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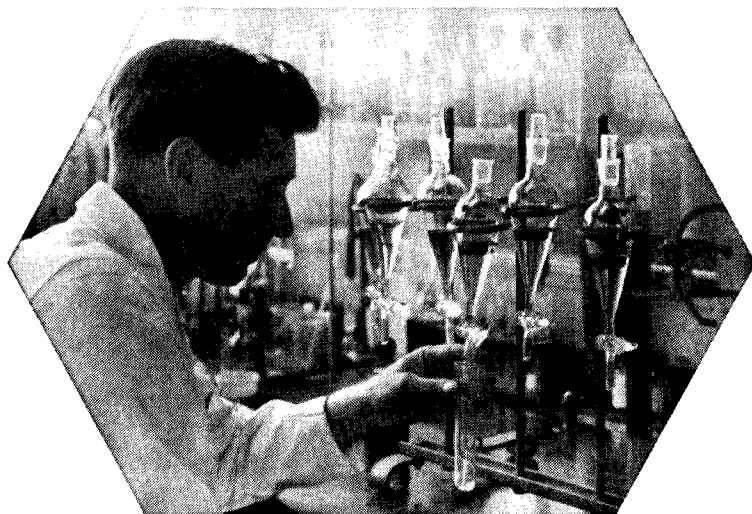
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Incidental information



*Items of
interest
from our
laboratory
notebooks*

► Most analysts know about 1,10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4,7-diphenyl-1,10-phenanthroline** is twice as sensitive as 1,10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 83 (1958) 80. The reagent is also called **Bathophenanthroline**, and we make it.

► Then, again the substitution of methyl groups in the 2,9 position has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 28 (1956) 1158). Hopkin & Williams make **2,9-dimethyl-**

1,10-phenanthroline (sometimes called **Neocuproin**).

► One does not think of sulphate as a radical one can determine absorptometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 29 (1957) 281 and *Anal. Chem.*, 30 (1958) 202. Hopkin & Williams make it.

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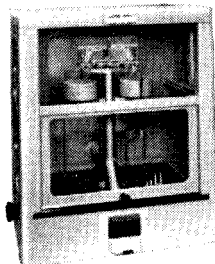
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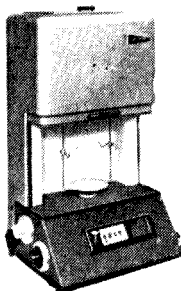


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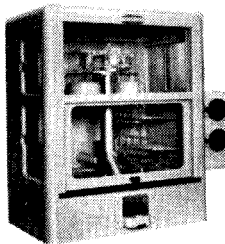
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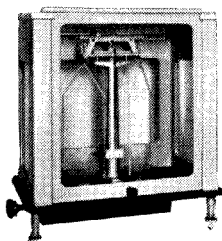
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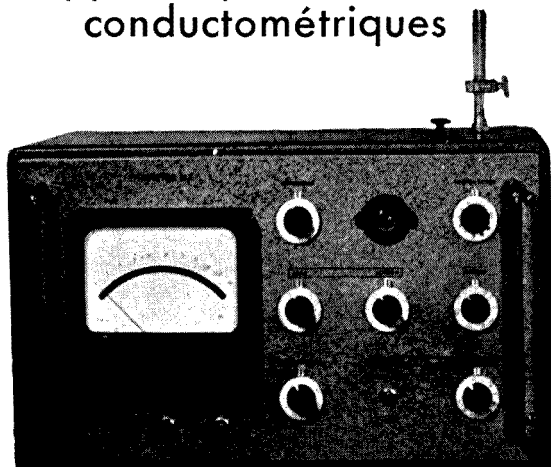
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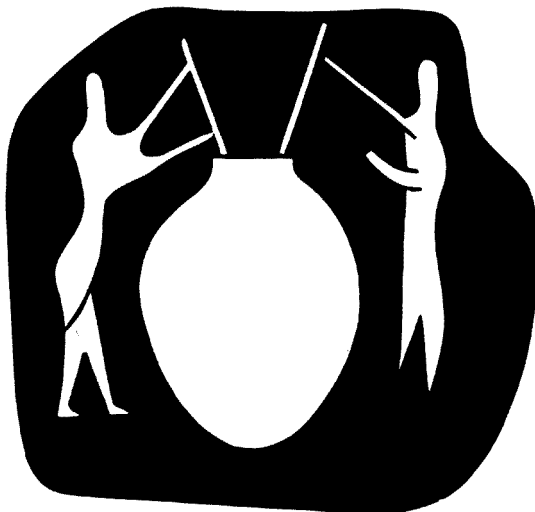
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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

II¹. DISCRIMINANTS IN ION COMBINATION REACTION CALCULATIONS

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In the calculation of ion concentrations in ion combination reactions, *e.g.* in titrimetry, there is often presented a choice of equations of differing precision or exactness². For example, in calculating the equivalence point pH in the titration of a weak base with a strong acid, if the ionisation of the solvent and the loss of cation by hydrolysis can both be ignored, a crude equation, the *simple* form (1), is employed,

$$[\text{H}^+] = \left(\frac{cK_w}{K_b} \right)^{\frac{1}{2}} \dots \dots \dots (1)$$

When the ionisation of the solvent is taken into account, but hydrolysis is ignored, one *approximate* form (2) which incorporates the solvent ionisation correction is applied,

$$[\text{H}^+] = \left(\frac{cK_w}{K_b} + K_w \right)^{\frac{1}{2}} \dots \dots \dots (2)$$

When, contrariwise, the loss of cation is taken into account, but the ionisation of the solvent is ignored, another *approximate* form (3), corrected for hydrolysis, is required,

$$[\text{H}^+] = \frac{1}{2K_b} \left\{ (K_w^2 + 4K_wK_b c)^{\frac{1}{2}} - K_w \right\} \dots \dots \dots (3)$$

Though these two corrections normally tend to be mutually exclusive, and the approximate equations are more nearly precise than the simple form, neither is yet entirely precise, and under certain conditions an *exact* form (4) is called into use which incorporates all the corrections and is exact under all conditions,

$$K_b a_{\text{H}^+}^3 + K_w a_{\text{H}^+}^2 - (K_b K_w + a_c K_w) a_{\text{H}^+} + K_w^2 = 0 \dots \dots \dots (4)$$

or, writing concentrations instead of active masses,

$$K_b [\text{H}^+]^3 + K_w [\text{H}^+]^2 - (K_b K_w + c K_w) [\text{H}^+] + K_w^2 = 0 \dots \dots \dots (4a)$$

Strictly, activities should be used in all the equations, but this does not alter the order of the equations.

In moving from the simple through the various approximate forms to the exact form, the order of the equations increases. With simple symmetrical binary compounds the movement is from a linear to various quadratics to a cubic equation. The labour and difficulty of solving these equations rises rapidly with increasing exactness

of the solutions, so it is desirable to use the simplest possible equation compatible with the required accuracy of the solution.

The error

In making calculations, the analyst has in mind a certain permissible error, which is set either by the precision required from the practical determination, or by the known precision of the measurements made in the course of the determination. For instance, if pH is the quantity concerned and the experimental technique permits of discrimination to ± 0.01 pH unit, the precision would be roughly 2% on the hydrogen ion concentration. This would then be the permissible error in the calculations, though it is customary to calculate to a slightly higher precision, so 1% would probably be chosen. The relative error incurred in using a less precise equation (giving a value Q_1) instead of a more precise equation (giving a value Q_2) in the calculation is given by

$$E = \pm \frac{Q_1 - Q_2}{Q_2} \dots \dots \dots (5)$$

Examination of the correction incorporated in the more precise equation will determine which sign should be employed to give E a positive value. Multiplication of E by 100 gives the percentage error.

The question now arises of deciding if and when it is necessary to change over from one equation to a more precise equation. To do this by trial and error can be as tedious as using the more precise equation throughout the whole series of calculations. Some simple means is needed of delineating the exact conditions under which the change over one way or the other is required. This decision may be placed on a simple quantitative basis by the use of expressions which discriminate between the alternative equations for a specified permissible error. For these discriminating expressions, the term *discriminant** is proposed.

Derivation of discriminants

The exact conditions under which the change from one equation to another should be made for a specific error can readily be defined by substituting the appropriate values in (5), simplifying to a *master discriminant*, and solving this equation for the particular condition in question, giving a series of *particular discriminants*. In the case quoted above, to decide when correction for ionisation of the solvent is necessary, substitution in (5) of the values for $[H^+]$ from (1) and (2) (which is the greater) gives.

$$\frac{\left(c \frac{K_w}{K_b} + K_w\right)^{\frac{1}{2}} - \left(c \frac{K_w}{K_b}\right)^{\frac{1}{2}}}{\left(c \frac{K_w}{K_b} + K_w\right)^{\frac{1}{2}}} = E \dots \dots \dots (6)$$

Simplification of (6) gives the *master discriminant* (7),

$$cE(2 - E) - K_b(1 - E)^2 = 0 \dots \dots \dots (7)$$

* The term is here used as an abbreviation for "discriminating expression", and should not be confused with the mathematical use of the term in the treatment of complex quantities.

which can be solved for E , c or K_b as required, and shows that the simple equation (1) is adequate when

$$c \geq \frac{K_b(1 + E)^2}{E(2 - E)} \approx \frac{K_b}{2E} \dots \dots \dots (8)$$

or when

$$K_b \leq \frac{E(2 - E)c}{(1 + E)^2} \approx 2Ec \dots \dots \dots (9)$$

These expressions are then the *particular discriminants*, (9), for example, being the base ionisation constant discriminant for solvent ionisation correction, indicating that if the ionisation constant of the base exceeds the given value, ignoring the ionisation of the solvent will incur an error greater than that stipulated.

A further use of discriminants is in the assessment or calculation of errors incurred by ignoring particular corrections³, by solving the master discriminant for the term E , as in equations (26), (34), (43) and (48).

The multiplicity of equilibria involved in titrimetric and other analytical calculations makes complete coverage too lengthy. The purpose of the following account is to give sufficient examples to permit direct treatment of the commoner calculations by means of discriminants, and to provide a pattern for the derivation of discriminating expressions wherever alternative equations of differing precision present themselves. For the classification of titrimetric processes, the utility and application of the various calculations and the derivation of the simple, approximate and exact equations, reference should be made to the standard texts². For brevity in the following account, the arguments and the algebraic working have been omitted.

I. *Discriminants in hydrogen ion concentration calculations*

(a) *Weak acids.* For a solution of molar concentration c of an acid of ionisation constant K_a ,

$$\text{Simple } [\text{H}^+] = (K_a c)^{\frac{1}{2}} \dots \dots \dots (10)$$

$$\text{Exact } [\text{H}^+] = \frac{1}{2} \{ K_a + (K_a^2 + 4K_a c)^{\frac{1}{2}} \} \dots \dots \dots (11)$$

Substitution in (5) and simplification gives the *master discriminant*,

$$cE^2(2 + E)^2 - K_a(1 + E)^2 = 0 \dots \dots \dots (12)$$

Solution of which gives the particular discriminants (13) and (14) which indicate that the simple form (10) is sufficiently accurate when

$$c \geq K_a \left(\frac{1 + E}{E(2 + E)} \right)^2 \approx \frac{K_a}{4E^2} \dots \dots \dots (13)$$

or

$$K_a \leq c \left(\frac{E(2 + E)}{1 + E} \right)^2 \approx 4E^2 c \dots \dots \dots (14)$$

(b) *Weak bases.* Although the simple and exact forms for $[\text{H}^+]$ are different from those for weak acids², the discriminants are the same, and substitution of K_b for K_a in (12), (13) and (14) gives the discriminants for weak bases.

(c) *Hydrolyzed salt solutions. Salts of weak bases with strong acids.* When the ionisation constant of the weak base is K_b and the concentration of the salt is c , equations (1) to (4) apply. Discriminants for ionisation of the solvent (7) to (9) have already been derived.

When loss of cation by hydrolysis must be taken into account, substitution of (1) and (3) in (5) yields the *master discriminant* for the hydrolysis correction,

$$E^2(2 + E)^2cK_b - (1 + E)^2K_w = 0 \quad (15)$$

The *particular discriminants* (16) and (17) show that the simple form (1) is valid when

$$K_b \gg \left(\frac{1 + E}{E(2 + E)} \right)^2 \frac{K_w}{c} \approx \frac{K_w}{4E^2c} \quad (16)$$

or when

$$c \gg \left(\frac{1 + E}{E(2 + E)} \right)^2 \frac{K_w}{K_b} \approx \frac{K_w}{4E^2K_b} \quad (17)$$

Salts of weak acids with strong bases. Despite the fact that simple, approximate and exact forms are different², the discriminants are the same as for salts of weak bases with strong acids, and substitution of K_a for K_b in (7), (8), (9), (15), (16) and (17) yields the appropriate discriminants.

Hydrolyzed salts in the presence of a small excess of strong acid or base. If the untitrated or excess of strong acid in the titration of a weak base is calculated from reagent strength and solution volume to be c_a , the concentration of the salt is c_s and the ionisation constant of the base is K_b , then

$$\text{Simple } [\text{H}^+] = c_a \quad (18)$$

$$\text{Exact } [\text{H}^+] = 1/2 \left\{ \left(c_a^2 + \frac{4K_w c_s}{K_b} \right)^{1/2} + c_a \right\} \quad (19)$$

Substitution of (18) and (19) in (5) yields the discriminant (20) which shows that the simple value c_a gives sufficiently accurate results when

$$c_a \gg (1 - E) \left(\frac{K_w c_s}{K_b E} \right)^{1/2} \quad (20)$$

that is, when there is sufficient strong acid present adequately to suppress hydrolysis of the salt.

Substitution of c_b and K_a in (20) gives the discriminant for free strong base concentration in the titration of a weak acid with a strong base.

(d) *Acid buffer solutions.* For a weak acid of ionisation constant K_a and concentration c_a in mixture with a concentration c_s of its salt with a strong base, when ionisation of the acid and hydrolysis of the salt are both adequately suppressed,

$$\text{Simple } [\text{H}^+] = \frac{c_a}{c_s} K_a \quad (21)$$

When ionisation of the acid is not adequately suppressed, but hydrolysis can be ignored,

$$\text{Approx. } [\text{H}^+] = 1/2 \left[\left((c_s + K_a)^2 + 4K_a c_a \right)^{1/2} - (c_s + K_a) \right] \quad (22)$$

When hydrolysis of the salt is taken into account, but ionisation of the acid can be ignored,

$$\text{Approx. } [\text{H}^+] = \frac{1}{2c_s} \left[\left((c_a K_a + K_w)^2 + 4K_a K_w c_s \right)^{1/2} + (K_w + c_a K_a) \right] \quad (23)$$

Though these two corrections are usually in opposition, they are not mutually exclusive, and in the rare cases when both ionisation of the acid and hydrolysis of the salt must be accounted for, the exact equation (24) is required.

$$\text{Exact } [\text{H}^+]^3 + (c_s + K_a)[\text{H}^+]^2 - (K_w + K_a c_a)[\text{H}^+] - K_a K_w = 0 \quad (24)$$

Correction for ionisation of the weak acid. Substitution of (21) and (22) in (5) and simplification yields the master discriminant (25)

$$c_a K_a + c_s K_a(1 + E) - E c_s^2(1 + E) = 0 \dots \dots \dots (25)$$

This carries four possible variables, E , c_a , c_s and K_a , and may be solved for the error incurred under any given conditions by (26),

$$E = \frac{1}{2c_s} \left[\left\{ (c_s - K_a)^2 + 4K_a(c_a + c_s) \right\}^{\frac{1}{2}} - (c_s - K_a) \right] \dots \dots \dots (26)$$

or may be sorted to give particular discriminants (27) to (29) for the variable of interest. These indicate that the simple form (21) is valid when

$$c_s \gg \frac{1}{2E} \left[\left\{ K_a^2 + \frac{4EK_a c_a}{1 + E} \right\}^{\frac{1}{2}} + K_a \right] \approx \left(\frac{c_a K_a}{E} \right)^{\frac{1}{2}} \dots \dots \dots (27)$$

$$c_a \leq \frac{c_s(1 + E)(E c_s - K_a)}{K_a} \approx \frac{E c_s^2}{K_a} \dots \dots \dots (28)$$

$$K_a \leq \frac{c_s^2 E(1 + E)}{c_a + (1 + E)c_s} \approx \frac{E c_s^2}{c_a} \dots \dots \dots (29)$$

The conditional approximations of (27) to (29) apply when c_a is large compared with $[H^+]$ and c_s , and like those in (8), (9), (13), (14), (16) and (17) must be used with caution.

Since the term c_a/c_s appears in (21), it is often convenient to work in terms of this ratio, denoted by the symbol n , when particular discriminants become, in favour of the corrected expression (22),

$$n \gg \frac{(1 + E)(E c_s - K_a)}{K_a} \gg \frac{1 + E}{2} \left[\left\{ 1 + \frac{4E c_a}{(1 + E)K_a} \right\}^{\frac{1}{2}} - 1 \right] \dots \dots \dots (30)$$

$$c_s \leq \frac{K_a(1 + E + n)}{E(1 + E)} \dots \dots \dots (31)$$

$$c_a \gg \frac{n K_a(1 + E + n)}{E(1 + E)} \dots \dots \dots (32)$$

A corresponding set of discriminants for the reciprocal of this ratio is also of occasional use.

