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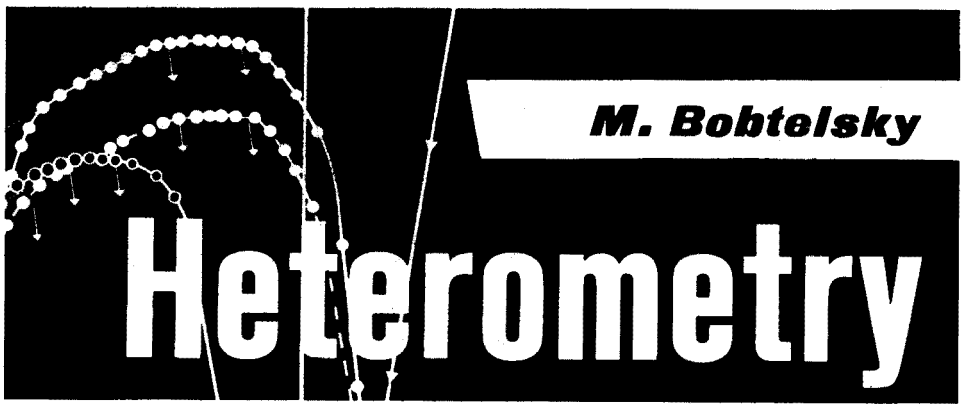

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Heterometry, a method of analysis devoloped by the author, deals with the quantitative photometric study of chemical reactions in which suspensions are formed. Optical density curves are measured in order to determine the location of the critical points.
This method has attracted the attention of chemists all over the world. Although the development of heterometry covers a period of less than ten years, a great deal of progress has been made and the author has attempted to summarize what has been achieved in this relatively short time.
Much of the book has been devoted to the use of heterometry in the rapid analytical determination of traces of metals, other ions or compounds, in the presence of a large excess of other substances, without any previous separation. The book contains a wealth of original material, generously supplemented with tables and figures, which demonstrate how hitherto unsolved problems can easily be solved by heterometry. Very often a few tenths of a milligram of material is sufficient for a whole investigation. The instrumentation as well as the various aspects of heterometry are thoroughly reviewed so that on the basis of information given chemists will be able to tackle their own problems by heterometry. This method will be of especially great value to all research workers as well as to industrial chemists working in the fields of analytical and microanalytical chemistry, complex chemistry, study of composition and structure of intermediates, lakes, complicated organic nitrogen compounds etc.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

V[1]. A SIMPLE METHOD OF CALCULATING ACID – BASE TITRATION ERRORS

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(Received May 25th, 1959)

The calculation of titrimetric errors receives relatively infrequent attention in standard texts[2], an empirical treatment more often being given[3], while the accounts in the literature tend to be impracticably, sometimes unrealistically, complicated[4]. If sets of theoretical titration curves are prepared, errors can readily be assessed by inspection[5], but where such aids are not to hand, the errors can be calculated directly from the colour transition intervals of the indicators and the ionisation constants of the electrolytes concerned.

The titration error is made up of three parts:

(a) the *chemical error* due to the difference between the end-point (at which the indicator changes colour) and the equivalence point (the theoretical neutral point);

(b) the *visual discrimination error* which is a measure of the scatter caused by the limited ability of the eye exactly to remember or compare colours, and corresponds to an interval of about 0.1 pH unit; and

(c) the *indicator error* due to consumption of the titrant by the indicator itself.

Factors (b) and (c) are normally small compared with (a), which is the factor of principal interest in this paper.

Equivalence and end-point conditions

Before the assessment of errors, or indeed selection of the appropriate indicator, is possible, the hydrogen ion concentration or pH of the titration solution at these points must be known. The hydrogen ion concentration ζ (and $p\zeta$ the pH) at the equivalence point is the calculated value for a solution of the pure salt in pure solvent, and in the case of strong acid – strong base titrations is equal to $K_w^{\frac{1}{2}}$. In other cases, ζ is the hydrogen ion concentration of the hydrolysed salt solution of appropriate concentration, and is calculated from the ionisation constant of the weak electrolyte in the usual way[5]. The end-point is the point at which the indicator changes colour, or, more strictly, the hydrogen ion concentration χ at which the indicator reaches the chosen colour. The value of χ may be determined from the pH of the comparison buffer solution, or from the known colour change interval of the indicator. When the chosen colour is the first perceptible colour change of the indicator, χ is given by the extreme value of the colour change interval. With an acid

titrant, $p\chi$ is the upper extreme, and with an alkaline titrant the lower extreme of the indicator pH interval. For example, with methyl red the pH interval is 4.4 to 6.0; with an acid titrant $p\chi$ will be 6.0, with an alkaline titrant $p\chi$ will be 4.4. Where the actual interval is not known, but the indicator constant pK_{ind} is available, the end-points can be taken to be at $p\chi = pK_{ind} \pm 1$.

The sign, or sense, of the error

Even in the most rigorous and comprehensive treatment[4] it is not possible to define the sign, positive or negative, of the error mathematically, since it will depend on whether the acid or the base is the titrant. Definition of the sign by inspection, however, permits a simple treatment. The error itself is defined as,

$$\text{Relative error} = k\,\frac{\text{equivalence point volume of titrant} - \text{end-point volume of titrant}}{\text{equivalence point volume of titrant}} \quad \ldots\ldots\ (1)$$

Conditions	*(k = sign of error)*	
	Acid titrant	*Base titrant*
$p\chi > p\zeta$	negative	positive
$p\chi < p\zeta$	positive	negative

The sign of the values given by the expressions below is a useful check on the values of χ and ζ used, since if the sign is negative before the application of k, this implies that impossible conditions are being applied to the titration. It will be observed in the expressions below that those derived for $p\chi > p\zeta$ contain the simple substitution of K_w/χ for χ in those derived for $p\chi < p\zeta$. Furthermore, unless the neutral salt concentration is excessive[4], activity coefficients may be neglected with very little error. The treatment is developed for monobasic acids and monoacid bases, and may be extended to polybasic or polyacidic compounds by substituting normalities for molarities.

THE CHEMICAL ERROR

1. *Strong acid – strong base titrations*

I. *$p\chi$ less than $p\zeta$.* If V ml of base of concentration M_B be titrated with an acid of concentration M_A, and the contribution of ions from the solvent is ignored (*vide infra*), then,

(i) the equivalence point volume of titrant

$$= V\,\frac{M_B}{M_A}\ \text{ml}$$

(ii) the total volume of the titration solution at this point will be

$$V + V\,\frac{M_B}{M_A} = V\left(\frac{M_A + M_B}{M_A}\right)\text{ml}$$

(iii) the numerator of expression (1) will be given by, as a first approximation ignoring solvent ionisation, the volume of titrant required to produce a hydrogen ion concentration of χ in the equivalence point volume of solution, *viz.*,

$$\frac{\chi\,V(M_A + M_B)}{{M_A}^2}$$

(iv) the relative error is then, from (1),

$$\frac{\chi\, V\,(M_A + M_B)}{M_A{}^2} \times \frac{1}{V\dfrac{M_B}{M_A}}$$

(v) the percentage error $E\%$ is then 100 times this,

$$E\% = \frac{100\,(M_A + M_B)\,\chi}{M_A M_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

If the two solutions are equivalent, and $M_A = M_B = M$,

$$E\% = \frac{200\,\chi}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2a)$$

If the base is the titrant, χ will, for the same indicator, have a different value from that used for the acid titrant, but the resultant expression for $E\%$ is identical with (2), and is derived by calculating the amount of acid unneutralised at the end-point in step (iii).

II. pχ *greater than* pζ. The expression is derived through the same argument as before. Working in terms of hydroxyl ion, the steps are parallel to those above. Working in terms of hydrogen ion, the amount of acid of equivalent concentration required to neutralise the amount of hydroxyl ion left at the end-point may be calculated. By either method, the following expression results

$$E\% = \frac{100\,(M_A + M_B)\,K_w}{M_A M_B \quad \chi} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

These expressions are adequate when pχ is less than 6 or greater than 8, but as pχ approaches pζ, or $\frac{1}{2}$pK_w, the contribution of ions from the solvent becomes more significant.

Ionisation of the solvent. When pχ is close to $\frac{1}{2}$pK_w, the amount of hydrogen or hydroxyl ions contributed by the solvent has to be subtracted from the amount to be supplied by the titrant in step (iii) above. When pχ < pζ the solvent contribution of hydrogen ions, from the ion product of water, will be equal to the total hydroxyl ion concentration at the end-point, *i.e.*, K_w/χ, and expression (2) becomes in the exact form

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{K_w}{\chi}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

By a similar argument, when pχ > pζ, expression (3) becomes in the exact form

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \chi\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

2. *Weak acid – strong base titrations*

In the presence of *excess of strong base* pχ will be greater than pζ and expression (3) applies.

In the presence of *excess of weak acid* pχ will be less than pζ and the solution will contain an acid buffer. Ignoring hydrolysis, the hydrogen ion concentration of the solution is given by the buffer equation[5],

$$[H^+] = \frac{c_a}{c_s} K_a \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where c_a and c_s are the weak acid and salt concentrations, and K_a is the ionisation constant of the weak acid. If V ml of strong base of concentration M_B is titrated with a weak acid of concentration M_A, ignoring hydrolysis and ionisation of solvent (*vide infra*) then,

(i) the volume of acid titrant required to reach the equivalence point

$$= V \frac{M_B}{M_A} \text{ ml}$$

(ii) the total volume of the titration solution at this point will be

$$V + V \frac{M_B}{M_A} = V \left(\frac{M_A + M_B}{M_A} \right) \text{ ml}$$

(iii) the salt concentration will be

$$c_s = \frac{M_B V}{V \left(\frac{M_A + M_B}{M_A} \right)} = \frac{M_A M_B}{(M_A + M_B)}$$

(iv) from (6) the concentration of free weak acid in conjunction with this salt concentration to give a solution of pH = pχ at the end-point will be

$$c_a = \frac{M_A M_B}{M_A + M_B} \cdot \frac{\chi}{K_a}$$

(v) the volume of acid titrant of concentration M_A required to give this concentration in the volume of solution defined in step (ii) will be

$$\text{volume} = \frac{M_A M_B}{M_A + M_B} \cdot \frac{\chi}{K_a} \cdot \frac{V(M_A + M_B)}{M_A^2} = \frac{M_B V \chi}{M_A K_a} \text{ ml}$$

This is then the numerator in (1).

(vi) The relative error from (1) is then

$$\frac{M_B V \chi}{M_A K_a} \frac{M_A}{M_B V} = \frac{\chi}{K_a}$$

(vii) the percentage error $E\%$ is then 100 times this,

$$E\% = \frac{100 \chi}{K_a} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

This very simple expression is independent of titrant and titrand concentration, and is applicable to acids with ionisation constants as low as 10^{-7} at concentrations around decimolar without loss of accuracy. With the strong base as titrant and the appropriate value of χ the same expression results, but the sign, k, will now be negative.

3. *Strong acid – weak base titrations*

As before, in the presence of *excess of strong acid*, expression (2) is valid. In the presence of *excess of weak base*, an argument similar to that above yields the expression for the percentage error $E\%$

$$E\% = \frac{100 K_w}{\chi K_b} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

This expression is also concentration independent, and is applicable to bases of ionisation constant as low as 10^{-7}.

Beyond the limits stated, it will be found that expressions (7) and (8) predict errors greater than those found in practice. Expressions (2) and (3) will similarly be found defective when applied to weak acid or base titrations. In such cases, the hydrolysis of the salt has to be taken into account. In a rigorous treatment, allowance must also be made for ionisation of the solvent, although in practice this factor makes a very small contribution, as can be shown by solution of expressions (27) to (30) for numerical examples, and can normally be neglected.

Hydrolysis of salts. It is necessary to distinguish between excess of strong electrolyte and excess of weak electrolyte. In both circumstances hydrolysis produces hydrogen or hydroxyl ions, depending on the nature of the salt, which contribute to the numerator of expression (1) and so reduce the amount of such ions which has to be furnished or neutralised by the titrant to reach the end point. At the same time, the value of c_s is reduced by the amount of salt lost by hydrolysis; this is a secondary effect which will be considered later. Two cases of each circumstance require consideration, and the sign of the error, k, being dependent on the nature of the titrant, is determined by inspection as described above.

Excess of strong acid in the titration of a weak base

The hydrogen ion concentration of the solution of the hydrolysed salt in the presence of an excess of strong acid of concentration calculated to be c_A is given by[5]

$$[H^+] = {}^1/_2 \left\{ \left(c_A{}^2 + \frac{4K_w c_s}{K_b} \right)^{\frac{1}{2}} + c_A \right\} \quad \ldots\ldots\ldots\ldots \quad (9)$$

which must derive from

$$H^+]^2 - c_A[H^+] - \frac{K_w c_s}{K_b} = 0 \quad \ldots\ldots\ldots\ldots \quad (10)$$

whence,

$$c_A = \left([H^+] - \frac{K_w c_s}{[H^+] K_b} \right) \quad \ldots\ldots\ldots\ldots \quad (11)$$

At the end-point, $[H^+] = \chi$, and c_A corresponds to the excess of acid required to produce the chosen end-point colour, and by arguments similar to those given in the derivation of (2) the percentage error $E\%$ will be,

$$E\% = \frac{100(M_A + M_B)\, c_A}{M_A M_B} \quad \ldots\ldots\ldots\ldots \quad (12)$$

Substitution of (11) in (12) then gives the error corrected for hydrolysis,

$$E\% = \frac{100(M_A + M_B)}{M_A M_B} \left(\chi - \frac{K_w c_s}{\chi K_b} \right) \quad \ldots\ldots\ldots\ldots \quad (13)$$

If required, the value of c_s (from step (iii), equation 7) can be inserted in this expression, giving

$$E\% = 100 \left\{ \frac{(M_A + M_B)\, \chi}{M_A M_B} - \frac{K_w}{\chi K_b} \right\} \quad \ldots\ldots\ldots\ldots \quad (13a)$$

Excess of strong base in the titration of a weak acid

If the excess of strong base is calculated to be c_B, the hydroxyl concentration is given by[5]

$$[OH^-] = {}^1/_2 \left\{ \left(c_B{}^2 + \frac{4K_w c_s}{K_a} \right)^{\frac{1}{2}} + c_B \right\} \quad \ldots\ldots\ldots\ldots (14)$$

whence, as before,

$$c_B = \frac{K_w}{[H^+]} - \frac{[H^+]c_s}{K_a} \quad \ldots\ldots\ldots\ldots (15)$$

and, as above,

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B} \left(\frac{K_w}{\chi} - \frac{\chi\, c_s}{K_a} \right) \quad \ldots\ldots\ldots\ldots (16)$$

Excess of weak acid in the titration of a strong base

The hydrogen ion concentration for a calculated excess of acid c_a is given by[5]

$$c_s[H^+]^2 - (K_w + c_a K_a)[H^+] - K_w K_a = 0 \quad \ldots\ldots\ldots\ldots (17)$$

whence

$$c_a = \frac{c_s[H^+]^2 - K_w([H^+] + K_a)}{K_a[H^+]} \quad \ldots\ldots\ldots\ldots (18)$$

At the end-point, $[H^+] = \chi$, and c_a is the concentration required in step (iv) in the derivation of (7), and by a similar argument, the percentage error $E\%$ will be

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B} \left(\frac{c_s \chi^2 - K_w(\chi + K_a)}{K_a\, \chi} \right) \quad \ldots\ldots\ldots\ldots (19)$$

Excess of weak base in the titration of a strong acid

The hydrogen ion concentration for a calculated excess of weak base c_b is given by[5]

$$K_b[H^+]^2 + (K_w + K_b c_b)[H^+] - c_s K_w = 0 \quad \ldots\ldots\ldots\ldots (20)$$

whence

$$c_b = \frac{K_w}{K_b} \left(\frac{c_s}{[H^+]} - 1 \right) - [H^+] \quad \ldots\ldots\ldots\ldots (21)$$

This gives a percentage error $E\%$ of

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B} \left\{ \frac{K_w}{K_b} \left(\frac{c_s}{\chi} - 1 \right) - \chi \right\} \quad \ldots\ldots\ldots\ldots (22)$$

Further corrections for decrease of salt concentration by hydrolysis and for ionisation of solvent

The expressions derived above suffice for most practical purposes, but rigorous treatment calls for two further adjustments. *Hydrolysis* of the salt causes a diminution in c_s. This is already included in equations (17) and (20), and therefore in (19) and (22), but where the strong acid or base is in excess, and hydrolysis is considerable,

further adjustment of (13) and (16) is required. In the case of the *strong acid*, the cation of the weak base is hydrolysed,

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

and the true concentration of B^+, assumed to be equal to c_s in the derivation of (9) is

$$[B^+] = c_s - [BOH]$$

From the ionisation constant of the base BOH and the ion product of water,

$$[B^+] = \frac{c_s[H^+]K_b}{[H^+]K_b + K_w} \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

Substitution of (23) for c_s in (13) then gives the percentage error corrected for loss of cation by hydrolysis

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{K_w c_s}{\chi K_b + K_w}\right) \quad \ldots\ldots\ldots \quad (24)$$

In the case of the *strong base*, by a similar argument, the true value of $[A^-]$ is

$$[A^-] = \frac{c_s K_a}{K_a + [H^+]} \quad \ldots\ldots\ldots\ldots\ldots \quad (25)$$

and substitution of (25) for c_s in (16) gives the percentage error corrected for loss of anion by hydrolysis

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \frac{\chi\, c_s}{K_a + \chi}\right) \quad \ldots\ldots\ldots \quad (26)$$

Further refinement may be achieved by correcting for *ionisation of the solvent* in the same way as in (4) and (5). This finally yields expressions which are fully rigorous and exact under all conditions. In the four cases cited, the expressions including ionisation of the solvent become:

Excess of strong acid in the titration of a weak base:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{c_s K_w}{\chi K_b + K_w} - \frac{K_w}{\chi}\right) \quad \ldots\ldots\ldots \quad (27)$$

Excess of strong base in the titration of a weak acid:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \frac{\chi\, c_s}{K_a + \chi} - \chi\right) \quad \ldots\ldots\ldots \quad (28)$$

Excess of weak base in the titration of a strong acid:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{c_s\chi^2 - K_w(\chi + K_a)}{K_a\chi} - \chi\right) \quad \ldots\ldots\ldots \quad (29)$$

Excess of weak acid in the titration of a strong base:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left\{\frac{K_w}{K_b}\left(\frac{c_s}{\chi} - 1\right) - \chi - \frac{K_w}{\chi}\right\} \quad \ldots\ldots\ldots \quad (30)$$

These further corrections make little difference to the value of the error, as solution for numerical examples would show, and are usually of less significance than the visual discrimination error.

THE VISUAL (OR INSTRUMENTAL) DISCRIMINATION ERROR

If the uncertainty in remembering or comparing colours corresponds to a pH interval of $\pm \Delta$ pH unit, then the end-point observed will fall within the pH range p$\chi \pm \Delta$, so that the hydrogen ion concentration at the end-point will be $\chi \cdot 10^{\mp\Delta}$. Consequently, in the expressions derived above, the percentage error, taking scatter into account will be

$$E \cdot 10^{\mp\Delta} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (31)$$

With visual observation of the colour change, Δ is usually about 0.1 pH unit, or somewhat less. Consequently the refinements in the calculation of E in equations (23) to (30) are usually of little significance. However, when the end-point is detected photoelectrically or electrometrically, the instrumental discrimination error may be much less, and Δ may be as little as 0.01 pH unit, in which case the refinements of equations (23) to (30) may become significant.

THE INDICATOR ERROR

The amount of titrant consumed by the indicator is normally very small unless the titrant concentration is very low. It must be remembered that only a fraction, about one tenth, of the indicator is titrated to give a first perceptible colour change. This may, however, be misleading, since it will depend on the form in which the indicator is added to the titration solution. Thus, if the alkaline form of the indicator is added to the titrand, and the titrant is acid, approximately one tenth of the indicator is titrated, and the error is positive, but if the acid form of the indicator were used in this titration it would all react with the base, and only one tenth would be restored to the acid form at the end-point, so that the error would be negative and correspond to about nine tenths of the amount of the indicator added. If the indicator solution were adjusted to the first perceptible colour change in the correct direction, or otherwise conditioned to the chosen end-point colour before addition to the titration solution, the indicator error would theoretically be nil, and in practice negligible.

If the indicator is used in the *same form as the titrand*, then the amount of the titrant required to react with the indicator will be the volume of the indicator solution used, multiplied by its concentration, divided by the concentration of the titrant, and the whole multiplied by the fraction of the indicator changed, normally about one tenth:

$$\text{Titrant consumption} = \frac{v_{\text{ind}}\, c_{\text{ind}}}{M_{\text{titrant}}} \cdot \frac{1}{10}.$$

If the initial volume of the titrand is V ml, then the percentage error $E_I\%$ will be:

$$E_I\% = \frac{v_{\text{ind}}\, c_{\text{ind}}\, 100}{M_{\text{titrant}}\, V \dfrac{M_{\text{titrand}}}{M_{\text{titrant}}}} \cdot \frac{1}{10} = \frac{10\, v_{\text{ind}}\, c_{\text{ind}}}{V\, M_{\text{titrand}}} \quad \ldots \ldots \ldots \quad (32)$$

Most indicators are used in solutions of concentrations between 1.5 and $2.5 \cdot 10^{-3}\, M$, and the amount required in a titration is normally specified as n drops per 10 ml of titrand. If c_{ind} is taken as $2 \cdot 10^{-3}$ and the drop size as 0.05 ml, then

$$E_I\% = \frac{n \cdot 10^{-4}}{M_{\text{titrand}}} \quad \ldots \ldots \ldots \ldots \ldots \quad (33)$$

If the indicator is used in the *same form as the titrant*, then the percentage error becomes negative,

$$E_I\% = -\frac{9\,n \cdot 10^{-4}}{M_{\text{titrand}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (34)$$

The total titration error is therefore,

$$\text{Total \% error} = E \cdot 10^{\mp\Delta} + E_I \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (35)$$

ACKNOWLEDGEMENT

The author is indebted to Dr. W. B. JEPSON for checking the mathematics, and for many helpful suggestions.

SUMMARY

The error in acid–base titrations is analysed into a chemical error due to disparity between end- and equivalence points, a visual (or instrumental) discrimination error due to uncertainty in remembering or comparing colours, and an indicator error due to consumption of titrant by the indicator. Simple expressions are derived for the calculation of the chemical error, and these are progressively refined ultimately to expressions which are rigorous and exact under all conditions.

RÉSUMÉ

L'erreur dans les titrages acide–base est analysée en trois composantes: l'erreur chimique, due à la différence existant entre le point final et le point équivalent; l'erreur visuelle due à l'incertitude de l'observateur lorsque celui-ci compare les couleurs; l'erreur d'indicateur due à la consommation de liqueur titrée par l'indicateur.

ZUSAMMENFASSUNG

Der Fehler bei Säuren–Basen Titrationen wird auf 3 Ursachen zurückgeführt: Nichtgleichheit des Endpunktes und Aequivalenzpunktes; Unsicherheit bei der Festlegung der Indikator-Farbnuance am Umschlagspunkt; Vernachlässigung des Verbrauchs an Titrierlösung durch den Indikator.

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THE SEPARATION AND DETERMINATION OF ALUMINUM IN PLUTONIUM–ALUMINUM ALLOYS*

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INTRODUCTION

Two methods have been reported for the determination of aluminum in plutonium–aluminum alloys. In one, developed by SMITH[1], plutonium is separated from aluminum by precipitation as the iodate. A mercury cathode is used to remove other interfering ions and aluminum is determined colorimetrically using aluminon. Although this procedure had not been applied to alloys of as high an aluminum content as were of interest in the work here, it did not appear likely that the precision could be improved sufficiently to meet the necessary requirements.

A second method, developed by CLEVELAND AND NANCE[2], measured the absorbance of the aluminum complex formed with oxine (8-quinolinol) in chloroform after plutonium is removed by precipitation and extraction as plutonium cupferrate.

Since both of these methods require operations difficult to carry out routinely with high precision in the glove box facilities in which plutonium is ordinarily handled, a simpler procedure was sought. The present work shows that an ion-exchange technique can be used to obtain a quantitative separation of aluminum and plutonium.

Colorimetric oxine and aluminon methods, a gravimetric oxine method, and volumetric oxine and EDTA methods were investigated for determining the aluminum after its separation from plutonium. Both the gravimetric and volumetric methods gave more precise results than either of the colorimetric methods. The precision and accuracy of the gravimetric and the volumetric methods are comparable, but the volumetric methods are faster.

PRINCIPLES OF THE ION-EXCHANGE SEPARATION

In a hydrochloric acid solution the ion-exchange behavior of both aluminum and plutonium(IV) is ideal for their separation. Plutonium(IV) forms anionic chloride complexes which are retained by an anion resin[3]. The higher the hydrochloric acid concentration, the greater the adsorption[4]. Table I, adapted in part from a graph by WISH[5], indicates this behavior.

Data on the distribution coefficients for iron(III) in hydrochloric acid are included in Table I to show how its behavior parallels that of plutonium(IV)[6]. Any interference from iron in the aluminum determination is obviated since the iron is retained on the column.

Aluminum does not form an anionic chloride complex at any hydrochloric acid

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TABLE I

INFLUENCE OF HCl CONCENTRATION ON ADSORPTION OF Pu(IV) AND Fe(III)

Pu: Dowex-2, Fe: Dowex-1

HCl N	*Distribution coefficient*	
	Pu(IV)	*Fe(III)*
1	0.10	0.33
2	0.15	1.94
4	0.40	67
6	30	460
8	1400	—
9	—	5900
10	5000	—
12	8000	—

concentration[7]. Plutonium and aluminum can be separated, therefore, by passing a solution of the two elements in 8 *N* or higher hydrochloric acid through an anion-exchange resin column. The plutonium is retained on the resin and the aluminum passes through. The plutonium can be eluted from the column with hydrochloric acid, 1 *N* or less in concentration.

REAGENTS

Al standard: (5.0 mg per ml). (Dissolve 5.000 g pure Al metal in HCl, dilute to 1 l). Dimethylglyoxime (1%): (Dissolve 1 g dimethylglyoxime in 100 ml 1% NaOH solution). Dowex® 1 × 4: (50–100 mesh, chloride form). Acid buffer: (108.9 g CH_3COONa and 2.3 ml glacial CH_3COOH diluted to 1 l). Basic buffer (26.5 g NH_4Cl and 7.5 ml conc. NH_4OH diluted to 1 l). EDTA: (ethylenedinitrilo) tetraacetic acid, 0.1 *M*. (Dry the disodium salt overnight at 80°, dissolve 37.22 g and dilute to exactly 1 l. Store in Pyrex or polyethylene bottle). $(CH_3COO)_2Zn$ (0.02 *M*) (Add two to three drops 8 *N* HCl per liter to prevent hydrolysis. Standardize against 0.1 *M* EDTA, using xylenol orange as indicator). Xylenol Orange (0.2%): (Dissolve 0.2 g in 100 ml H_2O). All other reagents used are of reagent grade.

PREPARATION AND TREATMENT OF THE ION-EXCHANGE COLUMN

An ion-exchange column was prepared by fitting a glass tube, 22 mm inside diameter and 35 cm long, with a stopcock and flaring the top. A small pad of glass wool was placed in the bottom of the column and it was filled to a height of 25 cm with resin that had been pretreated by washing several times with 8 *N* HCl. After filling, another small pad of glass wool was placed on top of the column and it was washed with approximately 250 ml of 8 *N* HCl. A column prepared in this manner will hold about 4 g of plutonium before regeneration is necessary. It can be regenerated using 0.4 to 1 *N* HCl.

Gas bubbles form within the column if plutonium is allowed to remain on the resin overnight. To prevent this, plutonium is eluted from the column at the end of each working day. If gas does form, it can be removed by stirring the column with a long glass rod.

METHOD

The size of an alloy sample to be used depends on its aluminum content. In developing the procedure which follows, 5 mg aluminum spikes were used. This could be varied, but appropriate changes would have to be made in column size and reagent concentrations.

Two ml of 8 *N* HCl are pipetted into a 10-dram vial. The alloy sample is added and allowed to dissolve completely. Then two ml of conc. HNO_3 are added slowly to oxidize the plutonium. This reaction generates heat and gas, so care must be exercised to prevent the solution from overflowing the vial. Oxidation is rapid: complete oxidation is indicated by a cessation of bubbling and a clear solution, deep brown

when viewed under daylight-type fluorescent lights. After oxidation is complete, the solution is transferred to the resin column and eluted at 2 ml per min with 8 *N* HCl. Sixty ml of eluate are collected.

The aluminum is determined in the eluate by one of the following methods.

Gravimetric oxine method

The eluate is neutralized to the blue of the bromphenol blue end-point by the careful addition of conc. NH_4OH. Dilute HCl is added until the color of the solution just turns back to yellow. The aluminum is then precipitated with oxine using a procedure essentially the same as described in KOLTHOFF AND SANDELL[8]. It differs in that the oxine is prepared in 8 *N* HCl instead of CH_3COOH and the solution containing the precipitate is heated almost to boiling to coagulate the precipitate and then filtered instead of letting it stand for an hour before filtering.

Volumetric oxine method

The procedure used for the volumetric method is similar to the procedure described in KOLTHOFF AND SANDELL[9]. No indicator is used, however, for determining when sufficient $KBrO_3$ has been added to produce the necessary small excess of bromine. A number of indicators have been suggested[10], but none is recommended as being particularly effective. Experimenting with several confirmed this recommendation. Instead, in initial work a spot test was used. This involved withdrawing, periodically, a small quantity of sample solution on the end of a stirring rod and mixing it on a test plate with a solution containing KI and starch. When this KI-starch solution turned blue, an excess of bromine was present indicating that sufficient $KBrO_3$ had been added.

This same test can be used, if necessary, when production samples are being analyzed. But when the alloy composition is constant for a number of samples, all samples can be cut the same size, the volume of $KBrO_3$ necessary to provide a slight excess of bromine determined on the first sample and that volume used on all of the remaining samples.

Volumetric EDTA method

A back titration procedure is used. After adding 5.00 ml of 0.1 *M* EDTA and two drops of 0.1% bromcresol green indicator to the column eluate, neutralize the solution by the careful addition of 12 *N* NaOH. Then add 5 ml of the acid buffer solution, five drops of xylenol orange indicator and titrate to the purple end-point using 0.02 *M* $(CH_3COO)_2Zn$.

A blank is run on the plutonium used in the preparation of the synthetic alloy samples to correct for its Al content. In the synthetic alloy samples, the Al concentration is calculated using the following equation:

$$\text{mg Al} = 26.98\ (\text{mequivs. Zn for blank} - \text{mequivs. Zn for sample})$$

In a true alloy sample, the mequivs. Zn for the blank in the equation would be replaced by the mequivs. Zn equivalent to the amount of EDTA initially added.

It has been reported that in order to complete the reaction between Al and EDTA, it is necessary to boil the solution after the addition of the EDTA and the pH adjustment[11]. In this work it was found that if the EDTA is added before neutralization, the

heat of neutralization is sufficient to ensure complete complexation of all the Al. Low results are obtained, however, if the solution is neutralized and allowed to cool before addition of the EDTA.

RESULTS AND DISCUSSION

Several methods are available for determining small amounts of aluminum. Five were selected for investigation: colorimetric oxine, colorimetric aluminon, gravimetric oxine, volumetric oxine and volumetric EDTA. The purpose of these investigations was to determine which of the methods was the most applicable to the samples and the working conditions. The methods were evaluated by analysis of a series of standard aluminum solutions.

The conclusion from this investigation was that the gravimetric oxine method and the two volumetric methods gave the best results. Not only was their precision better than either of the colorimetric methods, but also from an equipment and manipulation standpoint, the gravimetric and the volumetric methods offered less difficulty than did the colorimetric methods. This is a very important consideration when analytical work must be done in glove boxes.

Interferences

Interference would be expected from any cation that is not retained on the ion-exchange column and normally interferes with the method used for determining aluminum. In order to be retained on the resin column, the cation must form an anionic chloride complex in 8 *N* HCl. KRAUS AND NELSON[7] have summarized the anion-exchange behavior of a number of metal ions in hydrochloric acid solutions. From this summary, and from the knowledge of those metals that are usually found as impurities in samples, it was possible to anticipate interferences and alter methods to eliminate them.

Only iron, copper, nickel, chromium and aluminum have been present in samples at any one time in concentrations greater than 200 p.p.m. Of these, only iron is present consistently in high concentrations. Fortunately, iron(III) forms an anionic chloride complex which is retained by the resin. Chromium(III) is not retained by the resin. Its interference can be prevented, however, by oxidizing it to chromate[12,13].

The distribution coefficient for copper is quite low, so there was the possibility that it would come through the column[7]. If it did, it would interfere with all of the methods used for determining aluminum.

Nickel is not retained on the column and likewise will interfere with all of the methods used for determining aluminum.

A series of synthetic alloy samples were run to determine if copper was retained on the column and to determine the extent of interference from nickel. The results of these runs are shown in Table II. They indicate no interference from copper, but interference from nickel, if present in concentrations greater than 600 p.p.m. From these results it was apparent that the methods for determining aluminum had to be modified so that they could be used on those samples containing more than 600 p.p.m. nickel.

The literature offered several suggestions for determining aluminum in the presence of nickel. For the most part, however, they required either abandonment of the oxine or EDTA procedures or the use of equipment, such as a mercury cathode, that would

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TABLE II

EFFECT OF Cu AND Ni ON Al DETERMINATION

Impurity	*Impurity concentration*		*Method of determination*	*% recovery Al*
	mg	*Equivs. p.p.m.*		
Cu	1.0	2000	oxine (vol)	100
Ni	1.0	2000	oxine (vol)	110
Ni	1.0	2000	EDTA	109
Ni	0.7	1400	EDTA	107
Ni	0.5	1000	oxine (vol)	105
Ni	0.5	1000	EDTA	105
Ni	0.4	800	EDTA	103
Ni	0.3	600	EDTA	100
Ni	0.2	400	EDTA	100
Ni	0.1	200	EDTA	100

be difficult to manipulate in a glove box. The one suggestion that did appear feasible was the removal of nickel by masking or precipitation.

