvent extraction after rapid decomposition of the sample. In the chosen supporting electrolyte the wave is well formed and easy to measure, as shown in Fig. 1.

EXPERIMENTAL

APPARATUS—

A Sargent Polarograph, Model XV, was used to record all polarograms.

The electrolysis cell was an H-type polarographic cell, Sargent S-29405, that permits the use of a sample as small as 1 to 2 ml. However, in routine determinations, a simpler polarographic cell with a mercury pool can be used.

The conventional dropping-mercury electrode was used as the cathode. The reference electrode was the S.C.E., which filled one chamber of the cell.

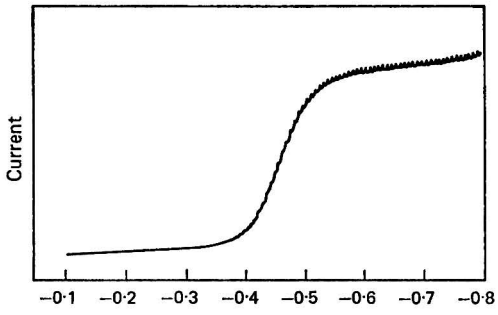


Fig. 1. Typical polarogram

MONAZITE SAND—

Samples I, II and III were separated from black sand concentrates obtained from the Uruguayan deposits of Atlántida, Aguas Dulces and San Luis, respectively. Sample IV was separated from a monazite sand from Cleveland County, North Carolina, U.S.A.*

REAGENTS—

Standard uranium solution—A solution containing about 1 mg ml^{-1} of uranium was prepared by dissolving uranyl nitrate in distilled water, diluting to an appropriate volume and mixing. The solution was standardised by reducing the uranium(VI) to uranium(IV) in a Jones reductor and then titrating with a standard potassium dichromate solution.

Commercial grade 2,2,4-trimethylpentane (isooctane)† and commercial grade tributyl phosphate‡ were used without further purification.

PROCEDURE—

Place 0·5 g of finely ground monazite (200 mesh) in a platinum crucible and mix it with 2 g of potassium hydrogen difluoride. Heat the mixture gently over a small flame. Gradually increase the flame to bring the contents to the melting-point. Cool for a few seconds, add 0·5 g of potassium pyrosulphate and continue heating until a clear melt is obtained. Cool, add 3 ml of 65 per cent. nitric acid, and evaporate to dryness. Repeat the treatment twice, taking care to ensure that the residue is well mixed with the acid after each addition.

Dissolve the residue in M nitric acid and filter the solution into a separating funnel. Wash the crucible and filter until a final total volume of about 30 ml is obtained. Add 15 g of aluminium nitrate. Extract the uranium by shaking the solution for 2 minutes with 20 ml of a 10 per cent. 2,2,4-trimethylpentane solution of tributyl phosphate. Discard the aqueous phase. Back-extract the uranium from the organic phase by shaking it with three successive 20-ml portions of water. Add 3 ml of 72 per cent. perchloric acid to the combined aqueous extracts and evaporate the resulting solution to dryness. Repeat the treatment with perchloric acid and again evaporate the solution to dryness.

Dissolve the residue in 5 ml of 4 M acetic acid - 4 M ammonium acetate solution. Transfer this solution to a 10-ml calibrated flask containing 176 mg of ascorbic acid. After dissolution of the ascorbic acid, dilute to volume with water and mix thoroughly. Transfer a suitable volume of this solution to the polarographic cell and record the polarogram between −0·2 and −0·7 V *versus* S.C.E. Measure the height of the step and determine the uranium concentration by reference to a calibration graph.

RESULTS AND DISCUSSION

DECOMPOSITION OF MONAZITE—

Many methods for the decomposition of monazite sands[5,6,7,8] have been considered with a view to selecting the most suitable according to the nature of the determination required.

* Supplied by Ward's Natural Science Establishment Inc., Rochester, N.Y., U.S.A.
† Supplied by Phillips Petroleum Corporation, U.S.A.
‡ Obtained from Matheson Coleman & Bell, U.S.A.

The classical treatment with sulphuric acid was excluded because sulphate interferes when it is present in large amounts in the uranium extraction, making its removal necessary. Fusion with sodium peroxide is very effective but produces a bulky precipitate that is difficult to filter off, while a mixed flux of sodium fluoride and potassium pyrosulphate sometimes failed to bring about complete decomposition.

On the other hand, fusion with potassium hydrogen difluoride followed by fusion with potassium pyrosulphate permits complete and rapid decomposition, and the residue is easily filtered off. After the fusion, repeated evaporations with 65 per cent. nitric acid ensure complete removal of fluoride. Moreover, in the presence of the sulphate introduced during the decomposition step, most of the lead remains in the residue when the melt is leached with M nitric acid. This moderate amount of sulphate does not interfere in the uranium extraction.

EXTRACTION OF URANIUM—

Among the various methods reported in the literature for the separation of uranium, solvent extraction with tributyl phosphate appears to be a simple and rapid way of isolating the element prior to the polarographic determination.

If aluminium nitrate is used as a salting-out agent, virtually complete removal of uranium is achieved with a single extraction.

The interferences caused by the phosphate present in the sample and the fluoride used for decomposition of the sample are eliminated by using aluminium nitrate at high concentration as salting-out agent.[9]

In the method of attack used sulphate will be present. Preliminary experiments indicated that aluminium nitrate was also effective in preventing interference by the sulphate, which may be present in amounts up to 1 g. The results given below were obtained by extracting an aqueous phase, consisting of 30 ml of M nitric acid containing 15 g of aluminium nitrate, 2·56 mg of U_3O_8 and various amounts of sulphate, with 20 ml of a 10 per cent. v/v solution of tributyl phosphate in 2,2,4-trimethylpentane. The uranium was back-extracted and determined polarographically—

Sulphate added/g	0	0·35	0·71	1·06	1·42
Uranium found, step height/mm ..	82	82	83	81	77

The presence of nitric acid is advantageous as it shifts the equilibrium

$$UO_2^{2+} + HSO_4^- \rightleftharpoons UO_2SO_4 + H^+$$

to the left, thereby favouring the formation of uncomplexed uranyl ion.[10]

2,2,4-Trimethylpentane was used as inert diluent because the solution of tributyl phosphate in 2,2,4-trimethylpentane separates cleanly and rapidly from the aqueous phase.

BACK-EXTRACTION OF URANIUM—

Many aqueous solutions of different substances have been investigated as extraction media in the back-extraction of uranium from the organic phase into the aqueous phase, selection being made according to the efficiency of back-extraction and the method used subsequently for the uranium determination.

In all respects, water is the most suitable back-extraction agent from the standpoint of the subsequent uranium determination. However, it has not been found very effective with tributyl phosphate containing nitric acid, the complete back-extraction being tedious and time consuming.

The nitric acid concentration of the organic phase has a marked influence on the efficiency of back-extraction. In general, the lower the nitric acid concentration of the organic phase, the more effective is the aqueous back-extraction.

In the procedure proposed in the present work, we use a M nitric acid solution to dissolve the uranium residue prior to the extraction with tributyl phosphate . Under these conditions, complete back-extraction from the organic phase was achieved with three successive extractions with equal volumes.

INTERFERENCE BY LEAD—

Lead interferes seriously in the supporting electrolyte used, as it gives a wave that coalesces additively with the uranium wave, and its extraction under the conditions used was, therefore, studied. The results given in Table I indicate that the amount of lead

extracted decreases as the nitric acid concentration in the aqueous phase increases and as the tributyl phosphate concentration in the organic phase decreases. Further, in the presence of sulphate the amount of lead extracted also decreases. Therefore, sulphate introduced into the analysis during the fusion is beneficial.

TABLE I

EXTRACTION OF LEAD

Aqueous phase: 15 ml of solution containing 10 mg of lead
Organic phase: 10 ml of a solution of tributyl phosphate in 2,2,4-trimethylpentane
Salting-out agent: 7·5 g of aluminium nitrate

Aqueous phase		Tributyl phosphate in organic phase, per cent.	Lead extracted, per cent.
Nitric acid concentration/M	Sulphate added/g		
0·1	—	20	1·55
1	—	20	0·70
0·1	—	10	0·80
1	—	10	0·60
1	0·2	10	0·30

In the procedure proposed the uranium is extracted from a M nitric acid solution containing 0·5 g ml^{-1} of aluminium nitrate with a 10 per cent. solution of tributyl phosphate in 2,2,4-trimethylpentane. Molar nitric acid is selected as it prevents the formation of uranyl sulphate complex, decreases the amount of lead co-extracted and prevents the formation of precipitates (of titanium, thorium, etc.) by hydrolysis, which produce emulsions. On the other hand, this level of acidity is sufficiently low to permit rapid and complete back-extraction with water.

Under the conditions of the proposed method and for the amounts of uranium and lead usually present in monazites, lead is not extracted in interfering amounts. However, with ratios of lead to uranium higher than about 5:1, trace amounts of lead may cause a small error. In this event, separation of lead is accomplished by extraction with dithizone as described below.

Add 1 ml of acetic acid and 100 mg of hydroxylammonium chloride, which prevents the precipitation of uranium, to the combined aqueous extracts, neutralise with ammonia solution (to a yellow colour with methyl red), and shake with a solution of dithizone (20 mg l^{-1}) in chloroform. If metals are precipitated by the ammonia solution, add 200 mg of citric acid and then neutralise the solution (with bromothymol blue as indicator) to give a higher pH than that obtained when methyl red is used. If citrate is used, it must be completely removed from the final solution to avoid changes in the diffusion current and in the wave form. It can be removed by repeated alternate evaporations with nitric and perchloric acids.

POLAROGRAPHY OF URANIUM: CHOICE OF SUPPORTING ELECTROLYTE—

The polarography of the uranyl ion has been studied by numerous workers, who used different supporting electrolytes.

Whichever supporting electrolyte was used, difficulties were experienced in the polarographic determination of uranium in monazite sands because of interfering elements that had to be removed. Many ions interfere in this determination, usually because they are reduced in the same potential region as the uranyl ion itself. Consequently, in the analysis of uranium ores, various methods have been used to remove interfering elements prior to the polarographic determination, namely, electrolysis at a mercury pool, chromatography, ion exchange and solvent extraction.

After separation of the uranium from the bulk of the impurities, the selected supporting electrolyte must enable a well defined wave to be obtained with no interference by any remaining impurities accompanying the uranium.

DeSesa, Hume, Glamm and DeFord[11] studied the polarographic characteristics of various metal ions in 2 M ammonium acetate - 2 M acetic acid solution containing 0·01 per cent. of gelatin. The uranyl ion showed a well defined and reversible wave with $E_{\frac{1}{4}}$ — 0·45 V *versus* S.C.E., corresponding to reduction to the +5 oxidation state, so that the use of this solution for analytical purposes has been suggested. Although the sensitivity in this supporting electrolyte is only moderate, it is adequate for determining normal uranium contents in monazite sands.

Among the elements present in monazite sands, only lead (E_i — 0·50 V *versus* S.C.E.) can interfere with the uranium wave, as discussed above.

Iron(III) extracted together with uranium may interfere with the base-line of the uranium wave if present in relatively large amounts. This interference is eliminated by reducing it to the iron(II) state, which is discharged at much more negative potentials than those of the uranium wave. This reduction is frequently accomplished by treating the solution with hydroxylammonium chloride and warming it for a few minutes. However, the reduction is more easily carried out by addition of ascorbic acid.[12]

Ascorbic acid has also been proposed as supporting electrolyte for the polarographic determination of uranium in the presence of many other cations.[13] The polarographic properties of ascorbic acid as supporting electrolyte are based on its strong reducing power and complex-forming capacity. Further, at pH values above 3·5 it is not necessary to remove dissolved oxygen by bubbling an inert gas through the solution because ascorbic acid rapidly reduces oxygen.

Thus, the supporting electrolyte finally selected consisted of a solution 2 M in ammonium acetate, 2 M in acetic acid and 0·1 M in ascorbic acid. In this medium the wave form is excellent, with E_i — 0·455 V *versus* S.C.E. and a well developed base-line. It is not necessary to de-aerate the solution, or use a maximum suppressor.

The calibration graph was almost linear over the range $2{\cdot}3 \times 10^{-5}$ to $1{\cdot}3 \times 10^{-3}$ M uranium(VI) concentration.

APPLICATION OF PROCEDURE—

The given procedure is suitable for the rapid and accurate determination of uranium in monazites and monazite sand concentrates containing not less than 0·005 per cent. of uranium oxide (U_3O_8).

The results obtained by the method proposed agree with those found by the peroxide - spectrophotometric method[5,14] and the thiocyanate - spectrophotometric method,[15] as shown in Table II.