Correction for hydrolysis of the salt. Substitution of (21) and (23) in (5) and simplification yields the master discriminant (33),

$$(1 - E)^2 c_s K_w + (1 - E) c_a K_w - E c_a^2 K_a = 0 \dots \dots \dots (33)$$

Solution for the error gives, in the most convenient form for series of calculations,

$$E = \frac{1}{2} \left[\left(\frac{K_a c_a^2}{K_w c_s} + \frac{c_a}{c_s} + 2 \right) - \left\{ \left(\frac{K_a c_a^2}{K_w c_s} + \frac{c_a}{c_s} + 2 \right)^2 - \frac{4(c_a + c_s)}{c_s} \right\}^{\frac{1}{2}} \right] \dots \dots \dots (34)$$

Particular discriminants derived from (33) show that the simple form (21) is valid for a specified error when

$$c_a \gg \frac{(1 - E)}{2E K_a} \left[K_w + \left\{ K_w^2 + 4E K_a K_w c_s \right\}^{\frac{1}{2}} \right] \dots \dots \dots (35)$$

$$c_s \leq \frac{c_a}{(1 - E)} \left(\frac{E K_a c_a}{(1 - E) K_w} - 1 \right) \dots \dots \dots (36)$$

$$K_a \gg \frac{(1 - E)}{E} \frac{K_w}{c_a} \left\{ 1 + (1 - E) \frac{c_s}{c_a} \right\} \dots \dots \dots (37)$$

Other discriminants in terms of $n = c_a/c_s$ or $n' = c_s/c_a$ can be derived and are often useful.

(e) *Basic buffer solutions.* When the concentration of weak base of ionisation constant K_b is c_b and the concentration of the salt with a strong acid is c_s , then equations of differing exactness are offered, in analogy to acid buffers.

$$\text{Simple } [H^+] = \frac{c_s}{c_b} \frac{K_w}{K_b} \dots \dots \dots (38)$$

Correction for ionisation of the weak base gives

$$\text{Approx. } [H^+] = \frac{K_w}{2K_b c_b} \left[(K_b + c_s) + \left\{ (K_b + c_b)^2 + 4K_b c_b \right\}^{\frac{1}{2}} \right] \dots \dots \dots (39)$$

Correction for hydrolysis of the salt gives

$$\text{Approx. } [H^+] = \frac{1}{2K_b} \left[\left\{ (K_b c_b + K_w)^2 + 4K_w K_b c_s \right\}^{\frac{1}{2}} - (K_b c_b + K_w) \right] \dots \dots \dots (40)$$

Correction for both ionisation of the weak base and hydrolysis of the salt gives

$$\text{Exact } K_b [H^+]^3 + (c_b K_b + K_w) [H^+]^2 - K_w (c_s + K_b) [H^+] - K_w^2 = 0 \dots \dots \dots (41)$$

Correction for ionisation of the weak base. Substitution of (38) and (39) in (5) and simplification yields the *master discriminant* (42)

$$E c_s^2 - (1 - E) K_b c_s - (1 - E)^2 c_b K_b = 0 \dots \dots \dots (42)$$

from which the error incurred in the use of (38) is, in the most convenient form involving the ratio c_s/c_b ,

$$E = 1/2 \left[\left(\frac{c_s}{c_b} \frac{c_s}{K_b} + 1 \right) + 2 \right] - \left\{ \left(\frac{c_s}{c_b} \frac{c_s}{K_b} + 1 \right) + 2 \right\}^2 - 4 \left(\frac{c_s}{c_b} + 1 \right) \right\}^{\frac{1}{2}} \dots \dots \dots (43)$$

From (42), *particular discriminants* may be derived showing that the simple form is valid when

$$c_b \ll \frac{E c_s^2 - (1 - E) K_b c_s}{(1 - E)^2 K_b} \dots \dots \dots (44)$$

$$c_s \gg \frac{(1 - E) K_b}{2E} \left\{ 1 + \left(1 + 4E \frac{c_b}{K_b} \right)^{\frac{1}{2}} \right\} \dots \dots \dots (45)$$

$$K_b \ll \frac{E c_s^2}{(1 - E)(c_s + (1 - E)c_b)} \dots \dots \dots (46)$$

Correction for hydrolysis of the salt. Substitution of (38) and (40) in (5) and simplification gives the *master discriminant* (47),

$$E(1 + E) K_b c_b^2 - (1 + E) K_w c_b - c_s K_w = 0 \dots \dots \dots (47)$$

from which the error incurred in using the simple form (38) is, in the most convenient form for calculation,

$$E = 1/2 \left[\left\{ \left(1 - \frac{K_w}{K_b c_b^2} \right)^2 + \frac{4K_w}{K_b c_b^2} (c_b + c_s) \right\}^{\frac{1}{2}} - \left(1 - \frac{K_w}{K_b c_b^2} \right) \right] \dots \dots \dots (48)$$

and solution for *particular discriminants* (49) to (51) indicates that the simple form (38) is valid when

$$c_b \gg \frac{K_w}{2EK_b} \left[1 + \left\{ 1 + \frac{4EK_b c_s}{(1 + E)K_w} \right\}^{\frac{1}{2}} \right] \dots \dots \dots (49)$$

$$c_s \ll \frac{(1 + E)c_b(EK_b c_b - K_w)}{K_w} \dots \dots \dots (50)$$

$$K_b \gg \frac{K_w[(1 + E)c_b + c_s]}{E(1 + E)c_b^2} \dots \dots \dots (51)$$

As before, the master discriminants may be converted into terms of the ratio $c_a/c_b = n$, or its reciprocal, and the new master discriminants solved for particular discriminants.

2. Discriminants in precipitation reaction calculations

(a) *Simple binary precipitates.* With a simple binary compound BA of solubility product S_{BA} , if one ion, say B^+ , is in excess to an amount calculated from reagent concentration and volume of titration solution to be c , then the ion concentrations are

$$\text{Simple } [B^+] = c; \quad [A^-] = \frac{S_{BA}}{c} \quad \dots \dots \dots (52)$$

Near the equivalence point the contribution of ions from the precipitate can no longer be neglected and the concentrations become,

$$\text{Exact } [B^+] = 1/2 \{ (c^2 + 4S_{BA}) + c \} \quad \dots \dots \dots (53)$$

$$\text{Exact } [A^-] = 1/2 \{ (c^2 + 4S_{BA}) - c \} \quad \dots \dots \dots (54)$$

Substitution of (52) and either (53) or (54) as appropriate in (5) results in the same discriminant, since the precipitate is symmetrical, whether A^- or B^+ is in excess, and demonstrates the validity of the simple form (52) when

$$c \gg \left(\frac{S_{BA}}{E(I + E)} \right)^{1/2} \quad \dots \dots \dots (55)$$

(b) *Binary precipitates of the first order of asymmetry.* Taking as an example the precipitate B_2A , since the precipitate is unsymmetrical, the equations will be unsymmetrical and different depending on which ion is in excess.

Anion in excess. Suppose the anion is in excess to an amount calculated to be c_A . The ion concentrations are then

$$\text{Simple } [A^{-2}] = c_A; \quad [B^+] = \left(\frac{S_{B_2A}}{c_A} \right)^{1/2} \quad \dots \dots \dots (56)$$

Near the equivalence point account must be taken of the contribution of ions from the precipitate and the concentrations become

$$\text{Exact } [A^{-2}] = c_A + 1/2[B^+] \quad \dots \dots \dots (57)$$

$$\text{Exact } [B^+]^3 + 2c_A[B^+]^2 - 2S_{B_2A} = 0 \quad \dots \dots \dots (58)$$

Substitution of the values of $[A^{-2}]$ from (56) and (57) in (5) yields the discriminant (59)

$$c_A = \frac{(I - 2E)}{2E} [B^+] \quad \dots \dots \dots (59)$$

which is impracticable. Solution of (56) for $[B^+]$ makes the assumption that $[A^{-2}] = c_A$, and will give a high value for $[B^+]$ while A^{-2} is in excess. Use of this value would mean that a change to the exact equation would be made while the error was still very slightly less than E . It is therefore safe to use this value in defining the limiting value of c_A , especially since it defines the point at which the difference between c_A and $[A^{-2}]$ becomes less than that which causes a relative error of E . Substitution of this value then gives the discriminant (60) which shows that the simple forms (56) are valid when

$$c_A \gg \left\{ \left(\frac{I - 2E}{2E} \right)^2 S_{B_2A} \right\}^{1/3} \quad \dots \dots \dots (60)$$

Cation in excess. If the calculated excess is c_B ,

$$\text{Simple } [B^+] = c_B; [A^{-2}] = \frac{S_{B_2A}}{c_B^2} \dots \dots \dots (61)$$

$$\text{Exact } [B^+] = c_B + 2[A^{-2}] \dots \dots \dots (62)$$

$$\text{Exact } 4[A^{-2}]^3 + 4c_B[A^{-2}]^2 + c_B^2[A^{-2}] - S_{B_2A} = 0 \dots \dots \dots (63)$$

A similar process to that above, allowing $[B^+] = c_B$ at the critical point, yields the discriminant (64) which shows that the simple forms (61) are valid when

$$c_B \gg \left(\frac{2(1-E)}{E} S_{B_2A} \right)^{\frac{1}{3}} \dots \dots \dots (64)$$

(c) *Simple binary precipitates which are salts of a monobasic weak acid.* In the case of the salt BA of the weak acid HA and the base BOH where $K_b \gg K_a$, the equations will be unsymmetrical and will differ according to which ion is in excess.

Anion in excess. If the calculated excess is c_A , then remote from the equivalence point,

$$\text{Simple } [A^-] = c_A; [B^+] = \frac{S_{BA}}{c_A} \dots \dots \dots (65)$$

Nearer the equivalence point the removal of A^- ions as unionized HA and the contribution of A^- ions from solution of the precipitate become significant,

$$\text{Exact } [A^-] = \frac{1}{2[K_a + [H^+]]} \left[c_A K_a + \left\{ c_A^2 K_a^2 + 4K_a S_{BA} (K_a + [H^+]) \right\}^{\frac{1}{2}} \right] \dots \dots (66)$$

Assuming $[A^-]$ to be greater than c_A , substitution of (65) and (66) in (5) gives the discriminant (67) which shows that the simple forms of (65) are valid when

$$c_A \gg (1-E) \left\{ \frac{K_a S_{BA}}{[H^+] + EK_a} \right\}^{\frac{1}{2}} \dots \dots \dots (67)$$

Cation in excess. For a calculated excess of c_B ,

$$\text{Simple } [B^+] = c_B; [A^-] = \frac{S_{BA}}{c_B} \dots \dots \dots (68)$$

$$\text{Exact } [B^+] = 1/2 \left[c_B + \left\{ c_B^2 + 4S_{BA} \left(1 + \frac{[H^+]}{K_a} \right) \right\}^{\frac{1}{2}} \right] \dots \dots \dots (69)$$

From (68) and (69) the discriminant (70) may be derived showing the validity of (68) when

$$c_B \gg \left\{ \frac{(1-E)}{E} S_{BA} \left(1 + \frac{[H^+]}{K_a} \right) \right\}^{\frac{1}{2}} \dots \dots \dots (70)$$

3. Discriminants in complexation reaction calculations

(a) *Simple symmetrical 1:1 complexes not involving the production of hydrogen ion.* In the case of a complex ML of instability constant K_{inst} present in concentration c , if the calculated excess of one ion be c_L or c_M as appropriate, the concentration of the other ion will be

$$\text{Simple } [M] = \frac{c K_{inst}}{c_L} \dots \dots \dots (71)$$

$$\text{Simple } [L] = \frac{c K_{inst}}{c_M} \dots \dots \dots (72)$$

Close to the equivalence point, if M is in excess, the true state of affairs is

$$\text{Exact [L]} = 1/2[\{ (c_M + K_{inst})^2 + 4c K_{inst} \}^{1/2} - (c_M + K_{inst})] \quad (73)$$

$$\text{Exact [M]} = 1/2[\{ (c_M + K_{inst})^2 + 4c K_{inst} \}^{1/2} + (c_M + K_{inst})] \quad (74)$$

Substitution of (72) and (73) in (5) followed by simplification gives the *master discriminant* (75).

$$E c_M^2 + E(1 - E)K_{inst} c_M - (1 - E)^2 c K_{inst} = 0 \quad (75)$$

Solution of (75) gives *particular discriminants* of which the most important is (76) showing that (72) is valid when

$$c_M \gg \frac{(1 - E)}{2} \left[\left\{ K_{inst}^2 + \frac{4c K_{inst}}{E} \right\}^{1/2} - K_{inst} \right] \quad (76)$$

Since the complex is symmetrical, substitution of c_L for c_M in the expressions above gives the appropriate equations when L is in excess.

(b) *Complexes of the first order of asymmetry, such as BA_2^-* . If one or other of the ions is present in excess, calculated to be c_A or c_B , sufficient adequately to suppress dissociation of the complex, whose calculated concentration is c , then ion concentrations can be calculated from the instability constant,

$$\text{Simple [A}^-] = \left(\frac{c K_{inst}}{c_B} \right)^{1/2} \quad (77)$$

$$\text{Simple [B}^+] = \frac{c K_{inst}}{c_A^2} \quad (78)$$

Close to the equivalence point, dissociation of the complex becomes significant, and expressions which differ according to which ion is in excess are required.

Cation in excess. The true concentrations are now obtained from

$$\text{Exact [B}^+] = c_B + 1/2[A^-] \quad (79)$$

$$\text{Exact [BA}_2^-] = c - 1/2[A^-] \quad (80)$$

$$\text{Exact [A}^-]^3 + 2c_B[A^-]^2 + K_{inst}[A^-] - 2c K_{inst} = 0 \quad (81)$$

To derive a discriminant from (77) and (81) is impracticable, but as in the derivation of (60), the use of (79) and the simple value c_B yields a safe working equation. Substitution of (79) and c_B in (5) gives

$$2Ec_B = (1 - E)[A^-] \quad (82)$$

Solution of (77) for $[A^-]$ gives a slightly low value, which is usable as it defines the point at which substitution of c_B for $[B^+]$ incurs a relative error of E . Substitution of this value in (82) gives the *particular discriminant* of immediate interest which shows that (77) gives valid results when

$$c_B \gg \left\{ \left(\frac{1 - E}{2E} \right)^2 c K_{inst} \right\}^{1/2} \quad (83)$$

Anion in excess. The true concentrations are now derived from

$$\text{Exact [A}^-] = c_A + 2[B^+] \quad (84)$$

$$\text{Exact [BA}_2^-] = c - 2[B^+] \quad (85)$$

$$\text{Exact } 4[B^+]^3 + 4c_A[B^+]^2 + (c_A^2 + K_{inst})[B^+] - c K_{inst} = 0 \quad (86)$$

From the simple value c_A and (84), and substituting the value of $[B^+]$ from (78), the *particular discriminant* (87) emerges, showing that the simple form (78) is valid when

$$c_A \gg \left(\frac{2(1 - E)}{E} c K_{inst} \right)^{1/2} \quad (87)$$

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SUMMARY

The use of discriminating expressions, termed *discriminants*, is proposed to place on a simple quantitative basis the selection of the appropriate equation for an analytical calculation for which alternative equations of differing degrees of exactitude present themselves. Sufficient examples of discriminants are given to permit direct treatment of the commoner calculations in titrimetric analysis, and to afford a pattern for their derivation whenever a choice of alternative equations is offered.

RÉSUMÉ

Des formules mathématiques („discriminants“) sont proposées, permettant de choisir, sur une base quantitative, l'équation qui convient le mieux pour un calcul analytique lorsque plusieurs de ces équations, mais de degré de précision différent, existent. Des exemples sont donnés pour permettre d'effectuer directement les calculs les plus courants de l'analyse volumétrique.

ZUSAMMENFASSUNG

Es wird die Verwendung von „Diskriminanten“ vorgeschlagen, um aus verschiedenen möglichen approximativen Gleichungen für analytische Berechnungen mit streuender Genauigkeit die geeignete Gleichung auszuwählen. Es werden verschiedene Beispiele für Diskriminanten angeführt, die eine direkte Durchführung der üblichen Berechnungen titrimetrischer Analysen gestatten.

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SEPARATIONS INVOLVING SULPHIDES

XI. SEPARATION OF ALUMINIUM OR URANIUM FROM SOME ELEMENTS FORMING THIOSALTS

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The present investigation deals with the separation of aluminium or uranium from the elements which are estimated by decomposing their thiosalts with hydrochloric acid. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide was filtered and weighed, and aluminium or uranium in the filtrate was estimated as oxinate. The separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from aluminium or uranium was studied.

EXPERIMENTAL

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium pyroantimonate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, gold chloride, platinum chloride, potassium perrhenate, potash alum, K_2SO_4 , $Al_2(SO_4)_3 \cdot 24H_2O$ (containing a little sulphuric acid) and uranyl acetate were used. Measured volumes of the two solutions were mixed and the mixture was treated with 2 *N* sodium sulphide reagent in excess. The mixture containing the thiosalt was acidified with a measured quantity of hydrochloric acid, heated to boiling and allowed to cool to room temperature. The precipitated sulphide was filtered through a sintered glass crucible (porosity 4) and weighed as $As_2S_5^1$, $Sb_2S_3^2$, $Sb_2S_5^3$, TeS_2^1 , SeS_2^1 , $MoS_3 \cdot 2H_2O^4$, HgS^5 , $Au_2S_3^2$, $PtS_2 \cdot 3H_2O^3$, or $Re_2S_7^5$.

The following points should be noted in precipitating the sulphides.

1. In the case of aluminium, the solution of potassium antimony tartrate should not be used, as tartrate interferes in the estimation of aluminium as oxinate.

2. With antimonate, the free acid of potash alum should be neutralized before antimonate is added, to avoid the precipitation of antimonic acid. In other cases the neutralization with caustic soda can be done after mixing the two solutions.

3. With uranium, any precipitate which appears on mixing the two solutions need not be dissolved in acid.

4. In the case of mercury, the mixture should be treated with ammonium hydroxide before sodium sulphide reagent is added.

5. For arsenic, platinum or rhenium, the final acidity should be 6 *N*, for selenium 2 *N* and for the other elements 1 *N*.