Cyanide is the logical ion for masking nickel. It does not prevent the precipitation of aluminum with oxine[12] or the formation of the aluminum–EDTA complex[14]. However, cyanide would present difficulties with waste disposal, so other complexing agents as well as precipitating agents were investigated. These included the citrate, oxalate and sulfosalicylate ions, sodium sulfide and dimethylglyoxime. Of these, the only one that was satisfactory was dimethylglyoxime.

In the three methods that have been described for determining aluminum, the determination is carried out in a slightly acidic solution. This prevented the formation of aluminum hydroxide. But it was determined experimentally that nickel could not be completely precipitated by dimethylglyoxime from the sample solutions at a pH lower than 8. It was therefore necessary to modify the methods for determining aluminum.

In a basic solution, aluminum hydroxide formation can be prevented by the presence of the tartrate ion. Tartrate does not prevent the precipitation of aluminum with oxine or nickel with dimethylglyoxime. The volumetric oxine method was modified on the basis of this information. This modification involved the addition of 0.2 g sodium tartrate to the column eluant, then neutralization to the phenolphthalein end-point. Thirty ml of the basic buffer was added followed by 2 ml of the dimethylglyoxime solution. After waiting a few minutes to permit formation of the dimethylglyoximate, 3 ml of the oxine solution was added and the determination completed as in the original volumetric method.

Since nickel dimethylglyoximate is present in the aluminum oxinate precipitate, the determination cannot be completed gravimetrically. The dimethylglyoxime does not interfere in the volumetric method, however.

The EDTA method was modified to eliminate the interference from nickel in a manner comparable to that used in the volumetric oxine method. After collecting the eluant from the column, 0.2 g sodium tartrate was added and the solution neutralized to the phenolphthalein end-point by the careful addition of 12 *N* NaOH. Two ml of the dimethylglyoxime solution was added and the solution stirred for one minute. After standing for a minute, the solution was filtered through a medium porosity sintered glass filter funnel and the precipitate washed with 1% NaOH. Fifteen ml

8 *N* HCl was added to the combined filtrate and washings, then 5.00 ml 0.1 *M* EDTA. The determination was then completed following the original method.

Plutonium(IV) forms a precipitate with oxine[15] and a complex with EDTA[16]. To determine if there was enough plutonium leaking through the column to interfere in the aluminum determinations, a column was loaded with plutonium almost to capacity and a sample of the eluate then analyzed for plutonium. The eluate contained less than a mg of plutonium per l. This is too low to affect any of the methods given for determining aluminum.

TABLE III

PRECISION AND ACCURACY OF METHODS (SYNTHETIC ALLOYS)

Method	*No. samples*	*Al concn.*		*S.D.*
		Known	*Exp. mean*	
Oxine (grav.)	12	5.00 mg	5.03 mg	±0.11 mg
Oxine (vol.)	17	5.00 mg	4.93 mg	±0.08 mg
EDTA	12	5.00 mg	4.92 mg	±0.10 mg

Precision and accuracy of methods

The precision and accuracy of the oxine and EDTA methods for determining aluminum in an alloy were determined by running a series of synthetic alloy samples. These were prepared by dissolving 500-mg portions of pure plutonium metal and adding aliquots of the standard aluminum solution. The results are shown in Table III.

TABLE IV

PRECISION AND ACCURACY OF VOLUMETRIC METHODS (MODIFIED PROCEDURES)

Method	*Ni concn.*	*No. samples*	*Al concn.*		*S.D.*
			Known	*Exp. mean*	
Oxine	1 mg	11	5.00 mg	4.98 mg	±0.09 mg
EDTA	1 mg	6	5.00 mg	4.98 mg	±0.03 mg

A statistical analysis of duplicate results on 22 individual alloy samples run over a period of five weeks by the volumetric oxine method showed a standard deviation of ±0.012%. The nominal aluminum content of these alloys was 1%.

The precision and accuracy of the volumetric methods were determined using

TABLE V

COMPARISON OF PRECISION OF METHODS FOR DETERMINING ALUMINUM IN PLUTONIUM–ALUMINUM ALLOYS

Method	*Coefficient of variation*	*Comments*
Iodate-Aluminon	6.4%	Based on 28 determinations on synthetic samples in 0.2 to 0.4 w/o Al range.
Cupferron-Oxine (Colorimetric)	2.6%	Based on 24 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-Oxine (Gravimetric)	2.2%	Based on 12 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-Oxine (Volumetric)	1.6%	Based on 17 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-EDTA	2.0%	Based on 12 determinations on synthetic 1 w/o Al alloy samples.

synthetic alloy samples after the methods had been modified to eliminate nickel interference. The data are given in Table IV.

Comparison with other methods

It is possible to compare the precision of the procedures discussed in this report with the precision of the two other methods reported for determining aluminum in plutonium alloys[1,2]. Data for these are given in Table V.

SUMMARY

An anion-exchange method has been developed for the separation of aluminum from plutonium in a 1% aluminum–plutonium alloy. After separation, the aluminum is determined using oxine, either volumetrically or gravimetrically, or by a complexometric titration using EDTA. The volumetric methods are favored because they are faster. On synthetic alloy samples containing 5.00 mg of aluminum the mean recovery and the standard deviation of the volumetric oxine method are 4.93 mg and ± 0.08 mg, respectively. Using the EDTA procedure, the comparable values are 4.92 mg and ± 0.10 mg, respectively. Of the elements commonly present as impurities only nickel interferes, but the volumetric procedures can be modified so that this interference is eliminated.

RÉSUMÉ

Une méthode par échange d'anions est proposée pour la séparation de l'aluminium d'avec le plutonium. Après séparation, l'aluminium peut être dosé soit par volumétrie, soit par gravimétrie, à l'aide d'oxine; on peut également effectuer un dosage complexométrique au moyen de l'acide éthylènediaminotétracétique (EDTA). Parmi les éléments généralement présents comme impuretés, seul le nickel gêne; on peut éviter cette perturbation en modifiant les procédés volumétriques.

ZUSAMMENFASSUNG

Aluminium lässt sich von Plutonium mit Hilfe eines Jonenaustauschers trennen. Die Bestimmung des Aluminiums als Oxychinolat kann gravimetrisch, volumetrisch oder komplexometrisch mit Aethylendiaminotetraessigsäure erfolgen. Von den üblichen Verunreinigungen stört nur Nickel, dessen Einfluss durch eine modifizierte volumetrische Methode eliminiert werden kann.

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PYROMELLITEIN INDICATORS

II. ADSORPTION INDICATORS

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The first paper[1] of this series introduced a new group of indicators prepared from pyromellitic dianhydride by condensing four phenolic molecules with one molecule of the dianhydride. Among these are two which resemble fluorescein; one containing four resorcinol groups and the other containing two resorcinol and two phenol groups. Two additional indicators were prepared from these by bromination, in the same manner by which eosin is made from fluorescein. There were therefore four possible adsorption indicators to work with, which will be designated in this article as roman numerals as follows: I. Tetra-resorcinol pyromellitein; II. Diresorcinol diphenol pyromellitein; III. Brominated product of I. IV. Brominated product of II.

Preliminary tests had determined that the other indicators listed in the first paper did not adsorb on silver halide precipitates. At the start of the study being discussed here, it was determined that compound IV did not adsorb, and that compound II, from which it was prepared, adsorbed very weakly, it being necessary to use so much of this indicator that it was considered that the pink color on silver chloride might be due to impurity (compound I).

As a comparison method, it was decided to titrate the soluble halides using 0.1 *N* $AgNO_3$ by Fajans method[2], and to compare the results obtained with those using dichlorofluorescein. The effect of acidity was determined by adding 3 *M* HNO_3 to some solutions, and titrations in the presence of colored ions were carried out in 1 *M* HNO_3 solutions. Eosin was included for comparison purposes. The results of these experiments may be summarized as follows:

A. *For the titration of chlorides*, indicator I gives results identical with those obtained in neutral and slightly acid solutions using dichlorofluorescein, but indicator II gives poor results. For the chloride titration in more acid solutions, however, where dichlorofluorescein cannot be used, indicator II gives good results, even in the presence of highly colored ions such as Cr^{+3}, Fe^{+3}, Cu^{+2}, Ni^{+2}, and Co^{+2} in 1 *M* HNO_3. In the absence of colored ions an excellent end-point was obtained in an acidity as high as 1 *M* HNO_3.

B. *For the titration of bromides*, indicator II gave excellent results over a wide range of acidities, from neutral to 1 *M* HNO_3, while indicator I gave results similar to those of dichlorofluorescein with bromides.

C. *For the titration of iodides*, indicator II also gave excellent results over a wide range of acidities, while indicator I gave results similar to those of dichlorofluorescein with bromides.

D. *In titrating thiocyanate solution,* indicator II gave very good results both in dilute and strong acid, the end-points being sharp and the checks excellent. The color of colored thiocyanate ions (such as ferric), of course, interferes.

E. *In the titration of very dilute solutions of all three halides,* indicator I gave results at least as good as those obtained with dichlorofluorescein in weak acid solutions, while indicator II gave better results for bromides and iodides in weak acid solution, and very good results for all three halides in solutions of HNO_3 which were 0.05 *M* or stronger.

The good results obtained for bromides and iodides may be due to the fact that the color of indicator II on adsorption has a more purple tinge than that shown by dichlorofluorescein, eosin, and indicator I which are shades of pink when adsorbed. The color changes of indicators I and II are listed in Table I.

TABLE I

Indicator	*Acidity*	*Solution color*	*Adsorbed color*
Indicator I	Neutral	Green-Yellow fluorescence	Pink (coral)
Indicator II	Neutral	Pink	Purple
Indicator I	0.05 *N*	Yellow	Pink (not at equiv. pt.)
Indicator II	0.05 *N*	Orange	Purple
Indicator II	1 *N*	Orange	Purple (more pink)

All indicator solutions in these tests were made up by dissolving 0.1 g of indicator in 100 ml H_2O, one drop of 6 *N* NaOH being added to aid in dissolving the indicator.

When 0.1 *N* halide solutions were tested, five drops of indicator were used for a total final volume of about 50 ml. When very weak halide solutions were titrated, only one drop of indicator solution was used.

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SUMMARY

Two new indicators have been made and tested, one of them being a substitute for dichlorofluorescein, the other showing excellent end-points in moderately strong nitric acid solutions for chlorides, bromides, iodides and thiocyanates even in the presence of colored ions.

RÉSUMÉ

Des indicateurs ont été préparés par condensation du dianhydride pyromellique avec le résorcinol. Ils ont été examinés en vue de leur emploi comme indicateurs d'adsorption.

ZUSAMMENFASSUNG

Die Reaktionsprodukte von Pyromellitsäure-dianhydrid mit Resorcin wurden auf ihre Eignung als Adsorptionsindikatoren untersucht.

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RAPID EXTRACTION OF IRON(III) WITH 2-THENOYL TRIFLUOROACETONE

DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

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Various metal ions react with 2-thenoyltrifluoroacetone (TTA) to give chelates which are intensely colored, relatively stable, insoluble in aqueous solutions, but soluble in many organic solvents. BERG AND MCINTYRE[1] reported the paper chromatographic separation of mixtures of TTA-chelates with iron(III), cobalt(II), copper (II), nickel(II) and manganese(II), by means of the mixed solvent system, benzene, methanol and glacial acetic acid. They prepared iron(III)–TTA chelate and determined its molecular weight as 718.8 which indicates the formula $Fe(TTA)_3$. They also noted the absorption spectrum in ethyl alcohol. In an earlier report BOLOMEY AND WISH[2] observed that the equilibrium constant for the iron(III)–TTA complex exceeds 1 and that the optimum pH for extraction into benzene is around 2 to 3. They measured the ferric chelate in the benzene phase spectrophotometrically at 470 mμ. But systematic extraction and colorimetric studies of iron(III) with TTA are lacking.

In the present work the brilliant red color of the iron(III)–TTA complex in benzene has been utilised in a rapid spectrophotometric method for iron(III) at the milligram level. The various factors involved in the extraction and colorimetric measurement have been critically studied. A preliminary note of this work is under publication[3].

EXPERIMENTAL

Apparatus

A Hilger Quartz Spectrophotometer, with matched 1-cm quartz cells, was used for absorbance measurements; pH values were measured with a Cambridge pH meter.

Reagents

All the chemicals used, unless otherwise mentioned, were chemically pure or reagent grade materials.

Approximately 0.15 *M* solutions of TTA (Columbia organic chemicals, U.S.A.) (m.p. 42–43°) in benzene were used. More dilute solutions (*ca.* 0.01*M*) were ineffective for rapid extractions.

A stock solution of iron(III) was prepared by dissolving about 4.5 g of ferric alum (Merck) in 500 ml of 5% sulphuric acid. The solution was standardized by permanganate titration. 1 ml of the solution contained 0.99 mg of iron. For the following studies the stock solution was diluted ten-fold so that the iron content was 99 μg per ml.

GENERAL PROCEDURE

A suitable aliquot (1 or 2 ml) of the diluted ferric alum solution was adjusted to pH 2.0 with 0.01 *N* hydrochloric acid and 0.01 *N* sodium hydroxide using the pH meter

and then diluted with water to 25 ml. For pH studies, the solution containing iron was adjusted to different pH values and then diluted as above. For interference studies, the solution containing the desired ion was introduced before the pH was adjusted. The aqueous solution thus prepared was transferred to a 250-ml separatory funnel and shaken for 10 min with 10 ml of 0.15 *M* TTA solution in benzene. The aqueous layer was drained into a beaker and the benzene layer into a 25-ml volumetric flask. The aqueous layer was rinsed with 5 ml of benzene in the separatory funnel and the benzene layer collected as before. The combined red benzene extracts were finally diluted to 25 ml with benzene and the absorbance measured at 460 mμ against a reagent blank. The corresponding iron concentration was obtained from a calibration curve (see below).

RESULTS AND DISCUSSION

Absorption curve

Fig. 1 illustrates the absorption spectra of solutions containing no iron or $7.1 \cdot 10^{-5}$ *M* iron(III) treated as above. The bright red iron(III)–TTA system has a strong ab-

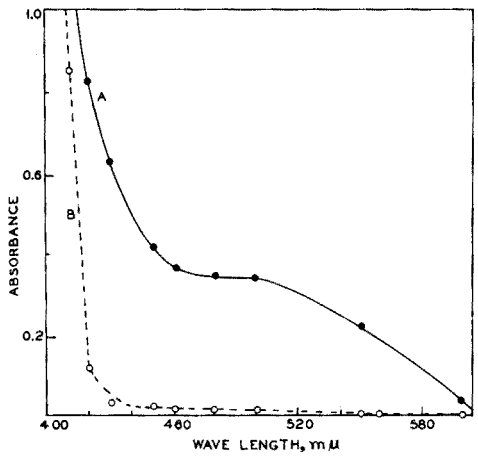

Fig. 1. Absorption spectra. A. Iron(III)–TTA complex in benzene against benzene as reference solution. Fe^{+3}, $7.1 \cdot 10^{-5}$ *M*; pH 2.0. B. Reagent blank against benzene, TTA, $15 \cdot 10^{-2}$ *M*; pH 2.0.

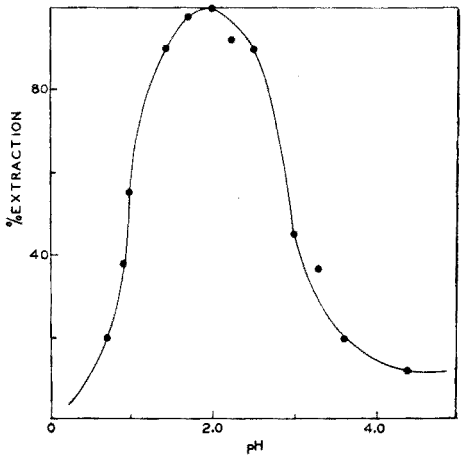

Fig. 2. Extraction of ferric–TTA complex with benzene as a function of pH.

sorption below 400 mμ which gradually decreases and becomes negligible beyond 650 mμ. All absorbance measurements were made at 460 mμ. The molar extinction coefficient at 460 mμ is 4880 $\pm$ 61 (on the basis of iron content).

Effect of pH

The extraction of iron(III) with TTA-benzene was investigated over the pH range 0.3–4.5. At higher pH the precipitation of ferric hydroxide causes trouble. The distribution constants, K_D, were calculated from extraction curves[4] (Table I). The

optimum pH for 90% or more extraction is 1.5 to 2.7 which agrees fairly well with the pH range, *viz.* 2–3, predicted by BOLOMEY AND WISH[2], who used more dilute solutions of TTA (*ca.* 0.01 *M*) and extracted for several hours. At pH 2.0 quantitative extraction (100%; $K_D = \alpha$) is observed (Fig. 2).

TABLE I

DISTRIBUTION CONSTANTS OF FERRIC-THENOYLTRIFLUOROACETONATE BETWEEN BENZENE AND AQUEOUS SOLUTION AS FUNCTION OF PH

pH	% *Iron extracted into benzene*	K_D
0.7	20	0.63
0.9	38	1.53
1.0	55	3.06
1.2	72	6.43
1.4	88	18.33
1.6	94	39.15
1.8	98	122.50
2.0	100	α
2.2	99	247.5
2.4	96	60
2.6	93	33.12
2.8	86	15.36
3.0	45	2.05
3.2	34	1.29
3.4	27	0.93
3.6	20	0.63
3.8	17	0.51
4.0	14	0.41
4.2	13	0.37
4.4	12	0.34

Calibration curve

Different amounts of iron (100, 150, 180 and 200 μg) were taken, and the absorbances measured at 450, 460 and 480 mμ against a reagent blank. Beer's law is obeyed at 460 mμ over a range of 1 to 10 μg iron per ml (Table II).

TABLE II

BEER'S LAW

Iron taken[a] μg	*Absorbance*		
	450 mμ	*460 mμ*	*480 mμ*
100	0.385	0.350	0.330
150	0.585	0.515	0.500
180	0.680	0.620	0.575
200	0.790	0.700	0.680

[a] Final volume of benzene solution was 25 ml containing the above amounts of iron.

Reagent concentration

The amount of TTA was changed from 0.008 *M* to 0.15 *M* while other factors were kept constant (Table III). The optimum concentration appears to be 0.15 *M*.

TABLE III

EFFECT OF REAGENT CONCENTRATION

200 μg of iron(III) gives an absorbance reading of 0.700 $\pm$ 0.008

TTA concentration (M)	*TTA added (ml)*	*Absorbance at 460 mμ*	*% extraction*
0.008	10	0.135	18.5
0.015	10	0.415	58.5
0.15	2	0.600	85.0
0.15	5	0.620	88.5
0.15	10	0.700	100
0.15	20	0.700	100

Stability of color

The absorbance of a solution of ferric–TTA complex (iron = 0.1 mg) was measured after 30 min, 2, 24, 48, 72, 96 and 168 h. The values obtained were 0.350, 0.352, 0.350, 0.345, 0.345, 0.345 and 0.335 respectively. The color was stable up to 96 h after which it underwent slow decomposition. At the end of 168 h the absorbance decreased by 4.3%.

Interfering ions

The following ions were taken through the procedure (iron = 0.2 mg): Ag^{+}, Cu^{+2}, Hg^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Bi^{+3}, Al^{+3}, Cr^{+3}, Ce^{+4}, Th^{+4}, Zr^{+4}, U^{+6}, PO_4^{-3}, citrate and tartrate (Table IV). Uranium, cerium, thorium, zirconium, copper,

TABLE IV

INTERFERING IONS

Iron(III) = 200 μg

Ion	*Concentration of ion (mg)*	*Added as*	*Absorbance at 460 mμ*	*Remarks*
None	—	—	0.700 $\pm$ 0.008	
Ag^{+}	20	$AgNO_3$	0.660	Interference
Cu^{+2}	21.3	$CuSO_4 \cdot 5H_2O$	1.23	Color reaction
Hg^{+2}	21.3[a]	$HgCl_2$	0.705	No interference
Mn^{+2}	10	$MnSO_4 \cdot 7H_2O$	0.560	Emulsion formed
Co^{+2}	20	$Co(NO_3)_2 \cdot 6H_2O$	0.700	No interference
Ni^{+2}	21.5	$NiSO_4 \cdot 7H_2O$	0.520	Interference
Bi^{+3}	0.5[b]	BiOCl	0.555	Interference
Al^{+3}	20	$Al_2(SO_4)_3 \cdot 18H_2O$	0.680	Interference
Cr^{+3}	20	$Cr(NO_3)_3 \cdot 9H_2O$	0.700	No interference
Ce^{+4}	25.6	$Ce(SO_4)_2 \cdot 4H_2O$	0.98	Color reaction
Th^{+4}	26.2	$Th(NO_3)_4 \cdot 4H_2O$	0.540	Interference
Zr^{+4}	1.0[c]	$ZrOCl_2 \cdot 8H_2O$	0.550	Precipitation of zirconium chelate
U^{+6}	24.6	$UO_2(NO_3)_2 \cdot 6H_2O$	0.940	Color reaction
PO_4^{-3}	20	$Na_2HPO_4 \cdot 12H_2O$	0.210	Strong interference
Citrate	20	Citric acid	0.265	Interference
Tartrate	20	Tartaric acid	0.420	Interference

[a] Larger amounts interfere.
[b] Extraction is difficult with larger amounts owing to increased oxysalt formation.
[c] Zirconium in larger amounts is troublesome because of voluminous precipitation of zirconium chelate.

phosphate and citrate interfere seriously. Silver, nickel, manganese, bismuth, aluminium and tartrate also interfere. The ferric–TTA system (iron = 0.2 mg) can tolerate 20 mg amounts of mercury(II), cobalt(II) and chromium(III).

RECOMMENDED PROCEDURE

Take an aliquot containing 25 to 200 μg iron, adjust to pH 2.0 with 0.01 *N* hydrochloric acid and 0.01*N* sodium hydroxide with the help of a pH meter and transfer the solution (*ca.* 25 ml) to a 250-ml separatory funnel. Extract for 10 min with 10 ml of 0.15 *M* TTA–benzene solution. Allow the phases to settle, withdraw the aqueous layer into a beaker and the benzene layer into a 25-ml volumetric flask. Pour the aqueous solution back into the separatory funnel and rinse with 5 ml of benzene. Collect the benzene layer in the flask. Dilute the combined organic extracts to 25 ml with benzene. Measure the absorbance at 460 mμ against a reagent blank and calculate the iron concentration from the calibration curve.

TABLE V

ACCURACY OF THE PROPOSED METHOD

Iron taken μg	*Absorbance at 460* mμ	*Iron found* μg	% *Error*
400[a]	0.695	398	—0.50
300[a]	0.522	302	+0.67
250[a]	0.395	252	+0.80
200	0.700	200	0.00
160	0.540	160	0.00
120	0.382	118	—1.60
100	0.345	99.5	—0.50

[a] The final volume of benzene solution was 50 ml.

To determine the accuracy of the method, known amounts of iron(III) were treated as above. The results (Table V) are accurate to within $\pm$ 1%. From six runs with 0.2 mg of iron(III), the absorbance found was 0.700 $\pm$ 0.008; the standard deviation was $\pm$ 1.14%. Thus the method enjoys good precision and accuracy. As little as 0.4 μg of iron per ml can be detected, which indicates the high sensitivity.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. A. K. MAJUMDAR for laboratory facilities, to the Council of Scientific and Industrial Research, India, for financial support and awarding a senior fellowship to one of them (S.M.K.), and to Columbia Organic Chemicals, Inc., Columbia, S. Carolina, U.S.A. for the gift sample of TTA.

SUMMARY

2-Thenoyltrifluoroacetone is investigated for the rapid extraction and spectrophotometric determination of iron(III) at the milligram level. The red extract absorbs strongly below 400 mμ. The color is stable for many hours; Beer's law is obeyed at 460 mμ for 1–10 μg of iron/ml. Interferences are studied. The method is reproducible to $\pm$ 1%.

RÉSUMÉ

La thénoyl-2-trifluoracétone est proposée comme réactif pour le dosage du fer(III). On peut ainsi effectuer une extraction rapide et une détermination spectrophotométrique directe du fer dans la phase organique.

ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Eisen(III) kann Thenoyltrifluoroaceton verwendet werden. Der gebildete Komplex ist Benzol-löslich. Die störenden Kationen und Anionen werden erwähnt.

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Anal. Chim. Acta, 22 (1960) 223–228

BEHAVIOUR OF BISMUTH NITRATE SPOTS IN INORGANIC PAPER CHROMATOGRAPHY

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In the course of a study of the chromatography of metal ions using butanol–water–thiocyanic acid as solvent, bismuth was found to give unusual crescent shaped spots.

EXPERIMENTAL

n-Butanol and aqueous 2.5 *N* thiocyanic acid (140:40) were mixed to give a single phase solvent, 0.53 *M* in thiocyanic acid. The chromatograms were prepared by the ascending technique of WILLIAMS AND KIRBY[1] using Whatman's No. 41 papers and were developed to a height of 15 to 18 cm without the appearance of an adsorption front. The paper used had a Tappi freeness[2] of 645 which corresponds[3] to a surface area of the order of 19 sq. metres per gram. The bismuth spots were located by treating the chromatograms successively with H_2S and NH_3 gases.

The bismuth solutions were in general 0.1 *M* in bismuth but varied in acid concentration. Where bismuth solutions of lower concentration were used these were made by diluting the 0.1 *M* solutions with acid of the appropriate concentrations. Five acids were used, nitric, perchloric, hydrochloric, hydrobromic and thiocyanic, and for the stock solutions the respective acid concentrations were 0.75 *M*, 0.6 *M*, 1 *M*, 0.5 *M* and between 1 and 2 *M* for the thiocyanic acid.

Approximately 0.005 ml of bismuth solutions was taken for each spot.

The perchlorate, thiocyanate and bromide solutions gave clear cut and slightly comet shaped spots at an R_F value of about 0.88. Solutions containing chloride and nitrate ions had R_F values of 0.45 and 0.65 respectively. These spots generally were of the shape shown in Fig. 1.

Varying the quantity of bismuth in the chloride (1 *M*) and nitrate (0.75 *M*) solutions from 10 to 100 μg per spot caused no significant change in either the R_F value of these groups or in

the shape of the bismuth chloride spots. However, as the concentration of bismuth was varied from 0.1 *M* to 0.01 *M* so the lower portion of the bismuth nitrate spot tended to assume a more regular oval shape.

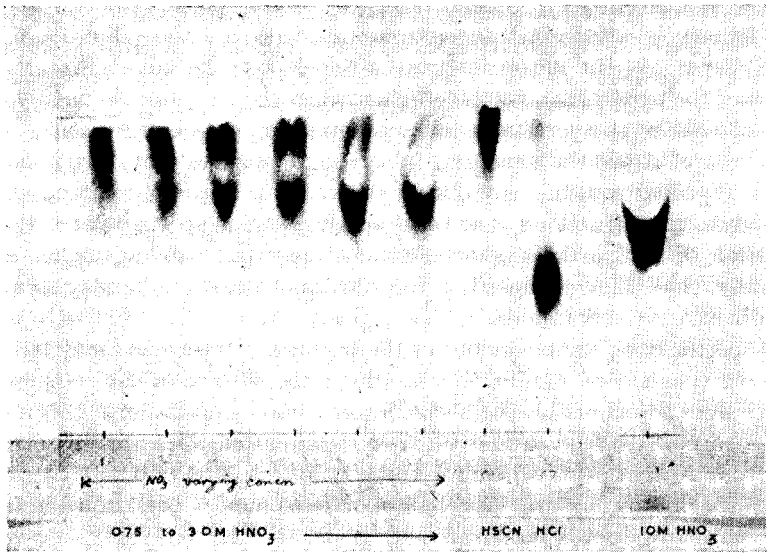

Fig. 1. Behaviour of $Bi(NO_3)_3$-spots in inorganic chromatography.

DISCUSSION

It might be expected that, of the five anions chosen, the chloride, bromide and thiocyanate bonds with bismuth would have a considerable degree of covalent character, while the nitrate and perchlorate link would be largely ionic. Whether bismuth in these latter was Bi^{+3} or BiO^{+} is not clear[4]. As MARTIN[5] has shown for antimony, bismuth as chloride and bromide may be expected to travel as covalent halides, $Bi(Ha)_3$ the thiocyanate may be of the same form or possibly $Bi(SCN)_6^{-3}$.

The bismuth chloride (except for a small amount), bromide and thiocyanate moved as colourless, pale buff and orange coloured spots respectively, at all times. The similarity between the R_F values for bismuth bromide and thiocyanate would appear to be incidental to this discussion. The bismuth chloride spot did furnish a bismuth thiocyanate spot amounting to 5–10% of the total bismuth. It appeared to be formed by a reaction between the developing solution and the spot material at the zone of the initial circular spot where its periphery and the horizontal interact. These two small spots travelled as bismuth thiocyanate, in some cases diffusing into one. In cases of mixed chloride and nitrate solutions, two systems of spots appeared, each system being characteristic for each ion.

The nitrate and perchlorate spots reacted with the developing solution as soon as it reached them but whereas the bismuth perchlorate travelled thereafter as thiocyanate to the normal position of the thiocyanate compound, the bismuth nitrate spot travelled in a hindered manner. This was due to the presence of a colourless spot of nitrate ion, oxidation product of nitrate and thiocyanate, or both, just ahead of it, and resulted in a variety of spot shapes, (Fig. 1.) and R_F values varying

between 0.5 and 0.7 depending mainly on the acidity of the solution of bismuth nitrate. The higher acidities gave a spot area of 3.6 sq.cm.

The behaviour of the bismuth nitrate spot suggests that the process of development is one of adsorption. In general terms the process of development may be pictured as follows. The ions of the solute are adsorbed by the cellulose on spotting on to the paper. As the chromatogram is developed, the advancing solvent first washes away the excess acid, water, etc., and then the ions are thoroughly desorbed into the solvent. As the portion of solvent containing the desorbed ions passes over the fresh area of paper the ions are readsorbed. The process of desorption and adsorption is repeated continuously during the running of the chromatogram. If this is essentially correct it follows that the R_F values of the spot is related to the time of adsorption of the particles, shorter time of adsorption giving higher R_F value, and secondly, that changes caused on the surface of the cellulose play an important role in influencing the R_F value.

In this specific case, the behaviour of the bismuth nitrate spots may be explained by assuming that the excess nitric acid affects the surface of the cellulose making it more strongly adsorbing for the bismuth compound, thus inhibiting its movement.

The evidence of data given above is not incompatible with this hypothesis. Calculating from an area of 3.6 sq.cm for the spot of 0.005 ml of 0.1 M Bi^{+3} in nitrate solution, a specific surface area of cellulose of 19 sq.metres per gram for the paper, we have an area of approximately 200 sq. A per Bi^{+3}.

This does not seem excessive if we take into account that the bismuth is not distributed evenly over the spot; a factor of 3 may be assumed both up to and down from the average. Furthermore, the specific area of the cellulose refers to a determination made in water while the solvent discussed above is only of the order of 0.6 mol fraction water, consequently the exposed surface area may be expected to be less.

SUMMARY

An investigation of irregularities found when chromatographing bismuth ions with butanol–water–thiocyanic solutions led to the conclusion that the process is one of absorption rather than partition for the development of this ion.

RÉSUMÉ

L'auteur a examiné le comportement du bismuth lors d'une étude de chromatographie sur papier d'ions métalliques, utilisant le mélange butanol–eau–acide thiocyanique comme solvant.

ZUSAMMENFASSUNG

Es wurde festgestellt, dass die bei der papier-chromatographischen Bestimmung von Wismut mit Butanol–Wasser–Thiocyanat beobachteten Unregelmässigkeiten auf Adsorptionserscheinungen zurückzuführen sind.

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SPECTROPHOTOMETRIC DETERMINATION OF NOBLE METALS WITH TIN(II) IN BROMIDE SOLUTIONS

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INTRODUCTION

The coloured products obtained from noble metals on treatment with tin(II) chloride have been used extensively for the colorimetric determination of these metals; but such reactions do not permit the determination of the metals in presence of one another. Recently, the reactions of rhodium[1] and iridium[2] with tin(II) bromide have been investigated. A broad study of all platinum metals has not hitherto been carried out, although a bromide medium appears to be very useful, since its sensitivity is greater than that of chloride.

In the present work we have examined from an analytical point of view the behaviour of platinum, rhodium, palladium, iridium and gold with tin(II) bromide, both in aqueous solutions and in organic solvents and extraction of the coloured products with isoamyl alcohol. The colours obtained are suitable for sensitive spectrophotometric determinations; it is possible also to perform several separations and simultaneous determinations. This work forms part of a wide investigation on noble metals which is being carried out in this Institute[3].

EXPERIMENTAL

Apparatus and solutions

Absorption measurements were made with a Beckman DU spectrophotometer, 1-cm Corex glass cells being used.

Reagent: 0.5 *M* $SnBr_2$ in 3 *N* HBr was prepared by dissolving pure tin in hydrobromic acid ($d = 1.48$) and diluting to the proper volume. Noble metals solutions in 0.2 *N* hydrobromic acid were prepared as follows:

Platinum: A suitable volume of standardized chloroplatinic acid solution was diluted with hydrobromic acid so that it contained 530 μg of Pt^{+4}/ml.

Rhodium: A solution containing 200 μg of Rh^{+3}/ml was made by dissolving $Na_3RhCl_6 \cdot 2\ H_2O$ in warm hydrobromic acid.