TABLE II

COMPARATIVE URANIUM DETERMINATIONS IN MONAZITE SAMPLES

Sample	U_3O_8, per cent., by Other methods	U_3O_8, per cent., by Proposed method	Mean value	Standard deviation	Relative standard deviation, per cent.
I	0·26	0·27, 0·24 0·24, 0·26	0·25	0·015	6·0
II	0·19	0·19, 0·19 0·16, 0·18	0·18	0·014	7·8
III	0·14	0·14, 0·13 0·13, 0·15	0·14	0·010	7·1
IV	0·36	0·35, 0·37 0·38	0·37	0·015	4·1

REFERENCES

1. Burstall, F. H., and Wells, R. A., *Analyst*, 1951, **76**, 396.
2. Habashi, F., *Metallurgia*, 1962, **65**, 255.
3. Schoeller, W. R., and Powell, A. R., "Analysis of Minerals and Ores of the Rarer Elements," Third Edition, Griffin, London, 1955, p. 110.
4. Smales, A. A., *Proc. Roy. Soc. Edinb.*, 1948, **63B**, Part II, 125.
5. Grimaldi, F. S., May, I., Fletcher, M. H., and Titcomb, J., "Collected Papers on Methods of Analysis for Uranium and Thorium," U.S. Geological Survey Bulletin, 1954, No. 1006.
6. Powell, R. A., and Kinser, C. A., *Analyt. Chem.*, 1958, **30**, 1139.
7. Sill, C. W., *Ibid.*, 1961, **33**, 1684.
8. Vickery, R. C., "Analytical Chemistry of the Rare Earths," Pergamon Press, New York, 1961, p. 6.
9. Burastero, J. J., and Martres, R. W., "*Octavo Congreso Latinoamericano de Química*," Buenos Aires, 1962, p. 148.
10. Collopy, T. J., and Stock, D. A., *U.S. Atomic Energy Commission Report*, NLCO–801, 1960.
11. DeSesa, M. A., Hume, D. N., Glamm, A. C., jun., and DeFord, D. D., *Analyt. Chem.*, 1953, **25**, 983.
12. Mashall, J., and Kendler, J., *Analytica Chim. Acta*, 1964, **31**, 490.
13. Susic, M. V., Gal, I., and Cuker, E., *Ibid.*, 1954, **11**, 586.
14. Rodden, C. J., *Editor*, "Analytical Chemistry of the Manhattan Project," McGraw-Hill, New York, 1950, p. 147.
15. Clinch, J., and Guy, M. J., *Analyst*, 1957, **82**, 800.

Analyst, August, 1971, Vol. 96, *pp.* 584–590

A Modified Spectrophotometric Method for the Determination of Ammonia (and Amino-acids) in Natural Waters, with Particular Reference to Sea Water

BY VICTOR W. TRUESDALE*

(East African Marine Fisheries Research Organization, P.O. Box 668, Zanzibar, East Africa)

Strickland and Parsons have described a method for determining ammonia (and amino-acids) in sea water. This method, in which ammonia is first oxidised to nitrite with sodium hypochlorite, was found to be very time consuming and often imprecise. The results of a critical examination of the underlying chemistry have led to a modified procedure in which the time required for analysis has been reduced from 3·5 hours to 17 minutes. The modified procedure gave a coefficient of variation of 1·6 per cent. from the analysis of thirteen replicate aliquots of a sample of sea water containing approximately 20 μg l^{-1} of ammonium-nitrogen, and hence is suitable for determining ammonia concentrations in the order of 0 to 200 μg l^{-1}. The response for 1 μg l^{-1} of ammonium-nitrogen, in either sea water or de-ionised water, was equivalent to an optical density change of $1{\cdot}6 \times 10^{-3}$ per cm of solution. The procedure is also suitable for the quantitative determination of ammonia (and amino-acids) in other natural waters.

STRICKLAND and Parsons[1] described a modified spectrophotometric procedure by Richards and Kletsch[2] for the determination of ammonia in sea water. A further description of the same method, which was not available to the author at the time of this study, has also been published.[3] In this method, dissolved ammonia is oxidised to nitrite with an alkaline solution of hypochlorite, and the nitrite so formed is allowed to react with sulphanilamide and *N*-1-naphthylethylenediamine dihydrochloride to form a pink azo compound. The concentration of ammonia initially present in each sample is determined by comparing the optical density (at 543 nm) given by the samples with those given by standard solutions of ammonium sulphate in de-ionised water.

Initial experience with the procedure recommended by Strickland and Parsons[1] showed that it has the disadvantage of being very time consuming, mainly because of a 3·5-hour period needed for the oxidation of ammonia in sea water, and also because it proved insufficiently precise to be used as a routine method for the determination of the small concentrations of ammonia encountered in the waters under examination (0 to 20 μg l^{-1} of ammonium-nitrogen). It was therefore evident that some further modifications were desirable. As a result of a study made of the chemistry involved in the method, this paper describes how it has been possible to modify it and thus overcome these disadvantages. The results of the study of the chemistry of each step in the analysis are also included.

EXPERIMENTAL

APPARATUS—

All optical density measurements were made by using a Unicam SP500 spectrophotometer with distilled water in the reference cuvette. The reagents were dispensed from Zipette automatic syringe pipettes. De-ionised water was prepared by passing distilled water through an Elga-stat mixed-bed ion exchanger. The analysis was performed with glass or polythene vessels equipped with tightly fitting polythene stoppers so that the reaction mixtures could be mixed by vigorously shaking them after the addition of successive reagents. The vessels were treated periodically with concentrated sulphuric acid and were always rinsed with de-ionised water immediately before use.

* Present address: Institute of Hydrology, Howbery Park, Wallingford, Berkshire.

These studies were performed at a room temperature of 25 °C, and all samples were filtered through Millipore membranes (0·8 μm average pore diameter).

Results of investigations

The oxidation—

When processing the solutions of ammonium sulphate in de-ionised water used for calibration purposes, Strickland and Parsons[1] found it advantageous to add potassium bromide as a catalyst to the reaction mixture, as the time required for oxidation was thereby reduced from 3·5 to 1·5 hours. They also stated that in the analysis of sea-water samples potassium bromide need not be added as there is sufficient bromide present naturally in sea water to act as a catalyst. In contrast, it was found during this study that the addition of 0·25 g of sodium bromide to each 1 litre of sea water being analysed increased the rate of oxidation in these waters sufficiently to allow the oxidation step to be completed in 1·5 hours. The experiments showed that under the same conditions still higher concentrations of the catalyst did not lead to an increased rate of oxidation but that the latter could be achieved if concentrations of hypochlorite in excess of those recommended by Strickland and Parsons[1] were used. With these greater amounts of reagents it has been possible to reduce the oxidation time required for up to 270 μg l^{-1} of ammonium-nitrogen in sea or fresh water to 17 minutes without any concomitant reduction in the yield of nitrite. Although it may have been feasible to reduce the time still further, by using even larger amounts of hypochlorite, this was not thought necessary as the above period fits well into the experimental routine evolved.

Variation in concentration of hypochlorite used—The results in Table I show that large changes in the recommended concentration of hypochlorite used in the alkaline oxidising agent have only a small effect on the yield of azo compound produced from a given amount of ammonia in sea water. It appears, therefore, that there is little chance that the slow deterioration of the stock hypochlorite reagent will affect the response of the method.

Table I

Variation in absorbance given by sea waters containing approximately 30 μg l^{-1} of ammonium-nitrogen for different concentrations of sodium hypochlorite and arsenite reagents

Amount used as a fraction of recommended amount		0·2	0·4	0·8	1·0	1·2	1·6	2·0
Optical density (10 cm)	Hypochlorite varied	0·650	0·690	0·720	0·713	0·700	0·680	0·683
	Arsenite varied	0·500	0·480	0·462	0·453	0·448	0·436	0·425

Destruction of excess of oxidising agent—

The results in Table I show that the yield of azo compound decreases with increasing amounts of arsenite and also that small variations in the recommended amount made while dispensing the reagent do not affect the final result unduly. With the recommended amount the reduction of excess of hypochlorite is complete within 3 minutes and no further change occurs when samples are stored for up to 18 minutes at this stage of the analysis.

Acidification—

Under the conditions recommended in the Strickland and Parsons hypochlorite method,[1] the high concentration of alkali necessary for the oxidation step is removed by reaction with an approximately 35 per cent. v/v solution of hydrochloric acid so as to produce a mixture at about pH 1·6. Although small, variable errors in dispensing the hydrochloric acid are reflected as relatively large errors in pH of the mixture and, as the yield of azo-compound is sensitive to pH, the yield of azo compound is lowered when the resultant pH becomes higher than 1·6. From the results shown in Fig. 1 it appears that the effect of these errors could be minimised by using a higher concentration of hydrochloric acid as the yield of azo compound is not then affected by small changes in pH. This was tested by using an acidic sulphanilamide reagent containing hydrochloric acid at a concentration of 45 per cent. v/v. Although this resulted in the anticipated maximum yield of azo compound, the reproducibility was adversely affected.

Experiments performed with separate solutions of acid and sulphanilamide instead of the combined reagent revealed that the nitrite ions, which were produced by oxidation of

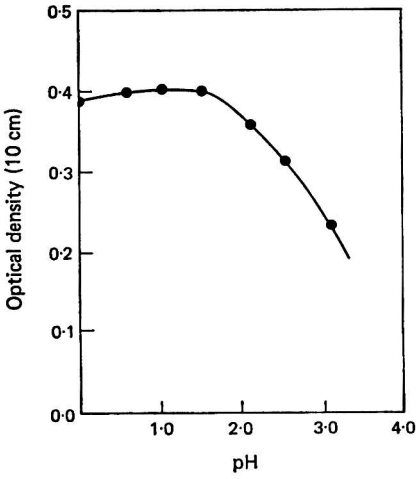


Fig. 1. Yield of azo compound as a function of the acidity of the mixture in which diazotisation occurs

ammonia with hypochlorite, were removed during the interval that elapsed between the addition of the acid and sulphanilamide reagents. Later experiments with sea water augmented with sodium nitrite showed that the hypochlorite solution used in the preparation of the oxidising agent was responsible for the removal of the nitrite ions. This was deduced from the fact that whereas they were not removed when the hypochlorite was omitted from the "blank" determination (see below) their removal did occur when the hypochlorite solution was included. As the excess of hypochlorite is reduced by the arsenite reagent, the acid decomposition of nitrite must be caused either by a contaminant of the hypochlorite solution, or by a product of the reaction between arsenite and hypochlorite solutions. Nevertheless, the rate of decomposition of nitrite increases with decreasing pH and is reduced by the addition of the sulphanilamide. The "half-life" period of nitrite in the absence of sulphanilamide (at 25 °C) is approximately 15, 45 and 180 s at pH 0·5, 1·5 and 2·0, respectively, for solutions containing 25 $\mu g\ l^{-1}$ of nitrite-nitrogen.

It seems, therefore, that the poor reproducibility observed when using the higher concentration of hydrochloric acid in the sulphanilamide reagents resulted from the rapid decomposition of nitrite during the brief period that elapsed between the addition of the acidic sulphanilamide and *N*-1-naphthylethylenediamine reagents. As this would be difficult to overcome, it seemed advisable to return to a mixture of pH 1·6, when a yield of azo compound near to the maximum is attained, and to make some other approach to the problem of the low precision encountered at this level of acidity.

It appeared that the problem could possibly be overcome by introducing a suitable buffer into the mixture and adopting a standard time between the addition of the acidic sulphanilamide and *N*-1-naphthylethylenediamine reagents. As phthalic and citric acids have acid-dissociation constants in the required range it seemed that either might be suitable as a buffer. Experiments showed that whereas citric acid could fulfil this rôle, phthalic acid did not as it produced a precipitate that interfered with subsequent measurements of optical density.

Because nitrite ions are decomposed in the acidified solution at the rate shown in Fig. 2, it is not advisable to delay the addition of the *N*-1-naphthylethylenediamine reagent. Experience has shown that a standard 1-minute period is most practicable.

Variation of recommended amount of citric acid - sulphanilamide reagent—The results of an experiment conducted with between 4·5 and 6·0 ml of the citric acid - sulphanilamide reagent instead of the recommended 5·0 ml (Fig. 3) show that the procedure easily accommodates any small errors made while dispensing this reagent.

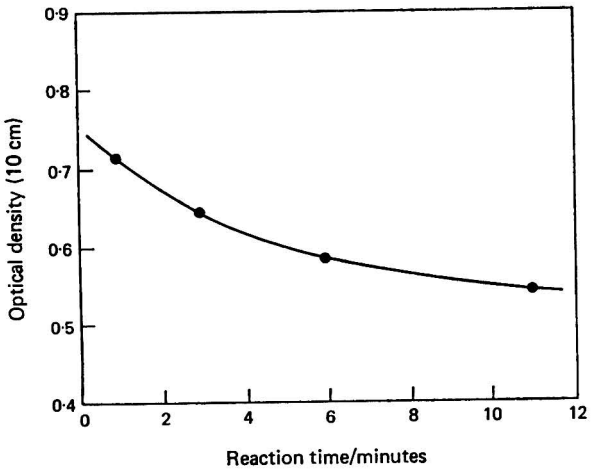


Fig. 2. Rate of decomposition of nitrite during the period elapsing between the addition of citric acid - sulphanilamide and *N*-1-naphthylethylenediamine reagents

BLANK DETERMINATION—

Any nitrite ions present either in the reagents or the waters being analysed are recorded as ammonia. Consequently, a correction must be made for nitrite contamination. Strickland and Parsons[1] recommended calculating the nitrate correction factor from a precise knowledge of the nitrite concentration of each individual sample. It seemed advisable to avoid the use of a correction factor calculated in this way because its magnitude might vary from one set of analyses to another. In any event, it is time consuming to have to perform additional analyses to determine nitrite content before the results of the ammonia determinations can be obtained. To overcome these objections, a "blank" procedure, which supplies the necessary correction factor for nitrite contamination during ammonia determination, has been developed.