6. After acidification the mixture should be treated with 10–15 g of ammonium acetate for platinum and with 10–15 g of ammonium sulphate for rhenium.

7. In filtering rhenium heptasulphide the suction should be slow.

After the sulphide had been filtered, the filtrate was evaporated to about 50 ml to remove hydrogen sulphide and aluminium⁶ or uranium⁷ was estimated as oxinate. 36–46 mg of arsenic were separated from 10–12 mg of aluminium, 38–39 mg of antimony were separated from 10–12 mg of aluminium, 44–55 mg of tellurium were separated from 10–13 mg of aluminium, 44–52 mg of selenium were separated from 10–23 mg of aluminium, 62–73 mg of molybdenum were separated from 10–12 mg of aluminium, 68–85 mg of mercury were separated from 10–13 mg of aluminium, 12–23 mg of gold were separated from 13–23 mg of aluminium, 34–45 mg of platinum were separated from 10–12 mg of aluminium, 31–38 mg of rhenium were separated from 10–12 mg of aluminium.

The metals were recovered with an accuracy of:

As: –0.27% to 0.0%, Al: 0.0% to +0.36%, Sb: –0.31% to 0.0%, Al: –0.09% to 0.0%, Te: –0.48% to 0.0%, Al: –0.34% to +0.36%, Se: 0.0% to +0.25%, Al: –0.55% to +0.43%, Mo: –0.13% to 0.0%, Al: 0.0% to +0.39%, Hg: 0.0% to +0.38%, Al: –0.46% to 0.0%, Au: 0.0%, Al: –0.71% to +0.27%, Pt: 0.0% to +0.34%, Al: 0.0% to +0.37%, Re: 0.0% to +0.40%, Al: 0.0% to +0.48%.

30–38 mg of arsenic, 47–58 mg of antimony, 44–68 mg of tellurium, 59–60 mg of selenium, 32–39 mg of molybdenum, 68–85 mg of mercury, 9–23 mg of gold, 23–28 mg of platinum or 31–38 mg of rhenium were separated from 61–76 mg of uranium.

The metals were recovered with an accuracy of:

As: -0.25% to $+0.15\%$, U: 0.0% to $+0.44\%$, Sb: 0.0% to $+0.47\%$, U: -0.22% to $+0.0\%$, Te: 0.0% , U: -0.08% to $+0.26\%$, Se: 0.0% to $+0.18\%$, U: 0.0% to $+0.55\%$, Mo: -1.1% to 0.0% , U: 0.0% to $+1.6\%$, Hg: 0.0% to $+0.4\%$, U: 0.0% to $+0.89\%$, Au: 0.0% , U: 0.0% to $+0.33\%$, Pt: -0.21% to 0.0% , U: 0.0% to $+0.33\%$, Re: 0.0% to $+0.4\%$, U: 0.0% to $+0.22\%$.

Notes

1. Even A.R. caustic soda contains aluminium as an impurity; errors can be compensated by adding an equal volume of caustic soda solution before standardizing the solution of aluminium or uranium.

2. As molybdenum also gives a precipitate with oxine, even a trace of it passing into the filtrate gives high results.

SUMMARY

2 N Sodium sulphide can be used to separate arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from aluminium or uranium.

RÉSUMÉ

Les auteurs proposent l'emploi du sulfure de sodium 2 N comme réactif pour la séparation de l'arsenic, de l'antimoine, du tellure, du sélénium, du molybdène, du mercure, de l'or, du platine ou du rhénium d'avec l'aluminium ou l'uranium.

ZUSAMMENFASSUNG

Mit Hilfe von 2 N Natriumsulfidlösung kann eine Trennung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium vom Aluminium oder Uran erzielt werden.

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SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. III

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In previous papers^{1,2}, equations which describe the extraction of metal chelates were derived and their validity was proved. In this final part, the use of these equations in analytical chemistry is described. It is therefore necessary to know a number of constants which hitherto have been seldom required.

Some of these constants can easily be determined, *e.g.* the solubility of a metal chelate in an organic solvent. The results of several determinations are shown in Table I.

TABLE I

<i>Chelate</i>	<i>Solubility in mmoles/ml</i>
CuOx ₂	3.4 · 10 ⁻³
NiOx ₂ (2 b.a.)	5.0 · 10 ⁻²
UO ₂ Ox ₂ · HOx	2.8 · 10 ⁻³
AlOx ₃	3.8 · 10 ⁻²
FeOx ₃	1.5 · 10 ⁻²
ThOx ₄	3.4 · 10 ⁻³

Other constants can easily be determined from the given extraction formulae. From the formula

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL_{MR_n}}{(R^-)^n MR_n \text{ sat.} + fL_{MR_n}}$$

L_{MR_n} can be calculated, if the percentage of extraction (giving $m^{+n} \text{ res.}/a$) is determined under known conditions (f and R^- known) and if $MR_n \text{ sat.}$ is known.

Example: To 1 mg of uranyl ion in 50 ml of aqueous solution a few drops of sulphuric acid were added, and the solution was shaken for 10 min with a solution of 100 mg of oxine in 10 ml of chloroform. After separation of the layers, the pH of the aqueous solution and the uranyl content of the chloroform phase were determined.

From the values obtained the values of $L_{UO_2Ox_2}$ are calculated (Table II).

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TABLE II

pH	mg UO_2^{+2} extracted	$\frac{m^{+2} \text{ res.}}{a}$	$L_{UO_2, O_2} \text{ calc.}$
2.80	0.05	0.95	$2.54 \cdot 10^{-25}$
2.86	0.09	0.91	$2.22 \cdot 10^{-25}$
2.99	0.19	0.81	$2.88 \cdot 10^{-25}$
3.13	0.39	0.61	$3.44 \cdot 10^{-25}$
3.18	0.52	0.48	$2.96 \cdot 10^{-25}$
3.47	0.87	0.13	$3.30 \cdot 10^{-25}$
3.55	0.94	0.06	$2.68 \cdot 10^{-25}$
3.90	1.00	0.00	—
mean value			$2.9 \cdot 10^{-25}$

The reasonable constancy of the solubility product is another proof of the correctness of our considerations. The values found in this way are given in Table III where the previous known values are also shown.

TABLE III

Chelate	Solubility product
$CuOx_2$	$5 \cdot 10^{-29}$
$NiOx_2$ (2 b.a.)	$7 \cdot 10^{-23}$
UO_2Ox_2 (HOx)	$2.9 \cdot 10^{-25}$
$AlOx_3$	$1.2 \cdot 10^{-35}$
$FeOx_3$	$7.5 \cdot 10^{-45}$
$ThOx_4$	$6.2 \cdot 10^{-47}$

The complete calculations have been described³.

THE PREDICTION OF THE CONDITIONS FOR A SEPARATION BY EXTRACTION

If all the necessary constants are known, the conditions for a possible separation can be calculated; or it can be shown that a separation of two elements is impossible under all conditions, with a particular reagent and a particular solvent. Some examples of each case are given below.

1. The separation of copper and uranyl with oxine-chloroform

Only conditions in which $f = 5$ are considered; it will be seen later that variation of f within practical limits has little effect.

For a proper separation at least 98% of one of the elements must be extracted while not more than 2% of the other element should be extracted. It is therefore necessary to know the pH required and the amount of oxine which should be present so that more than 98% of the copper can be extracted with 10 ml of chloroform without more than 2% of the uranyl ion being extracted.

Substituting the requirement, $Cu^{+2} \text{ res.}/a \leq 0.02$ and the known values, $f = 5$, $L_{CuOx_2} = 5 \cdot 10^{-29}$, and $CuOx_2 \text{ sat.} = 3.4 \cdot 10^{-3}$, in the extraction formula :

$$\frac{\text{Cu}^{+2} \text{ res.}}{a} = \frac{f L_{\text{CuOx}_2}}{\text{CuOx}_2 \text{ sat.} (\text{Ox}^-)^2 + f L_{\text{CuOx}_2}}$$

gives $(\text{Ox}^-)^2 \geq 3.6 \cdot 10^{-24}$.

Substituting the requirement, $\text{UO}_2^{+2} \text{ res.}/a \geq 0.98$ and the known values, $f = 5$, $L_{\text{UO}_2\text{Ox}_2} = 2.9 \cdot 10^{-25}$, and $\text{UO}_2\text{Ox}_2 \text{ sat.} = 2.8 \cdot 10^{-3}$, in the extraction formula gives $(\text{Ox}^-)^2 \leq 1.1 \cdot 10^{-23}$.

Combination of these results shows that for the separation of copper and uranyl:

$$3.6 \cdot 10^{-24} \leq (\text{Ox}^-)^2 \leq 1.1 \cdot 10^{-23} \quad \dots \dots \dots (1)$$

By means of table I, given in part II of this series², this requirement can be translated into actual conditions of pH and amount of oxine.

Suppose that we want to use 100 mg of oxine, or

$$B = \frac{100}{145} \cdot \frac{1}{50} = 1.38 \cdot 10^{-2} \text{ and } B^2 = 1.90 \cdot 10^{-4}.$$

When all terms in (1) are divided by $B^2 = 1.90 \cdot 10^{-4}$, then:

$$1.9 \cdot 10^{-20} \leq (\text{Ox}^-)^2_{B=1} \leq 5.8 \cdot 10^{-20}$$

and this can directly be "translated" into pH values by means of the above table I. By linear interpolation, it is found that the separation is possible between pH 2.57 and 2.71.

This result was checked by placing known amounts of copper and uranyl ions in 50 ml of a buffer solution of pH 2.60⁴ and extracting this solution once with 100 mg of oxine in 10 ml of chloroform. The copper content of the chloroform extract was determined by measuring the absorbance at 450 m μ and the pH of the aqueous phase was measured.

The pH of the aqueous phase was then brought to a value of 5 ± 0.5 with 2 N sodium hydroxide and uranyl oxinate was extracted with 10 ml of chloroform. In this extract the uranyl content was found by measuring the absorbance at 530 m μ *.

Because of the relatively large amount of oxine that remains in the aqueous phase after the first extraction, the uranyl oxinate can be extracted without further addition of oxine. This can easily be calculated. At pH 2.60, $R_{B=1}^- = 1.5 \cdot 10^{-10}$, hence in these extractions ($B = 1.38 \cdot 10^{-2}$) $R^- = 2.1 \cdot 10^{-12}$. With K_{HR}^2 , it can thus be calculated that $\text{HR}_w = 4.0 \cdot 10^{-5}$. From this value we calculate, using K_{HR}^2 that $\text{H}_2\text{R}^+ = 1.2 \cdot 10^{-2}$, and using E_{HR} that $\text{HR}_o = 8.2 \cdot 10^{-3}$. Finally $V_w = 50$ and $V_o = 10$ are known, hence $\text{Ox}_w^- = 1.0 \cdot 10^{-10}$ mmoles, $\text{HOx}_w = 2.0 \cdot 10^{-3}$ mmoles, $\text{H}_2\text{Ox}_w^+ = 6.0 \cdot 10^{-1}$ mmoles, $\text{HOx}_o = 8.2 \cdot 10^{-2}$ mmoles. Of the starting quantity of oxine, $6.9 \cdot 10^{-1}$ mmoles, there remains $6.0 \cdot 10^{-1}$ mmoles in the aqueous phase after the first extraction. In this calculation the small quantity of oxine ($3 \cdot 10^{-2}$ mmoles) extracted as copper oxinate is neglected.

The results of three checks are shown in Table IV.

* Although measuring the absorbance at 530 m μ is less sensitive than at 450 m μ , the former wavelength was chosen because of the better selectivity.

TABLE IV

mg added		pH aqueous phase	mg found	
copper	uranyl		copper	uranyl
1.00	1.00	2.60	0.98	1.00
0.20	1.00	2.60	0.20	1.00
1.00	0.20	2.62	0.99	0.21

2. The separation of iron and uranyl

In the same way, it can be calculated that the separation of iron and uranyl must be possible between pH values of 1.76 and 2.71 with 100 mg of oxine; iron oxinate is then extracted, while uranyl ion is extracted after the pH has been brought to 5 ± 0.5 .

The results of two separations carried out under these conditions are shown in Table V.

TABLE V

mg added		pH aqueous phase	mg found	
iron	uranyl		iron	uranyl
0.053	1.06	1.94	0.053	1.06
0.053	1.06	1.97	0.051	1.06

3. The separation of iron and aluminium

For the separation of iron and aluminium it is calculated that, with 100 mg of oxine, the pH must lie between 1.76 and 2.70; iron oxinate is then extracted, while aluminium is extracted after the pH has been brought to about 4.5. The results of two separations carried out under these conditions are shown in Table VI.

TABLE VI

mg added		pH aqueous phase	mg found	
iron	aluminium		iron	aluminium
0.053	0.200	1.96	0.053	0.203
0.053	0.200	1.89	0.053	0.200

For rapid and complete extraction of aluminium oxinate with chloroform after iron had been extracted, it proved necessary to allow the solution to stand for half an hour after it had been adjusted to a pH of about 4.5. This had already been observed by CLAASSEN, BASTINGS AND VISSER⁵.

4. The separation of aluminium and uranyl

By calculations similar to those in the above three examples, the requirements $Al^{+3} \text{ res.}/a \leq 0.02$ and $UO_2^{+2} \text{ res.}/a \geq 0.98$, lead to the contradiction: $Ox^- \leq 3.3 \cdot 10^{-12}$ (uranyl) and $Ox^- \geq 2.0 \cdot 10^{-11}$ (aluminium)

If the conditions for the reverse extraction are calculated, *i. e.* at least 98% of the uranyl ion present is to be extracted without extracting more than 2% of the alu-

minium present, then UO_2^{+2} res./ $a \leq 0.02$ and Al^{+3} res./ $a \geq 0.98$, another contradiction is obtained: $\text{Ox}^- \geq 1.6 \cdot 10^{-10}$ (uranyl) and $\text{Ox}^- \leq 3.2 \cdot 10^{-12}$ (aluminium).

These contradictions mean that the separation of aluminium and uranyl with oxine and chloroform is impossible under any conditions.

5. The separation of uranyl and thorium

In the same way it can be calculated that the separation of uranyl and thorium with oxine and chloroform is also impossible.

THE INFLUENCE OF f

It has been shown that some separations are impossible under any conditions. But at the start the restriction was made that only extractions in which $f = 5$ would be considered; thus such separations might be achieved by an extraction in which f had a different value. The influence of the value of f cannot be easily seen from the equations, but it appears when a definite problem is dealt with.

Consider the system water-oxine-chloroform.

In the equation

$$R^- = \frac{K_w K_a f \cdot B}{K_w H^+ (E+f) + f \{K_b (H^+)^2 + K_w K_a\}}$$

the value of each of the three terms of the denominator is calculated from the values $K_w = 10^{-14}$, $K_a = 10^{-10}$, $K_b = 10^{-9}$, $E = 200$; f is negligible with respect to E in the term $(E + f)$.

TABLE VII

pH	H^+	$K_w H^+ (E+f)$	$f \cdot K_b (H^+)^2$	$f K_w K_a$	Case
1	10^{-1}	$2 \cdot 10^{-13}$	$10^{-11} \cdot f$	$10^{-24} \cdot f$	A
4	10^{-4}	$2 \cdot 10^{-16}$	$10^{-17} \cdot f$	$10^{-24} \cdot f$	A — B
7	10^{-7}	$2 \cdot 10^{-19}$	$10^{-23} \cdot f$	$10^{-24} \cdot f$	B
10	10^{-10}	$2 \cdot 10^{-22}$	$10^{-29} \cdot f$	$10^{-24} \cdot f$	B — C
13	10^{-13}	$2 \cdot 10^{-25}$	$10^{-35} \cdot f$	$10^{-24} \cdot f$	C

From a practical point of view the value of f cannot vary to a large extent. For the subdivision into three cases the value $f = 10$ is assumed.

A. For the value of R^- , the second term in the denominator is the deciding one, thus we may write:

$$R^- = \frac{K_w K_a f \cdot B}{K_b (H^+)^2 \cdot f} = \frac{K_w K_a B}{K_b (H^+)^2}$$

and for the extraction error:

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL}{\left(\frac{K_w K_a B}{K_b (H^+)^2}\right)^n MR_n \text{ sat.} + fL}$$

Hence if f increases (less organic solvent) the extraction error increases too.

B. The first term is the deciding one, thus

$$R^- = \frac{K_{af} \cdot B}{H+E}, \text{ and } \frac{m^{+n} \text{ res.}}{a} = \frac{fL}{\left(\frac{K_{af} \cdot B}{H+E}\right)^n \text{MR}_n \text{ sat.} + fL} = \frac{L}{pf^{n-1} + L},$$

$$\text{in which } p = \left(\frac{K_a \cdot B}{H+E}\right)^n \text{MR}_n \text{ sat.}, \text{ independent of } f.$$

If f increases, the extraction error decreases in all cases except for monovalent metal ions when the extraction error is independent of f .

C. The third term in the denominator is deciding, thus

$$R^- = \frac{K_w K_{af} \cdot B}{K_w K_a \cdot f} = B \text{ and } \frac{m^{+n} \text{ sat.}}{a} = \frac{fL}{B^n \cdot \text{MR}_n \text{ sat.} + fL}, \text{ analogous to A.}$$

As a rule, the influence of f is small, therefore when we deal with extractions to which these considerations apply, only the variations of pH and reagent concentrations need be considered.

SUMMARY

The author shows how the equations derived and proved in the two previous papers can be useful in analytical chemistry. The solubility product of some oxinates is determined. The conditions for separation of Cu/VO₂, Fe/VO₂ and Fe/Al by extraction are calculated and shown to be correct. The separation of Al/VO₂ and VO₂/Th by extraction with oxine-chloroform are proved impossible under any conditions.