Palladium: $PdCl_2$ was dissolved in warm HBr to give a solution containing 576 μg of Pd^{+2}/ml.

Iridium: $IrCl_3$ was dissolved in warm HBr to give a solution containing 603 μg of Ir^{+3}/ml.

Gold: The metal was dissolved in aqua regia, evaporated almost to dryness and standardized gravimetrically. A solution containing 2 mg of Au^{+3}/ml was obtained by diluting a suitable volume of this solution with hydrobromic acid.

RESULTS

The optimal experimental conditions for the reaction between noble metals and stannous bromide were studied. The following results were obtained with pure solutions.

Platinum

The addition of reagent to a platinum(IV) solution caused a red colour to appear immediately and the colour was stable for several days. The absorption spectrum showed a peak at 463 mμ and the curve did not change on moderate heating of the solution. The optical density at the wavelength of the maximum was not affected by variations in the tin(II) concentration between 0.03 and 0.3 *M*. On increasing hydrogen ion concentration above 1 *N* the same spectral curves were obtained; at an acidity of less than 1 *N* no peak appeared. At 463 mμ Beer's law was followed strictly over the range 1 to 30 p.p.m. of platinum. The extinction coefficient was sufficiently high to provide a sensitive determination of this metal.

The colour was easily and completely extracted with isoamyl alcohol. The spectrum in this solvent, which was very similar to that obtained in aqueous solution, is shown in Fig. 1. The extracted colour was very stable and Beer's law was obeyed at 463 mμ; the determination could therefore also be done in isoamyl alcohol solution.

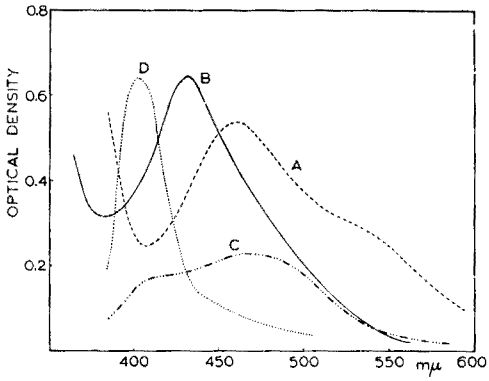

Fig. 1. Spectra in isoamyl alcohol: A. 10.6 μg Pt/ml. B. 2.3 μg Rh/ml. C. 10.1 μg Pd/ml. D. 6 μg Ir/ml.

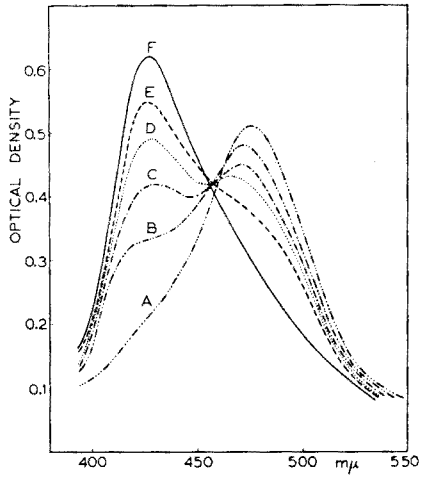

Fig. 2. Spectra of 2.3 μg Rh/ml with 0.5 *M* Sn(II) in 3 *N* HBr: A. after 6 min. B. 19 min. C. 44 min. D. 1 h. E. 1 h 30 min. F. 3 h 30 min.

Rhodium

When a rhodium(III) solution was mixed with the reagent at room temperature a red-orange colour first developed, its maximum being at 475 mμ in the spectral curve. After 1–2 hours the colour changed to yellow and a peak appeared at 427 mμ (Fig. 2). In solutions containing only hydrobromic acid the yellow colour was stable for only half an hour, but if perchloric acid was also added measurements could be made from 20–30 min to 2–3 h after mixing reagents; it was convenient to perfom all measurements at the same time in order to obtain good reproducibility. On gentle heating the yellow colour appeared in 2–3 min, but it was less stable than when obtained at room temperature and its optical density was lower. The optimal conditions were a tin(II) concentration of not less than 0.1 *M* and an acidity between 2.5 and 3 *N* (almost 50% of both HBr and $HClO_4$). Beer's law was followed at 427 mμ

from 0.1 to 5 p.p.m. of rhodium. The molar extinction coefficient was 3.10^4, hence the determination was very sensitive.

The yellow product could be extracted into isoamyl alcohol; the spectrum is shown in Fig. 1, the maximum lying at 429 mμ. When the extraction was made after the yellow colour had developed, the spectrum in the organic solvent did not change within 12 h. Beer's law was again followed. Thus rhodium can be determined in isoamyl alcohol as well as in aqueous solution.

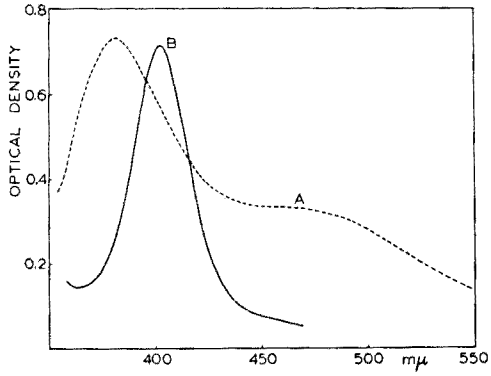

Fig. 3. Spectra in presence of 0.1 *M* Sn(II) and 3 *N* HBr: A. 10 μg Pd/ml. B. 5 μg Ir/ml.

Palladium

Palladium(II) gave a yellow-brown colour with tin(II) bromide. The spectrum is shown in Fig. 3; a peak at 385 mμ and a plateau in the range 440–460 mμ are noticeable. In view of the absorbance of tin-bromide complexes below 400 mμ, all measurements should be made on the plateau instead of at the maximum. The optical density was very sensitive to the concentrations of tin(II) and hydrogen ion. The optimal experimental conditions were an acidity of almost 3 *M* and a tin(II) concentration above 0.1 *M*. The colour was stable for only 1 h and Beer's law was followed from 1 to 10 p.p.m. With higher amounts of palladium, a calibration curve should be determined.

The yellow-brown colour was readily extracted by isoamyl alcohol. The spectrum in the organic solvent did not show a peak at 385 mμ, but only a rounded maximum at 450 mμ (Fig. 1). Since Beer's law was obeyed at this wavelength, a sensitive determination could be performed. The colour was more stable when perchloric acid was present in the aqueous solutions before extraction.

Iridium

No colour was observed on treating an iridium(III) solution with tin(II) bromide at room temperature for several days. A yellow colour developed on heating for some minutes[2]. The spectrum is shown in Fig. 3; the maximum optical density (at 403 mμ) and the greatest stability of the colour (several hours) were obtained with 0.1–0.2 *M* tin(II) bromide acidity of 2–3 *N*. The colour followed Beer's law and the useful range for determining iridium was 0.1 to 5 p.p.m.

Isoamyl alcohol could be used for extraction of solutions which were very high in

hydrogen ion concentration. The spectrum obtained in this solvent is shown in Fig. 1. However, the results were not very reproducible and determinations should be done only in aqueous solutions.

Gold

The behaviour of gold with tin(II) bromide was very different from that of the other noble metals. Finely divided gold metal seemed to be produced; in the absence of protective colloids a blue-gray colour appeared which gave a black precipitate within an hour. When 0.05% gelatine was present as protective colloid, a stable

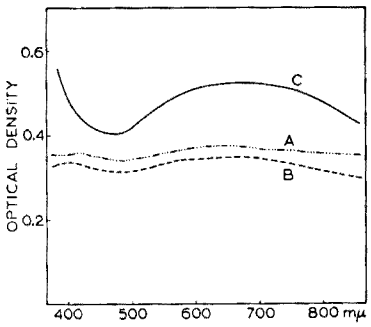

Fig. 4. Spectra of 40 μg Au/ml in presence of 0.05 *M* $SnBr_2$ without gelatine: A. H^+ = 1 *N*. B. H^+ = 2 *N*. C. H^+ = 6 *N*.

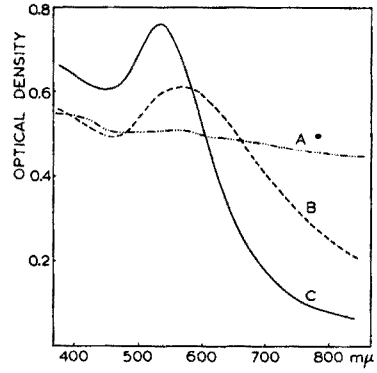

Fig. 5. Spectra of 40 μg Au/ml in presence of 0.05 *M* $SnBr_2$ with 0.05% gelatine: A. H^+ = 1 *N*. B. H^+ = 2 *N*. C. H^+ = 6 *N*.

reproducible violet colour was obtained which depended on the acidity of the solutions (Figs. 4 and 5). The concentration of stannous bromide should be greater than 0.05 *N* for rapid colour development, but it must be less than 0.15 *M* to avoid turbidity in solutions containing gelatine. Beer's law was obeyed between 540 and 550 mμ over the range 5 to 50 p.p.m. The colour could not be extracted with organic solvents.

The spectrophotometric data of the 5 elements investigated are summarized in Table I.

TABLE I

SPECTROPHOTOMETRIC DATA OF PLATINUM, RHODIUM, PALLADIUM, IRIDIUM AND GOLD IN PRESENCE OF TIN(II) BROMIDE

Metal	*Tin(II) concn. (M)*	*H^+ concn. (N)*	*λ_{max}*	*Molar extinction coefficient*	*Colour*
Pt	0.03–0.3	1	463	$9.3 \cdot 10^3$	red-orange
Rh	0.1	3	427	$3.0 \cdot 10^4$	yellow-orange
Pd	0.1	3	385	$6.7 \cdot 10^3$	yellow-brown
Ir	0.1 –0.2	2–3	403	$2.5 \cdot 10^4$	yellow[a]
Au	0.05–0.15	2	540	$3.2 \cdot 10^3$	violet[b]

[a] After heating for 3 min at 100°.
[b] In presence of 0.05% gelatine.

Separations and determinations of noble metals in presence of one another

The usefulness of the reactions with tin(II) bromide for the simultaneous determination of several noble metals was also studied.

a. Separation of gold from platinum metals. The formation of colloidal gold interferes seriously in the determinations of the other metals. Moreover, gold(III) in hydrobromic acid solutions is complexed as $HAuBr_4$. Since the dissociation of this complex is very small, it can be extracted by organic solvents such as ethyl ether, isoamyl alcohol, etc. Hence, gold should be extracted before the addition of tin(II) bromide; platinum metals are not extracted from hydrobromic acid solutions and remain in the aqueous phase so that they can be determined with tin(II) bromide.

b. Determination of platinum, rhodium and palladium in presence of iridium. As mentioned above, iridium does not react at room temperature, hence platinum, rhodium and palladium can be determined in presence of iridium, both in aqueous solutions and by extraction with isoamyl alcohol. Extraction is also advisable when iridium, which remains in aqueous solution, has to be determined. Some examples of determinations in presence of a large amount of iridium are shown in Table II; the coloured products were extracted with 25 ml of isoamyl alcohol from solutions containing 1 *N* hydrobromic acid, 1.5 *M* perchloric acid and 0.15 *M* tin(II) bromide.

TABLE II

DETERMINATION OF PLATINUM, RHODIUM AND PALLADIUM IN PRESENCE OF IRIDIUM

Metal (μg/ml)	*Wavelength (mμ)*	*Optical density*	
		Without Ir	*48.2 Ir μg/ml added*
Pt 8.5	463	0.428	0.434
Rh 2.4	429	0.580	0.571
Pd 9.2	450	0.365	0.366

c. Separation of platinum and rhodium from palladium. Several complex-forming substances can be used to eliminate palladium from a solution containing platinum and/or rhodium. Dimethylglyoxime forms a characteristic complex with palladium which can be used to precipitate this element[4]. But we have found that at acidities of 2 or 3 *M*, the results are better with α-nitroso-β-naphthol (or α-nitro-β-naphthol). Palladium is complexed by this ligand preferentially to platinum and rhodium. The complex can then be extracted with isoamyl alcohol and the other metals can be determined in the aqueous solution with tin(II) bromide. The results are rather low and errors of 5–7% can be expected.

d. Simultaneous determination of rhodium and platinum. It is not easy to extract or mask either of these elements when the other is present. However, it is possible to use the wavelengths corresponding to maxima in the spectrum of each. In solutions which are 1 *N* in hydrobromic acid, 1.5 *M* in perchloric acid and 0.15 *M* in tin(II) bromide, the optical density of platinum at 427 mμ is 51.5% of the density at 463 mμ; the optical density of rhodium at the latter wavelength is 59.5% of the density at 427 mμ. After the absorbances at these two wavelengths have been measured, the following equations must be solved:

$$D^{427}_{\text{total}} = D^{427}_{\text{Rh}} + 0.515\, D^{463}_{\text{Pt}}$$

$$D^{463}_{\text{total}} = D^{463}_{\text{Pt}} + 0.595\, D^{427}_{\text{Rh}}$$

In this way, the unknown D^{427}_{Rh} and D^{463}_{Pt} can be calculated and the amount of rhodium and platinum can be determined by comparison with a calibration curve. The results of some determinations by this method are shown in Table III.

TABLE III

SIMULTANEOUS DETERMINATION OF PLATINUM AND RHODIUM

Rh present μg	*Pt present* μg	D_{427}	D_{463}	*Rh found* μg	*Pt found* μg
40.6	53	0.465	0.347	40.5	53.5
40.6	106	0.516	0.441	40.8	102.7
40.6	159	0.562	0.547	39.8	161
40.6	212	0.620	0.649	40.5	213
20.3	53	0.263	0.230	20.5	55.6
20.3	106	0.312	0.329	20.2	108.5
20.3	159	0.367	0.434	20.4	163
20.3	212	0.420	0.534	20.6	215

ACKNOWLEDGEMENTS

This work was sponsored by the Italian National Research Council (C.N.R.).

SUMMARY

In presence of tin(II) bromide, noble metals give coloured products which are suitable for spectrophotometric determinations. The colours are: red (platinum), yellow-orange (rhodium), yellow-brown (palladium), yellow (iridium) and violet (gold). They are extracted, except for gold, with isoamyl alcohol. Platinum, rhodium and palladium can be separated from iridium, and rhodium and platinum from palladium. Rhodium and platinum can be determined simultaneously.

RÉSUMÉ

Les métaux nobles réagissent avec le bromure d'étain(II), en solution bromhydrique, pour donner des produits diversément colorés. On a pu ainsi établir des méthodes de séparation et de dosage spectrophotométrique de ces éléments.

ZUSAMMENFASSUNG

Die Edelmetalle geben mit Zinn(II)-bromid in bromwasserstoffsaurer Lösung verschieden gefärbte Reaktionsprodukte, die sich zur Trennung und spektrophotometrischen Bestimmung dieser Metalle verwenden lassen.

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ZINC ACETATE AS A REAGENT IN GRAVIMETRIC ANALYSIS. I.

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In an earlier publication[1] it was shown that the precipitation of some anions of the second group by means of zinc acetate is quantitative and provides a satisfactory means of separating these anions. As many of the separations thus accomplished cannot be done easily by other gravimetric methods, the method has been investigated

for the determination of these anions when they are present together in solution. It has been shown that zinc acetate gives satisfactory separations and permits the determination of anions in certain combinations which cannot be easily analysed otherwise.

For example, in the determination of iodide in presence of arsenate and selenite, the acidification of the solution liberates iodine with the reduction of arsenate and selenite. In the analysis of mixtures of phosphite and iodide, phosphite interferes with the estimation of iodide owing to the reduction of silver nitrate to metal. In the determination of iodide in presence of tellurite and tellurate, complexes are formed on acidification. All these difficulties can be overcome by the use of zinc acetate for separation.

Precipitation as Re_2S_7 is the most accurate method for the determination of rhenium but it cannot, of course, be used for its separation from metals such as arsenic, tellurium, etc., which also form thiosalts and are precipitated as sulphides. A preliminary separation by means of zinc acetate in presence of sodium carbonate permits the sulphide method to be used for the determination of these elements when present together.

EXPERIMENTAL

Determination of iodide in presence of arsenate, phosphite, selenite, tellurite or tellurate.

Measured volumes of standard solutions of sodium arsenate, sodium phosphite, potassium selenite, potassium tellurite, and potassium tellurate were made alkaline with sodium carbonate (0.5 g), mixed with a measured volume of a standard solution of potassium iodide and then treated with zinc acetate solution until no further precipitation occurred. The sodium carbonate was added to prevent the interaction of acids in neutral or acid solution and also to form zinc carbonate which simplified the filtration of the gelatinous precipitates obtained with zinc acetate. The mixture was heated nearly to boiling, digested on a hot plate for 10–15 min, cooled, filtered and washed thoroughly with distilled water.

The precipitate of the zinc salt was dissolved in dilute hydrochloric acid and the arsenate, selenite, tellurite and tellurate were estimated as sulphides[2,3]; the sodium sulphide was added after the acid present had been neutralized. The precipitate obtained with phosphite was dissolved in dilute nitric acid; the phosphite was oxidised to phosphate with an excess of permanganate (the excess being removed by adding a crystal of potassium nitrate) and determined as ammonium phosphomolybdate. In the filtrate from the zinc salts iodide was determined volumetrically using eosin as adsorption indicator or gravimetrically as silver iodide.

30–38 mg of arsenic were separated from 61–76 mg of iodine; 59–60 mg of selenium were separated from 61–76 mg of iodine; 44–55 mg of tellurium(IV) were separated from 61–76 mg of iodine; 57–65 mg of tellurium(VI) were separated from 61–76 mg of iodine; 3 mg of phosphite were separated from 61–76 mg of iodine.

The metals were recovered with an accuracy of:

As	= −0.2% to +0.3%	I	= −0.3% to +0.2%
Se	= −0.3% to +0.4%	I	= −0.2% to +0.1%
Te(IV)	= −0.2% to +0.3%	I	= −0.2% to +0.25%
Te(VI)	= 0.0% to +0.25%	I	= −0.1% to +0.25%
P	= −0.25% to +0.3%	I	= −0.2% to +0.1%

Determination of rhenium in presence of arsenate, tellurate and tellurite.

Measured volumes of standard solutions of sodium arsenate, potassium tellurite or potassium tellurate were mixed with a measured volume of a standard solution of potassium perrhenate, made slightly alkaline with sodium carbonate (0.5 g) and treated as above. The precipitate of the zinc salt was dissolved in dilute hydrochloric acid, and the arsenate, tellurite and tellurate were determined as sulphides[2,3]. The filtrate from the zinc salt was made slightly acidic with dilute hydrochloric acid and concentrated to about 50 ml, and rhenium was also determined as sulphide[4].

30–38 mg of As were separated from 37–41 mg of rhenium; 44–55 mg of Te(IV) were separated from 37–41 mg of rhenium; 57–65 mg of Te(VI) were separated from 37–41 mg of rhenium.

The metals were recovered with an accuracy of:

As	= −0.2% to +0.35%	Re	= −0.2% to +0.3%
Te(IV)	= −0.2% to +0.3%	Re	= −0.25% to +0.4%
Te(VI)	= 0.0% to +0.3%	Re	= −0.2% to +0.3%

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SUMMARY

Zinc acetate can be used for the gravimetric separation of iodide from arsenate, selenite, phosphite, tellurate and tellurite, and rhenium from arsenate, tellurate and tellurite.

RÉSUMÉ

L'acétate de zinc peut être utilisé pour la séparation gravimétrique des iodures d'avec les arséniates, sélénites, phosphites, tellurates et tellurites, et du rhénium d'avec les arséniates, tellurates et tellurites.

ZUSAMMENFASSUNG

Es wird gezeigt, dass mit Hilfe von Zinkacetat eine gravimetrische Trennung der Jodide von Arsenaten, Seleniten, Phosphiten, Telluraten und Telluriten sowie des Rheniums von Arsenaten, Telluraten und Telluriten erzielt werden kann.

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MASS-SPECTROMETRIC STUDY OF NITROGEN COMPOUNDS FROM PETROLEUM DISTILLATES*

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INTRODUCTION

Little detailed information is available on the type distribution of the nitrogen compounds in oil. Accordingly, characteristic petroleum distillates were subjected to careful fractionated distillations and chromatographic separations. Among the fractions obtained were basic and non-basic nitrogen concentrates having molecular weights from 220 to about 320.

In this paper a detailed description is given of the mass-spectrometric method which was developed to determine the type distribution of the compounds in the basic nitrogen concentrates. This includes the pyridine-quinoline type distribution and the subdistribution according to naphthenicity. In addition, some data are presented on basic nitrogen–sulphur compounds which were found to the present in the corresponding extracts.

MASS-SPECTROMETRIC DETERMINATION OF THE PYRIDINE-QUINOLINE TYPE DISTRIBUTION

Qualitative considerations

In concentrates of the type mentioned in the introduction the heteroaromatic nitrogen compounds that must be considered primarily are the pyridines and the (iso)quinolines. As naphtheno-aromatics – *e.g.* indanes and tetralins – are known to constitute an appreciable part of the aromatic hydrocarbons of similar molecular weight occurring in oil fractions the presence of mono- and dinaphthenopyridines along with alkylpyridines and of the corresponding quinolines should be reckoned with. Hence a mass-spectrometric method is required that is capable of determining not only the alkyl-substituted heteroaromatics but also their various naphtheno-substituted relatives. As will shortly be seen, this naphtheno-substitution necessitates the separate analysis of basic and non-basic nitrogen concentrates.

By analogy with aromatic hydrocarbons the various heteroaromatic nitrogen compounds are expected to show marked parent peaks, fragment peaks and/or rearrangement peaks at m/e-series corresponding to their molecular Z number** as well as to Z—1.

The parent ions of alkyl-, mononaphtheno- and dinaphthenopyridines have Z-values —5, —7 and —9, respectively; the corresponding quinolines have Z-numbers —11, —13 and —15, respectively.

* Presented at the Seventh Annual ASTM–E14 Meeting on Mass Spectrometry, Los Angeles 1959.
** Z is defined by the molecular formula $C_nH_{2n+Z}N$ and is a measure of the hydrogen deficiency.

Similarly the non-basic nitrogen compounds like alkyl-, mononaphtheno- and dinaphtheno-indoles or carbazoles have Z-values —9, —11 and —13 or —15, —17 and —19, respectively. Hence, dinaphtheno-pyridines and alkyl-indoles, alkylquinolines and mono-naphtheno-indoles, and other pairs appear indistinguishable as regards their Z-number.

As seen from the mass spectra* reproduced in Fig. 1, the basic heteroaromatic nitrogen compounds are indeed clearly characterized by their Z-numbers:

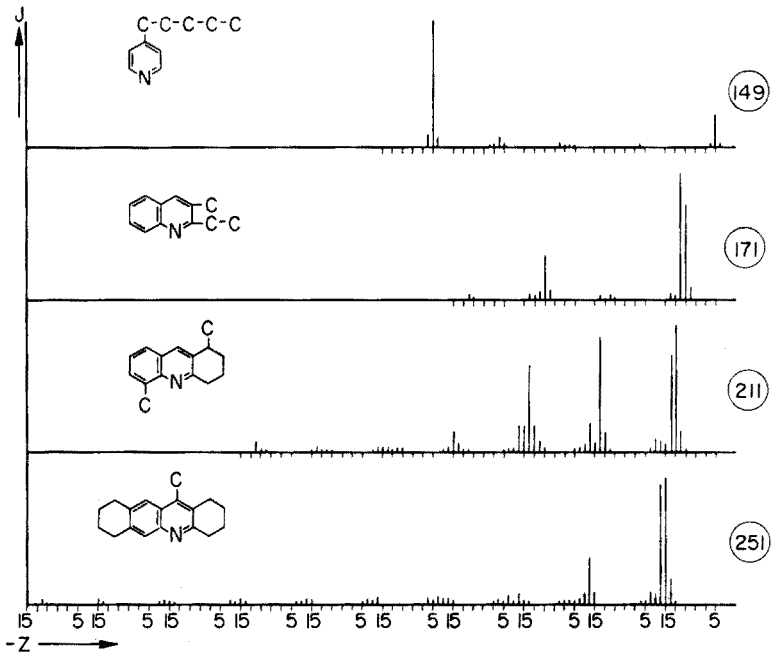


Fig. 1. Mass spectra of some basic nitrogen compounds. J = intensity in arbitrary units. The numbers at the right indicate the molecular weight. The spectra have been shifted horizontally with respect to each other by an integral multiple of 14 m/e units.

The strongest peaks of n-amylpyridine (Z = —5) appear at the mass/charge ratio: m/e = 93 (rearrangement peak) and at m/e = 149 (molecule ion) both belonging to the Z = —5 series; similarly methylethylquinoline (mol. wt. 171, Z = —11) has its major peaks confined to Z = —11 and Z = —12 positions; with the mononaphtheno-dimethylquinoline (mol. wt. 211, Z = —13) the major peaks are at Z = —13 and Z = —14 whereas with dinaphtheno-methylquinoline (mol. wt. 251, Z = —15) the strongest peaks are at Z = —15 and Z = —16 positions.

The mass spectra of these compounds and of others not given here are characterized by the following features:

(a) their base peak and other major peaks are found at series corresponding to Z and Z—1 if their molecular formula is given by $C_nH_{2n+Z}N$.

* Obtained with a Consolidated Model 21–103 C instrument, modified for high mass operation.

(b) the molecule ion peak is not necessarily the base peak but the latter and the other major peaks are found in the proper Z and Z—1 series down to the corresponding complete naphtheno-aromatic ring system without alkyl substituents.

Thus alkylpyridines as a class ($Z = -5$) are characterized by appreciable intensity in the sum S_1 of the ion currents at m/e values $\begin{matrix}78\\79\end{matrix} + i \times 14$. Mononaphthenopyridines would contribute mainly at m/e values $\begin{matrix}118\\119\end{matrix} + i \times 14$, sum S_2; as the first members of this class and of those of higher naphthenicity those with the maximum number of polycondensed five-membered rings for a given number of substituent C-atoms were chosen. The same applies to the quinoline classes starting with alkylquinolines ($Z = -11$) with the ion current sum (S_4) at m/e values $\begin{matrix}128\\129\end{matrix} + i \times 14$ and so on. Relevant data and symbols are given in Table I.

TABLE I

Py	*Q*	*Peak series*	*Intensity sum*	*Z-number*
0 n + (4 n)		$\left.\begin{matrix}78\\79\end{matrix}\right\} + i \times 14$	S_1	— 5
1 n		$\left.\begin{matrix}118\\119\end{matrix}\right\} + i \times 14$	S_2	— 7
2 n		$\left.\begin{matrix}144\\145\end{matrix}\right\} + i \times 14$	S_3	— 9
(3 n) +	0 n	$\left.\begin{matrix}128\\129\end{matrix}\right\} + i \times 14$	S_4	—11
	1 n	$\left.\begin{matrix}154\\155\end{matrix}\right\} + i \times 14$	S_5	—13
	2 n	$\left.\begin{matrix}180\\181\end{matrix}\right\} + i \times 14$	S_6	—15
	3 n	$\left.\begin{matrix}206\\207\end{matrix}\right\} + i \times 14$	S_7	—17

Ring systems (*Py* = pyridine, *Q* = quinoline, n = naphthenic ring), with corresponding peak series, intensity sums and Z-numbers.

Quantitative aspects

Once the characteristic peak sequences S_i have been selected the matrix for determining the pyridines and quinolines according to their Z-number should be devised; the choice of the S_i's described above already makes the diagonal elements s_{ii} the largest of each column.

The formal matrix is given in Table II. The matrix elements s_{ij} in each column j are to be obtained — except for a sensitivity factor — from model compounds. Intercomparability of columns — elimination of the sensitivity factor — can be obtained from total-ion-current (T_j) considerations and from data on synthetic blends of type concentrates: to the latter end a synthetic mixture of a pyridines concentrate (B91) and a quinolines concentrate (K76) — both having an average molecular weight of 231 — has been employed.

Let us first consider the intercomparability of columns. As shown by OTVOS AND STEVENSON[1] the total cross-sections of molecules for ionization under electron bombardment are additive in the cross-sections of the constituent atoms.

With the known atomic cross-sections of H, C and N the total molar cross-sections and hence the respective total molar ion currents Tm_1 and Tm_4 of an alkylpyridine

TABLE II

FORMAL MATRIX

	Py_{0n}	Py_{1n}	Py_{2n}	Q_{0n}	Q_{1n}	Q_{2n}	Q_{3n}
$-Z$	5	7	9	11	13	15	17
j	1	2	3	4	5	6	7
S_1	s_{11}	s_{12}	s_{13}	s_{14}	s_{15}	s_{16}	s_{17}
S_2	s_{21}	s_{22}	s_{23}	s_{24}	s_{25}	s_{26}	s_{27}
S_3	s_{31}	s_{32}	s_{33}	s_{34}	s_{35}	s_{36}	s_{37}
S_4	s_{41}	s_{42}	s_{43}	s_{44}	s_{45}	s_{46}	s_{47}
S_5	s_{51}	s_{52}	s_{53}	s_{54}	s_{55}	s_{56}	s_{57}
S_6	s_{61}	s_{62}	s_{63}	s_{64}	s_{65}	s_{66}	s_{67}
S_7	s_{71}	s_{72}	s_{73}	s_{74}	s_{75}	s_{76}	s_{77}
$\sum_i s_{ij}$	77	76	75	75	74	73	72

For the explanation of the $\sum_i s_{ij}$-values see text.

like $C_{17}H_{29}N$ (mol.wt. 247) and an alkylquinoline like $C_{18}H_{25}N$ (mol.wt. 255) are found to be 103.5 and 103.7, respectively, in arbitrary units. For the ratio of their "specific" total ion currents T_1 and T_4 — defined as total ion current per unit vapour density — follows $T_4/T_1 = 0.97$. This compares reasonably with the ratio $T_Q/T_{Py} = 1.01$ found experimentally with the synthetic blend (45.2% Py + 54.8% Q) of actual concentrates.

Accepting the T-values predicted for the successive Z-classes as correct, T_j would be 100, 99, 98, 97, 96, 95 and 94 in arbitrary units for $j = 1$ through $j = 7$, respectively, and for molecular weights around 250.

The next step is to ascertain what fraction f_j of T_j is present in the combined ion currents of the m/e series S_1 through S_7, in others words to find the quantity:

$$f_j = \sum_i s_{ij}/T_j.$$

To this end the f-values obtained from a variety of mass-spectra as given in Table III for mono(hetero)aromatics and in Table IV for di(hetero)aromatics may be considered. Some literature data on benzenes and naphthalenes—obtained on similar instruments—have been included in order to obtain a better balanced appreciation without making use of further model compounds.

The f-values increase with molecular weight: starting from $f \simeq 0.5$ for the low-molecular-weight members of the series an f-level of about 0.75 is approached in the C_{18}-region (mol.wt. $\approx$ 250) regardless of the Z-number of the molecular species. This further substantiated by the actual pyridine and quinoline concentrates which — despite a Z-difference of about 6 units — have almost identical f-values, *viz.* 0.77_5 and 0.79_2. In view of this near-identity, f_1 through f_7 will all be taken equal to 0.77 so that the sums of matrix elements per column $\sum_i s_{ij}$ attain the values given underneath the formal matrix (Table II).

Now the actual matrix elements s_{ij} per column j must be estimated from the mass patterns of model compounds and adjusted to give the proper $\sum_i s_{ij}$ value. Typical data are presented in Tables V and VI for mono- and di(hetero)aromatic compounds, respectively. From these the average s_{ij}-values for the final matrix are obtained: the columns s_{i3} and s_{i7} are estimated by inter- or extrapolation.

TABLE III

FRACTIONAL ION CURRENTS f_j OF MONO(HETERO)AROMATICS

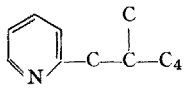
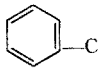
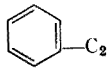
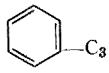
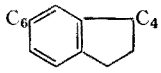
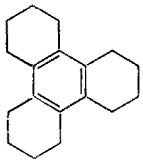
Compound	*Z-number*	*Molecular weight*	f_j
	—5	177	0.68_5
	(—6)	78	0.51
	(—6)	92	0.57
	(—6)	106	0.64
	(—6)	120	0.68
	(—8)	258	0.71
	(—12)	240	0.72
Pyridine concentrate B91	{—5 —7}	231	0.775

TABLE IV

FRACTIONAL ION CURRENTS f_j OF DI(HETERO)AROMATICS

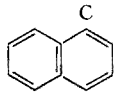
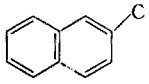
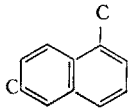
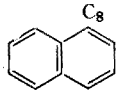
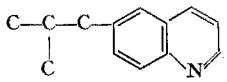
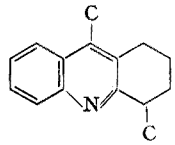
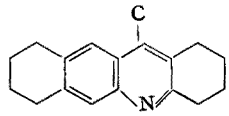
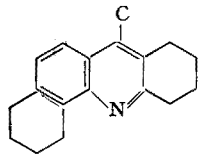
Compound	*Z-number*	*Molecular weight*	f_j
	(—12)	142	0.53
	(—12)	142	0.50
	(—12)	156	0.65
	(—12)	240	0.74

TABLE IV (continued)

	—11	185	0.62
	—13	211	0.693
	—15	251	0.703
	—15	251	0.753
Quinoline concentrate K76	{—11 —13}	231	0.792

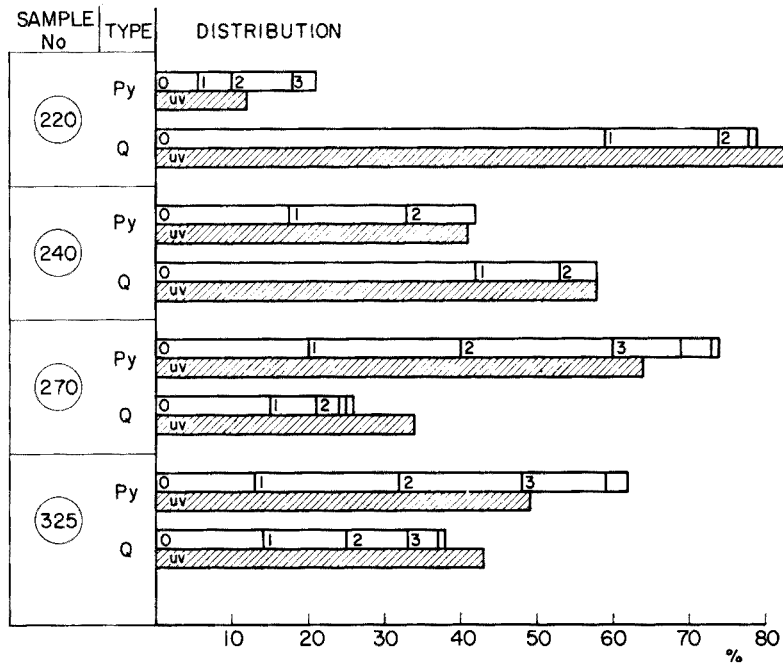


Fig. 2. Type distribution of pyridines and quinolines in four petroleum distillates according to mass-spectrometric and ultraviolet-spectroscopic analysis (u.v.) The figures in the horizonal bars indicate the number of naphthenic rings per molecule.