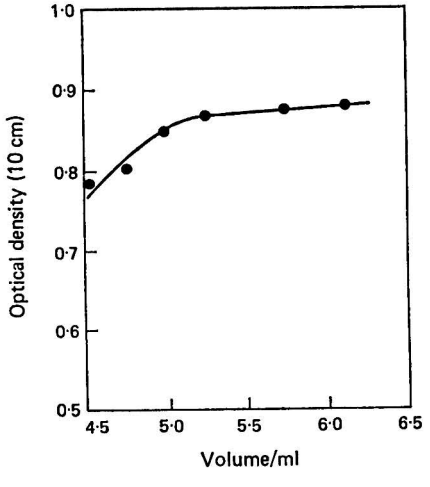


Fig. 3. Yield of azo compound as a function of the volume of citric acid - sulphanilamide reagent used

This "blank" procedure is similar to that for the ammonia determination, but is performed by adding the arsenite reagent before the alkaline oxidising agent, thus preventing the oxidation of ammonia in the sample and reagents, but leaving any nitrite ions to be carried through the remaining part of the procedure. The optical density measured from the "blank" procedure is deducted from that recorded for the full ammonia determination. The efficacy of this blank procedure was tested by analysing a sea water to determine ammonia both before and after 25 $\mu g\ l^{-1}$ of nitrite-nitrogen had been added. The same ammonia concentration was recorded for each portion.

Although it might appear that the correction for nitrite contamination could also be obtained by performing the analysis in the absence of any hypochlorite solution, this is not so, because the decomposition of nitrite, which occurs after acidification and as a result of the presence of the hypochlorite, would not be compensated for.

CALIBRATION—

It is desirable to calibrate the method by using the same water as that being tested so as to avoid any unforeseen variations in the response of the method to ammonia in different waters. However, during this study and previously recorded studies,[1,2,3] no significant difference has been observed in the response of the method to ammonia in several types of natural water, and so it is probably satisfactory to use de-ionised water as a calibration medium.

During this study a linear calibration graph was obtained for up to 270 $\mu g\ l^{-1}$ of ammonium-nitrogen, an optical density change of $5{\cdot}4 \times 10^{-2}$ per cm of solution corresponding to a change of 33 $\mu g\ l^{-1}$ of ammonium-nitrogen.

PRECISION—

The reproducibility of the procedure was tested by analysing thirteen replicate samples of sea water containing 20 $\mu g\ l^{-1}$ of ammonium-nitrogen. From the results shown in Table II, coefficients of variation of 1·8, 1·6 and 1·5 per cent. were obtained for determinations of the optical density of the blank, sample and sample spiked with 33 $\mu g\ l^{-1}$ of ammonium-nitrogen, respectively.

TABLE II

OPTICAL DENSITIES RECORDED DURING REPEATED ANALYSIS OF A SAMPLE OF SEA WATER

	Optical density (10 cm)		Optical density (4 cm) × 2·5 Sample spiked with 33 $\mu g\ l^{-1}$ of ammonium-nitrogen
	Blank	Sample	
	0·188	0·549	1·085
	0·199	0·562	1·120
	0·195	0·563	1·122
	0·196	0·566	1·080
	0·190	0·558	1·110
	0·191	0·561	1·102
	0·191	0·553	1·085
	0·193	0·556	1·110
	0·192	0·578	1·100
	0·190	0·572	1·127
	0·184	0·553	1·085
	0·189	0·551	1·085
	0·193	0·571	1·085
Average ..	0·191	0·561	1·099

INTERFERENCE—

Richards and Kletsch[2] found that this hypochlorite method, besides measuring the ammonia present in sea water, also records 6 per cent. of urea and up to 91 per cent. of amino-acid-nitrogen. However, these authors gave no information about the time required for the oxidation of the nitrogen in these compounds, and to avoid the possibility with this shortened method of quenching the oxidation reaction before the maximum yield of nitrite was obtained, a series of experiments was carried out to establish the kinetics of the oxidation of several amino compounds.

The compounds chosen were hydroxylamine, methylamine, urea, DL-α-alanine and ethylamine, and the yields of nitrite from each are shown in Table III. The maximum yield of nitrite from each compound was attained within 10 to 17 minutes of oxidation, and was maintained for at least a further 35 minutes. It is concluded, therefore, that the method shows a different response to various forms of amino compounds and that it will not be possible to correct this deficiency by a slight alteration in the experimental procedure.

TABLE III

YIELD OF AZO COMPOUND FORMED FROM VARIOUS AMINO COMPOUNDS EXPRESSED AS PERCENTAGE OF THAT GIVEN BY AMMONIA

Compound	Urea	Methylamine	Ethylamine	DL-α-Alanine	Hydroxylamine
Per cent.	<5	9	32	71	76

Thus, as the result given by this method represents the sum total of the effects of several amino compounds present in the sample and, as there is no way of determining the relative proportions of each without resorting to other techniques, the results obtained for natural waters from different sources will not necessarily be comparable. Strickland and Parsons[1] have suggested that the method might be suitable in productivity ecology studies as a good indicator of the amount of tervalent nitrogen potentially available for micro-organisms. Although this is probably correct when the studied system contains essentially only one form of tervalent nitrogen, it is difficult to envisage the method still retaining its usefulness when a mixture of interconvertible tervalent nitrogen compounds is involved.

CONTAMINATION—

Although the author doubts the validity of reports that contamination can occur by merely opening bottles containing ammonia solution in the laboratory it is advisable to maintain a set of glassware exclusively for use with this method, and to avoid any unnecessary contact with substances containing ammonium or amino groups.

Any de-ionised water used in the method should be prepared immediately before use.

STORAGE OF SEA-WATER SAMPLES PRIOR TO THEIR ANALYSIS—

Marvin and Proctor[4] found that the ammonium-nitrogen concentration of estuarine and coastal waters (as determined by using Nessler's reagent) was effectively stabilised when samples were stored at −23 °C. Strickland and Parsons[1] recommended that samples of sea water should be analysed within 1 to 2 hours of collection but that the samples should be deep-frozen if longer delays are anticipated.

When unfiltered samples of sea water, which had been collected at eighteen different depths down to 1500 m at an offshore station east of Zanzibar, were stored at −20 °C for 18 days, their ammonia concentrations increased from an initial value of between 0 and 5 $\mu g\ l^{-1}$ to between 30 and 863 $\mu g\ l^{-1}$. For tropical sea waters, therefore, it seems that this mode of storage is useless and should be avoided, and that until a suitable method of storage is found, samples must be analysed within a few hours of collection.

MODIFIED METHOD

REAGENTS—

Alkali solution—Prepare a 4 N solution by dissolving 160 g of sodium hydroxide or 224 g of potassium hydroxide in 1 litre of de-ionised water. Add 8 g of sodium bromide to each 1 litre of solution. The solution can be stored well in polythene containers.

Alkaline oxidising agent—Filter a stock solution of 1·0 N sodium hypochlorite in 0·1 N alkali through a Whatman GF/C glass-fibre filter that has been washed with 400 ml of de-ionised water. Mix 5 ml of the stock hypochlorite solution with each 100 ml of 4 N alkali solution. Experience has shown that the oxidising agent is stable for up to 4 hours and that more precise results are obtained if it is stored for 15 minutes before use.

Sodium arsenite solution—Dissolve 20 g of arsenic(III) oxide and 6 g of sodium hydroxide in approximately 75 ml of distilled water. Dilute this solution to 500 ml with distilled water and filter it through a Whatman GF/C glass-fibre filter.

Citric acid - sulphanilamide reagent—Titrate a mixture of 5 ml of the 4 N alkali solution and 1 ml of the arsenite solution with a solution of hydrochloric acid (50 per cent. v/v); bromothymol blue is a suitable indicator for this reaction. From the result, calculate the concentration of hydrochloric acid needed so that 5 ml of the acidic solution would exactly neutralise the hydroxide present in the mixture of alkali and arsenite solutions used in the titration (this value is approximately 36 per cent. v/v). Prepare a hydrochloric acid solution of this concentration but also containing 126 g l^{-1} of citric acid monohydrate and 10 g l^{-1} of sulphanilamide. Filter the solution through a Whatman GF/C glass-fibre filter. The solution can be stored, without undue deterioration, in a darkened glass bottle for at least 1 month.

N-1-*Naphthylethylenediamine reagent*—Dissolve 0·5 g of *N*-1-naphthylethylenediamine dihydrochloride in 500 ml of distilled water. Filter through a Whatman GF/C glass-fibre filter and store in an amber-glass bottle. Discard solutions that develop a strong red coloration.

Ammonium sulphate solution—Dry ammonium sulphate for about 1 hour at 110 °C and dissolve about 0·1322 g in de-ionised water; add 1 ml of chloroform and sufficient de-ionised water to make 1 litre of stock solution. Prepare standard working solutions by diluting the stock solution with de-ionised water.

PROCEDURE—

Add 5 ml of alkaline oxidising agent to 25 ml of the filtered sea-water sample and, after at least 17 minutes, add 1 ml of sodium arsenite solution. Let the mixture stand for at least 3 minutes, then add 5 ml of citric acid - sulphanilamide reagent. After a standard period of approximately 1 minute add 1 ml of *N*-1-naphthylethylenediamine reagent and allow the mixture to stand for at least 10 minutes before measuring its optical density in a spectrophotometer cell of appropriate path length.

Perform nitrite "blank" determinations by first adding 1 ml of sodium arsenite reagent and then 5 ml of alkaline oxidising agent to 25-ml aliquots of each sea-water sample. After at least 3 minutes, add 5 ml of the citric acid - sulphanilamide reagent followed, 1 minute later, by 1 ml of *N*-1-naphthylethylenediamine reagent; develop the azo compound and measure the optical density of the solution.

CALIBRATION—

Take 25-ml volumes of both de-ionised water and an appropriate standard solution of ammonium sulphate prepared with the same de-ionised water through the above procedure. A standard solution containing about 30 μg l^{-1} of ammonium-nitrogen is appropriate when analysing samples of offshore waters. Prepare a "blank" determination for de-ionised water.

CALCULATION OF RESULTS—

If A, B, C, D and E are the optical densities corresponding to the solutions derived from the sample, sample blank, de-ionised water blank, de-ionised water and standard, respectively, and if F is the concentration of ammonium-nitrogen added to the de-ionised water to prepare the standard, then the concentration of ammonium-nitrogen in the unknown sample

$$= \frac{(A - B) - (D - C)}{(E - D)} \times F \ \mu g \ l^{-1}$$

Thanks are given to Captain J. Cutcliffe for his invaluable assistance with the manuscript, and also to the Director of this Research Organization for his permission to publish this paper.

REFERENCES

1. Strickland, J. D. H., and Parsons, T. R., "A Manual of Sea Water Analysis," Second Edition, revised, Fisheries Research Board of Canada, Bulletin No. 125, 1955, p. 83.
2. Richards, F. A., and Kletsch, R. A., "Recent Researches in the Fields of Hydrosphere, Atmosphere and Nuclear Geochemistry," Maruzen, Tokyo, 1964, p. 65.
3. Strickland, J. D. H., and Parsons, T. R., "A Practical Handbook of Sea Water Analysis," First Edition, Fisheries Research Board of Canada, Bulletin No. 167, 1968, p. 81.
4. Marvin, K. T., and Proctor, R. R., *Limnol. Oceanogr.*, 1965, **10**, 288.

Received *May 4th*, 1970
Accepted *March 16th*, 1971

Analyst, August, 1971, Vol. 96, *pp.* 591–597

Photometric Determination of Small Amounts of Oxygen in Water with 3,3′-Dimethylnaphthidine

BY HUBERT FADRUS AND JOSEF MALÝ

(Central Sewage Treatment Plant, Brno-Modřice, Czechoslovakia)

The oxidation products of manganese obtained in Winkler's classical method for the determination of oxygen can be determined by a photometric method based on their reaction with 3,3′-dimethylnaphthidine in an acidic medium. This reagent is used in preference to *o*-tolidine because of its higher molecular weight, which results in greater sensitivity, and in the intense red - violet colour of the oxidised form of 3,3′-dimethylnaphthidine.

IN attempts to eliminate errors involved in Winkler's iodimetric method[1] and to increase its sensitivity several physicochemical methods have been applied, the most significant of which is photometric determination. Oxygen has been determined either indirectly by being allowed to react with oxygen-fixing substances or directly, by its action on certain organic compounds. Direct measurement of the red colour of the pyrophosphate - manganic complex[2] produced by dissolving manganese hydroxide precipitates in an acidified solution of pyrophosphate seems to be an exception, as does Gad's modification[3] of Winkler's process, in which manganese(II) salts are replaced with iron(II) salts, and the iron(III) ions produced by this reaction are determined photometrically with rhodanate or sulphosalicylic acid.[4] The indirect methods include reactions of oxidised forms of manganese with iodide (followed by determination of the liberated iodine[5,6]), with *o*-tolidine[7] and with some redox indicators.[8,9] In the method with *o*-tolidine, cerium(III) salts[10] have sometimes been used instead of manganese(II) salts for oxygen fixation.

In the direct method, oxidation of organic compounds such as polyphenols and aminophenols, *viz.*, pyrogallol,[11] hydroquinone,[12] 2,4-diaminophenol[13] and adurol,[14] and leuco compounds of dyes, *viz.*, indigo-carmine,[15] methylene blue[16] and safranine T,[17] was carried out.

3,3′-Dimethylnaphthidine as the redox indicator seemed to be preferable. In analytical procedure it has only been used for this purpose. Following its application as redox indicator for the detection of end-points in chelatometric titrations,[18] it has also been used in the catalytic determination of osmium,[19] in a spot test for vanadium,[20] and in the photometric determination of chlorine[21] and iodine,[8,22] which is formed in the determination of oxygen by Winkler's method. This method, however, seemed to be very demanding as it was necessary to control the acidity strictly. Acid concentrations higher than 0·01 N inhibited the reaction of 3,3′-dimethylnaphthidine with iodine and also the colour development. This method could be greatly simplified, without the use of iodine, by direct oxidation of 3,3′-dimethylnaphthidine with the oxidising product of manganese, which reacts with this reagent over a wide range of acid concentrations.