RÉSUMÉ

L'auteur montre l'utilité en chimie analytique des équations proposées dans les deux premiers articles de cette série. Les produits de solubilité de quelques oxinates ont pu être déterminés ainsi que les conditions de séparation par extraction des mélanges Cu/VO₂, Fe/VO₂ et Fe/Al.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die in den beiden früheren Veröffentlichungen erwähnten Gleichungen sich mit Vorteil in der analytischen Chemie verwenden lassen; so konnte mit deren Hilfe das Löslichkeitsprodukt einiger Oxinate bestimmt und die Bedingungen für eine Trennung von Cu/VO₂, Fe/VO₂ und Fe/Al durch Extraktion errechnet werden.

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SEPARATION AND DETERMINATION OF TITANIUM IN STAINLESS STEELS

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Numerous sensitive organic reagents are known for the spectrophotometric determination of titanium but WELLER's¹ hydrogen peroxide method is still widely used in the analysis of stainless steels owing to its selectivity. Even this reaction cannot be applied directly in presence of coloured cations, *e.g.* Fe⁺³, Cr⁺³, Ni⁺² etc., or in presence of Mo, V, etc., which form colours. Some procedures have been reported where the interferences are compensated²⁻⁴ either in the blank or in the standards. Other procedures involve the chemical separation of some of the interfering ions and compensation for the rest, but none of these is quite satisfactory. Alternatively, titanium is separated chemically^{5,6} before its colorimetric determination. The procedure recommended in this paper consists of coprecipitation of titanium along with zirconium as the phosphate after separation of iron by extraction with ether, conversion of the phosphates to sulphates, and spectrophotometric determination with hydrogen peroxide.

EXPERIMENTAL

Titanium sulphate solution. "M & B" titania was fused with potassium bisulphate and dissolved in 5% (v/v) sulphuric acid. The solution was standardized by the peroxide method against a solution of spec-pure titania as sulphate. 1 ml contained 0.66 mg Ti.

Zirconyl chloride solution. B.D.H. Zirconyl chloride was dissolved in hydrochloric acid, precipitated with ammonium hydroxide, and redissolved in a slight excess of hydrochloric acid. The zirconia content of the solution was determined by precipitation with ammonium hydroxide and ignition to ZrO₂; 20 ml contained 60.0 mg Zr. This solution did not contain titanium.

Other reagents. B.D.H. AnalaR or E. Merck reagent quality.

All absorption measurements were made on a Beckman spectrophotometer Model DU with 1.00-cm corex cells.

Estimation of titanium in stainless steels was often required in this laboratory. Attempts to extend the tannin method⁷ were without success. Further experiments to separate titanium by precipitation as phosphate were also unsuccessful but the results obtained are worth summarizing here. Titanium is quantitatively precipitated as the phosphate above pH 0.7. At pH 0.7, molybdenum, tungsten and vanadium are quantitatively separated from titanium by a single precipitation. But iron and chromium are strongly coprecipitated and are not removed completely by washing. Hence, coprecipitation of titanium along with zirconium at still higher acidity was resorted to.

Quantitative coprecipitation of titanium

To determine the minimum quantity of zirconium required for quantitative coprecipitation of titanium, varying quantities of zirconium and titanium solutions were mixed and the acidity was adjusted to 2 to 4 N with hydrochloric or sulphuric acids

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in a total volume of 150 ml. The solution was warmed to about 50°, and titanium and zirconium were precipitated with 20 g of diammonium hydrogen phosphate. The precipitate was allowed to settle for 5 to 10 min, filtered through Whatman No. 541 filter paper, and washed four or five times with wash liquid (10 g of the phosphate and 10 ml of conc. hydrochloric acid per l). With more acid in the wash liquid, coprecipitated titanium phosphate was found to dissolve slowly. The phosphates dissolved on heating with oxalic acid, but on addition of acid for the colorimetry of titanium with peroxide, slow precipitation was observed which could not be prevented by increasing the oxalic acid concentration. Hence the phosphate precipitate was transferred back to the original beaker with a jet of hot water, and the solution was made alkaline with sodium hydroxide, boiled for 3–5 min, filtered through the same paper and washed with 2% sodium hydroxide solution. The precipitate was dissolved in 10 ml of 1:1 sulphuric acid, 1 ml of 30 vol. hydrogen peroxide was added and it was then filtered through the same paper. The filtrate was made up to 100 ml and the titanium content was estimated using a spectrophotometer.

The results (Table I) show that 1.32 mg titanium required a minimum of 60 mg of zirconium for quantitative coprecipitation at an acidity of 2–4 *N*.

TABLE I
RECOVERY OF TITANIUM BY COPRECIPITATION ALONG WITH ZIRCONIUM UNDER DIFFERENT CONDITIONS

<i>Titanium solution taken mg of Ti</i>	<i>Zirconyl chloride added mg of Zr</i>	<i>Acidity of precipitation N</i>	<i>Titanium recovered mg</i>	<i>Difference mg</i>
0.33	15	2	0.25	— 0.08
0.33	30	2	0.32	— 0.01
0.33	45	2	0.33	0.0
0.33	60	2	0.33	0.0
0.33	30	4	0.32	— 0.01
0.33	45	4	0.32	— 0.01
0.33	60	4	0.33	0.0
2.31	60	2	2.29	— 0.02
2.31	75	2	2.30	— 0.01
2.31	75	3	2.01	— 0.30
2.31 ^a	80	3	2.03	— 0.28
1.32	60	3	1.32	0.00
1.32	60	4	1.31	— 0.01

^a 25 g phosphate used for precipitation.

SEPARATION OF IRON, CHROMIUM AND NICKEL

Titanium was determined using the above procedure in synthetic mixtures with iron, chromium and nickel (Table II). Chromium and nickel do not interfere whereas iron is partly coprecipitated. Hence iron was previously removed by ether extraction⁸ from 6 *N* hydrochloric acid solution (Expts. 7–10). The presence of chromium and nickel gave no difficulty.

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TABLE II
SEPARATION OF TITANIUM FROM IRON, CHROMIUM AND NICKEL

No.	Titanium solution taken mg of Ti	Ferric chloride taken mg of Fe	Chromium chloride taken mg of Cr	Nickel chloride taken mg of Ni	Titanium found mg	Difference mg
1	0.66	100	—	—	0.77	+ 0.11
2	0.66	100	—	—	0.76	+ 0.10
3	0.66	—	30	—	0.66	0.00
4	0.66	—	30	—	0.67	+ 0.01
5	0.66	—	—	10	0.66	0.00
6	0.66	—	—	10	0.67	+ 0.01
7	0.66	100	30	10	0.66	0.00
8	0.66	100	30	10	0.65	— 0.01
9	0.33	100	30	10	0.33	0.00
10	0.20	100	30	10	0.21	+ 0.01

To study the possible interference of niobium and tantalum, oxalate solutions of niobium and tantalum were added to a standard steel sample solution. Spectrophotometric determination of titanium was carried out in the presence of 0.2 g of oxalic acid. The results are given in Table III along with synthetic and stainless steel samples.

TABLE III
ANALYSIS OF SAMPLES OF STEEL FOR TITANIUM

No.	Approximate composition of synthetic mixtures %										Titanium found %	Difference %	
	Fe	Cr	Ni	V	Mo	Mn	Al	Cu	W	Ti			
1	64.0	18.0	8.0	2.0	1.0	0.8	3.0	1.0	2.0	0.071	0.07	+ 0.001	
2	56.0	25.0	10.0	—	—	0.8	4.0	2.0	2.0	0.17	0.17	0.0	
3	73.0	10.0	10.0	3.5	—	0.8	—	—	2.0	0.43	0.44	+ 0.01	
4	82.0	10.0	2.0	—	5.0	0.8	—	—	—	0.53	0.51	— 0.02	
5	69.0	5.0	5.0	2.0	2.0	5.0	5.0	5.0	2.0	0.33	0.32	— 0.01	
6	48.0	10.0	—	—	—	30.0	5.0	5.0	2.0	0.66	0.65	— 0.01	
7	Samples of standard steel supplied by British Chemical Standards (No. 235, 18/8 stainless steel)										0.62	0.62	0.0
8	Samples of standard steel supplied by British Chemical Standards (No. 235, 18/8 stainless steel)										0.62	0.61	— 0.01
9	Same B.C.S. Sample (0.1 g) + 2 mg Cb + 2 mg Ta added										0.62	0.61	— 0.01
10	Same B.C.S. Sample (0.1 g) + 2 mg Cb + 2 mg Ta added										0.62	0.60	— 0.02

PROCEDURE

Stainless steel samples were analyzed by the following procedure: dissolve 0.1 g of a homogeneous sample in 20 ml of 1:1 hydrochloric acid by warming, add about 1 ml of nitric acid and boil. Cool, neutralize with ammonium hydroxide and then add conc. hydrochloric acid to bring the acidity to 6 N. Cool to room temperature, transfer to a separating funnel and extract three times with 50-ml aliquots of ether.

Take the aqueous layer into a 400-ml beaker, heat to expel the ether, add 20 ml of zirconyl chloride solution, dilute to twice the volume and precipitate with 20 g diammonium hydrogen phosphate. Allow to settle for 5 to 10 min, filter through Whatman No. 541 filter paper, wash four or five times with the wash liquid and transfer the precipitate back to the original beaker with a jet of hot water. Make the solution alkaline with sodium hydroxide, boil for 1 min filter through the same paper and wash with 2% sodium hydroxide solution. Transfer the precipitate back to the original beaker with a jet of hot water, dissolve in 10 ml of 1:1 sulphuric acid, add 1 ml of 30 volumes hydrogen peroxide and 0.2 g oxalic acid, dilute to about 50 to 75 ml and filter through the same paper. Dilute the filtrate and washings to 100 ml. Measure the optical density of the solution and compute the titanium content from a calibration curve obtained under similar conditions (it is important to add the same amount of oxalic acid).

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SUMMARY

Titanium is separated from titanium-bearing stainless steels by coprecipitation with zirconium as phosphate from 2-3 N acid solutions after removal of iron by ether extraction. It is spectrophotometrically determined by the hydrogen peroxide method in the presence of oxalic acid, with an accuracy better than $\pm 0.02\%$. V, Fe, Cr, Ni, Al, Cu, Mo, W, Nb, and Ta do not interfere.

RÉSUMÉ

Lors de l'analyse des aciers inoxydables, le titane peut être séparé par coprécipitation avec le zirconium au moyen de phosphate, après extraction du fer par l'éther. Il est finalement dosé spectrophotométriquement par la méthode au peroxyde d'hydrogène en présence d'acide oxalique.

ZUSAMMENFASSUNG

Zur Bestimmung von Titan in titanhaltigen Edeltählen wird zunächst das Eisen nach dem Aether-Extraktionsverfahren entfernt; Titan wird dann zusammen mit Zirkon als Phosphate gefällt und ersteres nach der Wasserstoffperoxyd-Methode spektrophotometrisch bestimmt.

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MICRO-HETEROMETRIC DETERMINATION OF BISMUTH BY
TITRATION WITH THIOCARBANILIDE

A STUDY OF THE REACTION AND THE COMPOUNDS

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INTRODUCTION

Complex compounds of bismuth and thiourea have been reported by several investigators. Yellow or orange coloured solutions are obtained which can be used for the photometric determination of bismuth. The structure of these complexes is not known; different workers have suggested that the complexes contain a definite number of molecules of thiourea per atom of bismuth, this number varying from two to six¹.

We were interested in studying the heterometric behaviour of derivatives of thiourea-bismuth complex cations with large anions. We used the iodobismuthate anion, the properties of which had already been studied². Fairly large salt complexes of strictly stoichiometric composition were obtained and used for the heterometric determination of minute quantities of bismuth. Thus, *ca.* 0.2 mg of bismuth in 20 ml of a solution containing sufficient thiocarbanilide (TCA) could be precisely determined by titration with potassium iodide. The titration at room temperature usually took 7–15 min, and the error was negligible. The analyzed solution could contain *ca.* 99% of many metals, including thorium and uranium(VI). Part of the work deals with the study of the different compounds obtained.

EXPERIMENTAL

The apparatus and working conditions were the same as in previous heterometric investigations³.

All chemicals used were either AnalaR or chemically pure reagents. Special solutions were prepared as follows:

Bismuth nitrate, *M.* 48.5 g. of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Baker's Analyzed), were dissolved in 20 ml of conc. nitric acid and diluted to 100 ml. A 0.1 *M* solution in 2 *M* nitric acid was then prepared. More dilute solutions were prepared from this solution by dilution; the 0.0005 *M* solution was 0.1 *M* in nitric acid.

Thiocarbanilide, 0.01 *M.* 0.5707 of TCA (Eastman Organic Chemicals, Cat. No. 245), was dissolved in *ca.* 95% alcohol and diluted to 250 ml. More dilute 50% alcoholic solutions of TCA were prepared from this standard solution.

Potassium iodide, 0.1 *M.*, aqueous. (Baker's Analyzed).

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RESULTS AND DISCUSSION

When bismuth nitrate and thiocarbanilide solutions were mixed, no visible change occurred, but when potassium iodide was added, an orange precipitate appeared. As TCA seemed insoluble in water, a 50% alcoholic solution was used. Only a little TCA could be added to the analyzed solution without precipitation. If the solution contained too little alcohol, the TCA precipitated, which ruined the heterometric titration. But the insoluble Bi-TCA-I⁻ compound obtained dissolved in excess of alcohol. In spite of these difficulties, conditions were found for the study of the insoluble compounds obtained, and for the determination of bismuth.

Titrations of bismuth with TCA

The results of such titrations are given in Table I. Bismuth could be titrated with TCA only if the analyzed solution contained bismuth and iodide in a ratio of $1:\geq 8$ (Expts. 1-7). If less iodide was present, then only that part of the bismuth corresponding to the ratio of $1[\text{Bi}]:8[\text{I}^-]$ was titrated (Expts. 8-13). Two moles of TCA were always consumed at the first maximum density point per one mole of *titrated* bismuth. Any iodide present in excess of the above ratio had no influence. The use of a red filter did not improve the results, the maximum optical density value achieved being sometimes even lower with a filter than without. The compound obtained at the first maximum density point always had the stoichiometric composition $\text{Bi}_1(\text{TCA})_2\text{I}_8\downarrow\downarrow$ (or $\text{Bi}_1\text{H}_m(\text{TCA})_2\text{I}_8$). The smallest amount of bismuth which could easily be titrated was *ca.* 0.2 mg of bismuth (in 20 ml solution).

Titrations of TCA with bismuth nitrate

Some of the experiments carried out are presented in Table II and Fig. 1. When 5 ml of 0.0025 *M* (*ca.* 3.0 mg TCA) in 20 ml of solution were titrated with bismuth nitrate, the maximum optical density values obtained were rather high (Expts. 1-5) and the results were practically the same whether the $[\text{Bi}]:[\text{I}^-]$ ratio at the end-point was $1:16.7$ or $1:4.1$. In all these experiments the ratio of $[\text{Bi}]:[\text{TCA}]$ at the end-point was always $1:4$, and the whole TCA present in solution was determined. The amount of potassium iodide in the analyzed solution was gradually diminished in these experiments, but in all cases the molar ratio of $[\text{I}^-]:[\text{TCA}]$ was either $1:1$ or higher. However, when less than the above ratio of iodide was present, only that part of TCA corresponding to the ratio of $1[\text{I}^-]:1[\text{TCA}]$ was titrated (Expts. 6-7).

When the titration curves were analyzed, it was found that in almost all cases an intermediate intersection point ($=\downarrow$) was obtained in addition to the final critical point ($=\downarrow\downarrow$). This point always occurred at the molar ratio of $1[\text{Bi}]:8[\text{I}^-]$ (Table II). Again, excess of potassium iodide had no influence.

From the above calculations it may be concluded that the insoluble compound obtained at the end-point had the composition $\text{Bi}_1(\text{TCA})_4\text{I}_4\downarrow\downarrow$.

As to the analytical aspect of these titrations, this compound, which has a different composition from that obtained with TCA as titrant, is no longer suitable for the determination of the components. Although the compound $\text{Bi}[\text{TCA}]_4\text{I}_4$ was obtained stoichiometrically from the components, if the analyzed solution contained potassium iodide in a molar ratio of $[\text{I}^-]:[\text{TCA}] = \geq 1:1$, not less than *ca.* 3 mg of TCA was necessary for the titration of TCA with bismuth. This is more than ten times that needed for the reverse titration (compare Tables I and III).

TABLE I

General composition: 4 ml *mM* Bi(NO₃)₃ + 1 ml *M* HNO₃ + *a* ml *nM* KI + (15—*a*) ml H₂O + *x* ml *pM* thiocarbamide (50% a.c.) (= TCA) T = 20°

Expt. No.	Bi(NO ₃) ₃ Molarity	KI Molarity	Thiocarbamide (= TCA)			Titration time in min	Molar ratios at the end-point		Remarks
			Molarity	Init. ppt. at ml	End-point at ml		[Bi] : [TCA]	[Bi] : [I ⁻]	
1	0.00025	0.05	0.00125	0.4	i 1.6 h	0.395	11	1:2	1:250
2	0.00025	0.05	0.00125	0.4	i 1.60 h	0.328	7	1:2	1:50
3	0.0005	0.05	0.00125	0.2	i 3.2 h	0.538	8	1:2	1:50
4	0.0005	0.005	0.00125	0.4	i 3.18 h	0.429	10	1:2	1:12.5
5	0.001	0.005	0.0025	0.4	i 3.18 sh/h	0.862	11	1:2	1:12.5 Red filter (Corning 3480)
6	0.001	0.005	0.0025	0.4	i 3.20 h	0.497	11	1:2	1:8
7	0.001	0.005	0.0025	0.2	i 3.20 h	0.597	10	1:2	1:8 Red filter
8	0.001	0.005	0.0025	0.6	~ 2.4	0.593	11	1:1.5	1:6 Corresponds to: 3.20 × 3/4 = 2.40 ml TCA
9	0.001	0.005	0.0025	0.6	i 2.4 h	0.592	10	1:1.5	1:6 Corresponds to: 3.20 × 3/4 = 2.40 ml TCA red filter
10	0.001	0.005	0.0025	0.6	i 2.1 h	0.323	11	1:1.3	1:5 Corresponds to: 3.20 × 5/8 = 2.0 ml TCA
11	0.001	0.005	0.0025	0.6	c 2.1 h	0.308	10	1:1.3	1:5 Corresponds to: 3.20 × 5/8 = 2.0 ml TCA red filter
12	0.002	0.005	0.0025	0.1	c 3.2 h	0.561	10	1:1	1:4 Corresponds to: 4 ml Bi 0.001 M at 1[Bi]:8[I ⁻] = 3.20 ml TCA
13	0.002	0.005	0.0025	0.1	i 2.00 h	0.348	7	1:0.625	1:2.5 Corresponds to: 2.5 ml Bi 0.001 M at 1[Bi]:8[I ⁻] = 2.00 ml TCA

i = intersection point; h = horizontal maximum density line; sh = short; c = contact point.