TABLE V

s_{ij} PATTERNS OF MONO(HETERO)AROMATICS

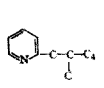
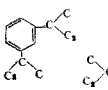
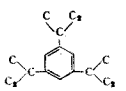
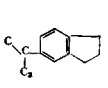
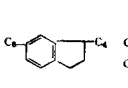
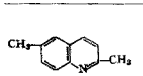
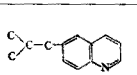
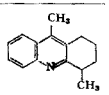
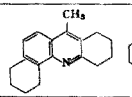
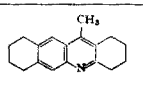
Class	*Alkylpyridines (benzenes)*						*Mononaphtheno compounds*				*Dinaphtheno compounds*	*Trinaphtheno compounds*
Compound						"Average"				"Average"	"interpolated"	
Molecular weight	177	190	190	246	288		202	258	272			240
—z	5	(6)	(6)	(6)	(6)		(8)	(8)	(8)			(12)
j	1	1	1	1	1	1	2	2	2	2	3	
s_{1j}	74	68	68	68	58	65	8	9	7	7	2	2
s_{2j}	3	6	6	5	13	8	62	57	56	59	10	2
s_{3j}	—	1	1	1	1	1	5	6	7	6	53	13
s_{4j}	—	2	2	1	3	2	1	4	6	4	6	47
s_{5j}	—	—	—	—	—	—	—	—	—	—	2	8
s_{6j}	—	—	—	—	—	—	—	—	—	—	2	2
s_{7j}	—	—	—	2	2	1	—	—	—	—	0	1

TABLE VI

s_{ij} PATTERNS OF CONDENSED DI(HETERO)AROMATICS

Class	*Alkylquinolines (naphthalenes)*				*Mononaphtheno compounds*	*Dinaphtheno compounds*			*Trinaphtheno compounds*
Compound				"Average"				"Average"	Estimated
Molecular weight	157	185	240		211	251	251		250
—z	11	11	(12)		13	15	15	15	17
j	4	4	4	4	5	6	6	6	7
s_{1j}	—	2	1	1	2	4	4	4	10
s_{2j}	—	1	1	1	1	2	2	2	3
s_{3j}	7	3	4	5	0	1	1	1	2
s_{4j}	68	56	65	59	8	1	1	1	0
s_{5j}	—	12	4	9	51	7	6	7	2
s_{6j}	—	1	0	0	11	50	51	50	10
s_{7j}	—	—	—	—	1	7	8	8	45

The resulting final s_{ij}-matrix is given in Table VII

TABLE VII

FINAL s_{ij}-MATRIX

$-Z$	5	7	9	11	13	15	17
j	1	2	3	4	5	6	7
S_1	65	7	2	1	2	4	10
S_2	8	59	10	1	1	2	3
S_3	1	5	53	5	0	1	2
S_4	2	5	6	59	8	1	0
S_5	0	0	2	9	51	7	2
S_6	0	0	2	0	11	50	10
S_7	1	0	0	0	1	8	45

Results

The analysis of the pyridine concentrate B91 with the final matrix is given in Table VIII; the result obtained with a provisional matrix ($s_{ij} = 1$ for $i = j$ or 0 for $i \neq j$) — which eventually appeared to have been a reasonable approximation — is

TABLE VIII

MASS-SPECTROMETRIC ANALYSIS OF PYRIDINE CONCENTRATE B91

		Final %*wt.*	*Provisional* %*wt.*
Py			
	$0n$	53	48
	$1n$	32	31
	$2n$	15	14
Q			
	$0n$	0	1
	$1n$	3	1
	$2n$	2	5
	$3n$	—	—

also given. The final matrix appears definitely more satisfactory in that it shows no "apparent" (5%) Q_{2n}-contents as does the provisional one; the actual quinolines content is negligible according to ultra-violet spectrometric analysis.

Further results with pyridine-quinoline concentrates obtained from petroleum distillate fractions are given in Fig. 2; underneath the detailed mass-spectrometric results the total pyridine and quinoline concentrations found by independent ultra-violet-spectrometric analysis are given in each case.

It is seen that indeed an important part of the basic fractions consists of various naphtheno-substituted compounds.

In a similar way certain *non-basic* nitrogen concentrates were found to consist predominantly (80+%) of carbazoles, including some 40% mono- and dinaphtheno-carbazoles (see Table IX).

TABLE IX

MASS-SPECTROMETRIC ANALYSIS OF A CARBAZOLE CONCENTRATE

Carbazoles	*%wt.*
alkyl-	34
mononaphtheno-	22
dinaphtheno-	15
total (MS)	~82
total (UV)	~80

BASIC NITROGEN–SULPHUR COMPOUNDS FROM PETROLEUM DISTILLATES

During the preparation of sulphur-free basic nitrogen concentrates, some fractions were found to contain both sulphur and nitrogen in the same molecule.

For the determination of these types of compounds a simple yet general approach as described in the first part of this paper is no longer possible. A combination of spectrometric and chemical techniques, however, was found very useful for unravelling the structure of such biheteroaromatic systems. The techniques employed may be summarized as follows:

1. Ultra-violet absorption spectra to judge the overall structure of the condensed heteroaromatic ring system.

2. Selective hydrogenation of the "pyridine part" of this system by means of tin and hydrochloric acid.

3. Mass spectra before and after the selective hydrogenation to ascertain the hydrogen uptake.

4. Ultra-violet spectra — after selective hydrogenation — in neutral and acidic solution to show among other things whether the basic nitrogen atom is attached directly to the remaining aromatic skeleton or separated from it by one or more nonaromatic carbon atoms.

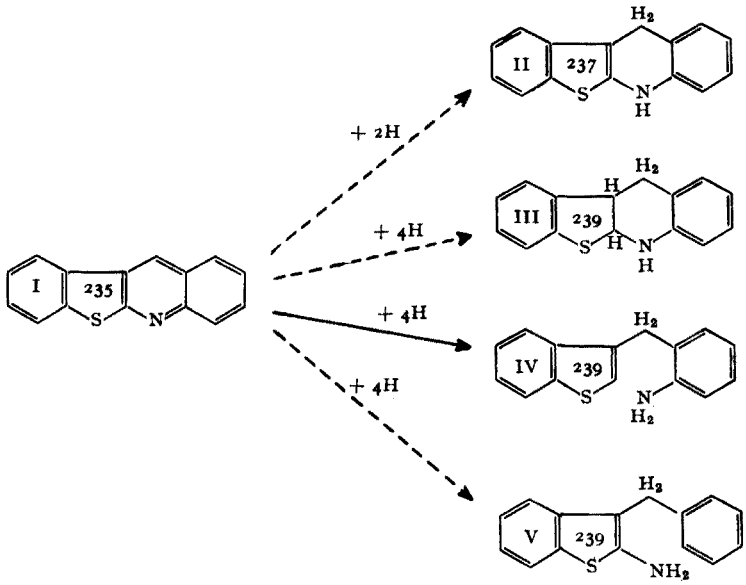


Fig. 3. Selective hydrogenation of 2,3-thionaphtho-2′,3′-quinoline.

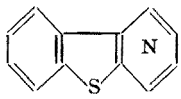
This procedure is perhaps best illustrated with a model compound of known structure, *viz.*: 2,3-thionaphtho-2′,3′-quinoline (mol.wt. 235); compound I of Fig. 3.

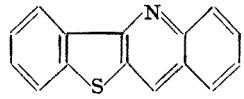
Upon selective reduction 4 H-atoms are taken up, as follows from the exclusive appearance of a parent peak at $m/e = 239$. This leaves III, IV and V as probable structures.

The ultra-violet spectra in neutral and acidic solution had a clearly composite character; they could be closely matched by superposition of an ortho-alkylaniline and an alkylthiophene spectrum in accordance with structure IV. The exceptional and unexpected ring opening giving the primary arylamino group was confirmed afterwards by other techniques.

Conversely, the evidence obtained ruled out the presence of a dibenzothiophene system in the original compound thus appreciably reducing the number of structures possible at the outset.

By means of this method the presence in actual concentrates of, among others, the following condensed biheteroaromatic ring systems could be demonstrated:



and


CONCLUSIONS

Mass-spectrometric analysis in proper combination with other techniques is capable of giving detailed information on the structure of heteroaromatic nitrogen compounds occurring in petroleum distillates.

Current concepts on total ionization have been verified for pyridines and quinolines having molecular weights of the order of 250. The data obtained were used in conjunction with other features to devise a matrix for the detailed analysis of pyridine–quinoline mixtures.

The presence of various naphtheno-substituted pyridines, quinolines and carbazoles in petroleum distillates has been demonstrated.*

A novel approach for the examination of heteroaromatic basic nitrogen-sulphur compounds from petroleum distillates is described and some results are presented.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the essential contributions of Dr. W. C. BREZESINSKA SMITHUYSEN, Mr. W. F. DE HAAS AND Mr. A. J. MULDER, who provided the concentrates and synthesized the model compounds, of Mr. J. SCHOUT who performed the ultra-violet-spectrometric examinations and of Mr. W. G. VAN WIJK who collaborated in the mass-spectrometric work.

SUMMARY

A mass-spectrometric method is given for the determination of the pyridine-quinoline type distribution, including subdistribution according to naphthenicity, in corresponding concentrates from petroleum fractions. Its results are in good agreement with those of ultraviolet spectrometry. In non-basic nitrogen concentrates indole-carbazole distributions can be determined similarly. The method uses peak intensity summations comprising the parent and parent-minus-one series,

* Independently, DINNEEN, COOK AND JENSEN came to a similar conclusion for nitrogen compound types from shale oil–gas oil. (*Anal. Chem.* 30 (1958) 2026).

starting from the first naphtheno-aromatic skeleton conceivable that is built up of condensed five-membered naphtheno rings. It is based on current concepts on total ionization. The presence of mono- and dinaphtheno-pyridines, mono-naphtheno-quinolines and naphtheno-carbazoles in oil fractions was demonstrated. Besides, basic nitrogen concentrates were obtained containing one sulphur atom per heteroaromatic ring system. Here, combined application of mass- and ultraviolet spectrometry before and after selective hydrogenation led to detailed conclusions regarding their heteroaromatic nucleus.

RÉSUMÉ

L'auteur discute une méthode d'application de la spectrométrie de masse, pour déterminer, dans des fractions de pétrole concentrées, la distribution des composés du type pyridine-quinoléine, y compris leur distribution secondaire selon leur caractère naphténique. Les résultats correspondent bien avec ceux qu'on trouve en se servant de la spectrométrie dans l'ultraviolet. Il est également possible de déterminer de cette façon les distributions indole-carbazole dans des composés azotés concentrés non-basiques. La présence de pyridines mono- et dinaphténiques, de quinoléines mononaphténiques et de carbazoles naphténiques dans des fractions de pétrole a pu être démontrée.

ZUSAMMENFASSUNG

Zur Bestimmung der Verteilung der Verbindungen vom Typ Pyridin-Chinolin in konzentrierten Erdölfraktionen, einschlieszlich deren Verteilung nach naphtenischem Charakter, wurde eine massenspektrometrische Methode entwickelt. Die mit dieser Methode erzielten Ergebnisse weisen gute Übereinstimmung mit den mittels UV-Spektrometrie ermittelten auf. In ähnlicher Weise läszt sich auch die Indol-Karbazol-Verteilung in nichtbasischen Stickstoffkonzentraten bestimmen.

Er wurde nachgewiesen, dasz in Erdölfraktionen Mono- und Dinaphtenpyridine, Mononaphtenchinoline, Naphtenkarbazole sowie schwefelhaltige heteroaromatische Ringsysteme enthalten sind.

REFERENCE

1 J. W. OTVOS AND D. P. STEVENSON, *J. Am. Chem. Soc.*, 78 (1956) 546.

THE COLORIMETRIC DETERMINATION OF DIALKYL PHOSPHITES USING CACOTHELINE

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(Received August 14th, 1959)

Cacotheline reacts with aqueous solutions of various inorganic ions such as tin(II), titanium(III), uranium(III) and rhenium(III) to give a lilac colour which is due to a reduction product of the reagent[1], the reaction also being given by numerous organic compounds[2]. The stronger reducing agents such as stannous ion or sodium dithionite yield lilac coloured solutions, a colour change which is reversible, but continued action results in a colourless solution from which the original colour of the reagent is not regained. Some doubt has been cast upon the suitability of cacotheline for the estimation of tin(II)[3] whilst it has been noted that the system does not follow Beer's law[4]. The colour reaction of alkyl phosphites with 3,5-dinitrobenzoic acid has been used for the estimation of alkyl phosphites[5], this method involving a period of about one hour

to develop the colour. Alkyl phosphites react with cacotheline in sodium carbonate solution to give an intense red solution the colour being formed immediately. A colorimetric method was required to deal with small quantities of alkyl phosphites and the use of the colour reaction with cacotheline for this purpose is described.

Experimental

The following dialkyl phosphites, available from laboratory preparations or supplied by Albright and Wilson Ltd., were examined: dimethyl, diethyl, di-isopropyl, di-*n*-butyl, and dibenzyl phosphite. All other materials used were of normal reagent grade. The spectra were recorded using a Hilger spectrophotometer with glass prism and 1-cm glass cells. This instrument was also used for the colorimetric estimations. The polarograms were recorded on Tinsley Recording Polarograph using a H-type cell one arm consisting of a saturated calomel electrode. All polarograms were recorded in media 0.1 *M* with respect to potassium chloride.

Results

The effect of increasing quantities of dimethyl phosphite upon the spectrum of cacotheline under the conditions used for the estimation is shown by Fig. 1. The red colouration produced in alkaline media is stable when the solution is made acid. The addition of dimethyl phosphite to a solution of cacotheline in pyridine resulted, after

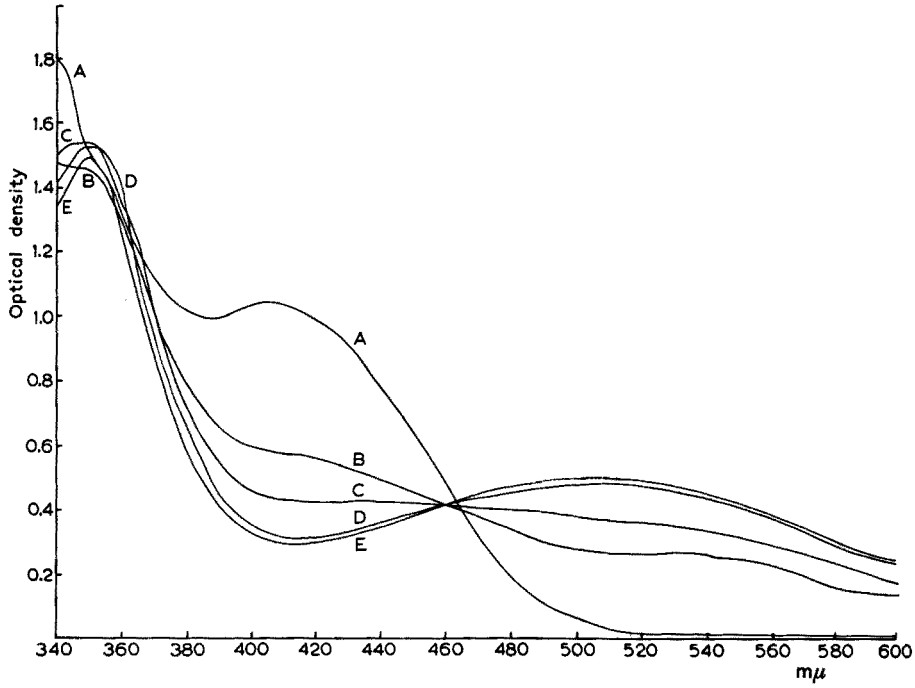

Fig. 1. Compositions of solutions: A. Cacotheline, $2 \cdot 10^{-4}$ *M*; sodium carbonate, $0.5 \cdot 10^{-1}$ *M*. B. cacotheline $2 \cdot 10^{-4}$ *M*; dimethyl phosphite, $2 \cdot 10^{-4}$ *M*; sodium carbonate, $0.5 \cdot 10^{-1}$ *M*. C. cacotheline $2 \cdot 10^{-4}$ *M*; dimethyl phosphite, $4 \cdot 10^{-4}$ *M*; sodium carbonate, $0.5 \cdot 10^{-1}$ *M*. D. cacotheline $2 \cdot 10^{-4}$ *M*; dimethyl phosphite, $6 \cdot 10^{-4}$ *M*; sodium carbonate, $0.5 \cdot 10^{-1}$ *M*. E. cacotheline $2 \cdot 10^{-4}$ *M*; dimethyl phosphite, $8 \cdot 10^{-4}$ *M*; sodium carbonate, $0.5 \cdot 10^{-1}$ *M*.

standing for a day, in the production of a green solution which eventually turned red. With the higher homologues some minutes were involved in colour production in aqueous sodium carbonate. The effect of dimethyl phosphite upon the polarographic response of cacotheline is shown by Fig. 2.

Other compounds containing the quinone group such as benzoquinone, chloranil, anthraquinone and alizarin showed no reaction with alkyl phosphites. Reagents which

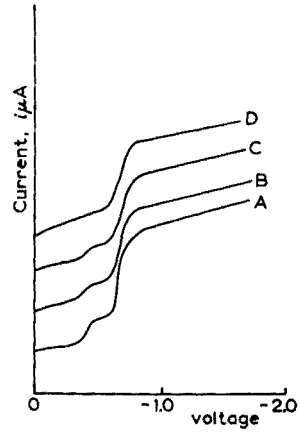

Fig. 2. Composition of solutions: All the solutions were 0.1 M in KCl and 0.1 M in Na_2CO_3. A. cacotheline $1 \cdot 10^{-4}$ M. B. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $1 \cdot 10^{-4}$ M. C. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $2 \cdot 10^{-4}$ M. D. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $3 \cdot 10^{-4}$ M.

in alkaline solutions gave colour reactions with 3,5-dinitrobenzoic such as ethyl malonate, ethylacetoacetate and acetophenone gave no reaction with cacotheline. Monoalkyl phosphites give no colouration with cacotheline.

Procedure

5 ml of 1 N sodium carbonate were added to 5 ml of $2 \cdot 10^{-2}$ M cacotheline in a 50-ml flask. The sample of aqueous or ethanol solution of phosphite was then added and the solution made up to the mark. The cacotheline at this reagent strength shows some tendency to come out of solution on

TABLE I

Mg of diethylphosphite	*Absorption: 560 mμ*
0.2	0.015
0.5	0.059
1.0	0.117
1.5	0.187
2.0	0.248
2.5	0.301
3.0	0.360
4.0	0.490
5.0	0.602

standing. By using 10 ml of $1 \cdot 10^{-2}$ M the reagent may be used for some time. The absorption of the solutions was measured at 560 mμ against the appropriate reagent blank using 1-cm cells. The choice of wavelength combined the required sensitivity with a reasonably low blank, and adherence to Beer's law. Typical calibration results are shown in Table I below for diethylphosphite.

The reagent blank at this wavelength had an absorption of 0.045 against water. Similar calibration curves were obtained for the other dialkyl phosphites. The absorption of the solutions was stable for at least three hours.

DISCUSSION

The spectra recorded indicate three moles of alkyl phosphite to one of cacotheline are required to develop the full colour. The reduction of cacotheline to its lilac product involves the addition of two hydrogen atoms to the reagent[6] and is the usual reduction product obtained. However a red colouration has been reported to be produced by the action of stannous chloride on the oxime of cacotheline[7].

The polarographic results confirm the spectrophotometric determinations in that the response at —0.40 V which is affected by the presence of dialkyl phosphite requires three times the molarity of cacotheline present before it is eliminated. By comparison with the collected data[8] this response is likely to be due to the quinone group whilst from the height and position the wave at —0.65 V to be due to the nitro-group which is not affected by the dialkyl phosphite. In the case of the interaction of dialkyl phosphites with 3,5-dinitrobenzoic acid in sodium bicarbonate media the polarograms show responses at —0.5 V and —0.65 V which are concerned with the reduction of the nitro groups. The heights of the waves are not affected by the presence of the dialkyl phosphite but instead a pronounced polarographic maximum the height of which is dependent on the concentration of dialkyl phosphite, occurs on the wave at —0.65 V.

SUMMARY

The estimation of dialkyl phosphites by means of its colour reaction with cacotheline in sodium carbonate solution is described. The effect of dialkyl phosphite upon the spectrum and polarographic response of the reagent is discussed to reveal the stoichiometry of the reaction and the group involved in colour production.

RÉSUMÉ

Les phosphites de dialcoyle donnent une réaction colorée avec la cacothéline, dans une solution de carbonate de sodium. Une étude spectrophotométrique et polarographique de cette réaction a été effectuée.

ZUSAMMENFASSUNG

Dialkyl-phosphite geben mit Kakothelin gefärbte Reaktionsprodukte, die sich zur spektrophotometrischen und polarographischen Bestimmung der Dialkyl-phosphite verwenden lassen.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

IV. A COMPARISON OF THE BAKER AND MORRISON CELL WITH THE RAlE.

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In a previous paper[1] it was mentioned that BAKER AND MORRISON[2] introduced a simple cell for the rapid amperometric determination of traces of fluoride in solution. They used a straight piece of aluminum wire, 0.125 inch in diameter and 0.5 inch in exposed length as one electrode, and a 10 inch long and 0.03 inch diameter platinum spiral as the other electrode. The spontaneous current measured two min after short-circuiting the cell was found to be approximately proportional to the fluoride concentration in a solution 0.2 *M* in acetic acid or saturated with benzoic acid. It was stated that chloride causes serious interference at it yields a large current even in the absence of fluoride while in our recommended amperometric procedure[1] with the RAlE chloride does not interfere. It appeared of interest to compare the performance of the Baker and Morrison cell with that of the RAlE *vs.* the saturated calomel electrode (SCE) at an applied potential of —0.75 V and to investigate whether the interference by chloride (and other halides and also of perchlorate) in the Baker and Morrison cell cannot be eliminated by the choice of a simple reference electrode, the potential of which is considerably more negative than that of the platinum spiral in air-saturated solutions.

The solution in the Baker and Morrison cell is air-saturated, the platinum spiral being the positive electrode at which reduction of oxygen must occur when the cell

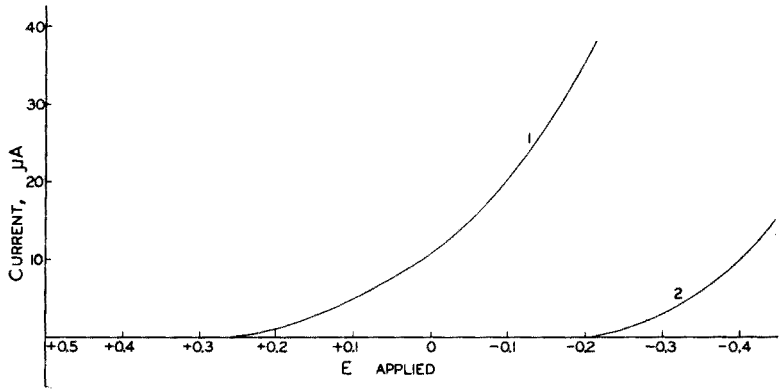

Fig. 1. Voltammograms at the platinum spiral *vs.* SCE in 0.2 *N* acetic acid. 1, saturated with air; 2, saturated with nitrogen.

yields a spontaneous current in the presence of fluoride. In order to establish the potential of the spiral under conditions when current flows, we have determined current–potential curves at this electrode in air-saturated 0.2 *N* acetic acid *vs.* the SCE. The platinum spiral was of the same dimensions as that used by Baker and Morrison. A voltammogram is illustrated by curve a in Fig. 1. Upon passage of a current of 10 μA the potential was about 0 V *vs.* SCE. It became more negative with increasing current and was of the order of —0.2 V with a current of 35 μA. When such a platinum spiral is short-circuited against an aluminum electrode in an air-saturated 0.2 *N* acetic acid solution which contains some fluoride, the aluminum electrode nearly adopts the potential of the platinum electrode. In a previous publication[3] it was shown that chloride and the other halides and also perchlorate depolarize the aluminum electrode when its potential becomes less negative than about —0.6 V (*vs.* SCE). Thus these ions must interfere with the fluoride determination in the Baker and Morrison cell while they do not interfere at a potential of —0.75 V. Curve 2 in Fig. 1 gives a voltammogram in 0.2 *N* acetic acid in the absence of oxygen. When oxygen is removed from the Baker and Morrison cell, fluoride still produces a large current. Again the platinum spiral was found to be the positive electrode at which reduction of hydrogen ions occurs upon passages of current. When this current is small, the potential of the platinum electrode is of the order of 0.4 V more negative than in air-saturated solutions. At the potential in nitrogen the interference by chloride and perchlorate is considerably less than at a potential of about 0 V (*vs.* SCE)[3], but these ions still have some depolarizing effect on the aluminum electrode at a potential of about —0.4 V (*vs.* SCE).

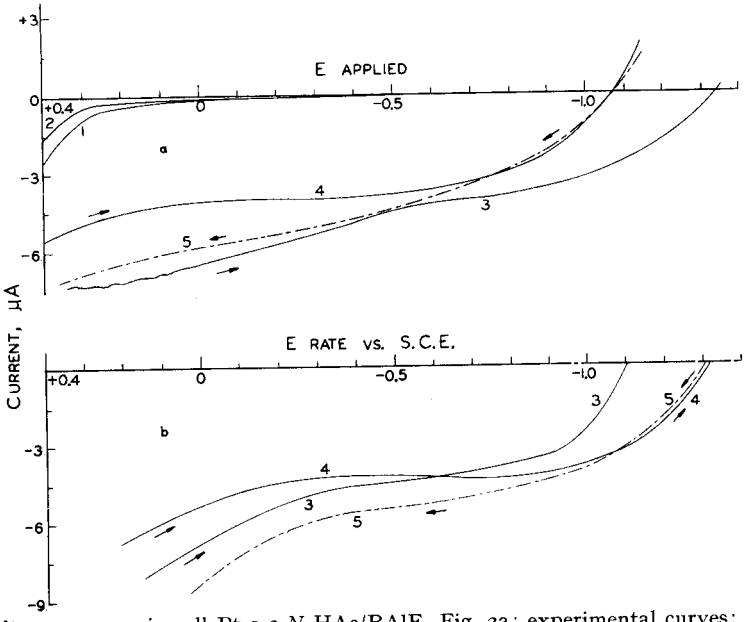

Fig. 2. Voltammograms in cell Pt 0.2 *N* HAc/RAlE. Fig. 2a: experimental curves; 1 and 2 no fluoride; 1, saturated with air; 2 in nitrogen; 3, 4 and 5 in $1 \cdot 10^{-4}$ *M* fluoride; 3, saturated with air; 4 and 5 in nitrogen. All run from + to — potentials except 5 in reverse direction (←). Fig. 2b: curves of Fig. 2a using the calculated potentials of RAlE *vs.* SCE as abscissa.

In order to substantiate the above conclusions several voltammograms were run in 0.2 *N* acetic acid using the RAlE *vs.* the platinum spiral as the electrode couple. As is to be expected hardly any current flows in the absence of fluoride over a wide range of potentials (from +0.5 to —1.5 V) as the two electrodes are highly polarized both in the presence and absence of oxygen (see Fig. 2a).

Curves 3, 4 and 5 are voltammograms of $1 \cdot 10^{-4}$ *M* fluoride in 0.2 *N* acetic acid in air (curve 3) and in nitrogen. The current in nitrogen is much better defined and smaller when run from positive to negative potentials (curve 4) than in the reverse direction. Qualitatively the same behavior was found in oxygen. Undoubtedly the reason is that the steady current value at a given potential cannot be registered by the polarograph when the applied potential is varied continuously with a reasonable speed. At a given potential the current, after rapidly attaining a large maximum value decreases to attain a steady value after about 40 sec in nitrogen and 70 sec in oxygen (see Fig. 3). The pattern of the curve of the residual current (in oxygen) is similar (curve 3, Fig. 3), but the current does not attain a steady value until after about 4 min.

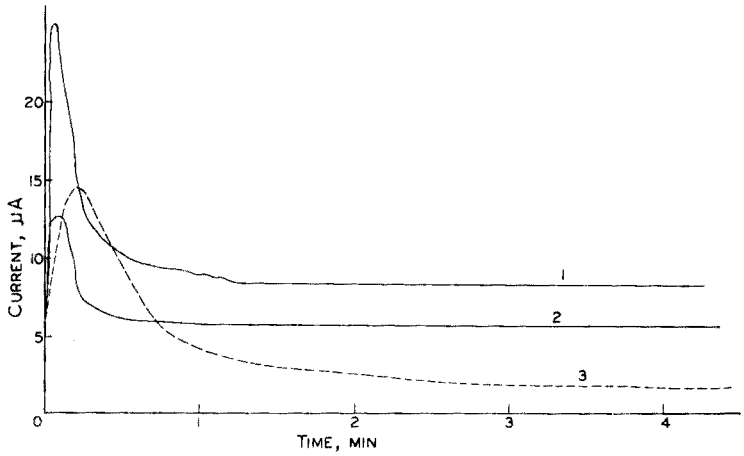

Fig. 3. Current–time curves in short-circuited cell Pt/0.2 *N* HAc/RAlE in the presence of $1 \cdot 10^{-4}$ *M* fluoride. 1, in air-saturated solution; 2, in nitrogen; 3 (dotted line) residual current in air (no fluoride).

In Fig. 2a the applied voltage is plotted on the abscissa. The current–potential curves plotted in oxygen and nitrogen can not be compared directly, because the potentials of both electrodes at a given applied voltage are quite different in oxygen than in nitrogen. For an intelligent understanding of Fig. 2a the potential of the RAlE *vs.* the SCE should be plotted instead of the applied e.m.f. If this is not done, the impression would be obtained from Fig. 2a that at zero current the aluminum electrode in air-saturated solutions is considerably more negative (—1.34 V) than in the absence of oxygen (—1.07 V). Actually, at zero applied voltage the potential of the platinum spiral was +0.24 V *vs.* the SCE and thus the potential of the RAlE becomes —1.1 V *vs.* SCE, while in nitrogen the potential of the platinum electrode was —0.24 V *vs.* SCE and the potential of the RAlE becomes —1.31 V *vs.* SCE. When current passes the potentials of the platinum electrode in oxygen and nitrogen become different

from the zero-current potentials as is evident from Fig. 1. When (with the aid of data in Fig. 1) correction is made in Fig. 2a for the potential of the platinum electrode upon passage of current, curves are obtained as illustrated in Fig. 2b in which the abscissa now refers to the potential of the RAlE *vs.* SCE. As is to be expected, these curves are now very similar to voltammograms presented in previous publications.

When the cell was short-circuited ($E_{applied} = 0$ in Fig. 2a) the potential of the RAlE was —0.5 V (SCE) in oxygen and —0.41 V in nitrogen. As is to be expected from previous publications[1,3] the anodic depolarization of the RAlE by perchlorates and halides should be much greater at the potentials in oxygen than in nitrogen. This was actually observed and an example of such a depolarization by perchlorate is presented in Fig. 4.

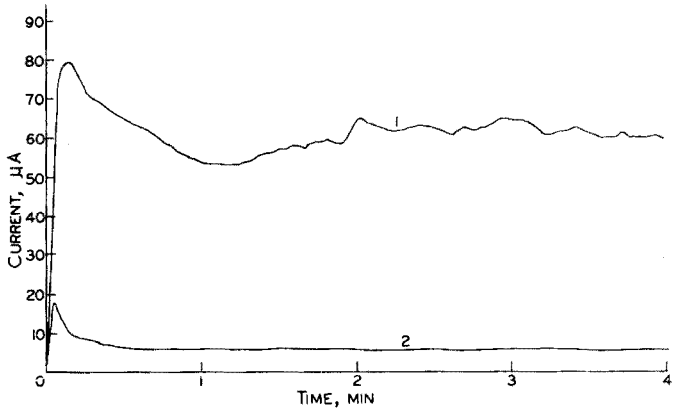

Fig. 4. Current–time curves in short-circuit cell Pt/0.2 *N* HAc + $2 \cdot 10^{-3}$ *M* $NaClO_4$/RAlE. 1, in air-saturated solution; 2, in nitrogen.