PRELIMINARY EXPERIMENTS

REAGENTS—

Potassium permanganate, 0·05 N—Solutions of lower concentration can be prepared by appropriate dilution.

Manganese(II) sulphate—A 40 per cent. solution of $MnSO_4.2H_2O$ in distilled water.

Potassium hydroxide—A 70 per cent. solution in distilled water.

Sodium thiosulphate, 0·05 N—This and more dilute solutions were stabilised by adding 1 mmole l^{-1} of sodium hydroxide and EDTA.

Sulphuric acid, concentrated.

Orthophosphoric acid, concentrated.

EDTA, 0·1 M.

3,3′-Dimethylnaphthidine—A 0·05 per cent. solution of 3,3′-dimethylnaphthidine in glacial acetic acid was used. The solution is stable for 2 weeks, after which the calibration graph should be checked. (In the solid state the reagent is permanently stable.)

The aqueous solutions of manganese sulphate and potassium hydroxide must be freed from oxygen by passing through them nitrogen that has previously been passed through an alkaline solution of pyrogallol.

APPARATUS—

Pulfrich photometer with ELPHO-2.
Filter S-50 (or 500 nm).
Measuring cells, 1 and 5 cm.

PREPARATION OF SYNTHETIC STANDARDS—

3,3′-Dimethylnaphthidine is used for the photometric determination of oxygen because it is readily and stoicheiometrically oxidised by multivalent manganese ions in an acidic medium in the final stage of Winkler's method, an intense red - violet colour being formed. It is possible to study the course of oxidation analytically, either by using water samples containing standard amounts of oxygen under routine conditions of Winkler's method, with iodide replaced by 3,3′-dimethylnaphthidine, or by using samples of standard solution and mixtures containing multivalent manganese compounds. The latter procedure appears to be more advantageous for studying the reactivity with 3,3′-dimethylnaphthidine as regards the rate and ease of the reaction.

Generally the determination of the oxidimetric equivalent of these mixtures involves some of the reductimetric titrations used for the determination of the permanganate value. It is, of course, necessary, in Winkler's classical method,[23] to continually verify the final redox effect of these standards for the oxygen concentration studied.

Previously prepared synthetic standards of the oxygen fixation products obtained by Winkler's method were not suitable for the study of modifications of this method. Usually the solutions of complex manganese salts prepared by oxidising manganese salts with permanganate in an orthophosphoric acid medium[24] were not stable enough; this applies to mixtures in which multivalent manganese hydroxides are not fully dissolved in strongly acidic media.[25] The difficulty in dissolving prepared manganese hydroxides in acidic solution is caused by their complexity as they consist essentially of the hydrolysates of manganese - manganic salts. From this complex system manganese(III) ions are extracted by acids to form relatively stable manganese(III) - acid complex salts, the particles of which contain manganese(IV) ions and remain intact and finely dispersed in the medium.[26] The rate of these processes is a function of the initial system composition of multivalent manganese hydroxides, which changes rapidly with ageing of the precipitate. The final condition of the suspensions and pseudo suspensions is further determined by the acidity of the medium and especially by the concentration of the excess of manganese(II) ions, in the presence of which the dissolution of residual precipitate particles by an auto-redox process between manganese(IV) and manganese(II) ions occurs more readily with the formation of easily liberated manganese(III) ions—

$$Mn^{4+} + Mn^{2+} = 2Mn^{3+}$$

The reliability of volumetric measurement of heterogeneous suspensions of imperfectly dissolved precipitates in these conditions is debatable. Solutions of manganese(III) and manganese(IV) salts are not suitable because of their lack of stability,[24] especially in a weakly acidic medium in which a reduction of the oxidimetric equivalent of the mixture by redox and auto-redox processes is involved. It was found that the preparation of true suspensions of the manganese hydroxides as an initial component and functionally most exact analogue of the fixation product in Winkler's method was not possible as there was no way of preventing the oxidation of residual manganese(II) ions in an alkaline medium—

$$2Mn^{2+} + 4OH^- + O_2 + xH_2O = 2MnO_2.yH_2O + (x + 2 - 2y)\ H_2O$$

Another method of preparing synthetic standards[26] involves the oxidation of manganese(II) ions with permanganate in a neutral medium of distilled water—

$$3Mn^{2+} + 2MnO_4^- + (x + 2)\ H_2O = 5MnO_2.xH_2O + 4H^+$$

$$4Mn^{2+} + MnO_4^- + (x + 11)\ H_2O = 5Mn(OH)_3.xH_2O + 7H^+$$

where, even after the minimal acidification resulting from this reaction, the final hydrated manganese dioxide seems to be stable enough and any residual manganese(II) ions are inactive to the oxygen from the air. It is not appropriate to express the resulting hydrated multivalent manganese hydroxide as $MnO_2.xH_2O$ as this does not represent the complicated system in which tervalent atoms are also present.

Replacement of this mixture of hydrated oxides with corresponding volumes of permanganate solution in an amount oxidimetrically equivalent to the calculated mixture of manganese(III) and manganese(IV) ions did not prove to be applicable because of the different oxidising effects of MnO_4^- and manganese(III) and (IV) ions on 3,3'-dimethylnaphthidine (Fig. 1). The method of preparing standard amounts of multivalent manganese hydroxides suspended in water with a neutral or weakly acidic reaction had the following advantages: an easy and ready preparation of standards immediately before use; the similarity of the activity and reaction conditions of the mixture to the reaction conditions of the precipitate obtained by Winkler's method; and the possibility of making an experimental study of the effects of multivalent manganese hydroxides in a neutral medium and in moderately weakly acidic solutions on 3,3'-dimethylnaphthidine, when with strongly acidic solutions conventionally prepared free and complex bound manganese(III) and (IV) salts could not be used.

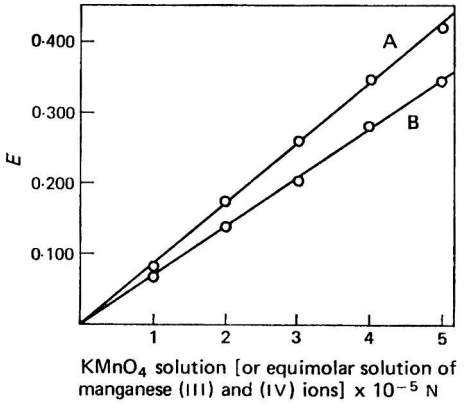


Fig. 1. Oxidation of 3,3'-dimethylnaphthidine with permanganate and manganese (III) and (IV) ions in an acidic medium: 0·00001 to 0·00005 N $KMnO_4$ [or equimolar concentrations of manganese (III) and (IV) ions] containing 2 ml of concentrated sulphuric acid and 1 ml of 0·05 per cent. 3,3'-dimethylnaphththidine in 100 ml of solution: A, with manganese (III) and (IV) ions; and B, with permanganate ions

Because the hydrated manganese oxides synthetically prepared according to the method given differ in structure from similar precipitates of analogous composition produced in Winkler's method, and the reactivity of the products towards acids varies, these synthetic standards could not in some instances, from the kinetic point of view, be used for the theoretical tracing of the redox system.

The subsequent procedure involves acidifying the suspensions of synthetically prepared manganese oxides with a given volume of the selected acid. After adding a solution of 3,3'-dimethylnaphthidine, the suspension of manganese hydroxides was dissolved and gave a red - violet solution which, after being made up to known volume, was measured photometrically. After further acidification the content of manganese hydroxides was determined iodimetrically in parallel samples. The oxygen content is obtained by using the following equivalence—

1 ml of 0·05 N sodium thiosulphate ≡ 0·4 mg of oxygen.

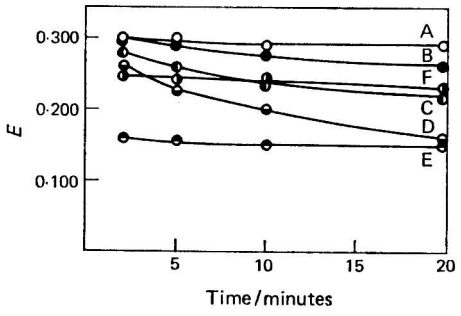


Fig. 2. Dependence of the colour intensity on the acidity of the solution: 0·00002 N equivalent concentration of manganese (III) and (IV) ions containing 1 ml of 0·05 per cent. 3,3′-dimethylnaphthidine in 100 ml of solutions with different acidities: A, B and C, 1, 5 and 10 ml of glacial acetic acid; D, 0·25 ml of concentrated sulphuric acid; E, 2·0 to 5·0 ml of concentrated sulphuric acid; and F, 5·0 ml of glacial acetic acid and 1·5 ml of 70 per cent. potassium hydroxide

An important factor in the reaction between manganese hydroxides and 3,3′-dimethylnaphthidine was the control of the acid conditions, the reaction being carried out in a wide concentration range of acetic, sulphuric, phosphoric and perchloric acids. Hydrochloric acid was not suitable as it contained traces of free chlorine, which reacted with the reagent. Higher concentrations of mineral acids gave the best results with respect to the stability of the colour, as did the buffered acetate medium resulting from adding acetic acid to the alkaline manganese hydroxide mixture, according to the procedure followed for oxygen fixation in Winkler's method (Fig. 2). The precipitate dissolved completely in high concentrations of phosphoric acid (3,3′-dimethylnaphthidine was not added) to give pink or red solutions of the triphosphate - manganic acid (Fig. 3). Because of the ease with which these complex salts are hydrolysed in the solutions mentioned, their stability decreases with decreasing phosphoric acid concentration.

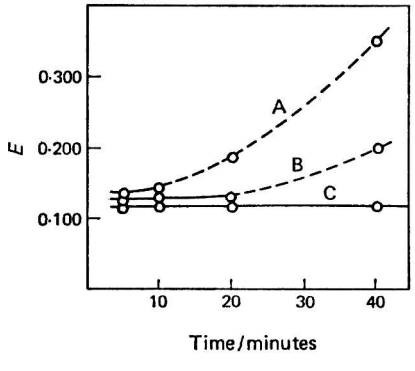


Fig. 3. Stability with time of triphosphate - manganic acid: 0·00002 N equivalent concentration of manganese (III) and (IV) ions containing 1 ml of 0·05 per cent. 3,3′-dimethylnaphthidine in 100 ml of solution with different concentrations of orthophosphoric acid: A, 0·8 M; B, 1·7 M; and C, 3·5 M orthophosphoric acid

The increase in the extinction values of solutions containing 0·8 and 1·7 M phosphoric acid (curves A and B in Fig. 3) seemed to be a result of the turbidity of the manganese hydrolysates evolved. A medium containing phosphoric acid in concentrations higher than 3 M was convenient for analytical use in the direct measurement of complex phosphate - manganites with higher contents of multivalent manganese hydroxides.

Reducing and strongly oxidising reagents interfered; their effect was similar to that in Winkler's classical process of oxygen determination. Of the ions occurring in waters, only Fe^{3+} and NO_2^- interfered in the determination. The reaction of nitrates and chlorine with 3,3′-dimethylnaphthidine, which is accompanied by the formation of a red colour, does not interfere under the experimental conditions stated in the final procedure for oxygen determination; for the former reaction higher concentrations of sulphuric acid are required and free chlorine must be eliminated before the determination, as the oxidation of manganese(II) ions in an alkaline medium interferes in the initial oxygen fixation. Readily oxidised organic matter interfered by reducing multivalent manganese in acidic medium. The effect of slowly reducing components (*e.g.*, sugar, phenols and amino-acids) could be eliminated by complexing manganese(III) ions to give a complex salt of manganese(III) - EDTA; EDTA was also used as its colour was suitable for the photometric determination of oxygen.[27] The stability of this complex is limited in a weakly acidic medium, and strongly acidic mineral acid media cause rapid decomposition of the complex as a result of auto-redox reactions between manganese(III) ions and the reducing EDTA.

Method

Basic procedure—

A conventional method was used to stabilise the dissolved oxygen in amounts from 1 to 80 μg in an oxygen reagent bottle by adding 1·0 ml of manganese(II) sulphate solution and 1·5 ml of potassium hydroxide solution.[23] After allowing the manganese hydroxide precipitate to settle and applying a surface layer of silicone oil (Lucooil-m, a product of VCHZ-Synthesia ČSSR, in which the solubility of atmospheric oxygen could be ignored), about two thirds of the solution volume in the reagent bottle were siphoned off carefully to avoid disturbing the precipitate. To the residue, 10 ml of dilute sulphuric acid (1 + 5) were carefully added and the solution stirred vigorously. If oil is not added, the procedure should be carried out sufficiently rapidly to prevent oxygen from the air diffusing through the surface while the solution is alkaline.

The mixture was transferred into a 100-ml calibrated flask, 1·0 ml of 3,3′-dimethylnaphthidine solution added, the volume made up to 100 ml and, after 5 to 10 minutes, the intensity of the red - violet colour was measured in 5-cm measuring cells with an S-50 filter (500 nm). For 5 to 40-μg amounts of oxygen in the reagent bottle a 1-cm measuring cell was used. With a suitable combination of size of reagent bottle and measuring cell oxygen concentrations of from 0·005 to 0·400 mg l^{-1} can be determined.