TABLE II

General composition: 5 ml 0.0025 M thiocarbamide (= TCA) + 1 ml M HNO_3 + b ml 0.005 M KI + ad 20 ml H_2O + x ml 0.001 M $Bi(NO_3)_3$
 $T = 20^\circ$

Expt. No.	ml KI	[I-] : [TCA]	Titrant $Bi(NO_3)_3$			Titrant time in min	Calculated molar ratios at the end-point		[Bi] : [I-] at the intermediate point	Remarks
			Initial ppt. at ml	Intermediate point at ml	End-point at ml		[Bi] : [TCA]	[Bi] : [I-]		
1	10	4:1	0.1	2.5	13.00 h	0.92	1:4.2	1:16.7	1:20	
2	5	2:1	0.1	2.6	13.10 h	0.97	1:4	1:8.1	1:9.6	
3	3.3	1.32:1	0.1	2	13.10 h	0.74	1:4	1:5.3	1:8.2	
4	3	1.2:1	0.1	1.9	13.06 h	0.88	1:4.1	1:4.9	1:7.9	
5	2.5	1:1	0.1	1.5	13.06 h	0.76	1:4.1	1:4.1	1:8.3	
6	2	4:5	0.1	—	12.44 h	0.69	1:5.1	1:4.1		$2.44 \times 5/4 = 3.06$
7	1.5	3:5	0.3	0.95	11.9 h	0.49	1:6.6	1:4	1:7.9	$1.9 \times 5/3 = 3.1$

= intersection point; h = horizontal maximum density line.

TABLE III

General composition: 4 ml mM Bi(NO₃)₃ + 1 ml M HNO₃ + *a* ml *nM* thiocarbamide (= TCA) + 1 ml *pM* salt + ad 20 ml H₂O + *x* ml *qM* KI
 T = 20°. Content: 0.2 to 0.4 mg bismuth

Expt. No.	Thiocarbamide		Salt solution		Titrant KI		Maximum density value	Titration time in min	% Bismuth	[Bi] : [TCA]	[Bi] : [I ⁻] at the end-point
	Molarity of Bi(NO ₃) ₃	ml	Name	Molarity	Molarity	Initial ppt. at ml					
1	0.0005 ^a	2.5	—	—	0.005	1.0	14.00 h	0.57	10	1:2	1:8
2	0.0005	3	—	—	0.005	1.4	13.20 h	0.34	9	1:3	1:8
3	0.0005	4	—	—	0.005	0.4	13.2 h	0.76	6	1:4	1:8
4	0.0005	8	—	—	0.005	0.4	13.20 h	0.86	10	1:8	1:8
5	0.0005	8	—	—	0.005	0.3	13.2	1.01	5	1:16	1:8
6	0.00025	8	—	—	0.0025	1.4	13.23 h	0.43	12	1:32	1:8
7	0.00025	8	Ca(NO ₃) ₂	1.0	0.0025	0.4	13.20 h	0.51	13	1:32	1:8
8	0.0005	8	Ba(NO ₃) ₂	0.1	0.005	0.8	13.20 h	0.82	13	1:8	1:8
9	0.0005	8	Mg(NO ₃) ₂	0.5	0.005	0.8	13.2 h	0.78	8	1:8	1:8
10	0.00025	8	Mg(NO ₃) ₂	1.0	0.0025	0.4	13.18 h	0.68	8	1:32	1:8
11	0.00025	8	Zn(NO ₃) ₂	0.5	0.0025	0.4	c 3.20 h	0.91	8	1:32	1:8
12	0.00025	8	Zn(NO ₃) ₂	1.0	0.0025	1.2	13.20 h	0.72	7	1:32	1:8
13	0.00025	8	Ni(NO ₃) ₂	0.1	0.0025	1.0	13.2	0.61	10	1:32	1:8
14	0.00025	8	Co(NO ₃) ₂	0.1	0.0025	0.8	13.2 h	0.55	10	1:32	1:8
15	0.00025	8	Al(NO ₃) ₃	0.5	0.0025	0.4	13.20 h	0.95	8	1:32	1:8
16	0.00025	8	Al(NO ₃) ₃	0.7	0.0025	1.6	c 3.20 h	0.62	9	1:32	1:8
17	0.0005	8	Cr(NO ₃) ₃	0.1	0.005	1.2	13.2 h	0.75	16	1:8	1:8
18	0.0005	8	Cd(NO ₃) ₂	0.1	0.005	1.4	13.21 h	0.64	16	1:8	1:8
19	0.0005	8	Pb(NO ₃) ₂	0.1	0.005	0.4	13.20 h	0.84	5	1:8	1:8
20	0.0005	8	Th(NO ₃) ₄	0.5	0.005	0.6	13.20 h	0.91	5	1:8	1:8
21	0.0005	8	UO ₂ (NO ₃) ₂	0.4	0.005	0.2	13.20 h	0.82	6	1:8	1:8
22	0.0005	8	ZrO(NO ₃) ₂	0.2	0.005	1.2	13.2 h	0.62	29	1:8	1:8
23	0.0005	8	Ce(NO ₃) ₃	0.125	0.005	0.8	13.20 h	0.74	6	2:2	1:8

^a 5 ml; i = intersection point; h = horizontal maximum density line; c = contact point.

20-21). In the case of magnesium, zinc or aluminium, the bismuth amounted to less than one per cent of the total metal content of the solution. In all other cases (except chromium) the foreign metal amounted to 95% or more. The foreign metal usually acted favourably on the titration.

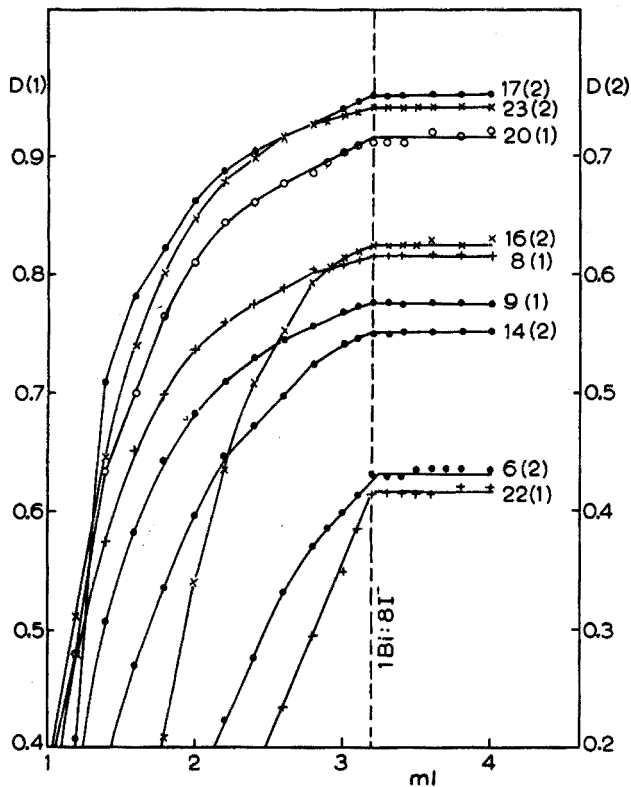
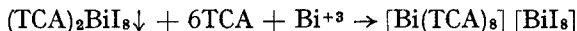


Fig. 2. Titrations of bismuth nitrate-thiocarbamide mixtures with potassium iodide.

Composition of the compounds

On titrating bismuth with TCA or with potassium iodide, we always found a molar ratio of $[\text{Bi}]:[\text{I}^-]$ equal to 1:8 in the final compounds obtained. In our previous investigations with bismuth iodide², we had never found a compound which contained iodide in excess of this ratio. No reaction between TCA and potassium iodide was traced. Therefore we must conclude that in all the previous cases the iodide entirely complexed the bismuth, and that the complex formed the insoluble compound $(\text{TCA})_2\text{BiI}_8 \downarrow \downarrow$, or better $(\text{TCA})_2\text{H}_m\text{BiI}_8 \downarrow \downarrow$. Conversely on titrating TCA-iodide mixtures with bismuth nitrate (Table II) we obtained the molar ratio of $1[\text{Bi}]:8[\text{I}^-]$ at the *intermediate point*. Evidently at this point a compound of the same composition as before was obtained. On further addition of bismuth nitrate, we obtained the final

compound $\text{Bi}(\text{TCA})_4\text{I}_4\downarrow$. This compound must be very stable as it was always formed at the final stage. The transformation of $(\text{TCA})_2\text{H}_m\text{BiI}_8\downarrow$ into $\text{Bi}(\text{TCA})_4\text{I}_4\downarrow$ by further addition of bismuth may be explained differently. Either the latter compound is a neutral insoluble compound in which both the iodide and the TCA are coordinately bound to the bismuth, or a further reaction occurs between the intermediate compound and bismuth nitrate, which might be represented as follows:



If this were true, the compound $\text{Bi}(\text{TCA})_4\text{I}_4$ obtained must be doubled and would contain bismuth both as a cation and as an anion. It remains uncertain which of these formulae is correct.

ANALYTICAL ASPECT

Bismuth nitrate can be titrated either with potassium iodide or with TCA (50% alc.). The former titration is to be preferred, the titration of TCA with bismuth as titrant is about ten times less sensitive.

METHODS

1. Titration of bismuth with potassium iodide

Approximately 0.2 mg of bismuth in 20 ml of solution containing 1 ml of *M* nitric acid, 1 ml of 0.5 *M* magnesium, zinc or aluminium nitrate, and 8 ml of 0.004 *M* TCA (50% alc.) are titrated at room temperature with 0.0025 *M* potassium iodide. The analyzed solution may contain 95 to 99% of the following metals as cations: Ca^{+2} , Ba^{+2} , Mg^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , Al^{+3} , Cr^{+3} , Cd^{+2} , Pb^{+2} , Th^{+4} ($\geq 99.7\%$), U^{+6} ($= \text{UO}_2^{+2}$) ($\geq 99.6\%$), Zr or Ce^{+3} .

Remark. The end-point comes exactly at the molar ratio $1[\text{Bi}]:8[\text{I}^-]$. The error in this method is always negligible.

2. Titration of bismuth with TCA

Approximately 0.5 mg of bismuth in 20 ml of aqueous solution containing 1 ml of *M* nitric and 2–5 ml of 0.05 *M* iodide are titrated with 0.001–0.00125 *M* TCA (50% alc.)

Remark. The end-point is reached exactly at the molar ratio of $1[\text{Bi}]:2[\text{TCA}]$.

3. Titration of TCA with bismuth nitrate

Approximately 2–2.5 mg of TCA ($= 4\text{--}5$ ml 0.0025 *M*, 50% alc.) in 20 ml of solution, containing 1 ml of *M* nitric acid and *ca.* 1 ml of 0.05 *M* iodide are titrated with 0.001 *M* bismuth nitrate.

Remark. The end-point is reached at the molar ratio of $1[\text{Bi}]:4[\text{TCA}]$.

SUMMARY

The composition, structure and behaviour of the large salt complexes formed between thiocarbanilide and bismuth iodide were studied heterometrically. Structural formulae for the compounds are presented. Methods are presented for the exact determination of *ca.* 0.2 mg of bismuth in 20 ml of solution by titration with potassium iodide (or with thiocarbanilide). The analyzed solution could contain 95–99% of the following metals as cations: Ca^{+2} , Ba^{+2} , Mg^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , Al^{+3} , Cr^{+3} , Cd^{+2} , Pb^{+2} , Th^{+4} , ($\geq 99.7\%$), U^{+6} ($\geq 99.6\%$), Zr^{+4} or Ce^{+3} .

RÉSUMÉ

Une étude a été effectuée sur les complexes formés entre iodure de bismuth et thiocarbanilide. Des méthodes de dosage du bismuth sont proposées par titrage hétérométrique au moyen d'iodure de potassium ou de thiocarbanilide.

ZUSAMMENFASSUNG

Die Zusammensetzung, Struktur und das Verhalten des Thiocarbanilid-Wismutjodid Komplexes wurde heterometrisch untersucht. Ferner wird eine titrimetrische Bestimmung von Wismut mit Kaliumjodid oder Thiocarbanilid beschrieben.

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THE DETERMINATION OF BORON IN BORIC ACID ESTERS

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INTRODUCTION

The determination of boron in an organic ester of boric acid is usually performed by hydrolysis¹ of the ester and titration of the resulting boric acid in the presence of mannitol². However, with esters of high hydrolytic stability³ it is necessary to maintain prolonged periods of reflux in boron-free glassware. Often low results are obtained and a second and more prolonged hydrolysis must be performed. In addition, with aromatic or alkanolamine^{3,4} esters, the phenols or alkanolamines liberated in the hydrolysis interfere with the titration of the boric acid. Hydrolysis followed by the "identical pH" method^{5,6} can be used but has never been reported. In such cases the boron was determined gravimetrically^{7,8} or by conversion to methyl borate with sulfuric acid and methanol⁹. This latter procedure adapted from the original method of CHAPIN¹⁰ is at best unwieldy and often suffers from incomplete volatilization of the boron as methyl borate. In addition it is not applicable at all to highly sterically hindered esters such as tri-(2-cyclohexylcyclohexyl)borate and tri-(diisobutylcarbonyl)borate³ since only a small percentage of these esters are transesterified in a reasonable time.

A general procedure which has been found to be applicable with slight modification to boric acid esters is the method for the determination of boron in acid insoluble minerals¹¹ which has also been used for the determination of boron in boric acid complexes of hydroxy acids^{12,13}, hydroxy ketones¹³, and catechol^{12,14}. The ester is fused with sodium carbonate in a platinum crucible. The cooled melt is dissolved in hydrochloric acid, boiled to expel carbon dioxide, and neutralized with dilute base. Excess mannitol is then added and the boric acid titrated to the phenolphthalein end-point.

EXPERIMENTAL

Reagents and materials

The boric acid esters excluding tri-(1-carboxy-11-heptadecyl) borate have been described.³ Tri-(1-carboxy-11-heptadecyl) borate was prepared by the azeotropic removal of water (with toluene) from a 3:1 molar mixture of 12-hydroxystearic acid and boric acid. The reaction mixture was then filtered and stripped of toluene under reduced pressure. The residue was triturated with cold acetone and filtered in a dry box to give a 60% yield of white granules melting at 111-120°.

Sodium hydroxide solution was prepared by dissolving reagent grade pellets in an equal weight of distilled water and filtering the insoluble carbonate. The filtrate was diluted to the proper volume and standardized with twice recrystallized boric acid. The recrystallized boric acid was previously dried in a vacuum desiccator over conc. sulfuric acid. All other materials were reagent grade.

The indicator solutions were prepared as follows: Phenolphthalein, 1 g in 100 ml of 60% (by volume) ethanol; methyl red, 0.1 g in 60 ml of methanol; methylene blue, 0.1 g in 100 ml of water.

Carbonate fusion procedure

A 35-ml platinum crucible is lined with sodium carbonate by melting about 4 g of the anhydrous reagent over a Fisher burner and gently swirling the vessel with crucible tongs while cooling. A 0.5 to 1.0 g-sample of the ester is accurately weighed into the crucible and covered (without mixing) with sodium carbonate (23 g) to within 1/4" of the crucible top. The crucible is placed in a muffle furnace at room temperature and heated to 850° at which temperature a clear melt is obtained. After cooling, the crucible is placed in a 500-ml wide mouth Erlenmeyer flask and covered with 100 ml of distilled water. Conc. hydrochloric acid (60 ml) is poured down the side of the flask which is then covered with a watch glass. After a few min solution is complete. Methyl red indicator (3 drops) is added and the excess acid neutralized with either a saturated solution of sodium hydroxide (stored in a polyethylene bottle) or sodium hydroxide pellets (8.5 g) and then reacidified with several drops of 4 N hydrochloric acid. The slightly acid solution is gently boiled on a hot plate for 10 min and cooled to room temperature in a cold water bath. Three drops of methylene blue solution are added and the solution and cover rinsings are adjusted to the methyl red end-point with 0.1 N sodium hydroxide. (The red-violet to green end-point effected by the methylene blue is more accurately discernable than the normal red to yellow change of methyl red itself.) Phenolphthalein (8 drops) and excess mannitol (30 g, the use of less than seven moles of mannitol per mole of boric acid at the dilutions used results in a hazy end-point and low boron determination) are then added and the boric acid complex is titrated with 0.1 N sodium hydroxide to the phenolphthalein end-point (green to red-violet).

Modified carbonate fusion procedure

A modified procedure is employed for the alkanolamine borates. A weighed sample is just covered with conc. hydrochloric acid in the platinum crucible and allowed to

stand at room temperature overnight. The acid is then neutralized by careful addition of conc. sodium hydroxide solution. Sodium carbonate is added as above and the usual procedure followed.