In order to check the accuracy and precision with the Baker and Morrison cell we have made experiments using an aluminum electrode of the same dimensions as recommended by these authors and following their directions. A 20-ml beaker was used as an electrolysis cell and the two electrodes were always placed at a distance of 2.6 cm of each other. Ten ml of solution was introduced into the cell and the contents stirred using a magnetic stirrer. Before each run the aluminum electrode was kept in 0.01 *N* hydrofluoric acid solution for 2 min. The reproducibility of residual currents and of fluoride currents in the measurement of current–time curves was found to be unsatisfactory in 0.2 *N* AcH. This could be attributed to a heating of the solution by the motor of the stirrer which became increasingly hot. Placing the beaker on a thick asbestos plate eliminated this interference. BAKER AND MORRISON[2] carried out most of their experiments in air-saturated 0.2 *N* acetic acid, but mention that a saturated benzoic acid solution is preferable when traces of fluoride (concentration of the order of 10^{-5} *M*) are to be determined. Indeed, we could confirm that the residual current is considerably smaller and better reproducible in saturated benzoic acid solution than in 0.2 *N* acetic acid. This is illustrated in Fig. 5.

After a short circuit of 2 min the current in 0.2 *N* acetic acid varied in 6 experiments between 15 and 22 μA after 2 min and between 8 and 14 μA after 5 min. In saturated

benzoic acid solutions the current varied between 8.5 and 10 μA after 2 min and 4 and 6 μA after 5 min. BAKER AND MORRISON measure the fluoride current after an electrolysis time of 2 min. Since this current must be corrected for the residual current a saturated benzoic acid solution would be preferable as a supporting electrolyte.

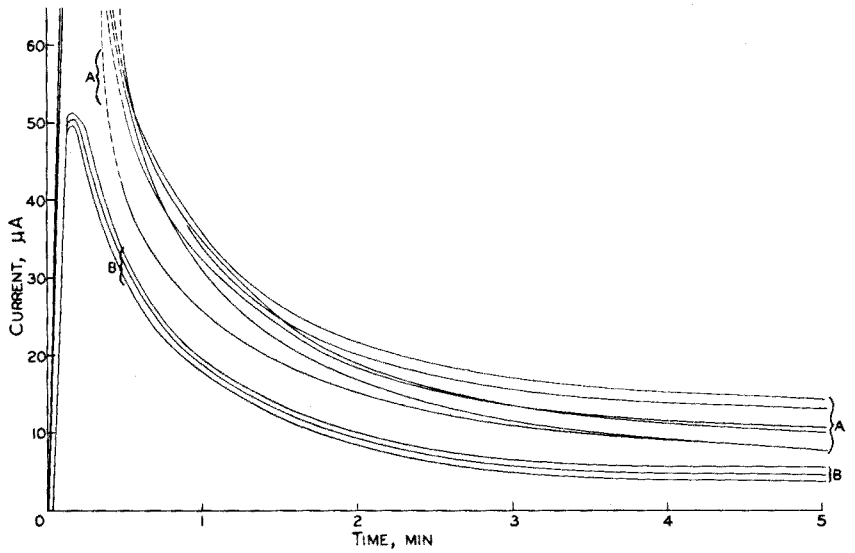

Fig. 5. Reproducibility of current–time curves of the residual currents. A, in 0.2 N acetic acid; B, in saturated benzoic acid; all air-saturated.

In agreement with BAKER AND MORRISON we find that upon short-circuiting the cell the residual current rapidly increases to a maximum value and then decreases. The same pattern is observed in a fluoride solution. However, when fluoride was added to the solutions after the cell had been short-circuited for five minutes and the residual current had become practically constant, the fluoride current increased rapidly, but the current–time curve did not exhibit an acute maximum. The behavior is illustrated in Fig. 6. The above behavior must be considered in the construction of a calibration curve and in the determination of fluoride in an unknown.

The method of BAKER AND MORRISON might find more general application if it were possible to eliminate the interference of some anions, particularly of chloride which yields a large current. The interference by halides and perchlorate in the Baker and Morrison method has been accounted for by the relatively large positive potential of the platinum electrode in an air-saturated solution. In our procedure with the RAlE the interference is eliminated by applying a potential of —0.75 V (*vs.* SCE). Using the Baker and Morrison method, but removing the oxygen with nitrogen, greatly improved the situation but did not eliminate the interference by chloride. This was to be expected since under these conditions the potential of the platinum electrode upon passage of spontaneous current was not negative enough to completely prevent depolarization of the aluminum electrode by chloride.

In the following experiments the supporting electrolyte was composed of 0.2 N acetic acid plus 0.02 M sodium acetate. From a practical point of view the use of a

well-buffered solution is to be preferred over the slightly buffered 0.2 N acetic acid or a saturated benzoic acid solution in water. Using a prismatic rod of 99.9% pure lead, 1.25 cm long with an exposed surface of 0.8 cm^2 constant values of the residual current and of the fluoride current were attained after short-circuiting for 30 sec against the

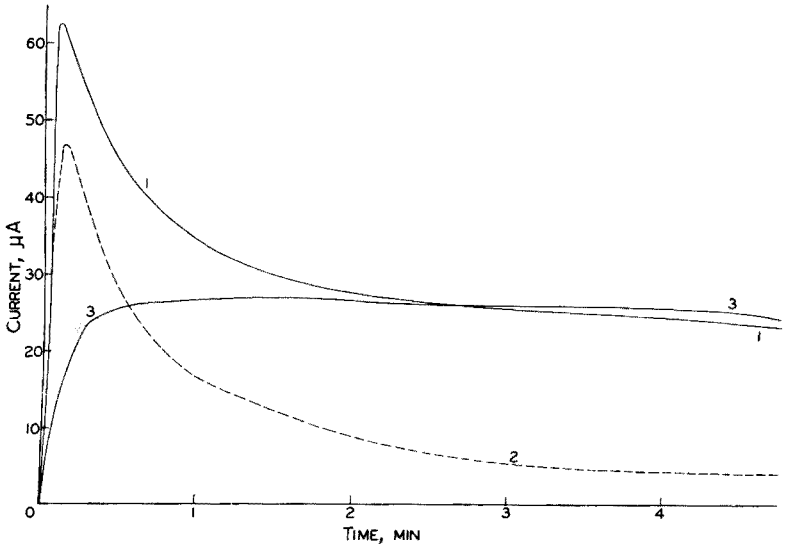

Fig. 6. Current–time curves (Baker and Morrison cell) in saturated benzoic acid. 1, clean electrode in $1.96 \cdot 10^{-5}$ M fluoride; 2, (dotted line) residual current (no fluoride); 3, $1.96 \cdot 10^{-5}$ M fluoride added after residual current had become constant.

RAlE. Both in air-saturated solutions and in the absence of oxygen proportionality was found between fluoride concentration (in the range between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ M) and current. Whereas the potential of the platinum spiral in oxygen is considerably more positive than in nitrogen, the difference of the lead potential in both media is very small. Upon short-circuiting with the RAlE the lead potential was found to be —0.50 V in air-saturated solutions and —0.54 V (*vs.* SCE) in the absence of oxygen. About the same values were found both in the presence and absence of fluoride. The potential of the lead electrode is not negative enough to completely eliminate interference by chloride. After studying various other electrodes we finally selected a cadmium amalgam electrode, five percent in cadmium, in a suitable electrolyte. The following half-cells with 5% cadmium amalgam were prepared and their potentials (*vs.* SCE) measured at 25°: saturated with cadmium sulfate —0.605 V; 1 M in cadmium sulfate —0.632 V, 1 M in cadmium sulfate and saturated with potassium chloride —0.715 V; 1 M in cadmium sulfate and saturated with potassium bromide —0.770 V. As is to be expected these potentials are hardly altered upon passage of small currents. The last two electrodes should be suitable for our purpose, and we selected the half cell saturated with potassium chloride. The preparation of such a half cell is extremely simple and can be done quickly. A wide-mouthed bottle was used as the container and electrolytic contact made with the solution in the beaker containing either the RAlE or the Baker and Morrison electrode by means of a glass

U tube filled with a saturated potassium nitrate solution which was solidified with agar. Experiments with the RAlE were carried out with 50 ml solution, both in the presence and absence of oxygen. With the Baker and Morrison electrode we used a beaker of 20 ml, a volume of solution of 10 ml, while the solution was stirred with a magnetic stirrer (a thick asbestos plate prevented heating of the solution). All experiments were carried out in a buffer which was 0.2 *M* in acetic acid and 0.02 *M* in sodium acetate (pH 3.6). In a nitrogen atmosphere the response of the RAlE was found the same as described in a previous paper. Instead of applying a potential of —0.75 V *vs.* the SCE the cadmium half cell can be used in a short-circuited cell. In a previous paper[4] it was stated that in air-saturated solutions the fluoride current (at —0.75 V) is less than in a nitrogen atmosphere, but the effect of oxygen at different fluoride concentrations was not investigated. Studying this effect with the present cell linear proportionality between fluoride concentration and current (corrected for the residual) was found in a range between $1 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ *M* fluoride, but the proportionality constant in air was found 30% smaller than in nitrogen. The residual current (which varies somewhat from day to day) in air was 0.2 to 0.3 μA (cathodic) and changed to 0.4 to 0.5 μA (cathodic) after short circuiting for 10 min. This final constant value must be added as a correction to the anodic fluoride currents. On the other hand, in nitrogen the residual current was anodic and its value after 5 min became constant and equal to 0.3 to 0.4 μA. It is preferred to carry out the fluoride determination in nitrogen. After applying the proper correction for the residual current constant values of i/c of 0.56 $\pm$ 0.01 per micromole per l were found in nitrogen over a concentration range between $1 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ *M*. In air-saturated solutions i/c became equal to 0.42 $\pm$ 0.02 over the same concentration range. The lower fluoride current in the presence of oxygen has been attributed[1] to an electroreduction of oxygen at the RAlE in the presence of fluoride which results in a decrease of the anodic fluoride current. It is surprising and unexpected that i/c remains constant in the presence of oxygen. This must mean that at the RAlE the cathodic oxygen current increases in proportion to the concentration of fluoride present.

Using the standard addition method 0.01 *M* chloride or perchlorate were found not to interfere either in nitrogen or in oxygen. However, in the presence of 0.01 *M* chloride the residual current after 5 min (when it became constant) was 0.8 μA (cathodic) in air-saturated solutions, while it was 0.4 μA (cathodic) in the absence of chloride. In a nitrogen atmosphere the presence of 0.02 *M* chloride did not affect the residual current. In the presence of 0.005 *M* chloride in air-saturated solutions the same results were obtained as described above in the absence of chloride, provided proper correction for the residual current was made.

Using the Baker and Morrison electrode in a volume of 10 ml with magnetic stirring, the residual current in nitrogen was found constant after 1 min and equal to only 0.5 to 1.0 μA (anodic) and unaffected by the presence of 0.01 *M* chloride. In air-saturated solutions the residual current was cathodic and increased from 1.0 μA after one minute to 3–4 μA after 2 to 3 min. The presence of 0.01 *M* chloride did not affect these values; however, the automatically recorded current–time curves exhibited irregular oscillations of the current in the presence of chloride.

Fluoride currents remained reasonably constant when measured between 1.5 and 3.5 min after short-circuiting the cell. In nitrogen i/c was found constant and equal to 5.5 $\pm$ 0.2 (per micromole per l) over the concentration range between $1 \cdot 10^{-5}$ and

$1 \cdot 10^{-4}$ *M* fluoride. The concentration in an unknown can be estimated by the standard addition method[1].

In air-saturated solutions a large correction must be applied for the residual (cathodic) current and no satisfactory constant value of i/c was found. For example, the following values of i/c were observed: 4.5 in $1 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$ *M* fluoride, 4.1 in $4 \cdot 10^{-5}$ *M*, 3.7 in $5.7 \cdot 10^{-4}$ an 2.9 in $7.4 \cdot 10^{-5}$ *M* fluoride.

In the presence of 0.0005 *M* chloride and in a nitrogen atmosphere the (anodic) residual current was 1 to 1.5 μA after 3 to 5 min and the value of i/c was the same as in the absence of chloride. In air-saturated solutions in the presence of 0.005 *M* chloride the residual current was the same as in the absence of chloride. However, periodic oscillations in the residual current and the fluoride current were observed. Again no linear proportionality between fluoride concentration and current was found. Thus the Baker and Morrison electrode short-circuited with the cadmium half cell is suitable for fluoride determinations when oxygen is removed from the solution. Using the RAlE removal of oxygen is recommended but not necessary.

In a previous paper[1] it was not stated that the RAlE, when not in use was kept in 0.01 *M* EDTA solution. When it was kept dry at the air the electrode became covered with a layer of oxide which could be removed by placing it in 0.01 *M* fluoride[2]. Similar observations were made with the Baker and Morrison electrode.

ACKNOWLEDGEMENT

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SUMMARY

In the amperometric determination of fluoride at the RAlE a half cell composed of 5% cadmium amalgam in equilibrum with a solution 1 *M* in cadmium sulfate and saturated with potassium chloride can be used as a reference electrode in a short-circuited cell instead of applying a potential of —0.75 V *versus* the saturated calomel electrode. The standard addition method can be used in the presence of air, although removal of oxygen is recommended. Using the Baker and Morrison electrode *versus* the above half cell and following their directions (10 ml solution, magnetic stirring) proportionality between current and fluoride concentration in a range between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ *M* was found in oxygen-free solutions. Halides and perchlorates do not interfere. The standard addition technique can be used in the determination of fluoride in an unknown.

RÉSUMÉ

Lors de leurs travaux sur l'emploi de l'électrode rotative en aluminium, en ampérométrie, les auteurs ont effectué une étude comparative entre cette dernière et l'électrode de BAKER ET MORRISON. Cette technique peut être utilisée pour le dosage des fluorures.

ZUSAMMENFASSUNG

An Hand von Studien über die Anwendung der rotierenden Aluminiumelektrode in der Amperometrie wird diese Elektrode im Vergleich mit der Elektrode von BAKER UND MORRISON betrachtet. Diese Methode eignet sich für die Bestimmung von Fluoriden.

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DETERMINATION OF SUBMICROGRAM QUANTITIES OF RUTHENIUM BY CATALYSIS OF THE CERIUM(IV)–ARSENIC(III) REACTION

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It has already been shown that amounts of osmium in the range 0.005–0.5 μg can be determined by the catalysis of the reaction

$$As(III) + 2\ Ce(IV) \rightarrow As(V) + 2\ Ce(III)$$

in sulfuric acid solution[1]. Even smaller amounts of ruthenium can be determined in the same way. The rate of the catalyzed reaction is conveniently determined spectrophotometrically by measuring the cerium(IV) concentration as a function of the time. A catalytic method is not likely to be of much value in practice unless the constituent being determined can be effectively separated from all the other constituents of the sample. The present paper, therefore, also deals with the separation of ruthenium as a necessary preliminary to the utilization of the method.

The catalytic method is intended for amounts of ruthenium that cannot be determined colorimetrically or by other methods (except such ultra-sensitive methods as neutron activation). There is no advantage in applying it when a colorimetric method can be used, since it is less convenient to carry out than the latter method. In general, the catalytic method will be of value for samples containing less than 1 p.p.m. Ru, or for larger relative amounts when the weight of sample available is limited.

Characteristics of the ruthenium-catalyzed reaction

The rate of the ruthenium-catalyzed ceric–arsenite reaction in 2.0 M sulfuric acid at 25.0° is given by the expression

$$-\frac{d[Ce(IV)]}{dt} = \frac{4.0 \cdot 10^{10}[Ru]\,[Ce(IV)]^{2.5}}{1 + 2.1 \cdot 10^{3}[Ce(IV)]^{1.5}}$$

where t is in minutes and concentrations are in moles/l[2]. The rate is thus first order with respect to ruthenium but is a complex function of the cerium(IV) concentration*. The rate is independent of the arsenic(III), arsenic(V), and cerium(III) concentrations. Moreover, the sulfuric acid concentration in the range 0.5–2.0 M has little, if any, effect on the rate if the ionic strength is kept constant with sodium bisulfate. An increase in the ionic strength (addition of sodium perchlorate) increases the reaction rate slightly. Provided the ruthenium solution is first mixed with the ceric solution,

* In the osmium catalysis, the rate is determined by the arsenic(III), not the cerium(IV), concentration.

it is immaterial whether ruthenium is originally present in the +4 or +8 oxidation state. If ruthenium (as RuO_4) is first added to the arsenite solution, the reaction rate is decreased and, moreover, depends on the manner of mixing the solutions[2]. The mechanism of the catalysis has not been elucidated.

The preceding rate expression shows that the sensitivity of the catalytic ruthenium determination can be increased by increasing, within limits, the concentration of cerium(IV). Thus, with an initial Ce(IV) concentration of 0.04 N in the reaction mixture, the initial reaction rate is 5.5 times that with an initial Ce(IV) concentration of 0.01 N (Fig. 1). The optimum concentration is close to 0.04 N Ce(IV). A similar initial concentration of As(III) is suitable.

Determination of ruthenium in pure solution

In the absence of interfering substances, the determination of ruthenium is simply carried out by mixing the sample solution with ceric sulfate solution, allowing to stand for a few minutes if necessary to oxidize Ru(IV) to Ru(VIII), adding the mixture rapidly to arsenious oxide solution, and noting the time for the absorbance of the solution to decrease to some specified value. The absorbance is measured at a wave length that will allow the change in the concentration of cerium(IV) to be determined with adequate photometric precision. It is convenient to utilize a wave length at or near 488 mμ, which, under the conditions of the recommended procedure gives a transmittance of about 22% at zero time (1-cm cell). The time required for the transmittance to increase to 60% is noted. This interval, corresponding to the reduction of about 2/3 of the original amount of cerium(IV), is called the reaction time.

A plot of the reciprocal of the reaction time against the ruthenium concentration gives a straight line (Fig. 2). The equation for the ruthenium line in this figure is

$$\mathrm{Ru} = 0.0057(1/t - 0.0015),$$

where Ru is the concentration of ruthenium in p.p.m. (μg Ru per ml of solution) and t is in minutes. The value 0.0015 in this expression represents the correction to be made for the rate of the uncatalyzed reaction. In this particular case, the reaction time of the blank is about 670 min, corresponding to an apparent ruthenium concentration of $\sim 1 \cdot 10^{-5}$ μg Ru/ml. The blank reaction time sets the limit to the lowest concentration of ruthenium that can be detected or determined. With the blank mentioned, $1 \cdot 10^{-5}$ μg Ru/ml would be detectable and could be roughly determined. The limiting ruthenium concentration can then be set at $1 : 10^{11}$. The blank reaction is in part due to a very slow uncatalyzed reaction between As(III) and Ce(IV) and in part to catalysis by impurities (iodine?). Although iodine, osmium and ruthenium are the only elements strongly catalyzing the ceric–arsenite reaction, it is conceivable that other elements or combinations of elements could have very weak catalytic activities, which might partly account for the blank reaction. Different batches of ceric sulfate have been found to give different blank reaction times, pointing to the presence of catalyzing impurities. The blank reaction time mentioned is not exceptional, *i.e.* some reagents have been found to give even slower reactions.

Under the conditions of the procedure, a convenient range of concentrations is from $5 \cdot 10^{-3}$ μg Ru/ml (reaction time a little longer than a minute) to $5 \cdot 10^{-4}$ μg Ru/ml (12 min). Reaction times other than the time corresponding to reduction of

two-thirds of the cerium(IV) can, of course, be adopted and made the basis of a standard curve. Thus, in determining low concentrations of ruthenium, it may be more convenient to choose a reaction time corresponding to reduction of a smaller fraction of cerium(IV). Instead of measuring the time interval required for a given fraction of ceric sulfate to be reduced, the analyst can determine the amount which has been reduced at the end of some convenient fixed time interval such as 30 or 60 min. This procedure (which was not investigated in the present work) would be superior

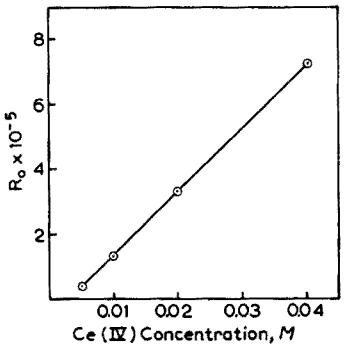

Fig. 1. Initial rate (R_0) of the ruthenium-catalyzed Ce(IV)–As(III) reaction as a function of the initial Ce(IV) concentration according to the rate equation in the text.

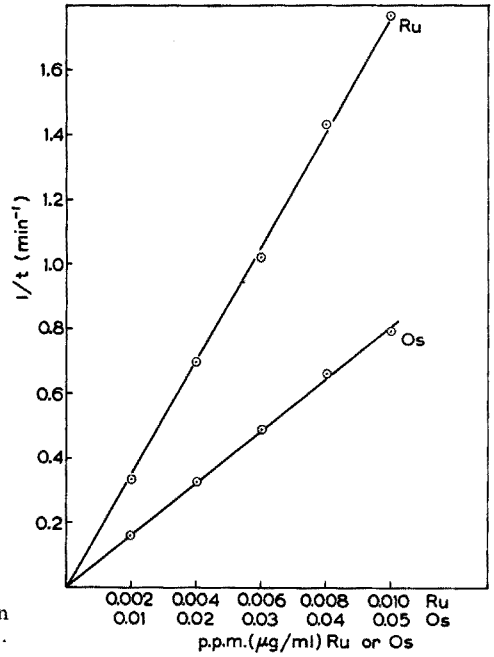

Fig. 2. Reciprocal of reaction time as a function of ruthenium and osmium concentration (25°).

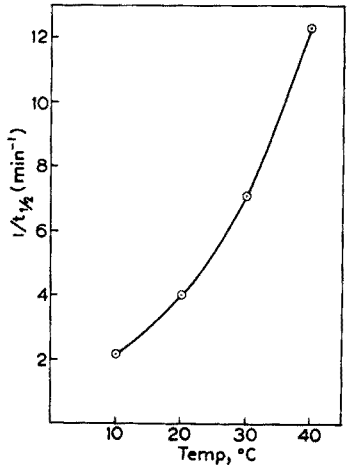

Fig. 3. Rate of ruthenium-catalyzed Ce(IV)–As(III) reaction as a function of the temperature. Rate is expressed as reciprocal of half-reaction time (0.02 *N* Ce(IV), 0.03 *N* As(III), 0.02 p.p.m. Ru).

for the lower ranges of ruthenium concentration. It would have the advantages of requiring less of the analyst's time and not requiring the use of a thermostated spectrophotometer; *i.e.*, the reaction mixture could be kept in a constant-temperature bath until shortly before the absorbance measurement. On the other hand, more work is needed to establish the standard curve, which is not linear.

As can be seen from Fig. 3, the temperature must be closely controlled in the catalytic determination. The reaction rate at 30° is 1.75 of that at 20°. A variation in temperature of 0.1° from 25.0° will cause an error of about 0.7%.

From the results in Table I it may be concluded that in pure solution, 0.005–0.1 μg Ru (in 2 ml) can be determined to within a few per cent, and 0.001 μg Ru to within 10%.

TABLE I

CATALYTIC DETERMINATION OF RUTHENIUM IN PURE SOLUTION[a]

Ru taken μg	*Ru found* μg		
0.0010	0.0011	0.0010	0.0010
0.0050	0.0049	0.0051	0.0049
0.0100	0.0098	0.0101	0.0098

[a] Two ml of Ru(IV) sulfate solution mixed with 1 ml of 0.160 *N* ceric ammonium sulfate solution and this solution added after 5 min to 1 ml of arsenious oxide solution.

Separation of ruthenium and subsequent determination

The volatility and extractability of ruthenium tetroxide offer the best means of isolating and separating ruthenium effectively from almost all elements. Extraction by an immiscible organic (non-oxygen) solvent is an attractive separation because final volumes can be kept small and ruthenium is obtained in an aqueous solution free from acids and other extraneous substances. Separation by extraction has therefore been adopted for use with the catalytic method. Carbon tetrachloride is a solvent providing a favorable extraction coefficient in neutral or acidic solutions[3]:

$$[RuO_4]_{CCl_4}/[RuO_4]_{H_2O} = 58.4 \quad (25°)$$

The chief problems in the extraction separation are the oxidation of ruthenium to the +8 state, the transfer of ruthenium from the carbon tetrachloride to an aqueous phase, and the elimination of osmium.

Because of the high oxidation potential of the Ru(IV)–RuO_4 couple ($E_0 \sim -1.4$ V), few oxidizing agents come into consideration for the oxidation to the tetroxide. Potassium peroxydisulfate and argentic oxide were tried. Quantitative oxidation could not be obtained with peroxydisulfate in the presence of ferric salt. Argentic oxide proved suitable (Tables II and III). The solution may be 2 to 5 *M* in nitric acid or 0.5 to 2 *M* in sulfuric acid. When a sulfuric acid medium is used, it is best to dissolve the argentic oxide in nitric acid before addition, since it dissolves only slowly in sulfuric acid. The oxidation of ruthenium(IV) to the tetroxide is complete within 5 min at room temperature.

The transfer of ruthenium from the carbon tetrachloride extract to an aqueous phase is not as easy as with osmium tetroxide. Arsenious oxide solution, which is very suitable for osmium tetroxide, cannot be used because ruthenium is reduced to forms which do not have full catalytic activity. Sulfurous acid, as an acidified sodium sulfite

TABLE II

DETERMINATION OF RUTHENIUM AFTER SILVER(II) OXIDATION AND EXTRACTION WITH CARBON TETRACHLORIDE[a]

Concn. H_2SO_4 *M*	*Ru taken* *μg*	*Ru found* *μg*		
2	0.0010[b]	0.0010	0.0011	
2	0.0100[b]	0.0105	0.0090	
2	0.100[b]	0.099	0.098	0.101
0.5	0.100	0.097		
1.0	0.100	0.098		
2.0	—	0.00035		
2.0	0.0010	0.0012		
2.0	0.0050	0.0053		
2.0	0.010	0.0092	0.0094	
2.0	0.050	0.0495	0.0484	
2.0	0.100	0.096	0.099	(0.087)
3.0	0.100	0.095		

[a] Fifty ml Ru(IV) solution treated with silver(II) oxide dissolved in nitric acid, RuO_4 extracted with three 10-ml portions of carbon tetrachloride, the combined extracts shaken for 2 h with 10 ml of 0.005 *N* H_2SO_3 in 2 *M* sulfuric acid and Ru determined catalytically in the aqueous solution.
[b] Ru added as RuO_4 and oxidation step omitted.

TABLE III

DETERMINATION OF RUTHENIUM IN PRESENCE OF IRON AFTER SILVER(II) OXIDATION AND CARBON TETRACHLORIDE EXTRACTION[a]

Ru taken *μg*	*Ru found* *μg*		
—	0.00012		
0.00100	0.0012		
0.0100	0.0101	0.0100	
0.0500	0.0519	0.0508	
0.100	0.096	0.097	0.095

[a] 0.5 g iron as ferric sulfate in each determination.

solution, was found to be satisfactory for reducing and returning ruthenium to the aqueous phase, although slow in action. When 30 ml of carbon tetrachloride containing 0.10 μg of ruthenium as the tetroxide was shaken with 20 ml of 0.005 *N* sulfurous acid at 250 cycles per min, 83% of the ruthenium was transferred to the aqueous phase in the first 30 min. Two hours of mechanical shaking are needed for essentially complete transfer of ruthenium from the carbon tetrachloride to the aqueous phase.

Separation of ruthenium and osmium

The separation of these elements from each other is based on the difference in the ease of their oxidizability to the tetroxides. Two procedures were studied:

1. *Ferrous sulfate reduction–nitric acid oxidation:* This procedure has already been applied in the catalytic method for osmium[1]. When a slight excess of ferrous ion is added to a solution containing osmium in the +8 state and ruthenium wholly or partly in this state, ruthenium(VIII) is quickly reduced to lower oxidation states which are not converted to the tetroxide on subsequent addition of nitric acid to 5–6 *M* concentration, whereas osmium(VIII) is only slowly reduced, and the small

part that is reduced is restored to the tetroxide by the added nitric acid. Osmium tetroxide can then be extracted with carbon tetrachloride; ruthenium is left in the aqueous phase. The success of this method depends on the reduction of only a small fraction of the osmium(VIII), which means that the nitric acid must be added soon (within a few minutes) after the ferrous salt. If much osmium(VIII) is reduced, quantitative reoxidation is difficult, as shown elsewhere[4].

TABLE IV

DETERMINATION OF OSMIUM AND RUTHENIUM BY CATALYSIS AFTER SEPARATION BY $FeSO_4$–HNO_3–CCl_4 METHOD[a]

Ru taken μg	*Os taken* μg	*Ru found* μg	*Os found* μg
	0.100		0.095 0.093
	0.50		0.50
0.100	0.100	0.096	0.095
0.100	0.100	0.099	0.096
0.100	1.00	0.097	0.99

[a] Solution of Ru(IV) and Os(IV) in 35 ml of 2 *M* sulfuric acid treated with 0.1 *N* potassium permanganate to appearance of pink color, which was discharged with a slight excess of ferrous ammonium sulfate solution. Conc. nitric acid (15 ml) added and OsO_4 extracted with four 10-ml portions of carbon tetrachloride. Ruthenium extracted with three portions of carbon tetrachloride after Ag(II) nitrate oxidation.

The separation of osmium by extraction is especially advantageous when both osmium and ruthenium are to be determined (Table IV). The separation of osmium in this way becomes less easy when the ratio Os/Ru exceeds $\sim$ 100, because of the large number of extractions needed for the satisfactory removal of osmium. For example, if 50 ml of aqueous solution is extracted with four 10-ml portions of carbon tetrachloride, 99.6% of the osmium will be removed if the extraction coefficient is 15 (it is 14.8 in a solution of 1 *M* ionic strength). Accordingly, if the original amount of osmium is 100 μg, 0.4 μg will be left in the aqueous phase after the four extractions. Since, weight for weight, the catalytic activity of osmium is about 1/11 that of ruthenium under the recommended conditions for the determination of the latter (Fig. 2), this amount of residual osmium corresponds to about 0.04 μg Ru. With 1 μg Ru, the error due to osmium would then be +4%.

2. *Boiling with hydrogen peroxide:* When a sulfuric acid solution of osmium(IV or VIII) is boiled with hydrogen peroxide, osmium tetroxide is volatilized. Under the same conditions ruthenium(VIII) is reduced to the +3 or +4 state and is not volatilized[5]. The results in Table V indicate that osmium can be separated fairly satisfactorily from ruthenium in this way. Even at an Os/Ru ratio of 1000 (100 μg Os, 0.1 μg Ru), the error is within 10% on the average. There may be some compensation of errors, a little osmium apparently tending to remain in the aqueous phase.

As may be seen from Table V, the other platinum metals and much ferric iron and nickel do not interfere with the determination of ruthenium. Chloride can be removed by evaporating and fuming the sample with sulfuric acid. As much as 0.1 mg of iodine as iodide has no effect when separations are made as described.

Reagents

Arsenious oxide, 0.160 *N*: Dissolve 7.91 g of analytical reagent As_2O_3 in 25 ml of 1 *N* sodium hydroxide, dilute to about 200 ml with redistilled water, and add dilute sulfuric acid until acidic

TABLE V

DETERMINATION OF RUTHENIUM IN THE PRESENCE OF OSMIUM AND OTHER FOREIGN ELEMENTS[a]

Addition	*Ru taken* μg	*Ru found* μg		
—	0.0100	0.0095	0.0100	
—	0.100	0.098	0.100	
100 μg Os	—	0.006	0.004	0.003
100 μg Os	0.100	0.093	0.087	
[b]	—	0.0003		
[b]	0.005	0.006		
[b]	0.100	0.096	0.097	
10 μg Os[b]	0.005	0.006		
100 μg Os[b]	0.010	0.010	0.011	
100 μg Os[b]	0.100	0.087	0.093	
100 μg Os, 1 ml 6 *N* HCl[b]	0.100	0.096	0.097	0.090
100 μg I^- [b]	0.100	0.093	0.092	
100 μg Os, 100 μg I^- [b]	0.100	0.094		

[a] Ag_2O_2 oxidation and CCl_4 extraction of RuO_4 after removal of Os by boiling with hydrogen peroxide.
[b] 0.5 g Fe(III), 0.1 g Ni and 100 μg each of Pt, Pd, Rh and Ir present. Fumed with sulfuric acid.

to litmus paper. Then dilute to 1 l in a volumetric flask after adding enough sulfuric acid to make the final concentration 2.0 *M*.

Ceric ammonium sulfate, 0.16 *N* in 2.0 *M* sulfuric acid: Dissolve 101 g of the dihydrate in dilute sulfuric acid and dilute to 1 l. It is advisable to check the oxidizing normality of the solution by standardization against the arsenious oxide solution, with ferrous 1,10-phenanthroline complex as indicator and osmium tetroxide as catalyst, according to the usual procedure. A variation of a few per cent in strength from 0.160 *N* is of no importance. The solution should preferably be allowed to stand for a week and any precipitate filtered off before standardizing.

Standard ruthenium solution: Prepare a stock solution of ruthenium(III or IV) sulfate of convenient strength, *e.g.* 1 to 2 mg Ru per ml, in 2 *M* sulfuric acid (*cf.* Note 1). Standardize by precipitating hydrous ruthenium oxide at pH 6 with sodium bicarbonate and igniting to ruthenium metal in hydrogen according to the usual procedure. Dilute the stock ruthenium solution stepwise with 2 *M* sulfuric acid to obtain solutions of convenient ruthenium concentration, *e.g.* 0.01 μg Ru/ml.