Modifications of the procedure—

When iron(III) is present, the dilute sulphuric acid is replaced with 10 ml of concentrated phosphoric acid, so that (3,3′-dimethylnaphthidine is present) the oxygen can be determined in the presence of up to 1000 mg l^{-1} of iron(III). The effect of nitrites up to a concentration of 10 mg l^{-1}, which in an acidic medium oxidise 3,3′-dimethylnaphthidine, can be eliminated by adding about 0·05 g of sulphamic acid to the oxygen bottle before sampling. The fixation of oxygen by manganese(II) salts and potassium hydroxide is carried out 5 to 10 minutes after sampling. With higher concentrations of nitrites the results were low as the nitrogen formed in the reaction of nitrites with the sulphamic acid displaces the dissolved oxygen. Sodium azide, recommended in Alsterberg's modification of Winkler's method, cannot be used as, in an acidic medium, the multivalent manganese ions are reduced.

$$2N_3^- + 2Mn^{3+} = 3N_2 + 2Mn^{2+}$$

If slowly oxidisable organic matter is present at a concentration generally occurring in surface waters, a mixture of 20 ml of 0·1 M EDTA and glacial acetic acid (1 + 1, v/v) is used to dissolve the precipitate completely before adding the solution of 3,3′-dimethylnaphthidine. At higher oxygen concentrations ranging from 0·2 to 2·0 mg l^{-1}, the precipitate can eventually be dissolved in 20 ml of concentrated phosphoric acid, the addition of 3,3′-dimethylnaphthidine being omitted. The red - violet colour of the phosphatomanganic acid complex was

measured after 5 to 30 minutes by using an S-50 filter and a 5-cm measuring cell. To determine the oxygen concentration, calibration graphs were used that had been prepared under identical conditions (with a medium of phosphoric acid and EDTA).

PREPARATION OF CALIBRATION GRAPH—

Distilled water (25 to 50 ml) and 0·5 ml of 40 per cent. manganese sulphate solution were introduced into a 100-ml calibrated flask and a volume of potassium permanganate solution added of concentration such that it was equimolar to the expected oxygen content in the reagent bottle, according to the relationship—

1 ml of 0·01 N potassium permanganate ≡ 0·08 mg of oxygen.

After the potassium permanganate solution was added the mixture became brown or yellow, depending on the amount of multivalent manganese hydroxide precipitate formed, which was treated further in accordance with the procedure previously described. The synthetic mixture of manganese hydroxides appeared to have unlimited stability, its reactivity varying with age as experienced with precipitates prepared by Winkler's method. The calibration graphs were linear.

RESULTS

The reliability of the photometric determination of oxygen with 3,3′-dimethylnaphthidine was confirmed (Table I) by using tap-water samples de-oxygenated with nitrogen. Residual oxygen concentration was determined by the method described and confirmed with Winkler's conventional procedure by titration with 0·0005 N sodium thiosulphate, with dead-stop indication.[28] The error of the given method on samples of unpolluted water containing dissolved oxygen in the range 5 to 40 μg in an oxygen reagent bottle is less than ± 2 μg of oxygen and in the range 50 to 400 μg is less than ± 10 μg of oxygen.

TABLE I

COMPARISON OF METHODS FOR THE DETERMINATION OF OXYGEN IN TAP-WATER SAMPLES INVOLVING 3,3′-DIMETHYLNAPHTHIDINE AND DEAD-STOP TITRATION

Sample No.	Volume of reagent bottle/ml	Weight of oxygen in the reagent bottle/mg		Δ/ mg of oxygen
		Photometric	Dead-stop	
1	113·6	0·082	0·090	−0·008
2	109·0	0·123	0·115	+0·008
3	122·5	0·045	0·057	−0·012
4	107·8	0·236	0·245	−0·009
5	104·1	0·312	0·302	+0·010
6	116·4	0·189	0·198	−0·009
7	113·1	0·263	0·256	+0·007
8	119·5	0·387	0·376	+0·011

The method was verified (Table II) by analysing contaminated surface waters (River Svratka, BOD ≡ 12 mg l^{-1} of oxygen), the oxygen concentration of which had been reduced to a suitable range by natural de-oxygenation by appropriate microbial fauna. Under the given conditions Anderson and Appelman's dead-stop titration method was used for confirmation.[29]

TABLE II

COMPARISON OF METHODS FOR THE DETERMINATION OF OXYGEN IN SURFACE-WATER SAMPLES INVOLVING 3,3′-DIMETHYLNAPHTHIDINE AND DEAD-STOP TITRATION

Sample No.	Volume of reagent bottle/ml	Weight of oxygen in the reagent bottle/mg		Δ/ mg of oxygen,
		Photometric	Dead-stop	
1	291·7	0·164	0·152	+0·012
2	303·2	0·217	0·198	+0·019
3	287·5	0·136	0·140	−0·004
4	299·1	0·065	0·072	−0·007
5	300·6	0·322	0·320	+0·002
6	293·0	0·183	0·192	−0·009
7	289·3	0·272	0·285	−0·013
8	309·5	0·042	0·050	−0·008

Conclusion

A sensitive and precise method for the determination of small concentrations of dissolved oxygen in waters by photometric determination with 3,3'-dimethylnaphthidine is presented. This reagent in an acetic acid and mineral acid medium produces a red - violet colour with multivalent manganese hydroxides, the intensity of which corresponds to Beer's law.

Errors occurring in the iodimetric determination by Winkler's method are eliminated and interferences are usually removed simply by modifications to the procedure. For unpolluted waters the accuracy of the oxygen determination is satisfactory; for contaminated waters errors are caused by the presence of interferences analogous to those in Winkler's method.

References

1. Winkler, L. W., *Ber. dt. chem. Ges.*, 1888, **21**, 2843.
2. Gad, G., and Hoppe, W., *Gesundheitsingenieur*, 1956, **77**, 343.
3. Gad, G., *Gas- u. WassFach*, 1938, **81**, 59.
4. Exton, W. G., *J. Lab. Clin. Med.*, 1945, **30**, 84.
5. Hansen, W. J., and Pieters, H. H., *Analytica Chim. Acta*, 1948, **7**, 712.
6. Johnson, M. L., and Whitney, R. J., *J. Exp. Biol.*, 1939, **16**, 56.
7. McCrumb, F. R., and Kenny, W. R., *J. Amer. Wat. Wks Ass.*, 1929, **21**, 400.
8. Banks, J., *Analyst*, 1959, **84**, 700.
9. Stones, W. F., *Chem. & Ind.*, 1957, 120.
10. Schumann, E., *Brennst.-Wärme Kraft*, 1954, **6**, 37.
11. Mackey, W. M., and Middleton, R. E., *J. Soc. Chem. Ind.*, 1898, **17**, 1127.
12. Tuwe, R., *Chem. Abstr.*, 1948, 6029d.
13. Gilcreas, F. W., *J. Amer. Wat. Wks Ass.*, 1935, **27**, 1166.
14. Winkler, L. W., *Z. angew. Chem.*, 1913, **26**, 135.
15. Meyling, A. H., and Frank, G. H., *Analyst*, 1962, **87**, 60.
16. Rotstein, V. P., and Schemjakin, V. N., *Teplotechnika*, 1954, **2**, 19.
17. Aleskovskij, V. B., *Zav. Lab.*, 1962, **28**, 159.
18. Brown, E. G., and Hayes, T. J., *Analytica Chim. Acta*, 1953, **9**, 1.
19. Bognar, J., and Sarosi, S., *Magy. Kém. Foly.*, 1961, **67**, 193.
20. Belcher, R., and Nutten, A. J., *Analyst*, 1951, **76**, 430.
21. Belcher, R., Nutten, A. J., and Stephen, W. I., *Analyt. Chem.*, 1954, **26**, 772.
22. Banks, J., *Analyst*, 1954, **79**, 170.
23. "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 12th edition, American Public Health Association, New York, 1965.
24. Freier, R., *Vom Wass.*, 1952, **19**, 124.
25. Buriánek, K., Sb. VŠCHT Praha 1958, *Technologie paliv a vody* 2, Part 1, p. 137.
26. Fadrus, H., and Malý, J., in preparation.
27. ——, ——, *Städtehygiene*, in the press.
28. Knowles, G., and Lowden, G. F., *Analyst*, 1953, **78**, 159.
29. Anderson, F. L., and Appelman, E. H., *Analyt. Chem.*, 1965, **37**, 298.

Rapid Determination of Solvent Occluded in Some Pharmaceutical Chemicals

By THOMAS R. LOWTHER and W. D. WILLIAMS
(Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow)

An infrared spectrophotometric method has been developed for the determination of occluded solvent in orciprenaline sulphate and warfarin sodium. In lesser detail ampicillin sodium, colchicine, the calcium and sodium salts of novobiocin and streptomycin sulphate have also been examined.

The 1968 edition of the British Pharmacopoeia[1] includes three chemicals, the monographs for which limit the content of solvent present either as residues or in the form of a clathrate compound. These compounds and solvents are ampicillin sodium (dichloromethane), orciprenaline sulphate (methanol) and warfarin sodium clathrate (isopropyl alcohol). To these the 1969 Addendum[2] adds streptomycin sulphate (alcohols). The solvent is not readily removed by conventional drying methods and the official determinations rely upon gas chromatography or chemical oxidation (for alcohols in streptomycin sulphate) for control of the solvents. Further examples of this type are believed to be chloroform[1] or ethyl acetate (D. Watt, private communication) in colchicine and a solvent of some kind in the salts of novobiocin.

A detailed study of the retention of water and organic solvents by carbohydrate materials has been described by Anderson and King,[3] who based their determinations of solvent upon an elegant vapour-phase infrared technique.[4]

The solvents mentioned above are readily vaporised and give satisfactory infrared absorption spectra at relatively low concentrations in conventional gas cells. It therefore appeared worthwhile to heat the pharmaceuticals with a liquid of high boiling-point to dissolve the sample and to examine the vapour in an evacuated gas cell for the presence of absorption characteristic of a particular solvent. It was hoped in this way to simplify the system involving the use of a cold trap and manometer, as described in detail by Anderson,[4] to a single small flask. The method would have the advantages of enabling the solvent to be identified directly without the two or more columns required initially by gas chromatography, the solvent to be determined quantitatively, and amounts of sample less than those required for gas chromatography to be used.

Infrared Method

Apparatus—

Instrument—A Perkin-Elmer 237 grating infrared spectrophotometer with a conventional gas cell of approximately 140-ml capacity and sodium chloride end windows was used.

Flasks—These were blown from Quickfit CNB.CNC10/19 cones to give capacities of approximately 1 and 2 ml, which are useful for light powders.

Assay procedure—

Weigh accurately sufficient of the compound to give a satisfactory absorption (Table I), transfer it to a small flask and add about 0·4 ml of polyethylene glycol (PEG) 300 (see below and Results and Discussion). Attach the flask to an evacuated gas cell (at a pressure of less than 0·5 mm of mercury), open the tap of the cell and immerse the flask in an oil-bath at a suitable temperature (Table I) for 4 minutes. Close the tap and place the gas cell in an oven at 100 °C for 2 minutes.

Record the absorption spectrum of the vapour, identify the solvent and measure the extinction of an appropriate peak. Calculate the percentage of solvent by reference to a calibration graph obtained by treating aliquot portions of a solution of the solvent in polyethylene glycol 300 in the same way.

Methanol in orciprenaline sulphate—Sample B (Table I) was examined as described above except that diethylene glycol (0·2 ml) was used instead of PEG 300. Methanol found was 4·21 per cent. w/w (mean of four determinations).

Gas-chromatographic method

Apparatus—

Instrument—A Perkin-Elmer F11 gas chromatograph fitted with a flame-ionisation detector and Hitachi Perkin-Elmer 159 recorder was used.

Conditions—

These were as specified in the 1968 edition of the British Pharmacopoeia for the determination of the solvent in ampicillin sodium, orciprenaline sulphate and warfarin sodium. The same conditions, with a temperature of 75 °C, were used for examination of colchicine, novobiocin salts and streptomycin sulphate.

Results and discussion

Preliminary studies (not reported here) with various liquids of high boiling-point indicated that polyethylene glycol 300 was satisfactory as a solvent except for orciprenaline sulphate. Although no condensate appeared on the walls of the gas cell, as occured with liquids of lower boiling-point, the practice of warming the cell before recording the spectrum was adopted as standard. Typical amounts of occluded solvent varied from 1 mg (for methanol) to 8 mg (for isopropyl alcohol) and it was felt that trace amounts of condensation might well be missed. The cell used was fitted with two taps which, in practice, proved convenient, as a stream of air could be drawn through the cell for a few seconds to ensure complete removal of solvent vapour after each determination. The results obtained for the compounds examined in PEG 300 are recorded in Table I, which also includes, within parentheses, the corresponding results for the gas-chromatographic determinations when these were carried out quantitatively. Qualitative tests by gas chromatography confirmed the presence of the solvents found. Calibration graphs were linear with all solvents, and indicated that the use of a single cell and flask under standard conditions suffered no interference by pressure effects.

Table I

Identification and determination of occluded solvents

Chemical	Weight of sample/ g	Temperature/ °C	Solvent				
			Identified	Peak selected (cm^{-1})	Per cent. w/w (Mean)	Standard deviation	No. of results
Ampicillin sodium ..	—	160	—	745	0	—	4
	(1)	—	Dichloromethane	—	(0·38)	—	(1)
Colchicine	0·1	140	Ethyl acetate	1250	7·5	—	1
Novobiocin calcium ..	0·15	105	Acetone	1750	1·78	0·048	7
Novobiocin sodium (A) ..	0·15	105	Acetone	1750	0·2	—	1
Novobiocin sodium (B) ..	0·15	105	Acetone	1750	0·56	0·022	7
Orciprenaline sulphate A	0·03	160	Methanol	1038	2·49	0·092	11
	(1)	—	—	—	(3·02)	(0·11)	(4)
Orciprenaline sulphate B	0·03	160	Methanol	—	4·00	—	3
	(1)	—	—	—	(4·25)	—	(2)
Streptomycin sulphate ..	0·17	160	Methanol	1038	0·48	—	1
Warfarin sodium	0·1	160	Isopropyl alcohol	1385	8·06	0·08	12
	(0·5)	—	—	—	(8·19)	(0·23)	(6)

Ampicillin sodium—

Although dichloromethane was readily recovered from standard solutions with and without added ampicillin sodium, no trace of characteristic absorption appeared in the vapour from the sample and at present no explanation can be offered for this result. The sample itself was not from a normal production batch but was deliberately left with more than the permitted level of dichloromethane for this investigation.