Blank

A blank determination using the amounts of reagents as specified in the analytical procedure possessed a titer equivalent to 0.11 mg of boron. The percentage boron is thus calculated:

$$\% B = \frac{10.82 \times N \times \text{ml} - (\text{blank, in mg boron})}{\text{sample wt. (mg)}} \times 100$$

Parr peroxide bomb procedure (adapted from procedure of SNYDER, KUCK AND JOHNSON¹⁵)

The ester sample (0.5 g) is weighed into a PARR bomb fusion cup (Series 2000, 22 ml, electric ignition, macro bomb) followed by one gram of potassium perchlorate and 15 g of sodium peroxide. After thorough mixing with a glass rod, the rod is wiped clean with a small piece of filter paper which is added to the charge and the mixture is ignited with the usual precautions. The fusion mixture is then dissolved in 100 ml

TABLE I
PERCENTAGE BORON IN BORIC ACID ESTERS

Ester	Formula	Calculated	Found		
			Carbonate fusion	Parr bomb	"Identical pH"
Aromatic:					
Triphenyl borate	C ₁₈ H ₁₅ O ₃ B	3.73	3.74		
Tri- <i>o</i> -cresyl borate	C ₂₁ H ₂₁ O ₃ B	3.26	3.24		
Tri- <i>o</i> -chlorophenyl borate	C ₁₈ H ₁₂ O ₃ Cl ₃ B	2.75	2.83	2.84	
Tri- <i>o</i> -phenylphenyl borate	C ₃₆ H ₂₇ O ₃ B	2.09	2.04		
Tri- <i>o</i> -cyclohexylphenyl borate	C ₃₆ H ₄₅ O ₃ B	2.02	2.02		
Alkanolamine:					
Triethanolamine borate	C ₈ H ₁₂ O ₃ NB	6.89	6.71	6.75	6.73
Triisopropanolamine borate	C ₉ H ₁₈ O ₃ NB	5.44	5.47	5.46	
High hydrolytic stability:					
Tri-(diisobutylcarbiny) borate	C ₂₇ H ₅₇ O ₃ B	2.46	2.40	2.36	
Tri-(2-phenylcyclohexyl) borate	C ₃₆ H ₄₅ O ₃ B	2.02	2.02		
Tri-(2-cyclohexylcyclohexyl) borate	C ₃₆ H ₆₃ O ₃ B	1.95	1.93		
Tri-(2,6,8-trimethyl-4-nonyl) borate	C ₃₆ H ₇₅ O ₃ B	1.91	1.92		
Tri-(dicyclohexylcarbiny) borate	C ₃₉ H ₆₉ O ₃ B	1.81	1.79		
Intermediate and low hydrolytic stability:					
Tri- <i>tert.</i> -amyl borate	C ₁₅ H ₃₃ O ₃ B	3.97	4.08		
Tri-(1,3-dichloro-2-propyl) borate	C ₉ H ₁₅ O ₃ Cl ₆ B	2.74	2.82		
Tri-(β,β,β-trichloro- <i>tert.</i> -butyl) borate	C ₁₂ H ₁₈ O ₃ Cl ₃ B	2.00	2.04		
Tri- <i>n</i> -dodecyl borate	C ₃₆ H ₇₅ O ₃ B	1.91	1.86		
Trioleyl borate	C ₅₄ H ₁₀₅ O ₃ B	1.33	1.35		
Tristearyl borate	C ₅₄ H ₁₁₁ O ₃ B	1.32	1.34		
Tri-(1-carboxy-11-heptadecyl) borate	C ₅₄ H ₁₀₅ O ₉ B	1.19	1.20		

of water in a 400-ml boron-free beaker after which the cup is removed and rinsed. The solution and rinsings are combined and neutralized with conc. hydrochloric acid (approximately 30 ml). After adding 1 ml of 50% sodium hydroxide, the basic solution is boiled to coagulate the metallic hydroxides which are then removed by filtration of the hot solution. The filtrate which is collected in a boron-free beaker and acidified with 4 *N* hydrochloric acid is then boiled and titrated as in the carbonate fusion procedure.

A blank determination using benzoic acid in place of the boron compound gave a negligible boron titer.

"Identical pH" method

A 30.5-mg sample of triethanolamine borate was analyzed by the method of WILCOX⁶ as further described by TAYLOR⁵. An end-point of pH 6.3 was used.

DISCUSSION

Table I records the analytical results for a variety of aromatic, alkanolamine, and stable boric acid esters. Several esters of lower hydrolytic stability are included to indicate the general applicability of the carbonate fusion procedure for primary, tertiary, polyhalo, olefinic, and carboxyl-containing esters as well.

The procedure led to low results for the alkanolamine esters presumably due to some loss of the sample by sublimation. Both triethanolamine borate and triisopropanolamine borate readily sublime. However, a preliminary treatment with hydrochloric acid followed by the usual procedure resulted in good values for boron. It might be expected that the more volatile aliphatic esters of low molecular weight such as tri-*tert.*-amyl borate (B.p. 235°) similarly would distill before complete reaction with the sodium carbonate and also lead to low results. However, this is not the case and it is possible that the cage-structured alkanolamine esters^{3,4} possess a resistance to reaction with sodium carbonate not shared by the other esters. Such unreactivity is consistent with the high hydrolytic stability found for triisopropanolamine borate³.

The PARR peroxide bomb method which has been used for boron fluoride complexes of esters and ammonia¹⁶ as well as boronic acids¹⁵ has also been applied to the boric acid esters. In general, the method is more time consuming than the carbonate fusion procedure.

It has been found that the carbonate fusion method is useful for various classes of boron-carbon compounds for which the more involved methods of peroxide oxida-

TABLE II
PERCENTAGE BORON IN VARIOUS BORON-CARBON AND BORON-NITROGEN COMPOUNDS

Compound	Formula	Calculated	Found
Triphenylboroxine	(C ₆ H ₅ BO) ₃	10.41	10.37
β-Aminoethyl diphenylborinate	C ₁₄ H ₁₆ ONB	4.81	4.88
Triphenylborane	C ₁₈ H ₁₅ B	4.47	4.40
Sodium tetraphenylboron	C ₂₄ H ₂₀ NaB	3.16	3.15
B-Triphenylborazole	C ₁₈ H ₁₈ N ₃ B ₃	10.51	10.42
Trisanilinoborane	C ₁₈ H ₁₈ N ₃ B	3.77	3.87

tion^{15,17} and mercuric chloride treatment^{18,19} are presently used. A variety of boron-nitrogen compounds have also been analyzed successfully (Table II).

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SUMMARY

Boric acid esters of high hydrolytic stability which would require prolonged periods of reflux for hydrolysis and subsequent titration of boric acid can be analyzed conveniently for boron by fusion with sodium carbonate, solution of the melt, and titration of the boric acid in the presence of mannitol. Boric acid esters of phenols or alkanolamines which cannot be analyzed by titration of the boric acid due to the interference of the acidic phenolic or basic amine residues can also be analyzed by the carbonate fusion method. The method has also been applied to esters of primary and tertiary alcohols as well as polyhalo, olefinic, and carboxyl-containing borates. Further applicability to organoboron compounds containing boron-carbon and boron-nitrogen bonds is indicated.

The PARR peroxide bomb method has also been found to be generally applicable for the determination of boron in boric acid esters.

RÉSUMÉ

Une méthode est proposée pour le dosage du bore dans les esters boriques, par fusion au moyen de carbonate de sodium et titrage de l'acide borique en présence de mannitol. Ce procédé peut être appliqué aux organocomposés renfermant des liaisons bore-carbone et bore-azote. On décrit également la méthode au peroxyde de sodium, utilisant une bombe de PARR.

ZUSAMMENFASSUNG

Zur Bestimmung von Bor in Borsäureestern wird der Ester mit Soda geschmolzen und die Borsäure acidimetrisch in Gegenwart von Mannitol titriert. Diese Methode lässt sich auch für Verbindungen mit Bor-Kohlenstoff und Bor-Stickstoff Bindungen anwenden. Der Aufschluss kann auch mit Natriumperoxyd in der PARR Bombe erfolgen.

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RAPID DETERMINATION OF THORIUM IN ORES

III. DETERMINATION OF MICROGRAM AMOUNTS OF THORIUM IN
ILMENITE SANDS

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It was necessary in certain projects to know exactly the residual monazite content in ilmenite sands and therefore, to determine thorium in ilmenite when less than 0.015% was present. In an earlier communication¹ from this laboratory a method was described for the determination of more than 0.01% of thorium in minerals and ores.

Thorin² has been used for the colorimetric determination of thorium by many workers. As it is not specific a preliminary separation of thorium has to be carried out. BANKS AND BYRD³ separated milligram and higher amounts of thorium from monazite by extracting with mesityl oxide from a solution of thorium fluoride in aluminium nitrate. CLINCH⁴ carried out a similar separation with oxalate at a controlled pH of 4 and with calcium as carrier. Recently GRIMALDI *et al.*⁵ have developed a method for selective precipitation of thorium as iodate in presence of tartaric acid and hydrogen peroxide. The method was used for the determination of thorium in silicate rocks and of 0.01% of thorium or more in black sands. The method followed in this laboratory¹ has now been modified to determine less than 0.05% of monazite in ilmenite sands.

PRINCIPLE

The ilmenite is opened up with sodium peroxide and thorium precipitated as hydroxide with ammonia without prior removal of silica. Silica is removed by volatilisation in hydrofluoric acid and thorium collected as fluoride with lanthanum. The fluorides are decomposed with sulphuric acid and finally taken up in 10% nitric acid. Thorium is precipitated as iodate with mercuric nitrate as carrier. Thorium is finally determined spectrophotometrically, with thorin as the colorimetric reagent.

Reagents

Mercuric nitrate: 1.58 g of mercuric nitrate (E. Merck) dissolved in 10 ml of (1:1) nitric acid and diluted to 1 litre (1 ml = 1 mg of HgO). Oxalic acid: 10% oxalic acid solution. Hydrogen peroxide: 10 ml of 30% H₂O₂ diluted to 100 ml with distilled water. Lanthanum nitrate: To contain 1 ml = 1 mg La₂O₃ in dilute HNO₃. Hydrofluoric acid wash solution: 5 ml of HF diluted to 100 ml with distilled water. Potassium iodate reagent: 15 g of KIO₃ (E. Merck) dissolved in 100 ml of HNO₃ (1:1) and filtered through a dry paper. Potassium iodate wash solution: 10 g of KIO₃ dissolved in 200 ml of HNO₃ (1:1) and made up to 1 litre with distilled water. Thorin reagent: 0.1 g of thorin (Eastman Kodak) dissolved in distilled water and made up to 100 ml. Standard thoria solution: 1 ml = 5 μg of thoria.

The standard curve

Aliquots of standard thorium nitrate solution were taken containing 5 to 100 μg of thoria. 2 ml of nitric acid were added and the volume made up to 16 ml. The thorium was precipitated as iodate in presence of oxalic acid with mercuric iodate as carrier. After washing and decomposing the iodates, thorin was added and the optical densities were measured against a blank taken through the same procedure. (Details are given below). Beer's law was obeyed from 5 to 100 μg of thorium (Table I).

TABLE I

OPTICAL DENSITIES OF STANDARD THORIUM SOLUTION

(5 to 100 μg) with thorin and 5 mg of mercuric oxide as carrier, against reagent blank

No.	Thorium oxide (μg) taken	Optical density against blank with standards taken directly	Optical densities against blank and standards run through the procedure
1.	5.00	0.008	0.008
2.	10.00	0.017	0.017
3.	20.00	0.035	0.035
4.	40.00	0.066	0.065
5.	60.00	0.107	0.107
6.	80.00	0.138	0.139
7.	100.00	0.180	0.182

Procedure

A 1-g sample was cautiously fused in a nickel crucible with 5–6 g of sodium peroxide, the mass being kept liquid for about 10 min. The crucible was cooled and transferred to a 250-ml beaker. About 100 ml of cold water were added and the melt was disintegrated. The crucible was removed and rinsed first with water and then with hydrochloric acid (1:1).

The solution was neutralized with (1:1) hydrochloric acid and then 10 mg of zirconium oxide were added as the nitrate. (If titanium or zirconium are present in the sample, which can be noticed from the ammonia precipitate, it is not necessary to add zirconium.) The solution was warmed to about 90° and ammonia was added in excess to give a precipitate. The contents of the beaker were then digested on a water bath for 30 min.

The solution was filtered on a Whatman No. 540, 11 cm paper, and the precipitate washed with the ammonia wash solution. The precipitate was then transferred to a 100-ml platinum dish. The paper was burned in a platinum crucible and the ash added to the dish. 20 ml of hydrofluoric acid were added and the mixture was digested on a steam bath, while stirring with a platinum rod, and evaporated to about 8 ml. 10 ml of hydrofluoric acid were then added and the solution was re-evaporated to about 8 ml and then diluted with 30 ml of water. The solution was warmed on the steam bath and 10 mg of lanthanum oxide in the form of nitrate were added. The solution was stirred with a platinum rod and allowed to stand overnight at room temperature.

The solution was filtered on a Whatman No. 40, 9 cm filter paper in a hard rubber or plastic funnel. The precipitate was washed twice with 10 to 15 ml of 5% hydrofluoric acid wash solution and then twice with water.

The paper and the precipitate were transferred back to the dish and carefully charred but not ignited. When fumes were no longer evolved the contents were heated at 600° until carbon was burnt off. The residue was carefully moistened with a few drops of water, 0.5 ml of sulphuric acid and one drop of hydrofluoric acid. The

dish was heated on the hot plate for about 25 min until dry and then over a low Bunsen flame below 450° until no more fumes appeared. 15 ml of conc. nitric acid were added and the solution was evaporated to dryness on the water bath. This was repeated two or three times, until all the thorium was in solution. 2 ml of (1:1) nitric acid and 5 ml of water were added to dissolve any residue and the solution was filtered through Whatman No. 42, 7 cm paper. The final volume of the solution in beaker was about 16 ml. To the solution, 5 drops of hydrogen peroxide, 0.5 ml of oxalic acid and 5 mg of mercuric oxide as the nitrate were added and thorium precipitated as iodate with 3 ml of potassium iodate solution. The beaker was placed in cold water overnight to ensure complete precipitation.

The precipitate was filtered through Whatman No. 541, 7 cm paper, being transferred with the potassium iodate wash solution, and washed four times with the wash solution. It was then washed back into the beaker with distilled water. The paper was washed with a mixture of hydrochloric acid and sulphurous acid until all the iodate had decomposed and no stains of iodine remained on the paper. The solution was evaporated and fumed with 1 ml of perchloric acid to dryness. 0.5 ml of hydrochloric acid and 20 ml of distilled water were then added and the mixture was heated on the water bath until all the residue was in solution. 3 ml of 0.1% thoria were added and volume made up to 25 ml.

After 30 min, the optical densities of the solutions were measured on a Beckman DU quartz spectrophotometer at $545\text{ m}\mu$ with a 1-cm cell against a blank which had been similarly treated. The thoria present in the sample was calculated from the standard curve.

Application of the method for the determination of thoria in ilmenite sands

In order to check the procedure, the recoveries of thorium added to ilmenite were determined. As no ilmenite containing thoria of the order of 0.001% was available, an artificial ilmenite was prepared containing about 40% FeO and 60% TiO₂. To a 1-g sample 10 to 50 μg of thoria were added and thorium was determined as given above. It was found that 1 g of the artificial sample contained about 8 μg of thoria and that the recoveries of added thoria were quantitative (Table II).

TABLE II
RECOVERIES OF ADDED THORIA (10 TO 50 μg) TO AN ARTIFICIAL ILMENITE, THROUGH THE ENTIRE PROCEDURE

No.	Artificial ilmenite taken	Thoria added μg	Thoria recovered μg	Remarks
1.	1.000	—	8	8 μg of thoria were found in 1 g of the artificial ilmenite
2.	1.000	10	17	
3.	1.000	20	27	
4.	1.000	40	46	
5.	1.000	50	54	

Thoria was then determined in three mixtures of ilmenite and monazite (Table III).

TABLE III
DETERMINATION OF THORIA IN SYNTHETIC MIXTURES OF ILMENITE AND MONAZITE

No.	Nature of sample	Wt. of sample taken g	Thoria		Remarks
			Expected %	Found %	
1.	Ilmenite (A)	1.000	—	0.0078	Mean of 3 readings
2.	Ilmenite (A) + Monazite (B) 99.950% + 0.050%	0.500	0.0119	0.0110	Mean of 2 readings
3.	Ilmenite (A) + Monazite (B) 99.900% + 0.099%	0.500	0.0159	0.0150	Mean of 3 readings
4.	Ilmenite (A) + Monazite (B) 99.850% + 0.15%	0.500	0.0201	0.0200	Mean of 3 readings
5.	Ilmenite (B)	0.100	—	0.053	Value by trace method ¹ = 0.052%

Monazite (B) contains 8.20% thoria.

The results show that the recoveries of thoria agree fairly well and that it is possible to estimate less than 0.05% of monazite in ilmenite samples.

SUMMARY

A previous method has been modified to determine less than 0.05% of monazite in ilmenite samples, with thorin as the colorimetric reagent; mercuric iodate serves as carrier.

RÉSUMÉ

Les auteurs proposent une modification de leur méthode utilisant l'iodate mercurique comme entraîneur. On peut ainsi déterminer, dans des échantillons d'ilménite, des teneurs en monazite inférieures à 0.05%. On utilise le thorin comme réactif colorimétrique.

ZUSAMMENFASSUNG

Es wird über eine Modifikation der früher beschriebenen Methode zur Bestimmung von Monazit in Ilmenit berichtet. Mit Quecksilber(II)-jodat als Trägersubstanz lassen sich weniger als 0.05% Monazit bestimmen, wobei Thorin als colorimetrisches Reagenz verwendet wird.