Carbon tetrachloride: Shake a reagent quality product with 0.1 *N* potassium permanganate for several hours. Separate the phases and shake the carbon tetrachloride with several portions of concentrated sulfuric acid and wash with water. Saturate the carbon tetrachloride with chlorine and reflux for a few hours. Remove chlorine by shaking with several portions of 2 *M* potassium hydroxide. Wash the carbon tetrachloride with water until neutral to litmus paper, dry with anhydrone, and distil. Store in the dark.

Silver(II) oxide: This can be obtained by adding a solution of potassium peroxydisulfate, which has been made strongly basic with potassium hydroxide, to a boiling solution of silver nitrate, boiling until oxygen evolution ceases, filtering and washing the precipitate with hot water[6].

Procedure

The sample solution may conveniently contain 0.005–0.1 μg Ru. If halides are present add 5 ml of 1 : 1 sulfuric acid, evaporate to fumes, and continue fuming lightly to moderately for 30–60 min. Especially if much solid separates, it is well to take up the residue in water after fuming for one-half hour and again evaporate and fume to assure elimination of halides. Strong oxidizing agents such as nitric acid which could lead to loss of ruthenium tetroxide must be destroyed, as by evaporation with conc. hydrochloric acid. If osmium is to be determined simultaneously, ferrous sulfate must be added to prevent loss of osmium tetroxide on fuming.

Separation of osmium. If the weight ratio Os/Ru does not exceed 50–100, proceed according to (a), otherwise, in general, by (b):

(a) Carbon tetrachloride extraction of osmium tetroxide. Make the sample solution approximately 2 *M* in sulfuric acid. If the solution was evaporated to fuming, dilute to roughly this acidity. The final volume of the solution should not be greater than about 40 ml for the volume of carbon tetrachloride specified below.

To the cold solution add 0.1 *N* (or stronger if necessary) potassium permanganate with mixing until the solution just becomes pink. After 2 or 3 min destroy the excess permanganate by adding 50 mg of ferrous ammonium sulfate hexahydrate dissolved in a milliliter or two of water and mix well. Within a minute or two add 15 ml of conc. nitric acid (or more as necessary to make its concentration 5 to 6 *M*).

Extract osmium tetroxide from the cold solution with four 10-ml portions of carbon tetrachloride, shaking vigorously for one-half minute each time. Discard the carbon tetrachloride extracts unless osmium is to be determined also[1].

(b) Elimination of osmium by boiling with hydrogen peroxide. Dilute the fumed solution to 100 ml with water (0.5–1 *M* in sulfuric acid). Add a few drops of 30% hydrogen peroxide or more (1–2 ml) if ferrous iron is present. Boil in a beaker, with protection against mechanical loss, until the volume is reduced to one-half. Repeat the evaporation twice after restoring the volume with water and adding more hydrogen peroxide.

Oxidation and extraction of ruthenium. Add 0.5 g argentic oxide to the cold solution from which osmium has been removed and stir to dissolve. (In the absence of nitric acid — removal of osmium tetroxide by boiling — dissolve the argentic oxide in a little 5 *M* nitric acid and add this to the solution). Allow to stand 10 min at room temperature. Extract ruthenium tetroxide with three 10-ml portions of carbon tetrachloride. Shake the combined carbon tetrachloride extracts with 5 ml of 2 *M* sulfuric acid containing a little argentic oxide and discard the aqueous phase. The phases must be carefully separated.

Shake the carbon tetrachloride extract in a mechanical shaker for 2 h with 10.0 ml of 2.0 *M* sulfuric acid to which 3.2 mg of Na_2SO_3 has been added. If necessary clarify the aqueous layer by centrifuging, separate the phases, and discard the carbon tetrachloride.

Determination of ruthenium. Bring the aqueous solution to 25.0° and introduce a 2.00-ml aliquot and 1 ml of ceric ammonium sulfate solution into a hypodermic syringe (see Note 3). Thermostat the loaded syringe for 10 min. Then inject the solution as rapidly as possible into 1.00 ml of arsenious oxide solution (25.0°) in a 20-ml beaker. Start a stop watch or chart driving motor simultaneously with the mixing. Transfer the solution to a dry 1-cm cell, thermostated at 25.0°, and obtain the time required for a transmittance of 60% (against water) to be reached at 488 mμ (Note 4).

Establish the standard curve by taking 2.00-ml portions of Ru(III or IV) sulfate (0.001–0.02 μg Ru) in 2 *M* sulfuric acid and proceeding as above. Plot the reciprocal of the reaction time against the ruthenium concentration.

Notes: 1. It may be possible to prepare ruthenium sulfate by long-continued fuming of ruthenium chloride or ammonium chlororuthenate with sulfuric acid. The last traces of chloride are difficult to expel however.

2. A standard ruthenium(IV) sulfate solution in 2 *M* sulfuric acid containing 0.01 μg Ru per ml has been found to show no apparent change in concentration in a year's time.

3. Instead of a syringe, a small beaker can be used, with addition of the sample and

ceric mixture at one stroke to the arsenic solution, followed by return of the mixture to the first beaker and then to the absorption cell.

4. The transmittance of a mixture of 1 ml each of ceric ammonium sulfate and arsenious oxide solutions and 2 ml of water should be approximately 22%.

5. When the concentration of ruthenium is low, it may be advantageous to measure the reaction rate by finding the amount of cerium(IV) reduced in a fixed time interval, as mentioned in the text.

SUMMARY

Ruthenium in amounts of 0.005–0.1 μg (and less if need be) can be determined by its catalysis of the slow reaction between cerium(IV) and arsenic(III) in sulfuric acid solution. The rate of the catalyzed reaction is obtained by measuring the concentration of cerium(IV) spectrophotometrically as a function of the time. Ruthenium is first separated by carbon tetrachloride extraction of the tetroxide, following argentic oxide oxidation. Osmium tetroxide is removed by prior extraction with carbon tetrachloride after differential oxidation with nitric acid. Osmium can also be removed by boiling an acid solution with hydrogen peroxide, ruthenium being left in solution.

RÉSUMÉ

Il est possible de doser des teneurs en ruthénium de 0.005–0.1 μg grâce à son action catalysante sur la réaction lente entre le cérium(IV) et l'arsenic(III), en solution sulfurique. On effectue la détermination en mesurant spectrophotométriquement les variations de la concentration en cérium(IV) en fonction du temps. Le ruthénium est séparé au préalable par extraction au moyen de tétrachlorure de carbone après oxydation en tétroxyde par l'oxyde d'argent(II).

ZUSAMMENFASSUNG

Spuren von Ruthenium (0.005–0.1 μg) können durch seine katalytische Wirkung auf die langsame Reaktion zwischen Cer(IV) und Arsen(III) in schwefelsaurer Lösung bestimmt werden wobei die Änderung der Cer(IV)-Konzentration in Abhängigkeit von der Zeit spektrophotometrisch verfolgt wird. Die Abtrennung des Rutheniums vom Osmium erfolgt durch Lösungsmittelextraktion nach dessen Oxydation mit Silber(II)-oxyd.

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REACTIONS BETWEEN ALKALOIDS AND BISMUTH IODIDE, THE COMPOUNDS FORMED AND THEIR ANALYTICAL APPLICATION

A HETEROMETRIC STUDY*

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INTRODUCTION

The reaction between pyramidon and bismuth iodide was studied by us heterometrically[1]. More than *ten* well defined stoechiometric compounds were obtained. Each of four of them could be used for a precise determination of either bismuth or pyramidon. The composition of these latter final compounds (= ↓↓) depended on which of the three components (iodide, bismuth nitrate, or pyramidon) was used as titrant.

We were interested to study other complicated cyclic N-compounds on a similar basis. This investigation had a double purpose. Firstly, to study the reactions with the individual N-compounds, so as to establish the *final* as well as the *intermediate* compounds obtained. We hoped in this way to obtain a deeper insight into the function of each nitrogen atom built into the organic molecule. In many cases, the type of final compound obtained depended on the stereochemistry of the compounds. Although our main attention was directed to the alkaloids, other specific N-compounds, such as phenanthroline, nitron, pyramidon, etc. were also included for comparison. Secondly, we were interested to investigate the analytical application of the reactions for a rapid and precise determination of alkaloids or other complex N-compounds. The next step may be the determination of individual N-compounds in mixtures.

The results presented here seem to justify our interest from both aspects, the general chemical and the analytical, which are very closely connected in heterometry.

EXPERIMENTAL

Reagents

The following reagents were used.

Bismuth nitrate. $Bi(NO_3)_3 \cdot 5H_2O$, Baker's 'Analyzed'. A 0.05 *M* solution in 1 *N* nitric acid was prepared. More dilute solutions were prepared from the stock solution by diluting with acidified water, so that in the final solutions the molar concentration of nitric acid was approximately 22 times that of bismuth.

Potassium iodide. Baker's 'Analyzed'. A 0.5 *N* aqueous stock solution was prepared. More dilute solutions were freshly prepared and kept in dark brown bottles.

Nitron. Eastman Organic Chemicals, for chemical purposes. 0.7802 g nitron + 7 ml *N* CH_3COOH were dissolved in water and made up to 250 ml giving a 0.01 *M* solution. More dilute so-

* Dedicated to Prof. WALTER FEITKNECHT, Bern, on his 60th birthday.

lutions were prepared from the standard solution. All solutions were kept in dark brown bottles. The dilute solutions were freshly prepared every few days.

Quinine. $C_{20}H_{24}N_2O_2 \cdot HCl \cdot 2H_2O$ (Pharmacie Centrale de Belgique SA. Bruxelles, M.W. 396.9. 0.3969 g were dissolved in 100 ml water (0.01 *M*).

Cinchonine. Fisher Scientific Company, $C_{19}H_{22}N_2O$. M.W. 294.58, 0.2946 g were dissolved in 100 ml 0.02 *M* HNO_3 (0.01 *M*).

Strychnine sulphate. (neutral I). Boehringer und Soehne. M.W. 856.97, B.P.C. 49, 0.4285 g in 100 ml water (0.01 *M*).

Sparteine sulphate. $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$, M.W. 422.5, 0.4225 g in 100 ml water (0.01 *M*).

Papaverine hydrochloride. Roche DAB, $C_{20}H_{21}NO_4 \cdot HCl$, M.W. 375.8, 0.3758 g in 100 ml water (0.01 *M*).

Rivanol. Bubeck & Dolder ex. S. H. Wolfensberger & Co. (lactate). $C_{15}H_{15}ON_3 \cdot C_3H_6O_3 \cdot H_2O$, M.W. 361.3, 0.3613 g in 100 ml water (0.01 *M*).

Acriflavine. I.C.I. $C_{14}H_{14}N_3Cl \cdot HCl$, M.W. 296.2, 0.2962 g in 100 ml water (0.01 *M*).

1 : 10 Phenanthroline. B.D.H., AnalaR. $C_{12}H_8N_2 \cdot H_2O$, M.W. 198.22, 0.1982 g in 100 ml water (0.01 *M*).

Atropine sulphate. May & Baker, $(C_{17}H_{23}O_3N)_2 \cdot H_2SO_4 \cdot H_2O$, M.W. 694.80, 0.6948 g in 100 ml water (0.02 *M*).

Antipyrine. B.P. May & Baker, $C_{11}H_{12}ON_2$, M.W. 188.22. 0.1882 g in 100 ml water (0.01 *M*).

Pyramidon. Bubeck & Dolder Ph. H.V., $C_{13}H_{17}ON_3$, M.W. 231.29, 0.2313 g in 100 ml water (0.01 *M*).

Method

The same instruments and the same working conditions were used as in previous heterometric investigations[2]. The fundamental principles of heterometry have been presented before[3]. The temperature was always 20°.

RESULTS AND DISCUSSION

General

A selection of experiments carried out, and the results obtained, are presented in tables and figures. Each of the Tables I–III presents experiments using a different titrant. The course of some experiments are also presented in figures which correspond to the tables (the same numeration is used in both cases). In the Figs. 1–3 are cited the molar ratios of [Bi] : [titrant] found at the critical points of the formation of the intermediate and the final compounds.

A glance at the curves shows that in most curves many critical points were established corresponding to definite compounds formed stoechiometrically. In most cases the end-points exactly coincided with the first maximum density point (= ↓↓), after which a horizontal maximum density line was obtained. Thus each curve presented a series of *intermediate* compounds terminating with a *final* compound. The sequence of compounds, their character and composition depended on the titrant used. Analysing the results of Tables I, IV and V we can classify the different N-compounds and can define the role of each nitrogen atom in the complicated organic molecules. The reactions and the compounds obtained were largely dependent on the stereochemical character of the individual N-compounds participating in the formation of the insoluble compounds.

Table I shows that the *first* maximum density point could almost always be used for the determination of the N-compound. A full titration took 10–15 min and the error was usually negligible. The sensitivity of the reaction towards different alkaloids varied. In most cases (Table V) 0.5 to 1.0 mg of alkaloid was sufficient for an analysis. The titration time of 10–15 min was somewhat extended because all the intermediate critical points were considered. For analytical purposes the first maximum point only has to be considered. This may probably rather shorten the titration time.

TABLE I

General composition: *a* ml *k M* nitrogen compound (= A) + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or ad 20) water + *x* ml *m M* $Bi(NO_3)_3$. T = 20°. Filter: red.

Expt. No.	*Solution of nitrogen compound*		$Bi(NO_3)_3$ *Molarity*	$Bi(NO_3)_3$ *ml calculated*	$Bi(NO_3)_3$ *ml found*	*% error*	*Optical density at the end-point*	*Molar ratio [Bi] : [A] at end-point*	*Titration time in min*	*Remarks*
1	5 ml 0.002 *M* Nitron (+ 1 ml *M* HNO_3)	+ 12 ml H_2O								Precipitation before the beginning of titration.
2	3 ml 0.001 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.002				>1.0			Sulfuric instead of nitric acid.
3	3 ml 0.0005 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.94	2 : 1	12	
4	3 ml 0.00025 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.0005				0.30			No definite end-point; low density
5	3 ml 0.0005 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 16 ml H_2O	0.001		>5.0		0.0			Blank: *without* KJ.
6	3 ml 0.0005 *M* Quinine	+ 14 ml H_2O	0.00083	3.60	i 3.60 h	0.0	0.81	2 : 1	14	
7	3 ml 0.001 *M* Cinchonine	+ 14 ml H_2O	0.00167				>1.0			Too high optical densities.
8	3 ml 0.0005 *M* Cinchonine	+ 14 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.67	2 : 1	14	
9	4 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.00167	2.40	2.40 h	0.0	0.81	1 : 1	12	
10	4 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.0013	3.20	i 3.20 h	0.0	0.88	1 : 1	14	
11	8 ml 0.0003 *M* Sparteine	+ 9 ml H_2O	0.00167	2.88	i 2.90 h	0.6	0.91	2 : 1	12	
12	5 ml 0.0005 *M* Papaverine	+ 2 ml H_2O	0.001	2.50	i 2.50 h	0.0	0.67	1 : 1	10	
13	4 ml 0.00167 *M* Rivanol	+ 3 ml H_2O								Precipitation before the beginning of titration.
14	4 ml 0.00167 *M* Rivanol	+ 13 ml H_2O								
15	3 ml 0.001 *M* Rivanol	+ 14 ml H_2O	0.001	3.00	i 2.99 h	0.3	0.84	1 : 1	12	
16	4 ml 0.000833 *M* Rivanol	+ 13 ml H_2O	0.00167	2.00	2.00	0.0	0.72	1 : 1	10	
17	3 ml 0.001 *M* Acriflavine	+ 4 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.64	1 : 1	15	
18	5 ml 0.001 *M* Phenanthroline	+ 2 ml H_2O	0.00167	3.00	i 3.00 h	0.0	0.84	1 : 1	12	
19	4 ml 0.0013 *M* Antipyrine	+ 3 ml H_2O	0.0033	3.00	i 3.00 h	0.0	0.68	2 : 1	12	
20	3 ml 0.002 *M* Atropine	+ 4 ml H_2O	0.00167	3.60	i 3.60 h	0.0	0.73	1 : 1	10	

i = intersection point; h = horizontal maximum density line.

TABLE II

General composition: a ml k M $Bi(NO_3)_3$ + 1 ml M HNO_3 + 2 ml 0.1 M KJ + ad 10 (or ad 20) water + x ml m M nitrogen compound. T = 20°. Filter: red.

Expt. No.	*Solution of bismuth nitrate*	*Titrated vol. ml*	*Nitrogen compound*				*Max. optical density*	*Ratio [Bi] : [A]*	*Titration time in min*	*% error*	*Remarks*
			Name	*Molarity*	*ml calculated*	*ml found*					
1	6 ml 0.0005 M $Bi(NO_3)_3$	20	Quinine	0.0005	3.00	i 3.00 h	0.89	2 : 1	14	0.0	
2	3 ml 0.001 M $Bi(NO_3)_3$	10	Papaverine	0.001	3.00	i 3.00 h	0.77	1 : 1	12	0.0	
3	3 ml 0.001 M $Bi(NO_3)_3$	10	Acriflavine	0.001	3.00	i 3.00 h	0.72	1 : 1	14	0.0	
4	1 ml 0.5 M H_2SO_4 + (5 ml 0.02 M HNO_3)	20	Nitron	0.0005		> 5.0	0.0				Blank, no precipitation.
5	3 ml 0.001 M $Bi(NO_3)_3$ + (1 ml 0.5 M H_2SO_4)	20	Nitron	0.001	3.00	i 3.00 h	0.96	1 : 1	12	0.0	
6	3 ml 0.0005 M $Bi(NO_3)_3$ + (1 mlo.5 M H_2SO_4)	20	Nitron	0.0005	3.00	i 3.00 h	0.69	1 : 1	14	0.0	
7	3 ml 0.001 M $Bi(NO_3)_3$	20	Cinchonine	0.0005	3.00	i 2.97 h	0.55	2 : 1	14	1.0	
8	4 ml 0.00167 M $Bi(NO_3)_3$	10	Rivanol	0.002							No definite end-point.
9	3 ml 0.001 M $Bi(NO_3)_3$	20	Rivanol	0.001	3.00	i 3.00 h	0.47	1 : 1	14	0.0	
10	4 ml 0.001 M $Bi(NO_3)_3$	10	Strychnine	0.001	4.00	i 4.00 h	0.96	1 : 1	12	0.0	
11	5 ml 0.001 M $Bi(NO_3)_3$	10	Phenanthroline	0.00167	3.00	i 3.00 h	0.85	1 : 1	12	0.0	
12	3 ml 0.00167 M $Bi(NO_3)_3$	10	Antipyrine	0.00133	4.00	i 4.00 h	0.51	1 : 1	15	0.0	
13	4 ml 0.00133 M $Bi(NO_3)_3$	20	Sparteine	0.00167							Too high optical densities.
14	4 ml 0.0005 M $Bi(NO_3)_3$	20	Sparteine	0.00083							Too low optical densities.
15	5 ml 0.001 M $Bi(NO_3)_3$	20	Sparteine	0.00083	3.00	i 3.00 h	0.49	2 : 1	14	0.0	
16	3 ml 0.002 M $Bi(NO_3)_3$	10	Atropine	0.002	3.00	i 3.00 h	0.86	1 : 1	12	0.0	

i = intersection point; h = horizontal maximum density line.

TABLE III General composition: *a* ml *k M* $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + *b* ml 1 *M* nitrogen

Expt. No.	*Composition*			*Molarity of KJ*
1	10 ml 0.01 *M* Nitron	+ 9 ml H_2O + (1 ml 0.5 *M* H_2SO_4)		0.5
2	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.001 *M* Nitron	+ 11 H_2O	0.01
3	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.0005 *M* Nitron	+ 11 ml H_2O	0.005
4	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.0005 *M* Nitron	+ 11 ml H_2O	0.01
5	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4	+ 4 ml 0.01 *M* Nitron	+ 11 ml H_2O	0.005
6	5 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.00084 *M* Sparteine	+ 1 ml H_2O	0.01
7	5 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Sparteine		0.01
8	5 ml 0.0005 *M* $Bi(NO_3)_3$	+ 3 ml 0.01 *M* Acriflavine	+ 1 ml H_2O	0.00625
9	5 ml 0.005 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Acriflavine	+ 1 ml H_2O	0.00625
10	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Rivanol	+ 13 ml H_2O	0.00625
11	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Papaverine	+ 3 ml H_2O	0.00625
12	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Papaverine	+ 1 ml H_2O	0.01
13	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.00625
14	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.002 *M* Strychnine	+ 3 ml H_2O	0.00625
15	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.0005 *M* Quinine	+ 13 ml H_2O	0.00625
16	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.01 *M* Quinine	+ 3 ml H_2O	0.00625
17	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 3 ml 0.00125 *M* Phenanthroline	+ 3 ml H_2O	0.00625
18	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 4 ml 0.004 *M* Phenanthroline	+ 2 ml H_2O	0.005
19	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 3 ml 0.00063 *M* Phenanthroline	+ 3 ml H_2O	0.00625
20	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.0005 *M* Cinchonine	+ 13 ml H_2O	0.01
21	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Cinchonine	+ 11 ml H_2O	0.01
22	3 ml 0.00167 *M* $Bi(NO_3)_3$	+ 4 ml 0.00125 *M* Antipyrine	+ 2 ml H_2O	0.01
23	3 ml 0.00167 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Antipyrine	+ 2 ml H_2O	0.01
24	3 ml 0.00333 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Antipyrine	+ 2 ml H_2O	0.02
25	3 ml 0.002 *M* $Bi(NO_3)_3$	+ 3 ml 0.002 *M* Atropine	+ 3 ml H_2O	0.025
26	3 ml 0.002 *M* $Bi(NO_3)_3$ + (2 ml 0.1 *M* Na_3-citrate)	+ 3 ml 0.002 *M* Atropine	+ 2 ml H_2O	0.025
27	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Atropine	+ 1 ml H_2O	0.01

i = intersection point; h = horizontal maximum density line.

TABLE IV INTERMEDIATES AND

Nitrogen compound	+ *x Bi* — *Compounds of molar ratio [Bi] : [A]*
Nitron	2 : 3↓ → 1 : 1↓ → 3 : 2↓ → 2 : 1↓↓
Sparteine	2 : 3↓ → 1 : 1↓ → 3 : 2↓ → 2 : 1↓↓
Chinine	1 : 1↓ → 3 : 2↓ → 2 : 1↓↓
Cinchonine	. . . . → 2 : 1↓↓
Antipyrine	1 : 1↓ → 2 : 1↓↓
Pyramidon	1 : 1↓ → 3 : 2↓ → 2 : 1↓ → 3 : 1↓↓
Strychnine	1 : 2↓ → 3 : 4↓ → 1 : 1↓↓
Rivanol	1 : 2↓ → 2 : 3↓ → 1 : 1↓↓
Papaverine	2 : 3↓ → 1 : 1↓↓
Acriflavine	1 : 2↓ → 1 : 1↓↓
Phenanthroline	1 : 2↓ → 1 : 1↓↓
Atropine	. . . → 1 : 1↓↓

A = N-compound.

compound + ad 10 (or ad 20) water + x *m M* KJ. T = 20°. Filter: red.

KJ								
Initial p.p.t.		*ml at end-point*	*ml calculated*	*% error*	*Optical density at max.*	*Molar ratio [Bi] : [J⁻]*	*Titration time in min*	*Remarks*
at ml	*molar ratio [Bi] : [J⁻]*							
		> 5.0			0.0			Blank: no precipitation.
1.4	1 : 7	i 4.00 h	4.00	0.0	0.54	1 : 20	14	
3.2		> 5.0			> 0.37			No end-point
1.8	∿1 : 10	i 4.00 h	4.00	0.0	0.43	1 : 20	12	
0.8	1 : 2	i 4.00 h	4.00	0.0	0.84	1 : 10	14	
2.2	∿1 : 4	i 3.90 h	4.00	2.5	0.14	1 : 8	12	
1.1	1 : 2	i 4.00 h	4.00	0.0	0.88	1 : 8	12	
0.9	1 : 2	i 3.20 h	3.20	0.0	0.61	1 : 8	14	
0.5	1 : 1	i 3.20 h	3.20	0.0	0.80	1 : 8	14	
0.8	∿1 : 2	i 3.82 h	3.84	0.5	0.73	1 : 8	14	
0.9	1 : 2	i 3.80 h	3.84	1.0	0.65	1 : 8	12	
0.3		i 3.20 h	3.20	0.0	0.60	1 : 8	12	
2.3	∿1 : 5	i 3.86 h	3.84	0.5	0.5	1 : 8	14	
0.9	1 : 2	i 3.80 h	3.84	1.0	0.68	1 : 8	12	
		> 5.0			0.0			
2.1	∿1 : 4	i 3.83 h	3.84	0.1	0.46	1 : 8	12	
0.2		i 2.40 h	2.40	0.0	0.78	1 : 4	12	
0.2		i 3.00 h	3.00	0.0	0.84	1 : 4	14	
2.9		> 4.0			0.16		10	Too low optical densities
		> 5.0			0.0			
1.6	1 : 4	i 3.20 h	3.20	0.0	0.81	1 : 8	14	
2.9		> 4.0		0.13			20	Too low optical densities
0.8	∿1 : 2	i 4.00 h	4.00	0.0	0.82	1 : 8	15	
0.6		i 3.93 h	4.00	1.7	0.84	1 : 8	14	
0.8	∿1 : 4	i 1.90 h	1.92	0.5	0.60	1 : 8	12	
		> 5.0		0.0				
0.9	1 : 2	i 3.20 h	3.20	0.0	0.75	1 : 8	12	

FINAL COMPOUNDS

+ x Nitrogen compound	*+ x KI*
Compounds of molar ratio [Bi] : [A]	*Compounds of molar ratio [Bi] : [I]*
3 : 1↓ → 3 : 2↓ → 1 : 1↓↓	1 : 8↓ → 1 : 10↓↓ (in excess of nitrogen comp.)
4 : 1↓ → 2 : 1↓↓	→ 1 : 20↓↓
4 : 1↓ → 2 : 1↓↓	1 : 8↓↓
3 : 1↓ → 2 : 1↓↓	1 : 6↓ → 1 : 8↓↓
2 : 1↓ → 1 : 1↓↓	1 : 8↓↓
4 : 1↓ → 3 : 1↓ → 2 : 1↓ → (3 : 2↓) → 1 : 1↓↓	1 : 4↓ → 1 : 8↓↓
	(1 : 2↑) → 1 : 4↓ → 1 : 8↓↓
3 : 2↓ → 1 : 1↓↓	1 : 2↑ → 1 : 4↓↓ (in excess of nitrogen comp.)
3 : 2↓ → 1 : 1↓↓	→ 1 : 8↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 8↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 6↓ → 1 : 8↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 8↓↓
2 : 1↓ → 1 : 1↓↓	→ 1 : 4↓↓
	→ 1 : 8↓↓

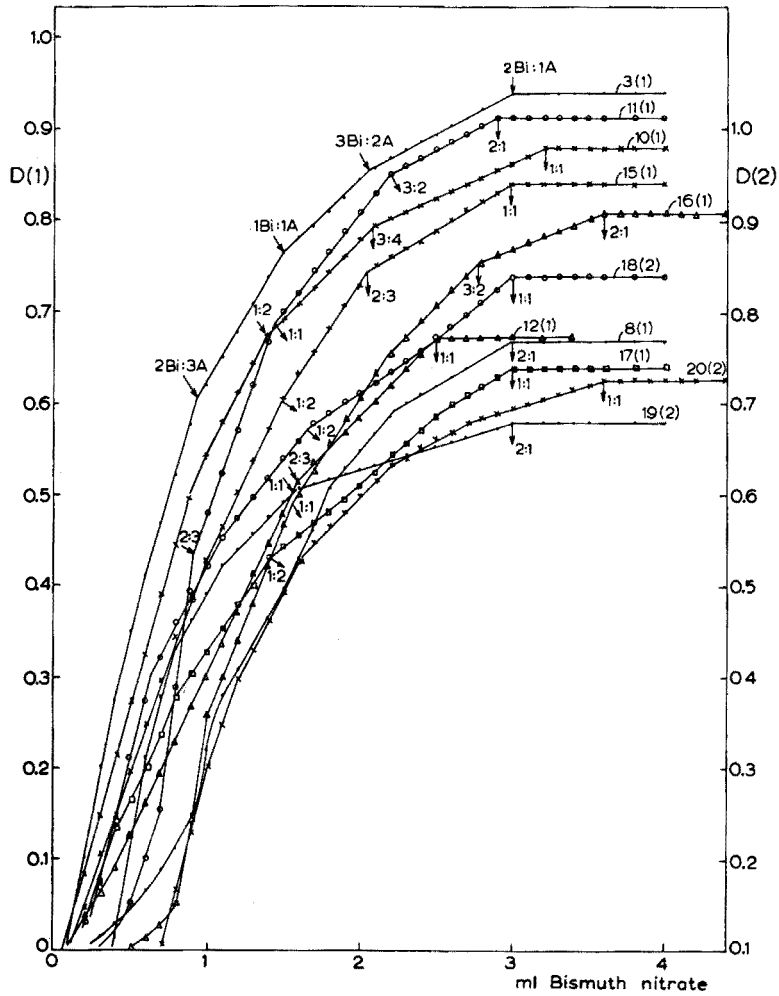


Fig. 1. Titrations of nitrogen compound (= A) with bismuth nitrate (= Bi). Molar ratios [Bi] : [A] found at the critical points. Nitrogen compound: (3) Nitron; (6) Quinine; (8) Cinchonine; (10) Strychnine; (11) Sparteine; (12) Papaverine; (15) Rivanol; (17) Acriflavine; (18) Phenanthroline; (19) Antipyrine; (20) Atropine.

TABLE V

General composition: *a* ml nitrogen compound (= A) + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or 20) ml H_2O + *x* ml $Bi(NO_3)_3$.

Nitrogen compound (= A)						*Optical density at maximum*	*End compound obtained*	*Relative sensitivity of nitrogen compound*
Name	*Content mg*	*No. of N atoms*	*Molar concentration [A]*	*Volume titrated [vol]*	*Molar amount used*			
Nitron	0.46	4	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.94	Bi_2A_1	4.0
Quinine	0.48	2	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.81	Bi_2A_1	4.0
Cinchonine	0.44	2	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.67	Bi_2A_1	4.0
Sparteine	0.56	2	$1.2 \cdot 10^{-4}$	20	$2.4 \cdot 10^{-6}$	0.91	Bi_2A_1	2.5
Papaverine	0.85	1	$2.5 \cdot 10^{-4}$	10	$2.5 \cdot 10^{-6}$	0.68	Bi_1A_1	2.4
Rivanol	1.1	3	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.84	Bi_1A_1	2.0
Acriflavine	0.8	3	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.64	Bi_1A_1	2.0

TABLE V (continued)

Name	Nitrogen compound (= A)					Optical density at maximum	End compound obtained	Relative sensitivity of nitrogen compound
	Content mg	No. of N atoms	Molar concentration [A]	Volume titrated [vol]	Molar amount[a] used			
Strychnine	1.3	2	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.88	Bi_1A_1	1.5
Phenanthroline	1.0	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.84	Bi_1A_1	1.2
Pyramidon	1.0	3	$4.3 \cdot 10^{-4}$	10	$4.3 \cdot 10^{-6}$	0.65	Bi_3A_1	1.2
Antipyrine	0.94	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.68	Bi_2A_1	1.2
Atropine	1.7	1	$6 \cdot 10^{-4}$	10	$6 \cdot 10^{-6}$	0.72	Bi_1A_1	1.0

[a] mole amount $= \frac{[A] \times [vol.]}{1000}$.

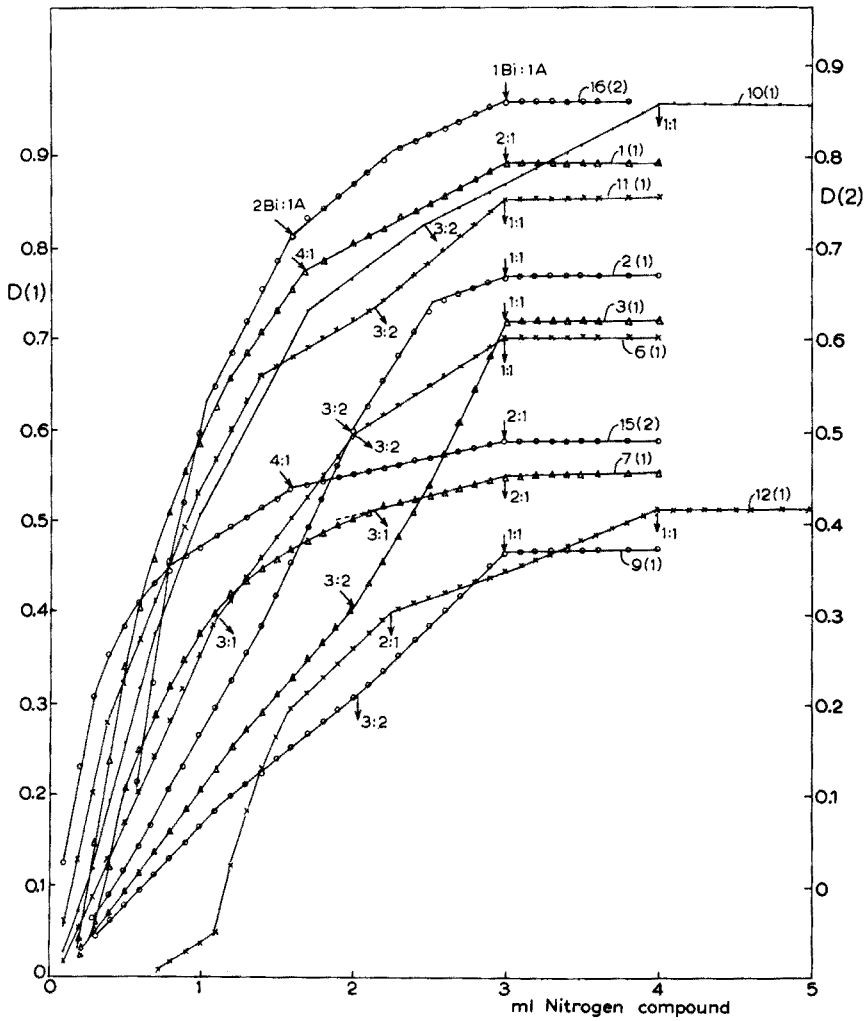
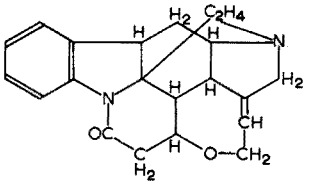


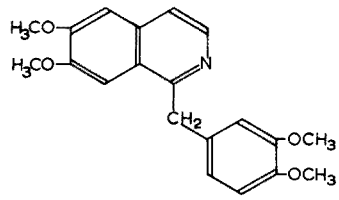
Fig. 2. Titrations of bismuth nitrate (= Bi) with nitrogen compound (= A). Molar ratios [Bi : [A] found at the critical points. Nitrogen compound: (1) Quinine; (2) Papaverine; (3) Acriflavine; (6) Nitron; (7) Cinchonine; (9) Rivanol; (10) Strychnine; (11) Phenanthroline; (12) Antipyrine; (15) Sparteine; (16) Atropine.