COLCHICINE—

No chloroform was found but ethyl acetate was present in considerable amount. This is in agreement with the expected result (D. Watt, private communication).

NOVOBIOCIN SALTS—

Although the solvent was not known with certainty, the identification of acetone in novobiocin calcium and the sodium salt (B), and the values found, were particularly gratifying in that the manufacturer confirmed that acetone was the solvent used and that the results were within specification.

ORCIPRENALINE SULPHATE—

The results obtained by the infrared and gas-chromatographic methods for sample A differed significantly. This difference is attributed mainly to the insolubility of the salt in PEG 300 although the particle size may also be important. Sample A was a coarse crystalline powder and a large discrepancy was observed, whereas sample B was a fine crystalline powder and the difference between the results was less (Table I). This is in agreement with Anderson and King's results[3] for water and methanol released from a powder prepared in 200 and 100-mesh sizes. The presence of solid, however, defeats the object of the method and another solvent was sought. Diethylene glycol (boiling-point about 238 °C) readily dissolved the sample on slight warming and the result was in agreement with that obtained by gas chromatography, *viz.*, 4·21 per cent. compared with 4·25 per cent. Unfortunately, it was not possible to repeat the determination on Sample A as no sample remained after the assays by gas chromatography.

STREPTOMYCIN SULPHATE—

The procedure given in the 1968 British Pharmacopoeia is for determining "alcohols" but methanol only was found in this sample.

WARFARIN SODIUM—

Good agreement between the results from both methods was observed, and the sample was completely soluble in PEG 300.

CONCLUSIONS

With this method several of the advantages over the gas-chromatographic methods are realised, but one compound that requires an extended investigation remains, *viz.*, ampicillin sodium.

We thank Mr. C. A. Johnson (Scientific Director, British Pharmacopoeia Commission), Beecham Research Laboratories, Boehringer Ingelheim Ltd., Merck, Sharp and Dohme Ltd. and Upjohn Ltd. for supplying samples of drugs. One of us (T.R.L.) thanks the Government of Northern Ireland for a grant during the tenure of which this work was carried out.

REFERENCES

1. "The British Pharmacopoeia 1968," The Pharmaceutical Press, London, 1968.
2. "The British Pharmacopoeia, 1968. Addendum, 1969," The Pharmaceutical Press, London, 1969.
3. Anderson, D. M. W., and King, N. J., *Talanta*, 1961, **8**, 497.
4. Anderson, D. M. W., *Analyst*, 1959, **84**, 50.

Received *October 22nd*, 1970
Accepted *March 25th*, 1971

The Gas-chromatographic Determination of Arsanilic Acid and Carbarsone in Animal Feeding Stuffs

By R. E. WESTON, B. B. WHEALS and M. J. KENSETT

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

Methods are described for the determination of arsanilic acid and carbarsone in animal feeding stuffs. These additives are extracted from the feed with an aqueous solvent. Carbarsone is converted by hydrolysis with sodium hydroxide into arsanilic acid, which is then reduced with Raney alloy to aniline. The aniline, separated from the reaction mixture by steam distillation and solvent extraction, is determined by gas chromatography with flame-ionisation detection.

Organoarsenical compounds such as arsanilic acid, 4-aminophenylarsonic acid and carbarsone, 4-ureidophenylarsonic acid, are incorporated in feeding stuffs for growth-promoting or prophylactic purposes. Analytical procedures are required for additives of the latter class in the enforcement of the Fertilisers and Feeding Stuffs Regulations, 1968.[1] The current method for the determination of arsanilic acid is based on its conversion into a water-soluble dye produced by diazotisation and coupling.[2] An analogous procedure can be used for carbarsone after it has been hydrolysed to arsanilic acid. The presence in feeds of other drugs that contain free amino groups, or those that may yield amino groups on hydrolysis, can cause interference in these procedures. Interferences are also encountered in some instances from substances co-extracted from feeds being examined for organoarsenic content.

The two arsenicals studied are incorporated in feeds at a level of 50 to 100 mg kg^{-1} for arsanilic acid and at a level of 375 mg kg^{-1} and over for carbarsone. Both of these compounds are soluble in water, but are poorly soluble in organic solvents other than alcohols, and are involatile. Few reactions of these compounds can provide the basis of a non-colorimetric analytical method, but an exception was found in the reductive cleavage of arsanilic acid to aniline effected by Raney nickel in alkaline solution.[3] The method described below has greater inherent specificity than the colorimetric methods and has considerable freedom from interferences arising from co-extractives.

Method

Apparatus—

Gas chromatograph—An isothermal instrument fitted with a flame-ionisation detector and incorporating a 150-cm glass column, 4·5 mm i.d., was used; the column packing was silanised Chromosorb W,* 80 to 100 mesh, coated with 10 per cent. Versamid 900† and 2 per cent. potassium hydroxide. The column temperature was 120 °C; the carrier gas was nitrogen and the flow-rate 50 ml $minute^{-1}$.

All-glass distillation apparatus—This consisted of a 100-ml round-bottomed flask connected to a side-arm Liebig condenser via a suitable still-head.

Reagents—

Arsanilic acid standard solution—Weigh a calculated amount of 4-aminophenylarsonic acid, dissolve it in water, and dilute to a concentration of 1000 μg ml^{-1}.

Carbarsone standard solution—Weigh a calculated amount of 4-ureidophenylarsonic acid, dissolve it in water, and dilute to a concentration of 1000 μg ml^{-1}.

Chloroform—Analytical-reagent grade.

Extraction solvent—Add 100 g of sodium chloride to 100 ml of N hydrochloric acid and dilute to 1 litre with water.

* Johns-Manville (G.B.) Ltd., 20 Albert Embankment, London, S.E.1.

† Applied Science Laboratories, Field Instruments Ltd., Tetrapak House, Orchard Road, Richmond, Surrey.

Raney alloy—Commercial nickel - aluminium alloy (42 + 58 w/w), in powder form.
Sodium hydroxide solution, 20 per cent. w/v.
Sodium sulphate, anhydrous, granular.

PROCEDURE—

Preparation of the feed—Grind a sample of the feed to pass a 1-mm sieve (B.S. No. 16) and carefully mix. Weigh 10 g of the prepared feed and transfer it to a 250-ml calibrated flask. Add 100 ml of extraction solvent and shake the mixture for 1 hour. Adjust the volume to 250 ml with water, mix, and allow the suspended material to settle. (The volume of 10 g of prepared feed was found to be approximately 7 ml and a suitable correction for this volume should be made in the final calculation of additive content.) Filter a portion of the solution through a Whatman No. 1 paper and reject the first 20 ml of the filtrate.

Feeds containing arsanilic acid—Transfer an amount of the solution containing 20 to 50 μg of arsanilic acid by pipette into a 100-ml round-bottomed flask, adjust the volume to approximately 30 ml with water, and add 15 ml of sodium hydroxide solution. Add 0·3 to 0·4 g of Raney alloy, loosely stopper the flask, and swirl the contents to effect an even suspension.

Swirl the flask periodically until no further reaction is apparent. When hydrogen evolution ceases, connect the flask to a side-arm condenser and distil the contents over into a separating funnel until 20 ml of distillate are collected. Wash the condenser with 10 ml of water and add 5 ml of sodium hydroxide solution to the combined distillate and washings. Add 2 ml of chloroform by pipette and shake the mixture vigorously. Transfer the chloroform extract to a stoppered test-tube containing about 1 g of anhydrous sodium sulphate. Treat arsanilic acid standards containing 25 and 50 μg in the same way as the sample by the addition of Raney alloy and sodium hydroxide solution, distillation and extraction, as described above.

Inject 2-μl amounts of the chloroform extracts on to the chromatographic column and measure the response of the aniline peak for each chromatogram. Plot a calibration graph of micrograms of arsanilic acid against chromatographic response and use this graph to determine the amount of arsanilic acid present in the unknown sample.

TABLE I

RECOVERIES OF ARSANILIC ACID AND CARBARSONE FROM SPIKED SAMPLES

	Arsanilic acid		Carbarsone	
Feed	Added/mg kg^{-1}	Found/mg kg^{-1}	Added/mg kg^{-1}	Found/mg kg^{-1}
Coarse grain balancer ..	100	97	100	93
	100	97	100	99
	200	192	200	200
	200	200	200	190
	—	—	375	369
	—	—	375	379
Layers mash	100	107	100	102
	100	104	100	103
	200	222	200	224
	200	208	200	184
	—	—	375	352
	—	—	375	370
Baby chick crumbs	100	100	100	100
	100	109	100	102
	200	187	200	214
	200	196	200	188
	—	—	375	377
	—	—	375	365
Growers mash	100	103	100	98
	100	100	100	102
	200	219	200	228
	200	196	200	188
	—	—	375	346
	—	—	375	377

Feeds containing carbarsone—With a pipette, withdraw from the prepared sample extract an amount expected to contain 20 to 50 μg of carbarsone and transfer to a 100-ml round-bottomed flask. Add 15 ml of sodium hydroxide solution and a suitable amount of water to bring the volume to approximately 25 ml. Boil gently under reflux for 1·25 hours. Wash down the condenser with 20 ml of water and allow the solution in the flask to cool. Carry out the reduction with Raney alloy, distillation and extraction with chloroform as described under "Feeds containing arsanilic acid." Treat amounts of a standard solution containing 25 μg and 50 μg of carbarsone by the procedure and inject 2-μl amounts of the extracts into the gas chromatograph.

Results

Under the chromatographic conditions described, the retention time of aniline was 4·25 minutes and its detection limit was about 2 ng. The peak height *versus* concentration graphs for arsanilic acid and carbarsone, as aniline, were linear over the range studied. No chromatographic peaks were encountered in feeds free from arsanilic acid or carbarsone.

Recoveries of arsanilic acid and carbarsone from spiked samples are shown in Table I. These compounds were added to feeds as solutions in methanol, and the solvent was subsequently removed in a gentle stream of air.

Discussion

The reductive cleavage of arsanilic acid to aniline proceeded to completion at the levels examined. Reduction with Devarda's alloy was less effective. The over-all recovery of aniline by the prescribed procedure was about 70 to 80 per cent. of the theoretical amount, the greatest loss occurring at the chloroform - water partitioning stage. The yield of arsanilic acid from carbarsone is dependent on hydrolysis time and the recommended time, 1·25 hours, was found to give at least 95 per cent. conversion. Other heating times resulted in a decreased yield. Of the additives likely to be present in feeding stuffs, only nitarsone, 4-nitrophenylarsonic acid, gave rise to aniline under the prescribed conditions. However, the present method was not directly applicable to the determination of this compound in feeds as initial investigation has shown that it is not completely extracted when present at the 200 p.p.m. level. The method does not distinguish between carbarsone and arsanilic acid in admixture, but such mixtures do not represent typical commercial practice. The detection of these compounds in admixture can be accomplished by the thin-layer chromatographic technique of Morrison.[4]

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

References

1. The Fertilisers and Feeding Stuffs Regulations, S.I. 1968 No. 218, H.M. Stationery Office, London, 1968.
2. Methods of Analysis of the A.O.A.C., Eleventh Edition, 1970, p. 731.
3. Feigl, F., *Analyt. Chem.*, 1961, **33**, 1118.
4. Morrison, J. L., *J. Agric. Fd Chem.*, 1968, **16**, 704.

Received *November 17th*, 1970
Accepted *April 19th*, 1971

Book Reviews

DETERMINATION OF ORGANIC COMPOUNDS: METHODS AND PROCEDURES. By FREDERICK T. WEISS. Pp. xii + 475. New York, London, Sydney and Toronto: Wiley-Interscience. 1970. Price £8·25.

Any author attempting to cover so broad a field in a single volume has a very difficult course to steer between the general and the particular. That Weiss succeeds is due in no small part to the fact that for most of the book he restricts his field to functional group analysis. To quote from his preface: "This volume contains a description of the functional analysis of organic compounds by chemical, spectroscopic and chromatographic techniques. The recommended methods, given in full detail, are in most cases of wide and general applicability and allow the determination of many of the compounds in a functional series. Laboratory data are given on the application of these methods to pure organic compounds and commercial materials. Critical evaluations, with tabulated results, are included to enable the analyst to choose methods and conditions and to understand their limitations and sensitivities."

The book is divided into three parts: determination of organic compounds, analysis of materials, and laboratory methodology and practice. Part 1, some two-thirds of the book, I found to be really excellent; it contains sixteen well written and informative chapters on functional groups from saturated hydrocarbons to sulphur compounds. However, my enthusiasm began to wane when I reached part 2, which in four chapters moves into the more specialised areas of applications to polymers, trace analysis, surface-active materials and petroleum and its products. Even so, there is some useful information for the non-specialist and one can sympathise with the intent to illustrate the methods in action. It is in part 3 that disaster strikes when the author, in attempting to round off his work, tries to deal briefly with topics both general and particular, *i.e.*, chromatography (in 47 pages), water (5), preparation of common reagents (15), analytical equipment (4) and safety in the laboratory (3). The result is an irritating mixture of the irrelevant and the useful, with the former predominating, and I would have been happier if this whole section had been omitted. However, it forms a relatively small part of the whole and therefore detracts little from the over-all value of the book. Anyone needing up-to-date information, with full practical details, on methods for determining the common functional groups will find this book invaluable.