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ANALYSIS OF SILVER SOLDERS BY ANION EXCHANGE AND EDTA TITRATION

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The recent pioneering work of KRAUS AND NELSON¹ on the anion exchange of metal chloride complexes with quaternary-amine type resins has opened a broad new field for metal separations. In the author's laboratory, it has been found that the anion-exchange separation of nickel, copper, zinc, and cadmium may be combined quite conveniently with the titration of these elements by the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA). As one or more of the above elements often occur along with silver in most commercial silver solder alloys, a procedure for their analysis by these techniques is presented.

In the procedure to be described, silver is first determined in dilute nitric acid solution by potentiometric titration with chloride. The solution is then prepared for anion-exchange chromatography by filtration and addition of the proper amount of hydrochloric acid. After adsorption on the column, the anions are eluted by washing the resin column with successively more dilute solutions of hydrochloric acid. Although zinc and cadmium may be titrated directly with EDTA in their respective eluates, it is necessary to evaporate the nickel and copper eluates to dryness on the steam bath first to rid them of their large excess of hydrochloric acid.

Whereas the anion-exchange separations reported in this present paper depend largely upon the original work of KRAUS AND NELSON¹, others such as BERG AND TRUEMPER², KALLMANN, OBERTHIN, AND LIN³ and JACKSON⁴ have applied anion exchange to the separation of two or more of the elements considered here.

APPARATUS AND REAGENTS

Standard glass chromatographic tubes commercially available (Fisher Scientific Co. #5-722) and measuring about 30 cm in length by 1.0 cm internal diameter were used. Each tube was filled to a height of 20 cm with about 10-12 grams of the anion-exchange resin Dowex 1-8X, 100 to 200 mesh, introduced as a water slurry. The liquid holdup of each column was about 9.5 ml.

A Beckman Model H-2 pH meter was used for the potentiometric titration of silver with chloride ion. A saturated calomel electrode and 1 M potassium nitrate-agar salt bridge were used as the reference electrode, pure silver wire as the other electrode.

Zinc and cadmium of "super purity" spectrographic grade, high purity nickel foil, electrolytic copper wire, and carefully dried reagent grade silver nitrate were used as standards. Other chemicals were the usual reagent or C.P. grades. EDTA (0.1 M) was standardized against zinc using Eriochrome Black T as indicator, and against copper using murexide as indicator.

Buffer of pH 9.2 used in the titration of zinc and cadmium was prepared from ammonium chloride and ammonium hydroxide so that the resulting solution was 0.5 M in each.

Zinc EDTA was prepared by the titration of a solution containing about 1% of zinc chloride with EDTA to its equivalence point. This solution was buffered with about 10 ml of pH 9.2 buffer and Eriochrome Black T was used as the indicator.

PROCEDURE

About 200 mg of sample are dissolved in a few ml of 8 *M* nitric acid, and the solution is evaporated just to dryness on the steam bath. The residue is then dissolved in about 10 ml of water and titrated potentiometrically with standard 0.1 *N* hydrochloric acid.

The silver chloride precipitate is now removed by filtration, care being taken to keep the wash water below a final volume of 45 ml.

If nickel is present in the filtrate, the filtrate should be made approximately 6 *M* in hydrochloric acid by the addition of an equal volume of conc. hydrochloric acid. If only copper, zinc, and cadmium are present, one eleventh volume of concentrated hydrochloric acid is added to the filtrate to make it 1 *M* in hydrochloric acid. The

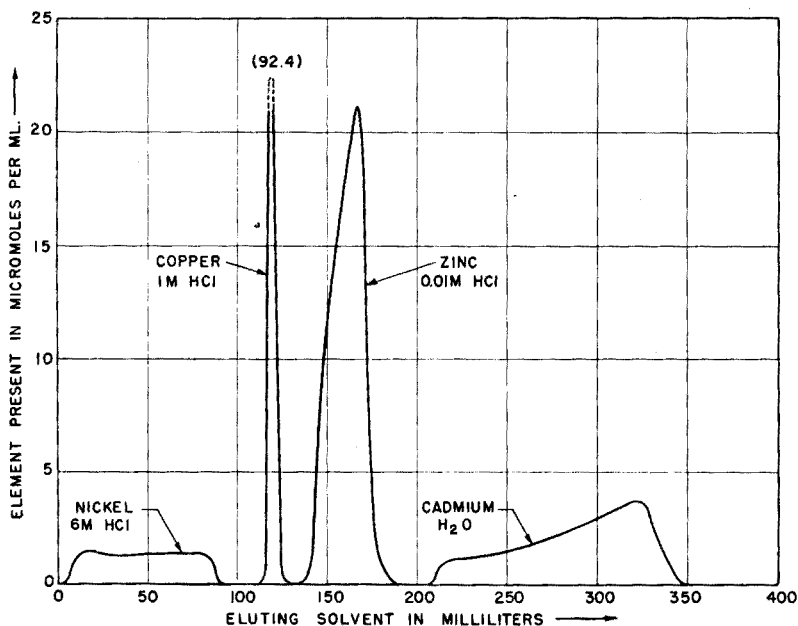


Fig. 1. Elution curves of Ni, Cu, Zn and Cd.

anion-exchange column is readied by a preliminary wash with a few ml of 6 *N* or 1 *N* hydrochloric acid as required, and the solution containing the unknown is introduced into the top of the column as soon as it has run dry. A reservoir on top of the chromatographic tube is quite helpful here. With 100–200 mesh resin, there is no danger of air being drawn into the interstitial spaces of the column if it should accidentally run dry. A final wash with 25 ml of 6 *N* hydrochloric acid serves to flush the nickel out of the interstitial spaces of the column without disturbing the other elements adsorbed on the resin.

Copper may be eluted from the column with 30 ml of 1 *N* hydrochloric acid. Zinc is eluted with 70 ml of 0.01 *N* hydrochloric acid, and the cadmium is finally eluted by a wash with 180 ml of water.

The progress of a typical elution is shown by the curves of Fig. 1, where small

fractions were separately collected and analyzed. Here it can be seen that in 6 *N* hydrochloric acid nickel passes quickly through the column, while copper, zinc, and cadmium are adsorbed. Copper is rapidly eluted by 1 *N* hydrochloric acid, however, while zinc and cadmium are completely eluted by 0.01 *N* hydrochloric acid and water respectively.

If nickel is absent, of course, one may proceed directly to the 1 *N* hydrochloric solution, and copper will pass through the column without adsorption.

The EDTA titration of the above eluates are carried out by methods already available in the literature⁵, with slight modification where necessary or expedient.

The eluates that contain the nickel and copper should first be evaporated to dryness on the steam bath because of the deleterious effect of a high concentration of ammonium salts on the murexide indicator. The nickel residue is dissolved in about 10 ml of concentrated ammonium hydroxide and titrated with EDTA after dilution with about 150 ml of water. Murexide is used as the end-point indicator.

Copper is also titrated with 0.1 *M* EDTA after solution of the dried residue in about 5 ml of 4 *N* ammonium hydroxide and dilution with water to about 300 ml murexide again is used as the indicator.

The eluate that contains the zinc may be titrated directly for zinc by EDTA after neutralization with a few drops of sodium hydroxide or ammonium hydroxide and addition of 10 ml of pH 9.2 buffer. Eriochrome Black T is used as the end-point indicator in this case.

Cadmium may be titrated in the same manner as zinc, except that a few drops of zinc EDTA must also be added.

Although each column may be re-used immediately after the elution of cadmium, a gradual loss of both speed and capacity takes place with continued use of the same column of resin. It has been found desirable to recharge the column with fresh resin after about four uses.

TABLE I
RECOVERY DATA ON SYNTHETIC SILVER SOLDERS

Sample No.	Element	Mg present	Mg found			
			A	B	C	Mean
1	Ag	100	99.6	100.0	100.1	99.9
	Ni	6	6.5	6.2	6.1	6.3
	Cu	31	31.1	31.0	30.9	31.0
	Zn	31	30.9	31.1	31.0	31.0
	Cd	32	32.3	32.5	32.5	32.4
2	Ag	90	90.3	90.1	—	90.2
	Cu	30	30.4	29.9	—	30.2
	Zn	32	32.0	32.0	—	32.0
	Cd	48	48.0	48.0	—	48.0
3	Ag	100	100.0	99.4	—	99.7
	Cu	68	—	67.8	—	67.8
	Zn	32	32.1	31.9	—	32.0
4	Ag	30	29.5	29.5	—	29.5
	Cu	160	159.7	159.5	—	159.6
	P	10	—	—	—	—

RESULTS

In Table I are the results obtained by this procedure on synthetic alloys prepared by weighing the pure metals and silver nitrate as required. A comparison of the results obtained by this procedure and those obtained by the more conventional ASTM methods is presented in Table II. Agreement between the methods is felt to be adequate.

TABLE II
COMPARISON OF ANION EXCHANGE AND ASTM METHODS ON UNKNOWN SILVER SOLDERS

Sample No.	Element	Anion exchange-EDTA %			ASTM %
		A	B	Mean	
1	Ag	25.76	25.57	25.67	25.64
	Ni	1.65	1.66	1.66	1.65
	Cu	56.99	56.88	56.94	56.70
	Zn	8.27	8.24	8.26	8.05
	Cd	7.86	7.85	7.86	7.93
	Total	100.53	100.20	100.39	99.97
2	Ag	44.84	44.75	44.80	44.83
	Cu	14.90	15.04	14.97	15.04
	Zn	15.87	15.82	15.85	
	Cd	24.46	24.35	24.41	24.51
	Total	100.07	100.06	100.03	
3	Ag	49.88	50.02	49.95	49.69 ^a
	Cu	34.06	34.10	34.08	32.24 ^a
	Zn	15.96	15.94	15.95	15.98 ^a
	Total	99.90	100.06	99.98	99.91 ^a

^a Mean of two values.

ACKNOWLEDGEMENTS

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SUMMARY

The separation of nickel, copper, zinc, and cadmium by anion-exchange chromatography has been found to be particularly suitable for the analysis of most commercial silver solders. After solution of the sample, the silver is separated by precipitation as the chloride. The components in the filtrate are separated as their chloro complexes by passage through an anion-exchange column and titrated in the eluates with EDTA. Results compare favorably with those obtained by the more conventional ASTM methods.

RÉSUMÉ

La séparation nickel, cuivre, zinc et cadmium par chromatographie d'échange d'anions convient particulièrement bien à l'analyse de la plupart des soudures d'argent du commerce. Après séparation de l'argent comme chlorure, les autres cations, sous forme de chlorocomplexes, sont séparés sur colonne d'échange d'anions et titrés ensuite par l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Die Trennung von Nickel, Kupfer, Zink und Cadmium nach dem Verfahren der Ionenaustauscher-Chromatographie hat sich als besonders geeignet erwiesen für die Analyse der meisten

Silberlote des Handels. Nach Abtrennung des Silbers als Silberchlorid werden die übrigen Kationen in Form der Chloro-Komplexe mit Hilfe einer Anionenaustauscherkolonne getrennt und in den Eluaten mit Aethylendiaminotetraessigsäure titriert.

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COULOMETRIC TITRATION WITH HIGHER OXIDATION STATES OF MANGANESE

ELECTROLYTIC GENERATION AND STABILITY OF +3 MANGANESE IN SULFURIC ACID MEDIA

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Quite recently TUTUNDŽIĆ AND MLADENOVIĆ¹ introduced the use of electro-oxidized manganese solutions for the coulometric titration of such reductants as +2 iron, +3 arsenic, and oxalic acid. They concluded that permanganate ion is produced by electro-oxidation at a platinum anode of solutions containing 0.02 to 0.45 *M* manganous sulfate in 1.8 *M* or higher concentrations of sulfuric acid. They appear to have based this conclusion merely on the red-violet color of the oxidized solutions and the fact that the oxidation potential of the solutions is in the vicinity of that of the permanganate ion-manganous ion couple. However, visual observation is unreliable because +3 manganese in sulfuric acid has a color quite similar to that of permanganate ion. Furthermore the potential of the +3/+2 manganese couple happens to be nearly the same as that of the permanganate-manganous ion couple, and hence cannot be used to distinguish the species present in the solutions.

That the solution, electro-oxidized under the conditions used by TUTUNDŽIĆ AND MLADENOVIĆ¹, does not contain permanganate is clearly evident from the absorption spectra shown in Fig. 1.

The work of SEM², CAMPBELL³, GRUBE AND HUBERICH⁴, and VETTER AND MANECKE⁵, suggests +3 manganese as the most likely species in solutions electro-oxidized under the conditions specified by TUTUNDŽIĆ AND MLADENOVIĆ¹. This has

been confirmed in the present study. We have also investigated the equilibrium between +2, +3 and +4 manganese over a range of sulfuric acid concentrations, and evaluated the current efficiency for the electro-oxidation of +2 manganese to

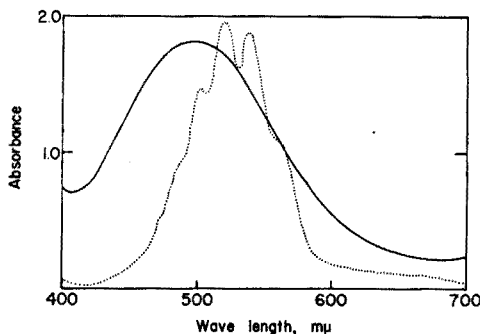


Fig. 1. Comparison of the absorption spectrum of 0.87 mM permanganate ion in 1 M sulfuric acid (dotted line) with that of +3 manganese (solid line). The +3 manganese solution was prepared by electrooxidizing 100 ml of a 0.2 M manganous sulfate solution in 7 M sulfuric acid for 5800 sec with a current of 24.8 mA.

the +3 state at a platinum anode as a function of sulfuric acid concentration, +2 manganese concentration and current density.

Equilibrium between +2, +3 and +4 manganese in sulfuric acid solution

For the disproportionation reaction:



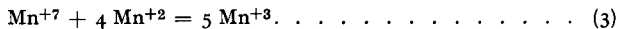
the formal equilibrium constant has the form:

$$K = \frac{[\text{Mn}^{+2}] [\text{Mn}^{+4}]}{[\text{Mn}^{+3}]^2} \dots \dots \dots (2)$$

In this study absorption spectrophotometry was used to determine the formal equilibrium constant, whose value varies from 10^{-3} in 4 M sulfuric acid to 10^{-4} in 7.2 M sulfuric acid. These values are about one-tenth those previously reported by GRUBE AND HUBERICH⁴, and VETTER AND MANECKE⁵, in studies using potentiometric measurements.

In order to determine the equilibrium constant spectrophotometrically it was necessary to evaluate the spectra of the various species of manganese involved in the equilibrium. The absorption spectrum of +2 manganese is easily obtained. Indeed, the extinction coefficient of this species is so small over the range of wave lengths at which measurements were made in this study that its contribution to the total absorbance can be neglected.

To obtain the absorption spectrum of +3 manganese, solutions of this species were prepared by the direct oxidation of +2 manganese with permanganate in strong sulfuric acid solutions. Fig. 2 shows a spectrophotometric titration curve of +2 manganese in 6.3 *M* sulfuric acid with a standard solution of potassium permanganate. The end-point corresponds closely to the reaction:



The reaction is quite rapid, as indicated by the fact that constant values of the absorbance are obtained almost immediately on addition of the permanganate titrant. The deviation from linearity of the absorbance in the region close to the end-point results from the disproportionation of +3 manganese. Prior to the end-point the solution contains only +2 and +3 manganese in significant concentrations, and the concentration of +4 manganese is negligible.

Because +2 manganese does not absorb significantly, the extinction coefficient, ϵ_3 , of +3 manganese can be evaluated from the observed absorbance, *A*, prior to the end-point by the relation:

$$A = \epsilon_3[\text{Mn}^{+3}] \dots \dots \dots (4)$$

Although the titration is fairly exact, there is nonetheless some reduction of permanganate by water concomitantly with its reduction by +2 manganese. Therefore

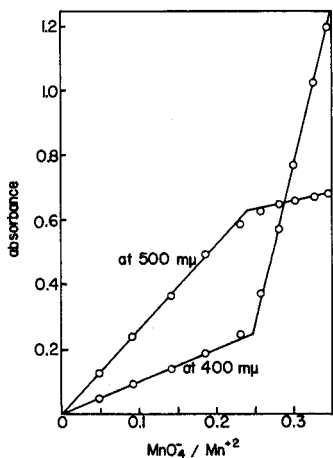


Fig. 2. Titration of 100 ml of 0.004 *M* +2 manganese in 6.3 *M* sulfuric acid with 0.02 *M* permanganate solution. Absorbance, corrected for volume change, was measured with a Beckman Model DU spectrophotometer using 1-cm silica cells. The abscissa represents the ratio of the moles of permanganate added to the moles of +2 manganese initially present.

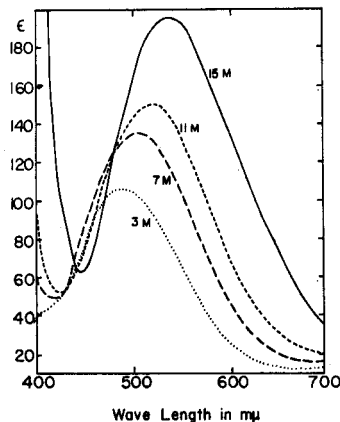


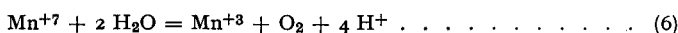
Fig. 3. Spectra of +3 manganese in sulfuric acid solutions of the concentrations indicated. Solutions were prepared by adding permanganate solution to a solution containing a large excess of +2 manganese. The exact concentration of +3 manganese resulting from the reaction was determined by titration with ferrous ion immediately after recording the spectrum with a Cary Recording Spectrophotometer.

the concentration of +3 manganese was evaluated by reductometric titration with ferrous ion, which is more accurate than its evaluation by calculation from the volume of permanganate added.