In this work, eleven heterocyclic nitrogen compounds were studied and twelve N-compounds were compared with one another. We present here the accepted structures for these compounds for comparison.

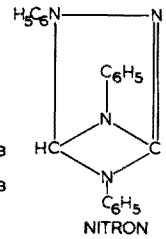
STRUCTURES OF N-COMPOUNDS



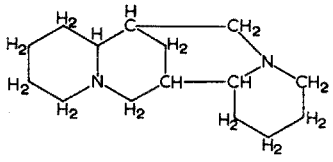
STRYCHNINE



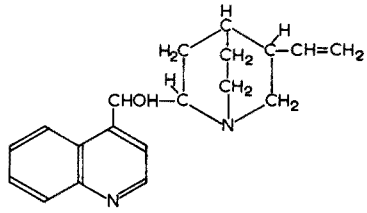
PAPAVERINE



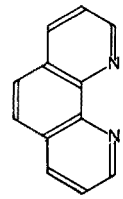
NITRON



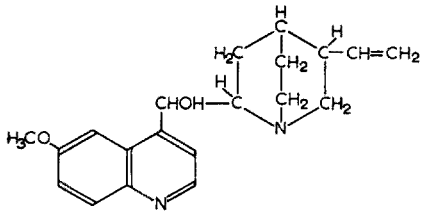
SPARTEINE



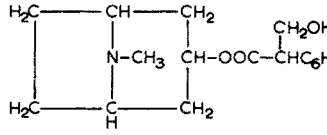
CINCHONINE



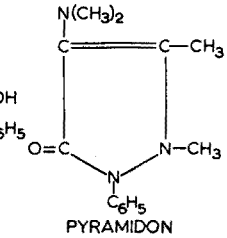
o-PHENANTHROLINE



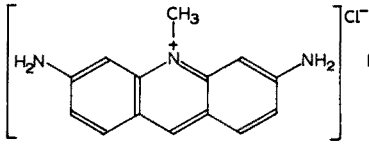
QUININE



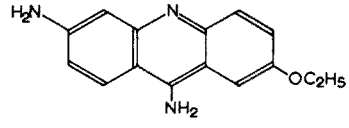
ATROPINE



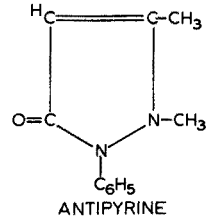
PYRAMIDON



ACRIFLAVINE



RIVANOL



ANTIPYRINE

All titrations were carried out only at pH $\sim$ 1, because of the character of the bismuth iodide reaction. Later on some experiments with other titrants will be presented which enabled us to study similar reactions at various pH values. If we consider the composition and the structure of the N-compounds investigated, we find that the molecules contain from *one* to *four* N-atoms. Some of the N-atoms are built in *closed* rings,

the others are *external* non-methylated amino groups. We will see later that the latter are insensitive towards the reaction with bismuth iodide.

Many alkaloids, or other N-compounds, have a smaller molecular weight than those mentioned above; they were less sensitive and gave precipitations only if used in higher concentrations than usual. They were therefore not included in our study. The following belong to this group: quinoline (3 ml 0.00125 *M*), caffeine (4 ml 0.002 *M*), theobromine (4 ml 0.005 *M*), urotropine (4 ml 0.001 *M*); streptomycin (4 ml 0.5%) and benzidine (1 ml 0.01 *M*).

1. *Titrations of N-compounds with bismuth nitrate*

Tables I and IV show the composition and the results. Table V contains calculations

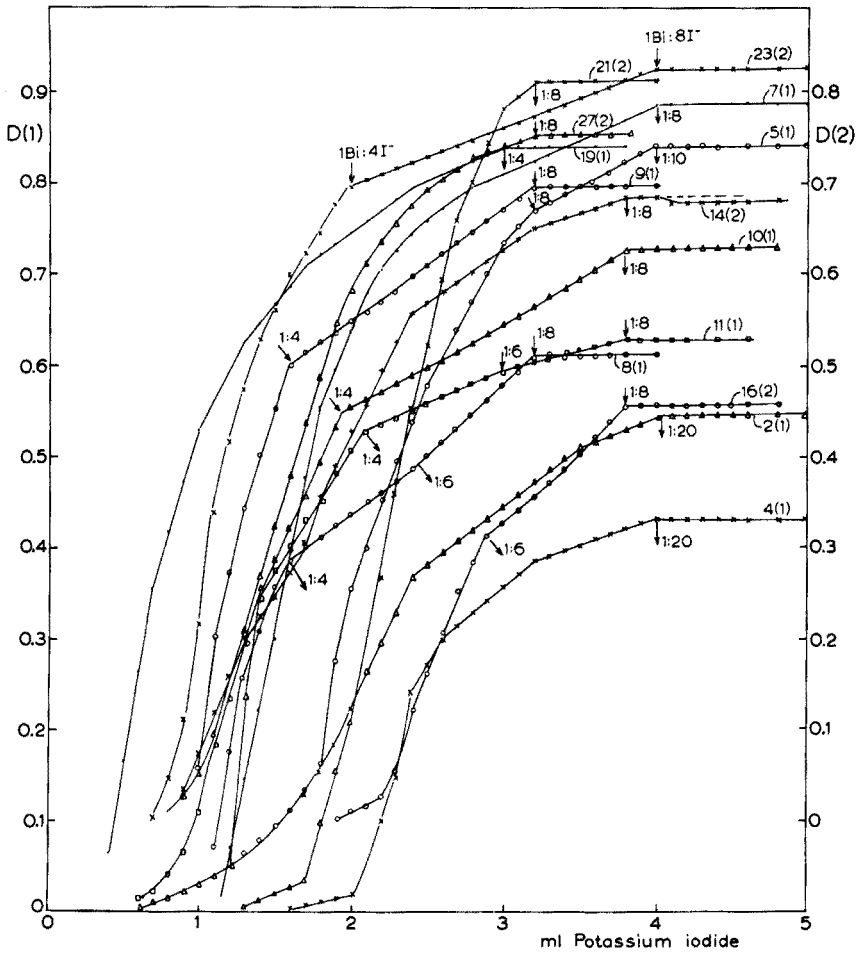


Fig. 3. Titrations of mixtures of bismuth nitrate and nitrogen compound with potassium iodide. Molar ratio [Bi] : [I^-] found at the critical points. Nitrogen compound: (2), (4) and (5) Nitron; (7) Sparteine; (9) Acriflavine; (10) Rivanol; (11) Papaverine; (14) Strychnine; (16) Quinine; (19) Phenanthroline; (21) Cinchonine; (23) Antipyrine; (27) Atropine.

based on Table I. The course of some of these experiments (Table I) is presented in Fig. 1. In Table IV we have summarized the different intermediate and final compounds obtained in Tables I–III.

Compounds

Final compounds

A glance at Tables I and IV shows that only *two* final compounds $Bi_2A\downarrow\downarrow$ and $BiA\downarrow\downarrow$ were ever obtained by titrating N-compounds ,with the exception of pyramidon, with bismuth nitrate. The compound $Bi_2A\downarrow\downarrow$ was always obtained if at least *two* N-atoms were built into the cyclic aromatic or aliphatic compound. Phenanthroline and strychnine were exceptions and gave $BiA\downarrow\downarrow$ instead. Evidently in phenanthroline, the two nitrogen atoms, although having similar construction, could not act separately with the bismuth iodide anion. In strychnine, one of the two nitrogen atoms is inactive, so that this alkaloid must be classified with those with one nitrogen atom. Both the above N-compounds act as *mono*basic N-compounds. In contrast to this, antipyrine, with two nitrogen atoms near each other, acted as a *di*-basic N-compound giving the compound $Bi_2A\downarrow\downarrow$ *with bismuth nitrate as titrant.*

Quinine, cinchonine and sparteine *always* acted as *two*-basic N-compounds. These all contain *two* N-atoms in aliphatic or aromatic rings, *distant* from one another, and acting separately.

Nitron is now considered as a "Zwitterion"; its electronic structure has not been finally established, and we do not know how the charges are distributed in the molecule. In any case it acts as a *di*-basic N-compound *when titrated with bismuth.*

All other N-compounds contain only one nitrogen atom in the ring and act as *mono*-basic N-compounds. Such is the case with rivanol and acriflavine which have external amino groups.

Intermediates

The sequences of intermediates traced remained in principle the same, whether the final compound ($= \downarrow\downarrow$) was BiA, Bi_2A or even Bi_3A. Thus, we obtained the following sequences of molar ratios [Bi] : [A].

With one active N-atom:

$$1 : 2\downarrow \rightarrow 2 : 3\downarrow \rightarrow 1 : 1\downarrow\downarrow$$

With *two* active N-atoms the sequence continued further giving:

$$\ldots 1 : 1\downarrow \rightarrow 3 : 2\downarrow \rightarrow 2 : 1\downarrow\downarrow$$

In the special case of pyramidon it continued:

$$\ldots 2 : 1\downarrow \rightarrow 3 : 1\downarrow\downarrow$$

Evidently there is even a possibility that an intermediate with the composition $BiA_2\downarrow$ is formed. It would be risky to present structures for such intermediates.

Analytical aspects

Sensitivity. Table V contains calculations carried out on the basis of table 1 which show us the sensitivity of the alkaloid titrations with bismuth nitrate. The reaction is most sensitive with N-compounds containing two *separate* ring systems in the mole-

TABLE VI

General composition: a ml $Bi(NO_3)_3$ + 1 ml M HNO_3 + 2 ml 0.1 M KJ + ad 10 (or 20) ml H_2O + x ml nitrogen compound (= A)

Nitrogen compound		*$Bi(NO_3)_3$*					
Name	*No. of N atoms*	*Molar concentration [Bi]*	*Vol. titrated [vol] (ml)*	*Molar amount[a] of bismuth nitrate*	*Optical density at max.*	*End compound obtained*	*Relative sensitivity of nitrogen compound*
Quinine	2	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.89	Bi_2A_1	2
Papaverine	1	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.77	Bi_1A_1	2
Acriflavine	3	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.72	Bi_1A_1	2
Nitron	4	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.69	Bi_1A_1	2
Cinchonine	2	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.55	Bi_2A_1	2
Rivanol	3	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.47	Bi_1A_1	2
Strychnine	2	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.96	Bi_1A_1	1.5
Pyramidon	3	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.66	Bi_1A_1	$\sim$1.5
Phenanthroline	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.85	Bi_1A_1	1.2
Antipyrine	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.51	Bi_1A_1	1.2
Sparteine	2	$2.5 \cdot 10^{-4}$	20	$5 \cdot 10^{-6}$	0.49	Bi_2A_1	1.2
Atropine	1	$6 \cdot 10^{-4}$	10	$6 \cdot 10^{-6}$	0.86	Bi_1A_1	1.0

[a] mole amount $= \frac{[\text{Bi}] \times [\text{vol}]}{1000}$.

cule, each with one nitrogen atom. These are quinine and cinchonine. The reaction is also sensitive towards nitron. The sensitivity is about four times as high as with atropine. Second in sensitivity come the *large* N-compounds containing one active N-atom in the molecule. These are sparteine and papaverine. They are about 2.5 times as sensitive as atropine. Rivanol and acriflavine act with *one* nitrogen atom in the ring, they are about twice as sensitive as atropine. Phenanthroline, antipyrine, atropine and pyramidon are the least sensitive.

2. *Titrations of bismuth nitrate with N-compounds*

Table II presents a selection of such experiments, their composition and the results obtained. Fig. 2 shows the course of some titrations. Table VI contains calculations made on the basis of Table II. Generally the differences in the results, using N-compounds as titrant, are less pronounced than in Table V.

Final compounds

It is interesting to establish that in only a very few cases a final compound $Bi_2A\downarrow\downarrow$ was obtained. These are the three alkaloids discussed separately before: quinine, cinchonine and sparteine. Compounds with two or more cyclic N-atoms such as nitron, antipyrine and phenanthroline, all gave final compounds $BiA\downarrow\downarrow$.

Intermediates

Table IV shows the intermediates obtained. If the N-compound (= titrant) contained *two* active N-atoms we obtained the sequence:

$$4 : 1\downarrow \rightarrow 2 : 1\downarrow\downarrow$$
$$\text{or } 2 : 1\downarrow \rightarrow 1 : 1\downarrow\downarrow \text{ (antipyrine)}$$

but if only *one* N-atom was active:

$$3 : 2\downarrow \rightarrow 1 : 1\downarrow\downarrow$$

Molecules with more than *two* nitrogen in the molecule (such as nitron or pyramidon) gave more intermediates:

Pyramidon: $4 : 1\downarrow \rightarrow 3 : 1\downarrow \rightarrow 2 : 1\downarrow \rightarrow 3 : 2\downarrow : \downarrow \rightarrow 1 : 1\downarrow\downarrow$

Nitron: $3 : 1\downarrow \rightarrow 3 : 2\downarrow \rightarrow 1 : 1\downarrow\downarrow$

TABLE VII

General composition: a ml $Bi(NO_3)_3$ + 1 ml M HNO_3 + b ml nitrogen compound + ad 10 (or 20) ml H_2O + x ml KJ

Nitrogen compound		*$Bi(NO_3)_3$*			*Optical density at max.*	*Molar ratio of [Bi] : [J⁻] at the end-point*	*Relative sensitivity of nitrogen compound*
Name	*No. of N atoms*	*Molar concentration [Bi]*	*Vol. titrated [vol] in ml*	*Molar amount[a] of bismuth nitrate*			
Nitron	4	$1 \cdot 10^{-4}$	20	$2 \cdot 10^{-6}$	0.43	1 : 20	3.0
Sparteine[b]	2	$2.5 \cdot 10^{-4}$	10	$2.5 \cdot 10^{-6}$	0.89	1 : 8	2.4
Acriflavine	3	$2.5 \cdot 10^{-4}$	10	$2.5 \cdot 10^{-6}$	0.80	1 : 8	2.4
Rivanol	3	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.73	1 : 8	2.0
Papaverine	1	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.63	1 : 8	2.0
Strychnine	2	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.48	1 : 8	2.0
Quinine[b]	2	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.46	1 : 8	2.0
Phenanthroline	2	$3.75 \cdot 10^{-4}$	10	$3.75 \cdot 10^{-6}$	0.78	1 : 4	1.6
Cinchonine[b]	2	$2 \cdot 10^{-4}$	20	$4 \cdot 10^{-6}$	0.81	1 : 8	1.5
Pyramidon	3	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.42	1 : 8	> 1.2
Antipyrine	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.13	1 : 8	1.2
Atropine	1	$6 \cdot 10^{-4}$	10	$6 \cdot 10^{-6}$	0.60	1 : 8	1.0

[a] mole amount $= \frac{[\text{Bi}] \times [\text{vol}]}{1000}$.

[b] Alkaloid present in large excesses.

Analytical aspect

Table VI contains calculations concerning the sensitivity of the bismuth determination using different N-compounds. The variations in sensitivity are relatively small. Thus, using atropine as titrant, the amount of bismuth analysed had only to be doubled in comparison with the action with quinine or nitron. The errors shown in Table II were equally negligible using the different N-compounds as titrant. 0.3–0.5 mg of bismuth were necessary for the determination.

3. *Titrations of bismuth nitrate with potassium iodide*

Tables III, IV and VII and Fig. 3 present the experiments made, the bismuth–iodo complexes obtained and the calculations of sensitivity.

Compounds

Final compounds. In the presence of almost all the N-compounds used, the final molar ratio of [Bi] : [I^-] was 1 : 8. Only phenanthroline behaved differently, giving a final ratio of $1 : 4\downarrow\downarrow$. The nitron also behaved differently, giving $1 : 10\downarrow\downarrow$ in excess of nitron, and if less nitron was used, the final ratio was $1 : 20\downarrow\downarrow$. Working in excess

of pyramidon, the final compound was also obtained at the ratio of 1 : 4↓↓. With sparteine, quinine and cinchonine, the final compound had the composition 1 : 8↓↓ if an excess of alkaloid was used.

Intermediates. The number of intermediates was relatively small. Thus, in general, the following sequences were traced:

$$1 : 4\downarrow \rightarrow 1 : 8\downarrow\downarrow$$
$$1 : 2\uparrow \rightarrow 1 : 4\downarrow\downarrow$$

The intermediate 1 : 2 was always soluble.

Sensitivity

The sensitivity in relation to bismuth was different than that towards the N-compound used. The variations in sensitivity towards bismuth were relatively small when using different alkaloids. The same was the case if the sensitivity towards the different alkaloids was compared (Table VII).

METHOD

0.5–1 mg of alkaloid in 10 (or 20) ml aqueous solution, containing 1 ml *M* HNO_3 and 2 ml 0.1 *M* KI, are titrated with 0.001–0.0015 *M* bismuth nitrate.

Remark: In the case of the less sensitive alkaloids, more of the alkaloid must be taken. The first maximum density point lies at BiA↓↓. Using quinine, cinchonine, sparteine or antipyrine, the end-point lies at $Bi_2A\downarrow\downarrow$.

SUMMARY

The reactions between nitron, quinine, cinchonine, strychnine, sparteine, papaverine, rivanol, acriflavine, phenanthroline, antipyrine and atropine with bismuth nitrate in potassium iodide solution were studied heterometrically. The individual structure of the N-compounds was discussed on the basis of the reactions and the large salt-compounds obtained. 0.5 to 1 mg of N-compound was necessary for a determination which lasted 10–15 min. The errors in almost all cases were negligible. 0.3–0.5 mg bismuth could also be determined by the titration of bismuth with N-compounds and the error was negligible.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique des réactions de divers alcaloïdes avec le nitrate de bismuth et l'iodure de potassium. On a pu ainsi établir une méthode de titrage des alcaloïdes et également une méthode de titrage du bismuth.

ZUSAMMENFASSUNG

Die Reaktion einer Anzahl Alkaloide mit Wismutnitrat in Gegenwart von Jodkalium wurde heterometrisch untersucht. Sie lässt sich zur titrimetrischen Bestimmung von Wismut bezw. Alkaloiden verwenden.

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DÉTECTION ET DOSAGE DE TRÈS PETITES QUANTITÉS D'EAU PAR LA MÉTHODE HYGROPHOTOGRAPHIQUE

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L'hygrophotographie, dont le principe est basé sur l'emploi de plaques ou de films spéciaux à l'iodure d'argent et de mercure, sensibles à la fois vis-à-vis de la lumière et de l'humidité, permet de fixer sur du papier ou des plaques photographiques ordinaires la trace de l'humidité enregistrée sur la plaque hygrophotographique exposée d'abord à l'influence de la lumière et ensuite à celle de l'eau[1]. Cette trace, dont l'intensité est proportionnelle à la quantité d'eau absorbée par la couche sensible, est ensuite comparée à une échelle densitométrique obtenue au moyen de quantités d'eau exactement connues. Leur mesure est faite, ainsi que nous allons l'exposer plus loin, à l'aide d'un densitomètre et d'une balance de précision sensible au millième de milligramme.

Lorsqu'on pose une goutte d'un solvant organique neutre, contenant de l'eau, sur une feuille de papier filtre, enfermée hermétiquement entre une plaque hygrophotographique noircie au préable par exposition à la lumière et une plaque de verre ordinaire transparente, l'ensemble étant serré fortement à l'aide de ressorts (dans un châssis-presse photographique, par exemple), on voit alors que le solvant ne pouvant pas s'évaporer rapidement, s'étale librement, par absorption, dans l'épaisseur du papier filtre; quand il a atteint son étalement maximum, le solvant commence à s'évaporer lentement, à partir de la périphérie, et, lorsqu'il s'agit par exemple de

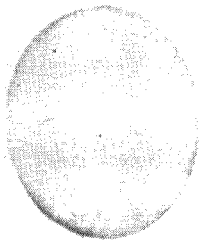

Fig. 1. Image hygrophotographique de l'humidité contenue dans une goutte d'alcool éthylique absolu du commerce.

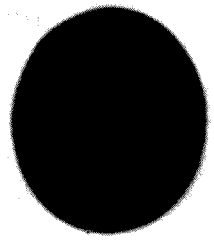

Fig. 2. Humidité dans une goutte d'alcool à 95%.

l'alcool éthylique, au fur et à mesure que s'évapore cet alcool, la très faible quantité d'eau qui peut se trouver dans la goutte passe du papier dans la gélatine et forme sur la plaque hygrophotographique, en allant de la périphérie vers le centre, une tache arrondie ou un anneau, dont l'aspect varie suivant la quantité d'eau contenue dans l'alcool.

Avec l'alcool éthylique absolu du commerce, on obtient un anneau périphérique jaune clair, ayant une partie centrale qui se détache sur la plaque hygrophotographique par une teinte moins claire et qui, sur les épreuves positives se traduit par une couleur grisâtre, alors que le cercle périphérique y figure en noir (Fig. 1). Avec les alcools à 95 et à 90%, on obtient des taches uniformément noires (Fig. 2).

Dans le cas de l'alcool méthylique, comme il est encore plus difficile d'avoir un échantillon absolument privé d'humidité, sur notre demande, M. PESEZ, dans les laboratoires de l'UCLAF, a bien voulu faire quelques essais en vue d'obtenir un méthanol rigoureusement anhydre. La méthode de déshydratation qu'il a utilisée, est l'ébullition avec du magnésium, selon BJERRUM ET ZECHMEISTER[2].

Partant d'un méthanol à 0.06% en eau, dosée par la méthode de Fischer, il a obtenu un distillat qui, recueilli dans les meilleures conditions possibles, montrait encore au dosage une teneur en eau de 0.01%. Un second traitement n'a pas fait baisser la teneur en eau. C'est avec cet échantillon que j'ai obtenu la figure 3 en mettant sur le papier filtre et à une certaine distance l'une de l'autre, deux gouttes du liquide maintenues enfermées entre la plaque hygrophotographique et la plaque transparente.

Ici, comme dans le cas de l'alcool éthylique ou des alcools propyliques, l'étalement de l'eau dans le papier filtre a lieu simultanément avec son solvant organique; le passage de cette eau du papier dans la plaque ne peut avoir lieu par conséquent qu' après l'évaporation du solvant à la limite de son étalement maximum; l'inscription de la tache humide sur la plaque se fait donc uniquement en progressant de la périphérie vers le centre, au fur et à mesure de l'évaporation (Fig. 3).

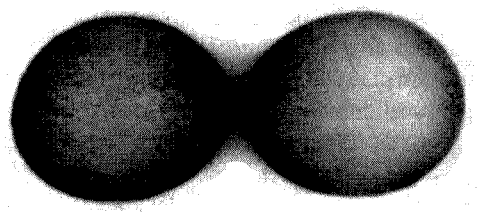

Fig. 3. Hygrophotographie obtenue avec deux gouttes d'alcool méthylique absolu distillé sur du magnésium.

Par contre, dans le cas de l'alcool butylique tertiaire, l'étalement de la goutte dans le papier filtre n'ayant pas lieu simultanément pour l'alcool et pour l'eau, en particulier si l'on a préparé deux mélanges binaires composés respectivement de 20 et de

30 parties d'eau pour 80 et 70 parties d'alcool, en volumes, dès que la goutte se trouve appliquée sur le papier et enfermée hermétiquement entre les deux plaques, elle semble s'y étaler normalement ; mais en réalité, l'eau ne suit pas constamment l'étalement de l'alcool ; elle reste en majeure partie au centre de l'étalement, tandis que l'alcool se porte de plus en plus vers la périphérie ; au bout d'une minute, on voit alors l'eau centrale passer presque intégralement et d'un seul trait dans la gélatine en formant instantanément sur la plaque une tache jaune intense (Fig. 4), dont le diamètre est par conséquent bien inférieur à celui du liquide resté sur le papier.

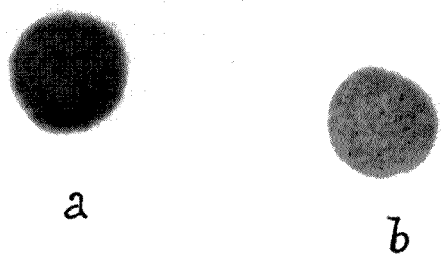

Fig. 4. Hygrophotographie de l'eau contenue dans une goutte d'alcool butylique tertiaire en: a. mélange binaire alcool–eau 7/3; b. mélange binaire 8/2. Diamètre de l'étalement maximum sur papier 2.3 × 2.7 diamètre de la tache de l'eau sur la plaque 1.5 × 1.4.

Dès nos premières applications de l'hygrophotographie à l'enregistrement et à l'étude de la transpiration des plantes, notre principale préoccupation a été de rendre cette méthode quantitative et ses résultats mesurables. Pour cela, il nous fallait une échelle densitométrique convenable et un procédé d'étalonnage facile et rapide.

Lorsque nous avons remarqué que la cellophane était capable de se saturer, dans certaines conditions, d'une quantité déterminée d'humidité, toujours la même, qu'elle cédait ensuite à la gélatine des plaques ou des films hygrophotographiques, nous avons pensé pouvoir utiliser ces pellicules cellulosiques de diverses épaisseurs et, par conséquent, chargées de quantités d'eau différentes; mais nous avons vite remarqué qu'avec les feuilles cellulosiques naturelles No. 600, 500, 400 et 300, dont les épaisseurs respectives sont 0.02, 0.03, 0.04 et 0.05 mm, malgré les différences indéniables dans la gamme densitométrique obtenue, ces différences n'étaient pas bien tranchées; en outre, l'échelle, qui n'avait que quatre points de repères, ne pouvait pas être complète et elle exigeait autant de pesées à la microbalance.

Finalement, nous avons pu construire une échelle densitométrique, correspondant à six degrés de décolorations obtenues avec des quantités déterminées d'eau de plus en plus faibles, en utilisant pour cela, en plus de l'eau pure, cinq solutions de bromure de sodium à (1, 2.5, 3, 4.5 et 5 M), solutions dont les tensions de vapeur, à la température de 25°, ont été déterminées avec un très grand soin par PEARCE, TAYLOR et BARTLETT[3].

Un calcul simple permet de ramener cette tension de vapeur à celle de la température du laboratoire au moment de l'expérience.

Comme

$$p = p_0(1 + \alpha t),$$

on a par conséquent

$$p_0 = \frac{p}{1 + \alpha t},$$

dans laquelle $\alpha = 0.003662$.

Dans le cas qui nous occupe, p_0 est la tension de vapeur des solutions à la température du laboratoire, 22° au moment de l'étalonnage et p, celle qui est donnée dans les tables des auteurs cités pour la température de 25°, donc $t = 25 - 22° = 3°$.

Ainsi, on trouve

$$\frac{p}{1 + 0.003662 \times 3} = \frac{22.973}{1.010986} = 22.723 \text{ mm}$$

pour la tension de vapeur, à 22°, de la solution à une molécule de bromure de sodium par litre, dont la tension de vapeur à 25° est 22.973 mm, d'après la détermination des auteurs précités.

Pour le calibrage de l'échelle densitométrique constituée de cette manière, nous avons pris un petit flacon de 8–10 ml environ, muni d'un couvercle souple et hermétique, et rempli de moitié avec de l'eau distillée.

On recouvre l'ouverture de ce flacon avec une feuille de cellophane naturelle, c'est-à-dire non imperméabilisée, (No. 600), trempée dans l'eau et on la fixe au goulot du flacon à l'aide d'un fil de coton. On la laisse sécher à l'air, on coupe et on enlève les parties de la pellicule cellulosique qui dépassent l'enroulement du fil et on bouche de nouveau le flacon avec son couvercle souple en plastique.

En conservant le récipient ainsi bouché pendant plusieurs heures, la vapeur dégagée par l'eau contenue dans celui-ci est absorbée au fur et à mesure par la cellophane qui se sature d'humidité. Nous estimons qu'une période de 24 heures de repos est largement suffisante pour obtenir l'état de saturation exigé pour le calibrage.

Lorsque, après avoir retiré rapidement le couvercle, on applique immédiatement sur l'ouverture du flacon, pendant trois minutes exactement, et en la pressant avec un poids convenable, une plaque hygrophotographique, l'humidité contenue dans la cellophane passe dans la gélatine de la plaque en y produisant une zone arrondie de décoloration. En pesant le flacon bouché avant et après cette opération, on peut connaître exactement la quantité d'eau cédée par la cellophane à la plaque. La pellicule cellulosique se comporte ici comme un condensateur qui se charge d'électricité et se décharge ensuite.

Connaissant la surface de décoloration et la quantité d'eau absorbée par cette surface, il est facile de calculer la quantité d'eau fixée par unité de surface de la plaque.

On place ensuite cette même plaque sur un bloc transparent en plexiglas, portant dans son épaisseur six creux identiques arrondis, de 8 mm de profondeur et de 10 mm de largeur, remplis successivement de l'eau pure et de cinq solutions de bromure de sodium, de concentrations croissantes et on y maintient celle-ci, sous une pression suffisante, jusqu'à ce que la décoloration obtenue avec l'eau pure soit identique à celle produite par la cellophane, ce qui demande de 10 à 15 min. L'égalité des décolorations peut d'ailleurs être établie avec l'une quelconque des cinq solutions salines du bloc.

Quand cette égalité est obtenue, cela indique que la quantité de vapeur d'eau absorbée par la partie de la plaque au-dessus de l'eau pure est telle qu'elle a fixé, par unité de surface, une quantité d'eau égale à celle fixée sur la zone de comparaison.

Ici, le diamètre de cette zone imprimée par la cellophane et qui est rendue en noir sur les images positives, étant de 21 mm, sa surface est de 346.36 mm^2; la quantité d'eau absorbée par cette surface est de 3169 μg dans une première pesée, et de 3193 μg dans une seconde. On voit que cette quantité est à peu près constante, ce qui permet de ne pas avoir recours constamment à la balance, lorsqu'on travaille surtout loin du laboratoire. Le calcul montre que la quantité d'eau fixée est de 9.1 μg et de 9.2 μg par mm^2 de surface.

Si une mole d'eau pure (18 g), à la pression atmosphérique (760 mm) occupe 22,400 cm^3, 0.0000091 g d'eau pure doit occuper

$$\frac{22{,}400 \times 0.0000091}{18} = 0.0113 \text{ cm}^3.$$

La tension de vapeur de l'eau pure, à 25°, étant 23.752 mm, à 22° elle est 23.493 mm et comme 9.1 μg d'eau sous 760 mm occupe un volume de 0.0113 cm^3, sous 23.493 mm, elle occupe

$$\frac{0.0113 \times 760}{23.493} = 0.3655 \text{ cm}^3.$$

D'autre part, dans l'échelle densitométrique ainsi constituée (Fig. 5), le degré densitométrique de la figure 5a témoin, obtenue avec la pellicule cellulosique, étant identique à celui de la figure 5b, qui correspond à l'eau pure, la quantité d'eau fixée par unité de surface pour cette figure est donc 9.1 μg par mm^2.

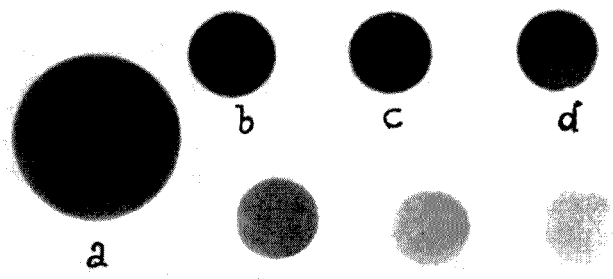

Fig. 5. Échelle densitométrique établie avec de l'eau pure (en a et en b) et de 5 solutions de bromure de sodium de concentrations croissantes.

Mais, si sous une tension de 23.493 mm, on a obtenu l'évaporation de 0.3655 cm^3 d'eau, sous 19.289 mm (tension de vapeur, à 22°, de la solution de bromure de sodium 4.5 M), on a dû obtenir l'évaporation de

$$\frac{19.289 \times 0.3655}{23.493} = 0.3008 \text{ cm}^3$$

d'eau et comme 0.3655 cm^3 d'eau pèse 9.1 μg, 0.3008 cm^3 d'eau pèse

$$\frac{0.3008 \times 9.1}{0.3655} = 7.4 \ \mu\text{g}.$$

Un raisonnement analogue nous montre que sous une tension de vapeur de 18.671 mm, qui est celle de la solution de bromure de sodium 5 *M* pour la même température, la plaque hygrophotographique a dû absorber 0.2904 cm^3 de vapeur d'eau, d'un poids de 7.2 μg.