G. E. PENKETH

DEVELOPMENTS IN APPLIED SPECTROSCOPY. VOLUME 7B. Edited by E. L. GROVE and A. J. PERKINS. Pp. xii + 291. New York and London: Plenum Press. 1970. Price £5·85; $12.50.

This volume contains four groups of papers on infrared and Raman spectroscopy (8 papers), internal reflectance spectroscopy (3 papers), nuclear magnetic resonance spectroscopy (4 papers) and spectrochemical applications to textiles and fibres (4 papers), selected from the programme of the 19th Annual Mid-America Spectroscopy Symposium held in Chicago during May 13th to 17th, 1968. The companion volume (7A) contains papers on X-ray spectroscopy, emission, flame and atomic-absorption spectroscopy, mass spectrometry and nuclear particle spectroscopy. Previous volumes in this annual series have appeared within a year of the Symposium, as did Volume 7A, but the additional material contained in Volume 7B has delayed the appearance of this part by a further year.

In view of the wide range of spectroscopic techniques covered in Volume 7B, it is only possible to note the actual subjects of the papers and to indicate the extent to which they may be regarded as meeting, in both content and treatment, the interests of applied spectroscopists.

Three of the papers in the section on *IR and Raman Spectroscopy* are concerned with inorganic solids. A study of the carbonate ion in natural and synthetic apatites takes account of both infrared (KBr disc) and X-ray data and contains the felicitous phrase "The apatite structure is a hospitable one, allowing varied substitutions to take place without significant change in its symmetry." A second paper on apatites deals with polarised infrared reflectance of single crystals, which is shown to provide much more structural information than powder absorption techniques.

The least appropriate paper in this section is "Spectroscopic Studies of Hydrogen Bonding." The intrinsic importance of hydrogen-bonding processes in molecular spectroscopy and nuclear magnetic resonance spectroscopy is undeniable, but to consider 310 references in less than 30 pages of text can only result in a catalogue, with no reference to hydrogen bonding within the context of applied spectroscopy. It is difficult to envisage this paper in terms of a conference presentation.

An excellent example of the way in which improvements in spectroscopic technique are rapidly spreading into applied spectroscopy is the brief but lucid account by D. S. Cain and A. B. Harvey entitled "Raman Spectroscopy of Polymeric Materials, Part I. Selected Commercial Polymers," in which the advantages of laser excitation are discussed. It is interesting to learn that sample "fluorescence" (the continuous background emission often seen in Raman spectra) is still something of a problem, even with helium - neon laser excitation at 632·8 nm! The authors conclude, however, that laser-excited Raman spectroscopy of commercial grades of polymers is feasible without sample pre-treatment and can make a useful contribution to the study of polymer structure.

The three papers on *Internal Reflection Spectroscopy* are brief and very limited in scope, with emphasis on the experimental aspects. The specific topics are inorganic halides in liquid sulphur dioxide, band sharpening effects at low temperature, and an elementary discussion of combined chromatographic, infrared internal reflection and mass-spectrometric techniques for the analysis of drug mixtures.

The section *NMR Spectroscopy* contains two brief papers that may be regarded as applied spectroscopy. The first is on the effect of substitution in the A and D rings on the positions of the $C_{(18)}$ and $C_{(19)}$ methyl group proton resonances in the androstane structure and the findings are relevant to the assignment of configuration. The second, on the analysis of acrylic copolymers, reports on the use of bromoform as the best solvent for this purpose. Of the two further papers on nuclear magnetic resonance spectroscopy, the first is a superficial account of computer procedures for the analysis of experimental data and the calculation of spectra from chemical shifts and coupling constants. In the other, by contrast, the analysis of ABX spectra is dealt with in great detail, with specific consideration of all possible combinations of the six magnetic parameters, particular attention to the avoidance of ambiguous solutions and a few examples of actual spectra. This treatment is fundamental and by no means easy to assimilate, but is clearly authoritative.

The final group of four papers on *Spectrochemical Applications to Textiles and Fibres* is at the level more commonly thought of as applied spectroscopy, but here again the quality is uneven. A general paper lists ten applicable spectroscopic (in the broadest sense) techniques, but discusses only atomic emission, X-ray fluorescence and atomic-absorption methods for the estimation of inorganic constituents. The value of the potassium bromide disc method for the infrared spectroscopy of cellulose products is excellently reviewed, with particular reference to the identification of new functional groups in modified celluloses and the detection of changes in crystallinity and polymorphic forms. A paper on the spectrophotometric control of dyeing procedures is much less impressive, while the final article is a brief practical note on the use of internal reflectance infrared spectroscopy for the quantitative analysis of mixed fibres.

It will be seen from these comments that, considered as a whole, many of the papers in Volume 7B are not well chosen as examples of applied spectroscopy. Of those which may be regarded as falling within this admittedly broad range, some are quite superficial. Only a small part of this book can be recommended for the consideration of applied spectroscopists.

G. H. BEAVAN

NMR SPECTROSCOPY IN ORGANIC CHEMISTRY. By B. I. IONIN and B. A. ERSHOV. Pp. x + 382. New York and London: Plenum Press. 1970. Price £11·70; $25.00.

This book on applications of n.m.r. spectroscopy to organic chemistry is a translation from the Russian original. On the whole the translation is good, although one is aware, perhaps inevitably, of some unusual phraseology and sentence structures.

A particular feature of this book, in comparison with those already available that concentrate on organic aspects of nuclear magnetic resonance, *e.g.*, the recent book by Jackman and Sternhell, is the considerable discussion of spectra from organic molecules that contain magnetic nuclei other than hydrogen, *e.g.*, ^{13}C, ^{31}P and ^{19}F. There is a less complete and systematic treatment of results from hydrogen nuclei than can be found elsewhere, but the book offers a good cross-section of applications of n.m.r. to structural and mechanistic aspects of chemistry. In the reviewer's opinion there is a rather greater emphasis on theory, *e.g.*, analysis of complex spectra, than an organic chemist would normally need.

This is a useful addition to the books available on this subject. However its price is very high and the quality of the book production is not satisfactory in relation to the price. For example, many of the symbols and formulae are in very small print and many of the spectral diagrams are also small and poorly drawn (or re-drawn).

N. SHEPPARD

INFRARED VAPOUR SPECTRA. By D. WELTI. Pp. xii + 211. London, New York and Rheine/Westf.: Heyden & Son in co-operation with Sadtler Research Labs. Inc., Philadelphia. 1970. Price £8·50; DM 77; $21.00.

The difficulty in interpreting infrared spectra of mixtures has led to increased interest being shown in the coupling of infrared spectrometers with efficient separation processes, notably gas chromatography. With the development of suitable sample trapping techniques and fast-scanning spectrometers it is now possible to obtain rapidly vapour spectra of the fractions from gas - liquid chromatographic columns and this book provides a timely and up-to-date review of developments in this field. It also includes a compilation of 306 vapour-phase spectra for application in this type of analysis, which will complement other compilations of liquid-phase spectra. The spectra, all of which were recorded on a single instrument, cover a variety of types of compounds, are clearly presented and adequately indexed. The infrared spectra of vaporised organic molecules in general exhibit small but discrete shifts of the frequency of the band maxima compared with liquid-phase spectra, the direction and extent of the shift being dependent on the particular molecular transition. Mr. Welti's book includes a chapter on frequency correlations of the vapour spectra in which he also compares directly the frequency of band maxima in both liquid and vapour phases and comments on the differences observed. The book will be invaluable as a reference for analytical spectroscopists working in this field and it is to be hoped that it will be brought up to date with new editions as the number of available spectra increases.

J. M. OTTAWAY

IR: THEORY AND PRACTICE OF INFRARED SPECTROSCOPY. Second Edition. By N. L. ALPERT, W. E. KEISER and H. A. SZYMANSKI. Pp. xiv + 380. New York: Plenum Press. 1970. Price £8·80; DM 75.00.

A review of the previous edition of this book (*Analyst*, 1964, **89**, 753) suggested its entire suitability for the student or beginner in a commercial laboratory. Its success in these spheres has apparently warranted this second edition, embodying some degree of re-writing under joint authorship. Apart from the re-orientation of chapters, the changes are in detail only, involving minor corrections, expansion of tables and some general improvements. It is claimed that the text has been updated to match the current state of the art and while this is very largely true one is compelled to reflect how little the art has changed and how little one wants to amend the observations made in the previous review.

The price has approximately doubled, the quality of both the binding and the paper is comparatively inferior, but the sketches and typescript remain both clear and well annotated. The volume is again a valuable standby for the beginner but I would not incur the expense of purchase solely to change editions.

W. L. SHEPPARD

GILLAM AND STERN'S INTRODUCTION TO ELECTRONIC ABSORPTION SPECTROSCOPY IN ORGANIC CHEMISTRY. Third Edition. By E. S. STERN and C. J. TIMMONS. Pp. vi + 277. London: Edward Arnold Publishers. 1970. Price £5·50.

The glamour and growth of infrared, the resonance techniques, atomic-absorption and photoelectron spectroscopy have attracted the limelight recently, and ultraviolet has become the Cinderella of spectroscopy. With so many new techniques to find jobs for, it is easy to overlook the fact that many modern problems in analytical chemistry are still best tackled with one or other of the older methods. The ultraviolet and visible spectroscopic techniques are inexpensive and powerful; they will always have their part to play in analytical chemistry, and for some time now an authoritative text, fresh and up to date in outlook, has been required to help keep this in mind. This new edition of "Gillam and Stern" serves this purpose excellently.

Although the declared object of this book is "to introduce ultraviolet and visible spectrophotometric techniques to graduates entering on research in organic chemistry," it will be a most useful acquisition for more senior chemists as well. The previous edition of "Gillam and Stern" appeared in 1957; as in all branches of spectroscopy, there has been great progress since then and—the only quibble that can be raised—this revision was overdue.

It is important to state clearly that the text has been re-written completely; this book now bears little resemblance to the late Dr. Gillam's original notes. It is indeed a nice gesture that the book has been re-written in its present form by Stern and Timmons in order to keep the name of Gillam fresh in the memory.

After a brief introduction that deals with selection rules, the laws of light absorption, definitions, etc., chapters deal with: Determination and Presentation of Absorption Spectra; General Principles and Simple Examples of Assignments of Bands; Selective Absorption of Molecules containing one Functional Group; Conjugated Chromophores; Benzenoid Absorption; Aromatic Heterocyclic Compounds; Application of Absorption Spectrophotometry to Qualitative Analysis; Spectrophotometric Determination of Organic Compounds; and Ultraviolet Absorption Spectroscopy applied to Problems of Molecular Structure. Appendices deal with Bibliography of Electronic Absorption Spectroscopy; Solvents; Temperature Effects and Tables of Logarithms and Reciprocals. There are good indices. The bibliography is up to date but (a wise decision, this) no attempt has been made to treat the literature exhaustively.

The authors and publishers of this book are to be congratulated on the very high quality of production they have attained. The tables of data, diagrams, spectra and formulae are all very clear, and I detected only one misprint—the excusable "hyspochromic" (p. 29). By today's standards, the cost of this book represents excellent value. For all those who have found the earlier editions of "Gillam and Stern" to be useful, it is now time to part with some cash.

D. M. W. ANDERSON

ATOMIC ABSORPTION SPECTROCHEMICAL ANALYSIS. By B. V. L'VOV. Translated by J. H. DIXON. Pp. xii + 324. London: Adam Hilger Ltd. 1970. Price £12·30.

Those of us actively engaged in this expanding branch of analysis recognise the value of Professor L'vov's contributions, in particular his exploitation of the furnace that is so frequently associated with his name.

In the early 1960s, L'vov proposed the use of a pulsed method of atomising samples in a graphite furnace in which the sample, after application to the tip of a carbon electrode, was introduced into a heated furnace through a transverse aperture situated at the centre of the tube. To accelerate atomisation, the electrode head was pre-heated by a powerful d.c. arc struck between this electrode (introduced into the furnace) and a second electrode positioned below the tube. This method of pre-heating electrodes was later replaced by a more effective and, technically, simpler resistance method of heating.

Hence it can be appreciated why this pioneering work of L'vov is so often regarded as having laid the foundations of all that has been profitably revealed by the use of a graphite cuvette as an ancillary to the vital process of atomisation; a concept that has been developed to a stage where it now constitutes a "powerful weapon in the armoury of the analytical chemist."

The book is largely devoted to theoretical and experimental research carried out by the author since about 1956 in the Spectrographic Laboratory at the Russian State Institute of Applied Chemistry. Understandably, therefore, a book written by L'vov himself, an undisputed expert in atomic-absorption spectrophotometry, cannot fail to appeal to the experimentalist in this field.

In addition to making available a comprehensive description and discussion of his personal observations and conclusions, the book presents a detailed and masterly treatise of the physical principles on which modern methods of atomic-absorption spectrophotometry are based.

It must not be concluded, however, that the book is simply a translation of the original Russian publication, or solely an exposition of L'vov's work. In co-operation with the translator, the author has wisely and sensibly recognised the value of bringing the book up to date; hence, many of the sections in the original Russian version have been completely revised. This observation is not based on the reviewer's intimate knowledge of the original publication, but can be deduced from the preface to this current edition, in which the author makes it apparent that extensive modifications were made to the original work before its publication in English. Further evidence of this is shown by the fact that the English text, compared with that of the original Russian, has been increased by almost 50 per cent. Thus, the book can be regarded as a translation of the manuscript for the second edition of the 1965 Russian publication.