Le calcul final donne les résultats suivants:

TABLE I

	Tension de vapeur à 22°	*Vapeur dégagée en*	
		cm^3	μg
Eau pure	23.493	0.3655	9.1
BrNa, *M*	22.723	0.3535	8.8
BrNa, 2.5 *M*	21.435	0.3334	8.3
BrNa, 3 *M*	20.950	0.3259	8.1
BrNa, 4.5 *M*	19.289	0.3008	7.4
BrNa, 5 *M*	18.671	0.2904	7.2

La comparaison des enregistrements hygrophotographiques obtenus au contact des échantillons soumis à l'analyse (feuille végétale, terre arable, matières plastiques, etc.) à l'échelle densitométrique peut être faite par simple examen à l'oeil nu, mais elle peut aussi être effectuée avec une précision bien plus grande, par l'emploi d'un densitomètre.

Nous avons pu doser par cette méthode la quantité d'eau qu'une plante est susceptible de perdre par la transpiration foliaire, ainsi que la proportion d'humidité qui peut traverser par diffusion et dissolution les matières plastiques de structures et de compositions différentes.

Fig. 6. La transpiration de la face supérieure d'une feuille d'Arachide.

Sans entrer dans les détails de ces analyses, dont les résultats paraîtront ailleurs, nous reproduisons, à titre d'exemples, deux hygrophotographies, dont l'une représente la transpiration de la face supérieure d'une feuille d'Arachide (Fig. 6) et l'autre, la perméabilité de deux échantillons de matières plastiques à l'humidité (Fig. 7) et il suffit de les comparer à l'échelle densitométrique de la figure 5, pour obtenir le résultat analytique cherché.

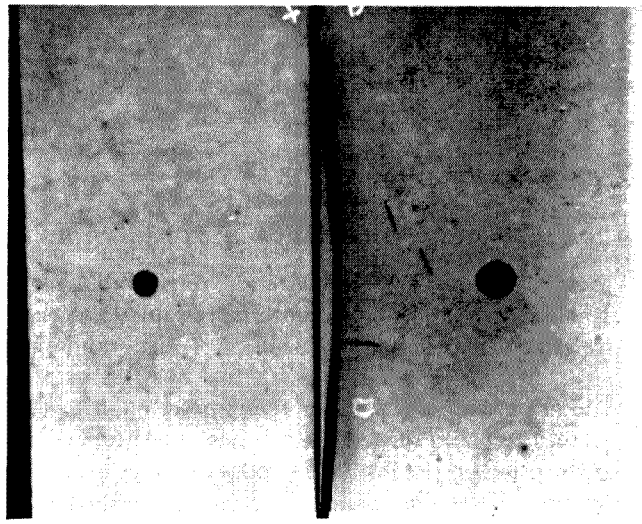

Fig. 7. La perméabilité à l'eau de deux échantillons de matières plastiques.

RÉSUMÉ

L'auteur qui avait exposé ici même, en 1953, le principe d'une nouvelle méthode analytique, dite hygrophotographie, destinée à la détection de l'eau, donne, dans le présent travail, quelques exemples sur l'application de cette méthode à la recherche de l'humidité dans les solvants organiques neutres, tels que les alcools, l'acétone, le dioxane, etc. Il décrit en outre la technique qui permet d'obtenir des résultats quantitatifs par l'étalonnage de la plaque hygrophotographique au moyen de l'eau pure et de solutions aqueuses de bromure de sodium à des concentrations croissantes. On obtient ainsi une échelle densitométrique de comparaison qui donne le moyen de doser les quantités d'eau absorbées par la gélatine de la plaque hygrophotographique au contact des feuilles végétales, de la terre arable, de matières plastiques perméables à l'eau, etc.

SUMMARY

Some applications of a method called "hygrophotography" for the detection and determination of water are described. The method is suitable for the determination of small quantities of water in organic solvents, plants, soil samples, etc.

ZUSAMMENFASSUNG

Es werden einige Anwendungen der als „Hygrophotographie" bezeichneten Methode zum Nachweis und der Bestimmung von Wasser mitgeteilt. Die Methode eignet sich zur Bestimmung von geringen Mengen Wasser in organischen Lösungsmittel, Pflanzenteilen, Erdproben usw.

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COULOMETRISCHE PERMANGANATOMETRISCHE BESTIMMUNG VON WASSERSTOFFPEROXYD

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Durch Elektrolyse saurer wässriger Lösungen von Mangansulfat wird an der Anode die Oxydation des Mn^{+2} Ions in MnO_4^- Ion bewirkt. Auf Grund des Studiums der Anodenpotentiale und der anodischen Oxydationsprozesse bei der Elektrolyse schwefelsaurer Lösungen von Mangansulfat haben TUTUNDŽIĆ UND MLADENOVIĆ[1] die Bedingungen für die quantitative anodische elektrolytische Bildung von Permanganationen ermittelt und haben auf dieser Grundlage die coulometrische Permanganatometrie aufgebaut. Anodische Oxydation der Mn^{+2} Ionen zu MnO_4^- Ionen ist quantitativ bei der Elektrolyse wässriger 0.45 bis 0.027 *M* Lösungen von Mangansulfat und 3.6 *N* und stärkerer Schwefelsäure. Das Anodenpotential muss positiver als 1.40 V sein und darf den Wert $e_h = 1.7$ V nicht überschreiten. Unter diesen Bedingungen ist die anodische Reaktion

$$Mn^{+2} + 4\,H_2O \rightarrow MnO_4^- + 8\,H^+ + 5\,e$$

quantitativ und mit den entwickelten MnO_4^- Ionen können verschiedene quantitative analytische permanganatometrische Bestimmungen ausgeführt werden.

Bis jetzt sind die Methoden für coulometrische permanganatometrische Mikrobestimmungen von Oxalat-, Ferro- und Arsenitionen ausgearbeitet worden[2,3].

Die coulometrische Permanganatometrie haben wir nun auch zur Mikrobestimmung von Wasserstoffperoxyd angewandt.

In saurer Mitte reagiert Wasserstoffperoxyd, bekanntlich, mit Permanganationen nach der Gleichung

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ = 5\,O_2 + 2\,Mn^{+2} + 8\,H_2O$$

Bei Zimmertemperatur tritt die Sauerstoffentwicklung auf, während bei niedrigerer Temperatur das Erscheinen von Sauerstoff ausbleibt[4,5]. Durch unmittelbare anodische Oxydation des Wasserstoffperoxyds wird ebenfalls Sauerstoff entwickelt[6,7]. TANATAR[6] und SCHÖNE[7,8] haben festgestellt, dass es bei der Elektrolyse saurer wässriger Lösungen von Wasserstoffperoxyd zu seiner Zersetzung unter der Einwirkung des atomaren Sauerstoffs, der an der Anode entwickelt wird, kommt.

Die katalytische Zersetzung des Wasserstoffperoxyds tritt unter dem Einfluss der Platinelektrode, auch ohne Elektrolyse, ein[6,9,10] und kann auch durch Glas[11,12], Fe^{+2} und Fe^{+3} Ionen[13,14] und MnO_2[15], als Substanzen die bei der coulometrischen

Permanganatometrie von Bedeutung sind, hervorgerufen werden. Mn^{+2} Ion beschleunigt die katalytische Zersetzung des Wasserstoffperoxyds unter dem Einfluss des Glases[12]. Auf Grund des Studiums der Kinetik der Reaktion des Wasserstoffperoxydes mit Kaliumpermanganat nehmen BAILEY UND TAYLOR[16] an, dass Wasserstoffperoxyd die partiell reduzierten Manganionen, wie z.B. MnO_3^- Ionen[17] reoxydiert, was niedrigere Resultate bei der Bestimmung des Wasserstoffperoxyds ergeben könnte.

Bei der coulometrischen permanganatometrischen Bestimmung der Oxalat-, Ferro- und Arsenitionen haben TUTUNDŽIĆ UND MLADENOVIĆ das Ende der Titration mit Hilfe von *o*-Phenanthrolin–Ferro-Komplex, Feroin, festgestellt[1,2]. Das Normaloxydationspotential des Feroins hat den Wert von 1.06 V, während die Farbänderung bei 1.12 V, für pH = 0, eintritt[18,19]. Das Ende der Titration haben TUTUNDŽIĆ UND MLADENOVIĆ bei Bestimmung des Ferroions unmittelbar durch Farbänderung des Indikators festgestellt, während sie bei den coulometrischen permanganatometrischen Titrationen der Oxalat- und Arsenitionen sich der indirekten Endpunktbestimmung, mittels desselben Indikators, bedienten.

VERFAHREN

Bei der Ausarbeitung der coulometrischen permanganatometrischen Methode zur Mikrobestimmung von Wasserstoffperoxyd wurden die direkte, sowie die indirekte Methode der Endpunktbestimmung, angewandt.

Das Oxydationspotential des Wasserstoffperoxyds hat, unter unseren Arbeitsbedingungen, einen Wert bei dem sich das Feroin grösstenteils in seiner Oxydationsform befindet und wenn dem Grundelektrolyten, in dem schon das Feroin in seiner Oxydationsform vorhanden ist, das zu bestimmende Wasserstoffperoxyd zugegeben wird, erscheint die Farbe der Reduktionsform des Indikators nicht mehr, weswegen das Feroin als Indikator zur direkten Endpunktbestimmung nicht geeignet ist.

Daher muss bei der Bestimmung des Wasserstoffperoxyds ein Indikator mit positiverem Normaloxydationspotential verwendet werden. Die Anwendung des 5-Nitro-*o*-Phenanthrolins zur Endpunktbestimmung durch die direkte Methode hat zu sehr zufriedenstellenden Resultaten geführt. Das Normaloxydationspotential dieses Indikators ist positiver als das Normaloxydationspotential des Feroins und beträgt 1.25 V, während die Farbänderung bei 1.31 V, für pH = 0, eintritt[20]. Gibt man dem Grundelektrolyten diesen Indikator zu und oxydiert man ihn nachher durch elektrolytisch erzeugte Permanganationen bis zu der Ferriform und fügt man dem so bereiteten Anolyten das zu bestimmende Wasserstoffperoxyd zu, so bemerkt man, dass schon die ersten zugegebenen Tropfen die rote Farbe der Reduktionsform wieder hervorrufen. Nur im Falle, dass der Grundelektrolyt mehr als 10 *N* Schwefelsäure enthält, erscheint die rote Färbung des vorher oxydierten Indikators nach der Zugabe des Wasserstoffperoxydes nicht mehr wieder und unter diesen Bedingungen kann das Nitro-Feroin für unmittelbare Bestimmung des Endpunktes der Titration nicht angewandt werden. Zahlreiche Bestimmungen haben bewiesen, dass 5-Nitro-*o*-Phenanthrolin als Indikator mit gutem Erfolg für die direkte Endpunktbestimmung bei der coulometrischen permanganatometrischen Titration des Wasserstoffperoxyds angewandt werden kann. Die Indikatorlösung wird auf dieselbe Weise wie die Feroinlösung bereitet, wovon 6–8 Tropfen einer 1 : 3 Lösung (1 Teil 0.025 *M* und 3 Teile Wasser) benutzt werden.

Bei indirekten Endpunktbestimmungen kann mit Erfolg als Indikator ebenfalls 5-Nitro-*o*-Phenanthrolin, sowie auch Feroin verwendet werden.

Das Verfahren, sowie die Apparatur für coulometrische permanganatometrische Mikrotitration des Wasserstoffperoxyds sind dieselben wie diejenigen für die Bestimmung von Oxalat-, Ferro- und Arsenitionen[2]. Die Elektrolyse wird bei konstanter und genau bekannter Stromstärke, ausgeführt. Die Änderungen der Stromstärke, durch Änderung der Leitfähigkeit der Zelle, sowie durch Wärme-Effekt in Aussenwiderständen hervorgerufen, kann leicht kompensiert werden. Anolyt und Katholyt müssen auch für diese Bestimmungen getrennt werden, um die Reduktion der gebildeten Permanganationen an der Kathode zu vermeiden. Der Grundelektrolyt, der als Anolyt, sowie als Katholyt dient und auch den elektrolytischen Schlüssel ausfüllt, enthält meistens eine 0.2 *N* Lösung von Mangansulfat in 6 bis 7 *N* Schwefelsäure. Es wurde auch mit verschiedenen Konzentrationen der Schwefelsäure von 3.6 *N* bis 14 *N* gearbeitet und festgestellt, dass es beim Arbeiten mit einem Anolyten mit 3.6 *N* und 4 *N* Lösung von Schwefelsäure zur Bildung einer MnO_2-Schicht an der Anode kommt, was positive Fehler von 0.3 bis 0.8% verursacht.

Durch diese coulometrische permanganatometrische Methode können sehr leicht und genau 1 bis 5.5 mg Wasserstoffperoxyd in 50 ml des Grundelektrolyten mit Stromstärken von etwa 8 und 10 mA bestimmt werden, wobei in einer Sekunde etwa $1.5 \cdot 10^{-3}$ mg, bzw. $1.8 \cdot 10^{-3}$ mg Wasserstoffperoxyd oxydiert werden. Während der Titration soll die Temperatur des Anolyten von 30° bis 32° eingehalten werden, um die Zersetzung des Wasserstoffperoxydes unter dem Einfluss der erhöhten Temperatur in annehmbaren Grenzen zu halten. Während der Ausführung der Bestimmung wird der Anolyt mechanisch mässig gerührt. Durch Änderung der Elektrodenoberfläche konnte nach Bedarf die Stromdichte variiert werden.

Bei indirekten coulometrischen Analysen mit konstanter Stromstärke muss die angewandte Stromstärke kleiner sein, als der Grenzstrom des Elektrodenprozesses, durch welches das Reagens primär erzeugt wird. Bei der anodischen Oxydation des Mn^{+2} Ions zum MnO_4^- Ion hängt die Grenzstromstärke von der Temperatur, von der Konzentration der Schwefelsäure und des Mangansulfats, sowie vom dessen Verhältnis ab, wobei alle drei Faktoren die Grenzstromstärke erhöhen und hauptsächlich die Konzentration des Mangansulfats, in Abhängigkeit von der zu bestimmenden Wasserstoffperoxydmenge. Die Analysenresultate stimmen mit den theoretischen Betrachtungen überein und zeigen, dass die festgestellten Bedingungen für Indikatoren[21] auch für die coulometrische permanganatometrische Bestimmung des Wasserstoffperoxydes ihre Gültigkeit haben.

Bei der indirekten Methode ist es bei ungenügender Reinheit der Reaktive nötig eine Prätitration auszuführen, während bei der direkten Methode der Endpunktbestimmung die Prätitration der Begleitstoffe mitinbegriffen ist. Beide Methoden, mit gleichzeitiger Prätitration, stellen zu gleicher Zeit ein Verfahren für die Einstellung des Anolyten auf das Potential des Endpunktes der Titration durch Anwendung des Indikators dar, analog der Einstellung des Elektrolyten auf das Potential des Endpunktes der Titration durch Anwendung der potentiometrischen Methode der Endpunktbestimmung[22,23], was man als ein allgemeines Verfahren für die Anwendung der Redox-Indikatoren bei der coulometrischen Titration betrachten kann.

TABELLE I

INDIREKTE COULOMETRISCHE METHODE

Indikator Feroin: i = 10.40 mA

Stromdichte mA/cm²	Temperatur °C	Grundelektrolyt, 50 ml H_2SO_4 N	Grundelektrolyt, 50 ml $MnSO_4 \cdot 4H_2O$ M	mg H_2O_2 Genommen	mg H_2O_2 Gefunden	Fehler mg	Fehler %	Dauer sec
0.20	30°	6	0.067	1.143	1.151	0.008	0.7	628.0
				2.285	2.272	—0.014	—0.6	1.238.9
0.45	21–22°	6	0.54	2.794	2.786	—0.008	—0.3	1.520.0
				4.192	4.166	—0.026	—0.6	2.272.6
		6.5	0.13	0.699	0.703	0.004	0.6	383.4
				1.397	1.391	—0.006	—0.4	758.6
				2.794	2.790	—0.004	—0.1	1.521.9
	20° (±1)	7	0.18	1.590	1.579	—0.011	—0.7	861.3
				2.385	2.373	—0.012	—0.5	1.294.5
				3.180	3.164	—0.016	—0.5	1.725.9
	21–22°	14	0.045	1.397	1.407	0.010	0.7	767.3[a]
				1.397	1.403	0.006	0.4	765.1[a]
	30° (±2)	6	0.045	4.219	4.196	—0.023	—0.6	2.288.7
			0.090	4.219	4.209	—0.010	—0.2	2.296.5
			0.36	4.219	4.208	—0.011	—0.3	2.295.7
1.5	20° (±1)	7	0.54	1.590	1.587	—0.003	—0.2	865.9
				1.590	1.595	0.005	0.3	870.0
				2.385	2.382	—0.003	—0.1	1.299.7
				2.703	2.693	—0.010	—0.4	1.689.3
				3.180	3.178	—0.002	—0.1	1.733.5
				3.975	3.969	—0.006	—0.2	2.165.4
	30° (±2)	6	0.36	4.219	4.214	—0.005	—0.1	2.298.6
		8	0.18	4.220	4.207	—0.013	—0.3	2.294.8
			0.27	4.221	4.215	—0.006	—0.1	2.301.4
			0.36	4.220	4.219	—0.001	—0.0	2.301.7
			0.45	4.221	4.209	—0.012	—0.3	2.294.2
			0.36	4.219	4.216	—0.003	0.1	2.299.9
				5.627	5.598	—0.029	—0.5	3.053.6
		10	0.36	4.219	4.224	0.005	0.1	2.304.5

[a] Indikator Nitro-Feroin

TABELLE II

DIREKTE METHODE

Indikator Nitro-Feroin: i = 10.40 mA

Stromdichte mA/cm²	Temperatur °C	Grundelektrolyt ml	Grundelektrolyt H_2SO_4 N	Grundelektrolyt $MnSO_4 \cdot 4H_2O$ M	mg H_2O_2 Genommen	mg H_2O_2 Gefunden	Fehler mg	Fehler %	Dauer sec
0.4	30° (±1)	50	6	0.067	1.143	1.141	—0.002	—0.2	622.2
					1.143	1.146	0.003	0.3	625.1
1.5	21–22°	25	7	0.45	1.397	1.404	0.007	0.5	765.8
			7	0.54	1.397	1.386	—0.011	—0.8	756.2
					1.397	1.404	0.007	0.5	765.7
			6	0.54	1.397	1.409	0.012	0.9	768.5
					1.397	1.393	—0.004	—0.3	760.0
			10	0.45	1.590	1.576	—0.014	—0.9	860.0
	30° (±2)	50	8	0.36	4.220	4.218	—0.002	—0.1	2.301.0
					4.220	4.219	—0.001	—0.0	2.301.0

ERGEBNISSE

Einige der erzielten Resultate, unter den schon angegebenen Bedingungen, enthalten Tabellen I und II.

Aus den Tabellen I und II ersieht man, dass die meisten Bestimmungen einen negativen Fehler aufweisen. Ein Grund dafür liegt, unserer Meinung nach, in der Einwirkung des Platins, da wir feststellen konnten, dass es unter unseren Arbeitsbedingungen auch zu katalytischer Zersetzung des Wasserstoffperoxyds an der Anode kommen kann. Deswegen ist es, unserer Erfahrung nach, ratsam mit einer Anode aus Platin, die so klein als möglich ist, und schnell zu arbeiten, auf welche Weise man, wie die Ergebnisse zeigen, sehr gute Resultate erzielen kann.

ZUSAMMENFASSUNG

Es wurde eine coulometrische permanganatometrische Methode zur Mikrobestimmung von Wasserstoffperoxyd entwickelt. Die Endpunktbestimmung wird mit Hilfe des *o*-Phenanthrolin–Ferro-Komplexes und des 5-Nitro-*o*-Phenanthrolin–Ferro-Komplexes als Indikator bewirkt.

Die Resultate bewegen sich in den üblichen Fehlergrenzen der schon ausgeführten coulometrischen permanganatometrischen Mikrobestimmungen, wobei die specifischen Eigenschaften des Wasserstoffperoxyds, sowie seine Unbeständigkeit in Betracht gezogen werden müssen.

SUMMARY

A method has been developed for the quantitative coulometric permanganatometric microdetermination of hydrogen peroxide. The end-point is ascertained by the colour changes of the indicators ferroin, and nitro-ferroin respectively.

RÉSUMÉ

Une méthode coulométrique par permanganatométrie est présentée pour le dosage de l'eau oxygénée à l'échelle micro. La détermination du point final est effectuée à l'aide de ferroïne ou nitro-ferroïne comme indicateur.

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Short Communications

Determination of niobium in the presence of tantalum after extraction with methyl isobutyl ketone

In a recent paper[1] it was shown that germanium extracted from hydrochloric acid solution with methyl isobutyl ketone can be made to react directly in the organic phase with phenylfluorone and then determined spectrophotometrically.

Niobium(V) was found to interfere in this procedure and had to be removed before performing the germanium extraction, but no interference due to the presence of tantalum(V) was observed.

On the basis of these findings it seemed possible that a method for the determination of niobium in the presence of tantalum could be developed.

The efficiency of the extraction was investigated by using solutions containing sulfuric + tartaric acids, which were made 7.5 *N* in hydrochloric acid. 1.0 ml of the aqueous hydrochloric solution was extracted with 1.0 ml of methyl isobutyl ketone, the content of niobium being varied from 10 to 200 μg. In every case 90% of the niobium was extracted in a single operation.

The extracted niobium reacts instantaneously in the organic phase with an alcoholic solution of phenylfluorone, giving a stable colored solution. Experiments performed according to the procedure given below showed that at the wave length of maximum absorption, 502 mμ, Beer's law is obeyed in the range studied, which was 0.2 to 2.0 μg Nb/ml; a Ringbom plot indicated the optimum concentration range to be 0.5 to 1.6 μg Nb/ml (final dilution). Spectrophotometric readings were found to be reproducible within 24 h after exposure to ordinary light at room temperature.

It was found that tantalum was not extracted by the treatment outlined above. Extraction experiments were carried out with pure tantalum solutions containing 10 and 1000 μg Ta/ml and the element was always quantitatively recovered in the aqueous phase. Furthermore, evidence was obtained that tantalum does not react with phenylfluorone in organic solution under the conditions of the procedure studied.

Experiments for the determination of niobium in the presence of tantalum were run with solutions containing 10 μg Nb and either 10, 200, 500 or 1000 μg Ta. Results were in perfect agreement with those obtained with the same concentration of niobium in absence of tantalum and no interference was observed in any region of the spectrum of the colored solution. It was also found that tantalum can be quantitatively extracted from the remaining aqueous phase with methyl isobutyl ketone after addition of sufficient hydrofluoric acid to make the solution about 2% in HF. Thus if necessary, tantalum can be determined, after separation of niobium, by the procedure given by LUKE[2].

The procedure reported in this communication is intended for application to the determination of niobium in mixtures of niobium and tantalum pentoxides, which are fused in the usual manner in a platinum crucible with excess potassium pyrosulfate. The melt is brought into solution with the aid of a mixture of 10% sulfuric and 10% tartaric acids.

Procedure

Place in a test tube with a ground glass stopper 1.0 ml of the tartaric–sulfuric solution, which should preferably contain 5 to 15 μg of niobium. Add 2.0 ml of concentrated hydrochloric acid ($d = 1.18$) and extract successively with one 1-ml and two 0.7-ml portions of methyl isobutyl ketone, shaking vigorously each time. Collect the extracts in a 10-ml volumetric flask. Add 3.0 ml of an alcoholic solution of phenylfluorone (0.02% phenylfluorone in a mixture of 95 ml ethyl alcohol and 5 ml H_2SO_4 (1 : 6))[1] and fill up to the mark with ethyl alcohol. Read the transmittance at 502 mμ against a blank.

In the course of this study a Beckman DU spectrophotometer and 1-cm Corex cells with ground glass stoppers were used. The same extraction technique previously reported[1] was employed.

A detailed paper on this subject including an investigation of the influence of foreign ions will be published later.

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A simple and rapid determination of small amounts of adenine

The determination of small quantities of adenine usually demands complicated analytical techniques, such as spectrophotometry[1], polarography[2], colorimetry after bromination[3] etc. We have developed a new method for the determination of small

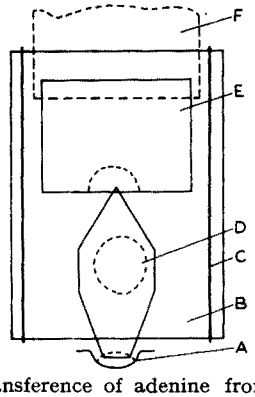

Fig. 1. Arrangement for direct transference of adenine from a chromatographic spot to the impregnated paper. A = water container, B = glass plates, C = plastic, D = spot, E = impregnated paper, F = blotting paper.

quantities of adenine (in the range 3–10 μg). The method is based on the measurement of the size of the spots formed on paper impregnated with silver arsenate when an aqueous solution of adenine is spotted on the paper and the spot is developed. The size of spot is proportional to the amount of adenine added.

The impregnated paper was prepared by immersing a strip of Whatman No. 1 chromatographic paper in an aqueous 0.1% silver nitrate solution, and after drying, in an aqueous 0.2% potassium arsenate solution; the method of impregnation has already been described in detail[4]. The paper impregnated with silver arsenate is very sensitive to light, and must be kept in the dark.

The aqueous solution of adenine can be placed on the impregnated paper directly from a micropipette or microextractor[5], or by means of the arrangement described previously for the analysis of phosphorus[6]. When adenine is to be estimated directly on a chromatogram, the elution process can be omitted; the adenine can be transferred directly from the spot on to the impregnated paper as illustrated in Fig. 1.

After the test solution has been placed on impregnated paper, the spot obtained must be diluted with 0.2–0.3 ml of distilled water.

The spot is then made visible by immersion for 1–2 min in photographic developer Ilford 1D2[7]. A white fleck of the complex of adenine with silver appears on the black background. The white spot is fixed by acid photographic solution. The spot is stable in the dark and its area can be measured by some suitable method[8]. The size of the spot is then compared with the control series on a suitable diagram. The analysis must be done in the dark.

The error in the results is about $\pm$ 5%.

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BOOK REVIEWS

Qualitative analysis and analytical chemical separations, by P. W. WEST AND M. M. VICK. 2nd Ed., The Macmillan Company, New York 1959, Pp. xv + 302, $ 4.5.

The authors of this book have presented a new approach to the teaching of qualitative inorganic analysis in order that students may better derive the maximum benefit from their work in this field. The basis of the new approach is a non-sulphide scheme of analysis which, it is claimed, offers advantages, both in theory and in practice, over the classical hydrogen sulphide scheme.

The contents of the book are divided into three parts: *Experimental*, *Fundamental Theory* and *The Metals*.

Part I, *Experimental* (84 pp.), is devoted mainly to the actual cation separation scheme. The latter involves the successive precipitation, from a single portion of sample solution, of a Chloride Group (Hg_2^{+2} and Ag^+), a Basic Benzoate Group (Sn^{+4}, Bi^{+3}, Sb^{+3}, Ge^{+3}, Al^{+3} and Cr^{+3}), a Fluoride Group (Pb^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2} and Ca^{+2}), a Hydroxide or Non-amphoteric Group (Mn^{+2}, Fe^{+2}, Hg^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2} and Cd^{+2}), leaving only an Amphoteric Group (Sn^{+2}, As^{+3} and Zn^{+2}) in the final solution. Examination is made for a Soluble Group (Na^+, K^+ and NH_4^+) on a second portion of the sample solution. The subject matter is arranged so that the reason behind every operation is to be derived from the carrying out of preliminary exercises, while discussions and explanations follow in the portion of the text dealing with the running of an unknown sample.

The method adopted for analysis of the anions, inherently more difficult than for analysis of the cations, contains nothing particularly new. It is based on such classical procedures as precipitation of anions with Ba^{+2}, Ca^{+2} and Ag^+ in solutions of varying acidity. These results are then considered in conjunction with those derived from preliminary tests, such as gases evolved upon acidification, oxidizing and reducing properties.

Peculiarly, there appears to be no mention of how much sample to take nor of how to prepare a solution of the sample for cation analysis. Directions given in the separation scheme seem to indicate a semi-micro scale of working. Advantages to be gained by working at less than macro levels might usefully be mentioned. The remarks on apparatus and technique (2½ pp.) are, in the reviewer's opinion, much to condensed. They could profitably be expanded and preferably illustrated. It is, however, pleasing to see the need to avoid contamination of reagent solutions (p. 8) and the advisability of carrying out both *control* and *blank* tests (p. 13) receive more emphasis than usual.

The authors have found it "not practical to delay the beginning of laboratory work until the student has mastered all of the theory which is required for the proper understanding of all of the procedures". *Fundamental Theory* (124 pp.) is, therefore, placed in Part II after the *Experimental* in Part I. Many people would doubtless still prefer the alternative arrangement. Close inspection of chapters comprising Part II confirms the authors' view that presentation of theory is much easier when associated with their non-sulphide scheme than when combined with classical hydrogen sulphide-based analysis. The inclusion of a series of questions and problems at the end of nearly every chapter is a useful feature.

Part III, *The Metals* (64 pp.) is sub-divided into *Metals and Metallurgy* and into *Reactions of the Metals and Metal Ions*. The material on metallurgy and chemistry of the metals appears for the first time in the second edition, having been added to provide a text suitable also for requirements of general chemistry. The need to make this change is greatly regretted by the reviewer for, in his opinion, the real value of the book lies rather in its attempt to present a new approach to qualitative inorganic analysis than in its expansion into a "several purpose" text. Only the summarised reactions of the various metal ions are particularly relevant to the teaching of analysis.

Two interesting additions have been made to the *Appendix* (21 pp.) short sections on spot test procedures and on mathematical operations. The spot tests should provide a valuable means of double-checking results obtained by the systematic scheme of analysis.

Non-sulphide approaches to qualitative analysis have previously been introduced, but none has stood the test of time in comparison with the classical hydrogen sulphide scheme. It is, therefore, significant that, in student hands for over four years at more than sixty institutions in the United States, the present scheme has proved itself capable of getting results comparable or superior to the classical scheme. This is the ultimate proof of the worth of any scheme. Since the book is specially designed for use in a United States teaching institution, its adoption can confidently be expected to become more widespread in that country.

Elsewhere, particularly where the classical hydrogen sulphide scheme still enjoys an almost complete ascendancy, it is more difficult to visualise the non-sulphide approach gaining rapid recognition. Such problems as acid and sulphide fumes have been largely eliminated by the universal scaling down of the hydrogen sulphide scheme from a macro to a semi-micro level of opera-

tion. At the same time much sharper group separations are possible. Further, at least one group of workers (*Mikrochim. Acta*, 12 (1956) 1842) is actively concerned with general improvement of the hydrogen sulphide scheme. The many teachers not seeking a change from the use of hydrogen sulphide would do well, however, to read this book carefully. The new ideas it puts forward present a serious challenge to the supremacy so long enjoyed by the classical scheme of qualitative inorganic analysis.

Finally, the title of the book is somewhat misleading. The contents might be better described by *"Qualitative Inorganic Analysis. A New Approach"*.

M. WILLIAMS (Birmingham)

Anal. Chim. Acta, 22 (1960) 299–300

Continuous Analysis of Chemical Process Systems, by SIDNEY SIGGIA, John Wiley and Sons, Inc., New York 1959, Pp. XIII 381, $ 8.50.

In industry today, continuous analysis of chemical processes is rapidly gaining importance. Such analyses are necessarily instrumental, frequently automatic and are sometimes geared to activate control circuits which automatically make adjustments to the chemical system being analysed. However much one may deplore increasing mechanisation of the analysts art and the replacement of the analyst and plant control chemist by automatic analytical-cum-reaction-control instruments, one must recognize that the situation does now exist.

This book represents the first monograph on continuous analysis of chemical process systems. The author has been faced with the paucity of published papers and has had to rely very largely on technical data and, to a lesser extent, advertising literature supplied by the instrument manufacturers. The material is therefore classified alphabetically according to manufacturer's name within sixteen chapter headings which deal with the physical property being determined *e.g.* refractive index, U.V. absorption, mass spectrometry, etc. Five other chapters are devoted to the measurement of moisture, oxygen, carbon dioxide, combustibles and water hardness; the final two chapters are concerned with automatic chemical analysis and instruments in the research or development stage.

The overall impression gained from a survey of this book is that it will be invaluable to those who desire to select and install such instrumentation; nowhere else is such a compilation available. It does not constitute a text-book of instrumental analysis and consequently its use to the analytical chemist is very largely restricted to interest-value. The coverage is very wide and must be virtually complete. For such a restricted specialist reading public, the cost is extremely moderate.

T. S. WEST (Birmingham)

Anal. Chim. Acta, 22 (1960) 300

Communication

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY ANALYTICAL CHEMISTRY SECTION

During the XXth Conference of the I.U.P.A.C. which was held in Munich in August, 1959, the Committee of the above Section discussed certain points of confusion in the literature. Recommendations were made as follows:

1. *Notation of indicators in titrimetric analysis.* Many dyestuffs have been recommended as indicators in chelatometric and redox titrations and a host of trivial names often exists for the same compound. Examples can be found in the literature of a compound having been recommended as a new indicator because it has a different name when the compound has in fact been in use for years under a different name.

To avoid future confusion and embarrassment of authors and editors, the Committee recommends that when a dyestuff is proposed as an indicator in any type of titration, and particularly when it is claimed as new, the British Colour Index or Schultz Number be quoted along with the trivial name.

2. *Terminology of complexing agents.* Because of the existing confusion regarding terminology in the use of complexing agents as titrants, the committee tentatively recommends the use of the following terms until such time further action is taken.

a. The group of polyamino-polycarboxylic acids which form *anionic* complexes shall be termed "complexans".

b. Titration processes in which any type of complexing titrant is used shall be termed "complexometric".

c. Those complexometric titrations which involve titration with a chelating agent shall be termed "chelatometric titrations" and represent a special type of complexometric titration.

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