Of the book's six main chapters, the number of pages (59) devoted to *The Graphite Cuvette* is about equal to those on *Atomic Absorption Spectrophotometers* and *The Flame*; other chapters, each dealt with in a smaller number of pages, are: *Theory of Atomic Absorption Measurement, Atomization of Samples—General Principles,* and *Special Fields of Application for the Atomic Absorption Method of Measurement.*

To avoid the use of a common cliché in summarising the unquestionable potential value of this book, with full marks to its translator, let me simply add that £12·30 is a lot of money.

W. T. ELWELL

SURFACTANT BIODEGRADATION. By R. D. SWISHER. Pp. xxiv + 496. New York: Marcel Dekker Inc. 1970. Price £15·95; $33.50.

This is a book which must be recommended to experts in the surfactant and biodegradation fields, to those who are newly entering the field and to all who are interested in the subject. There is little doubt that this work must for many years prove the "bible" on this subject and both the author and the organisation he is associated with are to be congratulated; the quality of the text and the degree of coverage on the subject are first-class. It will undoubtedly satisfy the needs of all who refer to it.

The lay-out of the subject matter is well conceived and the information included is commendable. It provides an excellent reference text and an excellent instructional book, but so concise and concentrated is the information therein, that the text can only be absorbed in small doses. The quality of the subject matter will, however, amply repay the reader's perseverance. Its primary use may, therefore, prove to be as a reference book.

In the chapter dealing with analytical methods the author states that "each method has its own advantages and none is free from limitations." This comment highlights the weakness in the biodegradation field, namely, the lack of adequate analytical procedures suitable for all purposes. This aspect of biodegradation work is undoubtedly one of the most difficult fields in analytical chemistry for development of analytical procedures. Much work is still necessary, but the author has more than adequately covered the present state of knowledge in this field. This weakness is again apparent from the author's recommendation that as many techniques as possible should be studied before a final decision is taken on the biodegradability of a chemical.

It is very apparent from the innumerable tables provided in Chapter 8, where data collected are often contradictory, that the degree of degradation reported is very dependent upon the technique used and upon the analytical procedure used to assess biodegradation. These tables highlight the anomalies that require clarification. As yet one can only conjecture which of the variable data reported are the most reliable. This chapter emphasises the differences that result from interpretation of biological oxygen demand and methylene blue methods. The text points out that the latter method assesses only the original surfactant and none of its possible intermediate biodegradation products. This could explain the difference between opinions based on interpretation of biological oxygen demand and methylene blue results.

In discussing the use of the desulphonation reaction to study the nature of the biodegradation reaction, the author has failed to stress that any fatty acids, fatty alcohols or fatty esters that may contaminate the "surfactant" extract will be converted into unsaturated hydrocarbons, and this holds also for any sulphocarboxylic acid degradation products. Care is therefore necessary in the interpretation of the desulphonation results. Again, when discussing the German Emschergenossenschaft the author adds "The bacteria can be propagated indefinitely by further transfers in the same manner." Elsewhere in the text he warns that such transfer produces a specialised bacterial system. The results under these conditions may thus bear little relation to behaviour in natural sewage systems.

The chapter dealing with chemical structure and primary biodegradation is very instructive and obviously great care has been exercised in collating knowledge on this aspect. In short, readers will find this book useful, instructive and enjoyable. The price is high but reasonable for a book of this nature.

G. F. LONGMAN

A Field Method for the Determination of Zinc Oxide Fume in Air

A method is described for the determination of zinc oxide fume in industrial atmospheres at concentrations up to 20 mg m^{-3} of zinc oxide. The fume is collected on a filter and dissolved in acid, and the zinc is determined spectrophotometrically or visually with 4-(2′-thiazolylazo)resorcinol reagent. The apparatus used is simple and the time required for a determination is about 20 minutes. A dynamic method for the generation of atmospheres of zinc oxide is also described.

B. S. MARSHALL, I. TELFORD and R. WOOD

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

Analyst, 1971, **96**, 569–578.

Polarographic Determination of Uranium in Monazite Sands

A practical method is described for the extraction of uranium from monazite sands and its subsequent polarographic determination.

The sample is decomposed by fusion with potassium hydrogen difluoride followed by fusion with potassium pyrosulphate. Uranium is extracted from nitric acid solution with tributyl phosphate in 2,2,4-trimethylpentane, with aluminium nitrate as a salting-out agent, and back-extracted from the organic phase with water.

The final polarographic determination is carried out in 2 M acetic acid - 2 M ammonium acetate - 0·1 M ascorbic acid solution as supporting electrolyte. Neither a maximum suppressor nor removal of oxygen is needed.

The interference by lead and some factors influencing the extraction of uranium are studied.

The results are reproducible and agree with those obtained by other, more laborious, techniques. The proposed procedure is suitable for the determination of uranium in monazites and monazite sand concentrates containing not less than 0·005 per cent. of uranium oxide, and is superior in speed, reliability and convenience to other methods previously reported.

R. W. MARTRES and J. J. BURASTERO

Administración Nacional de Combustibles, Alcohol y Portland, Centro de Investigaciones Tecnológicas, Pando, Uruguay.

Analyst, 1971, **96**, 579–583.

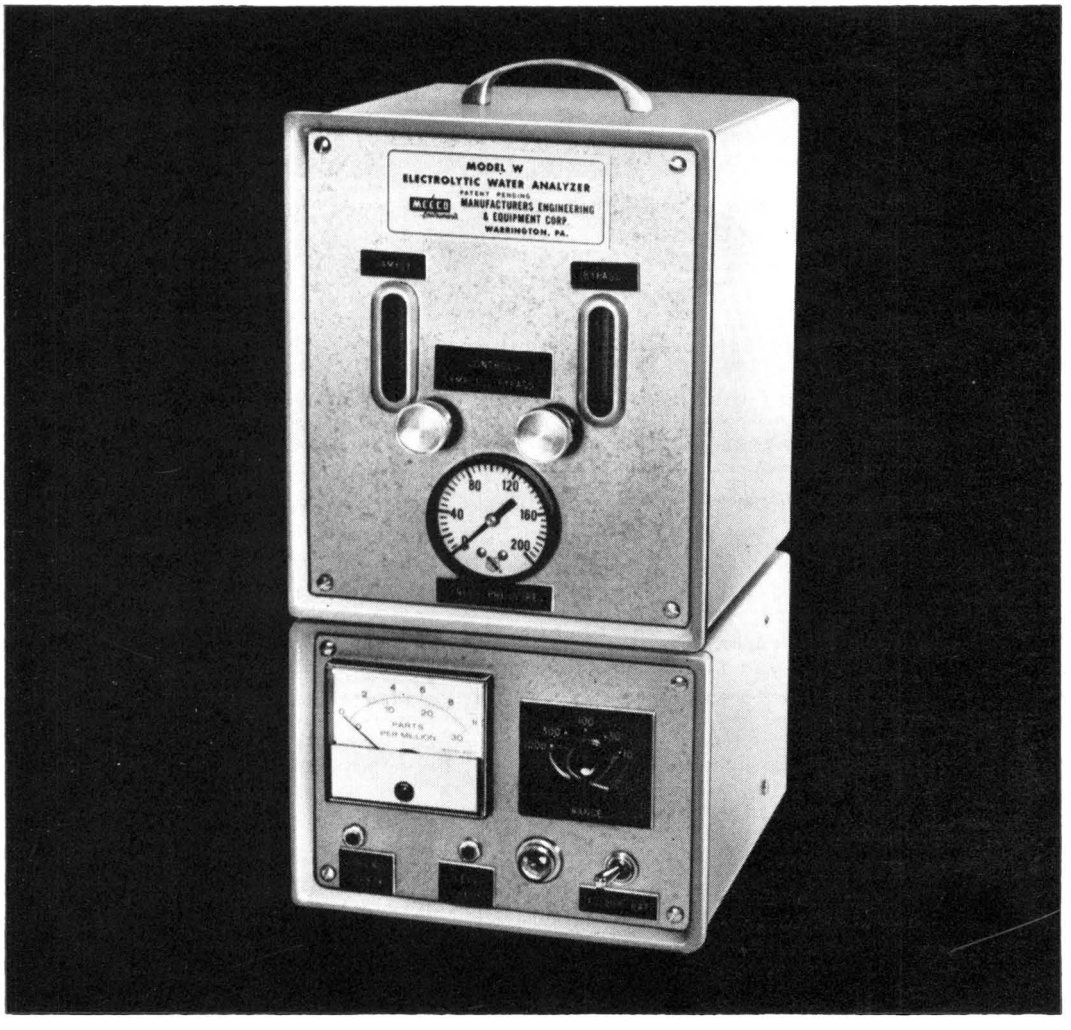
A Modified Spectrophotometric Method for the Determination of Ammonia (and Amino-acids) in Natural Waters, with Particular Reference to Sea Water

Strickland and Parsons have described a method for determining ammonia (and amino-acids) in sea water. This method, in which ammonia is first oxidised to nitrite with sodium hypochlorite, was found to be very time consuming and often imprecise. The results of a critical examination of the underlying chemistry have led to a modified procedure in which the time required for analysis has been reduced from 3·5 hours to 17 minutes. The modified procedure gave a coefficient of variation of 1·6 per cent. from the analysis of thirteen replicate aliquots of a sample of sea water containing approximately 20 $\mu g\ l^{-1}$ of ammonium-nitrogen, and hence is suitable for determining ammonia concentrations in the order of 0 to 200 $\mu g\ l^{-1}$. The response for 1 $\mu g\ l^{-1}$ of ammonium-nitrogen, in either sea water or de-ionised water, was equivalent to an optical density change of $1{\cdot}6 \times 10^{-3}$ per cm of solution. The procedure is also suitable for the quantitative determination of ammonia (and amino-acids) in other natural waters.

VICTOR W. TRUESDALE

East African Marine Fisheries Research Organization, P.O. Box 668, Zanzibar, East Africa.

Analyst, 1971, **96**, 584–590.



High accuracy moisture analyser for gases

The Meeco Electrolytic Moisture Analyser gives accurate and continuous measurement of moisture in gases over the range 0 to 1,000 v.p.m.

By utilising rhodium filaments in the measuring cell the catalytic recombination error normally obtained when analysing hydrogen is eliminated.

When used with the BOC low volume regulator the Meeco can be operated at 10 bar pressure, so accurate measurements in the 1 v.p.m. range are possible.

The instrument is suitable for use with all permanent gases. It's ideal as a process control instrument and being compact and portable can be operated by mains or battery giving exceptional flexibility in use.

For more information on the model illustrated and other versions write or phone BOC Analytical Services, Deer Park Road, London, S.W.19. Tel: 01-542 6677.

BOC

Photometric Determination of Small Amounts of Oxygen in Water with 3,3′-Dimethylnaphthidine

The oxidation products of manganese obtained in Winkler's classical method for the determination of oxygen can be determined by a photometric method based on their reaction with 3,3′-dimethylnaphthidine in an acidic medium. This reagent is used in preference to *o*-tolidine because of its higher molecular weight, which results in greater sensitivity, and in the intense red - violet colour of the oxidised form of 3,3′-dimethylnaphthidine.

HUBERT FADRUS and JOSEF MALÝ

Central Sewage Treatment Plant, Brno-Modřice, Czechoslovakia.

Analyst, 1971, **96**, 591–597.

Rapid Determination of Solvent Occluded in Some Pharmaceutical Chemicals

An infrared spectrophotometric method has been developed for the determination of occluded solvent in orciprenaline sulphate and warfarin sodium. In lesser detail ampicillin sodium, colchicine, the calcium and sodium salts of novobiocin and streptomycin sulphate have also been examined.

THOMAS R. LOWTHER and W. D. WILLIAMS

Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow.

Analyst, **1971**, **96**, 598–600.

The Gas-chromatographic Determination of Arsanilic Acid and Carbarsone in Animal Feeding Stuffs

Methods are described for the determination of arsanilic acid and carbarsone in animal feeding stuffs. These additives are extracted from the feed with an aqueous solvent. Carbarsone is converted by hydrolysis with sodium hydroxide into arsanilic acid, which is then reduced with Raney alloy to aniline. The aniline, separated from the reaction mixture by steam distillation and solvent extraction, is determined by gas chromatography with flame-ionisation detection.

R. E. WESTON, B. B. WHEALS and M. J. KENSETT

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

Analyst, 1971, **96**, 601–603.

County Councils Association
Association of Municipal Corporations
Urban District Councils Association
Association of Public Analysts

Joint Survey of Pesticide Residues in Foodstuffs sold in England and Wales

1st August, 1967—31st July, 1968 (second year)

This is a Report of Results obtained during the second year of the National Pesticide Residues Survey. The programme for the year was planned on the basis of results and experience gained during 1966–67, the range of foods examined being adapted accordingly. The slight increase in the number of foodstuffs found to contain residues was not considered significant. The result of the two years' tests are combined and compared, and details are included of findings for mercury residues in a large number of samples analysed for the survey.

Published by the Association of Public Analysts
325 Kennington Road, London, S.E.11 **Price £1·10 inc. postage**

Volume 96 No. 1145, Pages 537-608 August, 1971

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

CONTENTS

Printed for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England
Communications to be addressed to the Editor, J. B. Attrill, 9/10 Savile Row, London, W1X 1AF
Enquiries about advertisements should be addressed to J. Arthur Cook, 9 Lloyd Square, London WC1 9BA

Entered as Second Class at New York, U.S.A. Post Office