Fig. 3 shows the spectrum of +3 manganese, determined in this fashion, at a number of sulfuric acid concentrations. All spectra were obtained in solutions where the concentration of +2 manganese was at least ten times that of the +3 species. The spectra of solutions electro-oxidized under the conditions specified by TUTUNDŽIĆ AND MLADENOVIĆ¹ are identical with the spectrum of +3 manganese obtained by direct oxidation of +2 manganese with permanganate.

After the end-point in the titration shown in Fig. 2, the addition of permanganate results in oxidation of +3 manganese to the +4 state. That +4 manganese is indeed the product of this further oxidation is inferred from the fact that the absorbance at 500 $m\mu$ is too small, and the absorbance at 410 $m\mu$ too large, to be ascribed only to the excess permanganate added. In view of the known high degree of instability of +5 and +6 manganese in acid solutions, it is assumed that neither of these species is present in significant concentration.

However, one cannot obtain a second end-point in the titration, corresponding to complete oxidation of +3 manganese to the +4 state. This is prevented by the competition between the reduction of permanganate by water and by +3 manganese according to:



The following rate expression for the reduction of permanganate agrees relatively well with the observed data:

$$-\frac{d[\text{MnO}_4^-]}{dt} = k_1[\text{MnO}_4^-] + k_2[\text{MnO}_4^-][\text{Mn}^{+3}] \dots \dots \dots (7)$$

Shortly after the end-point of the titration shown in Fig. 2, when the concentration of +3 manganese is relatively high, reaction (5) is the predominant reaction. As the concentration of this species becomes less, reaction (6) predominates.

To obtain the spectrum of +4 manganese, solutions containing known concentrations of +3 and +4 manganese were prepared. By subtracting from the absorption spectra of such solutions the contribution of +3 manganese to the absorption, one obtains the spectrum of the +4 species.

For the preparation of solutions containing a mixture of +3 and +4 manganese the following procedure was followed. A standard solution of potassium permanganate (*ca.* 0.02 *M*) was added dropwise to exactly half its volume of concentrated sulfuric acid, with vigorous stirring in an ice bath. The final concentration of sulfuric acid was 6.3 *M*. This solution was then diluted to an appropriate volume with 6.3 *M* sulfuric acid, to give a solution in which the concentration of total manganese was between 0.002 to 0.0065 *M*. The solution was then allowed to stand at room temperature for at least 36 h. During this period there was a rapid change in the spectral properties of the solution and a concomitant loss of oxidizing titer. After this period a brown colored solution was obtained, the spectrum and oxidizing titer of which then remained relatively constant.

The results of a spectrophotometric titration of this brown-colored solution with both ferrous ion and with +2 manganese are shown in Fig. 4. Titration with +2 manganese results only in the reduction of +4 manganese to the +3 state. In the titration with ferrous ion the +4 manganese is first reduced to the +3 state and then to the +2 state. The fraction of manganese in the original solution existing in

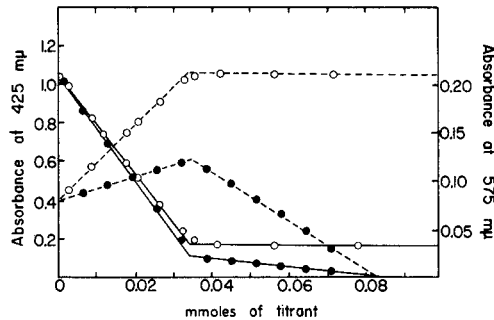


Fig. 4. Titration of solution obtained by allowing 0.0494 mmoles of permanganate contained in 25 ml of 6.3 *M* sulfuric acid to stand for 36 h. Solid circles represent titration with 0.0129 *N* ferrous ion, open circles represent titration with 0.00296 *M* +2 manganese. Solid line represents absorbance at 425 $m\mu$, and the dotted line represents absorbance at 575 $m\mu$ measured in 1-cm silica cell.

the +4 state is the ratio of the volume of ferrous ion required to reach the first end-point to the volume required to go from the first to the second end-point.

In the early part of the titration where the linearity of absorbance indicates that the disproportionation of +3 manganese has been repressed by the +4 manganese present, the solutions contain essentially only +3 and +4 manganese with only a negligible amount of the +2 species, and the extinction coefficient of +4 manganese at a particular wave length can be calculated from:

$$[\text{Mn}] = [\text{Mn}^{+3}] + [\text{Mn}^{+4}] \quad \dots \quad (8)$$

$$[\text{Ox}] = [\text{Mn}^{+8}] + 2 [\text{Mn}^{+4}]. \quad \dots \quad (9)$$

$$A = \epsilon_3[\text{Mn}^{+3}] + \epsilon_4[\text{Mn}^{+4}]. \quad \dots \quad (10)$$

in which $[\text{Mn}]$ is the total concentration of manganese and $[\text{Ox}]$ is the oxidizing titer as determined by titration with ferrous ion. In Fig. 5 the spectrum of +4 manganese determined in this way is shown, together with the spectra of +3 manganese and permanganate for comparison.

Knowing the extinction coefficients of +3 and +4 manganese and permanganate at a particular wave length, it is then possible to calculate the concentrations of these three species during the course of decomposition of permanganate in sulfuric acid solution. These concentrations were calculated from data on the variation of absorbance and oxidizing titer with time, together with the value for the total manganese concentration. Fig. 6 presents the results of such a calculation.

The final composition of the solutions depends on the initial concentration of permanganate. Solutions initially 0.002 *M* in permanganate give a final composition in which 70% of the manganese exists in the +4 state and 30% in the +3 state. Solutions initially 0.0065 *M* in permanganate give a final composition in which 90% of the manganese exists in the +4 state and 10% in the +3 state.

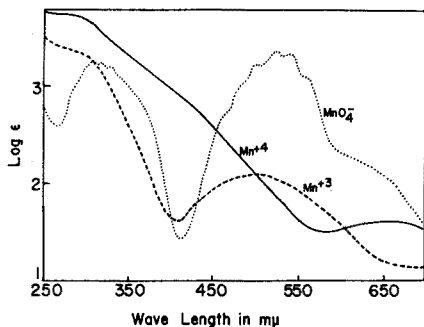


Fig. 5. Spectra of +3 and +4 manganese in 6.3 *M* sulfuric acid, and permanganate in neutral aqueous solution.

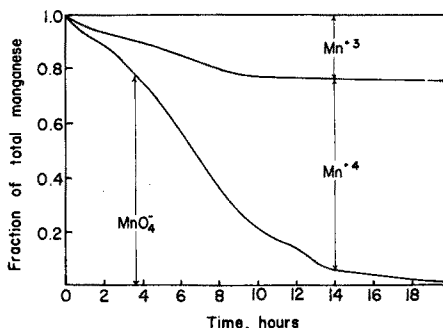


Fig. 6. Rate of decomposition of permanganate, initially 0.002 *M*, in 6.3 *M* sulfuric acid at room temperature.

After three or four months a precipitate formed in which the average oxidation number of manganese was +3.7. In the more dilute solutions the precipitate formed a tightly adherent film on the walls of the vessel, while the solution itself remained clear. In the more concentrated solutions the precipitate formed in the solution itself. This precipitate probably is a non-stoichiometric mixture of oxides of +3 and +4 manganese.

It appears that +4 manganese does not exist in these solutions in the colloidal state. This is inferred both from the fact that no Tyndall effect is exhibited by solutions containing large concentrations of +4 manganese and from chronopotentiometric measurements, which indicate that the diffusion coefficients for both +3 and +4 manganese are about equal (*ca.* $0.2 \cdot 10^{-5}$ cm²/sec) in 6.3 *M* sulfuric acid.

In 6.3 *M* sulfuric acid the decomposition of +3 and +4 manganese via reduction by water is quite slow. The half life for +4 manganese is about 2 months, while the half-life for +3 manganese is about 30 months. In solutions of both higher and lower acid concentrations decomposition of +3 and +4 manganese is more rapid.

When all three species are present in significant concentrations (the situation which obtains in the region close to the first end-point) the complete system of equations describing the system is:

$$K = \frac{[\text{Mn}^{+2}][\text{Mn}^{+4}]}{[\text{Mn}^{+3}]^2}$$

$$[\text{Ox}] = [\text{Mn}^{+3}] + 2[\text{Mn}^{+4}]$$

$$A = \epsilon_3[\text{Mn}^{+3}] + \epsilon_4[\text{Mn}^{+4}]$$

$$[\text{Mn}] = [\text{Mn}^{+2}] + [\text{Mn}^{+3}] + [\text{Mn}^{+4}]$$

Knowing the extinction coefficients of +3 and +4 manganese, this system of equations can be solved for K , the formal disproportionation constant. Maximum accuracy will be obtained when measurements are made exactly at the first endpoint, where $[\text{Mn}] = [\text{Ox}]$ and $[\text{Mn}^{+2}] = [\text{Mn}^{+4}]$.

The procedure for the determination of the equilibrium constant consisted in titrating an aliquot of the solution of +3 and +4 manganese, obtained by the decomposition of permanganate, with +2 iron to determine $[\text{Ox}]$. To a second aliquot was then added a volume of a standard solution of +2 manganese such that $[\text{Mn}]$ was made exactly equal to $[\text{Ox}]$, and the absorbance, A , was measured. To the same solution was then added an amount of solid $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, such that after solution of this salt the concentration of total manganese was more than ten times greater than the oxidizing titer. Under these conditions the concentration of +4 manganese is negligible. The measured absorbance, A° , is then equal to $\epsilon_3[\text{Ox}]$. The expression for the equilibrium constant then takes the simple form:

$$K = \frac{(A/A^\circ) - 1}{(\epsilon_4/\epsilon_3) - 2(A/A^\circ)}$$

The equilibrium constant was measured by this procedure at several acid concentrations. Optical measurements were made between 410 and 440 $\text{m}\mu$ where A/A° and ϵ_4/ϵ_3 are the largest, giving maximal precision in the evaluation of the equilibrium constant. The results obtained are shown in Fig. 7. The estimated probable error is shown by the vertical lines at each point.

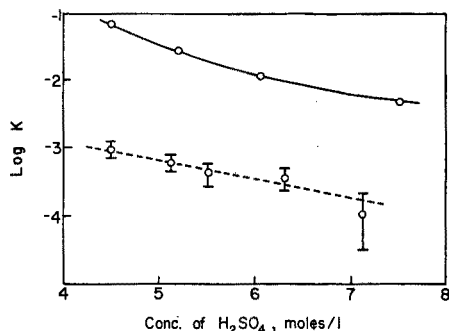


Fig. 7. Log of formal equilibrium constant for disproportionation of +3 manganese. Solid line represents values obtained by GRUBE AND HUBERICH⁴, and the dotted line represents values obtained in this study.

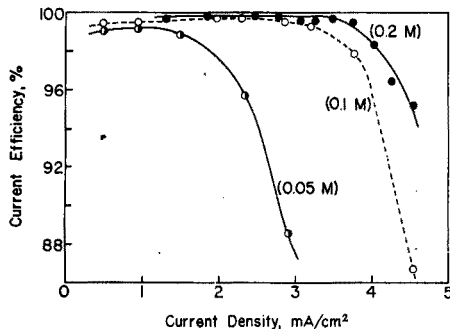


Fig. 8. Current efficiency for generation of +3 manganese in 5 M sulfuric acid as a function of current density and concentration of +2 manganese (in parentheses).

The formal equilibrium constants reported by GRUBE AND HUBERICH⁵ are shown for comparison in Fig. 7. These authors evaluated the constant from e.m.f. measurements of the +2/+3 and +3/+4 couples. For the +2/+3 couple no problems are involved since constant values of the potential are rapidly obtained, which obey the Nernst expression for a one-electron oxidation-reduction couple. In solutions containing +4 manganese this is not the case. From our experience, even after 48 h

there is a slow positive drift of the potential. The thermodynamic validity of potentials obtained under such conditions is questionable. The measurement of the equilibrium constant by spectrophotometry is, in our opinion, more reliable.

CURRENT EFFICIENCY FOR ELECTROGENERATION OF +3 MANGANESE

The current efficiency was determined for the generation of +3 manganese in solutions in which the concentration of +2 manganese and sulfuric acid were varied, and which were 0.025 *M* in +3 iron. A constant anodic current was passed for a measured period of time, and the +3 manganese so generated was then back-titrated by electrogeneration of ferrous iron. This procedure assumes 100% titration efficiency for the titration of +3 manganese with the electrogenerated ferrous iron. Support for this assumption lies in the fact that the cathode was maintained at a potential of about +0.5 V *vs.* N.H.E., and at this potential the contribution to the cathodic current from the reduction of hydrogen ion is known to be negligible.

A rotating platinum electrode was used to determine the end-point amperometrically in the titration of +3 manganese with +2 iron. The potential of the rotating electrode was maintained constant at +1.1 to +1.2 V *vs.* N.H.E. Sufficiently long generation times were used, so that the error in the measurement of the current efficiency is less than 0.1%.

For each solution, containing varying concentrations of +2 manganese and sulfuric acid, the current efficiency was determined over a range of anodic currents. The results shown in Fig. 8 are for solutions 5.0 *M* in sulfuric acid, in which the +2 manganese concentration was varied as indicated. The results obtained at other acid concentrations are similar. The current efficiency is not sensitive to the sulfuric acid concentration between 1 and 7 *M*, but is dependent on the +2 manganese concentration and the current density. The current efficiency decreases significantly at elevated temperatures.

The low values for the current efficiency observed at low current densities result from the fact that the over-potential for the oxidation of water (or perhaps sulfate or bisulfate) decreases with current density at a rate greater than the decrease in the overpotential for the oxidation of +2 manganese. At low current densities the contribution to the anodic current arising from reactions other than the oxidation of +2 manganese thus becomes more significant.

At high current densities the decrease in current efficiency results from the fact that the limiting current for oxidation of +2 manganese has been exceeded. However, in the oxidation of +2 manganese the limiting current is not diffusion controlled but rather is kinetically controlled. This has been confirmed by a chronopotentiometric study of this oxidation.

From this study the optimum conditions for the practical use of electrogenerated +3 manganese in coulometric titrations include a sulfuric acid concentration between about 2 and 7 *M*, a generating current density between about 1 and 4 mA/cm², and a relatively large concentration of +2 manganese (*e.g.*, at least 0.2 *M*). Although +3 manganese becomes less stable with increasing temperature, this does not necessarily preclude coulometric titration at an elevated temperature when the rate of the titration reaction is greater than the rate of disproportionation of +3 manganese and/or the rates of reduction of +3 and +4 manganese by water.

EXPERIMENTAL PROCEDURE

The titration cell was similar to that shown by LINGANE⁶, and consisted of a 200-ml tall form, lipless beaker closed by a Teflon stopper. The auxiliary electrode consisted of a 2-cm² platinum foil immersed in a solution of sulfuric acid of the same concentration as in the supporting electrolyte. This solution was contained in a glass tube whose bottom was closed by a sintered glass disc, and which was immersed in the test solution. The generator electrode consisted of a round disc of perforated platinum foil with a total surface area of 10.7 cm². The generator electrode lay horizontally in the solution directly below the sintered glass disc at the bottom of the auxiliary electrode chamber. The solutions were continuously deaerated with nitrogen, and a magnetic stirrer provided efficient stirring.

The auxiliary electrode for the amperometric end-point detection consisted of a mercury-mercurous sulfate-6.3 *M* sulfuric acid electrode, in contact with the solution through a 6.3 *M* sulfuric acid salt bridge.

The rotating electrode consisted of a length of platinum wire, 0.5 mm in diameter, sealed in a length of soft glass tubing, with about 1 cm of the wire protruding from the end of the tube and bent in a U-shape. The glass tube was filled with mercury, providing contact between the platinum wire and the external measuring apparatus. The electrode was rotated at 780 r.p.m.

The constant current source was essentially that described by LINGANE⁶.

ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (R.G.S.).

SUMMARY

The equilibrium constant for the disproportionation of +3 manganese into the +2 and +4 states in sulfuric acid media has been evaluated spectrophotometrically. The formal disproportionation constant varies from 10⁻³ in 4 *M* sulfuric acid to 10⁻⁴ in 7 *M* sulfuric acid at 25°. In 5 to 7 *M* sulfuric acid both +3 and +4 manganese are quite stable with respect to both their reduction by water and to the precipitation of their oxides. The current efficiency for the generation of +3 manganese is nearly 100% in 2 to 7 *M* sulfuric acid solution, providing the concentration of +2 manganese is at least 0.2 *M*. A sulfuric acid concentration of about 6 *M* is most satisfactory when +3 manganese is generated for coulometric titration because of the maximal stability of +3 manganese in this medium.

RÉSUMÉ

La constante d'équilibre de la dismutation du manganèse(III) en manganèse(II) et (IV) a pu être déterminée spectrophotométriquement. Une méthode est proposée pour un titrage coulométrique.

ZUSAMMENFASSUNG

Die Gleichgewichtskonstante für die Disproportionierung von Mangan(III) in Mangan(II) und Mangan(IV) konnte spektrophotometrisch ermittelt werden. Es wird eine Methode beschrieben zur coulometrischen Titration von Mangan.

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ELECTROSTATIC DISCHARGE METHODS OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

IV. RAPID APPROXIMATE ESTIMATIONS OF ZONE CONTENT BY STATIC DISCHARGE CURRENTS

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The writer described both rectified radio-frequency and low-frequency methods in parts I to III^{1,2}. The present paper presents a simple method whereby the solute content of spots or zones may be rapidly estimated by means of condenser discharges.

The required electrical circuit is indicated in Fig. 1. R is a sensitive mirror galvanometer which is highly damped by means of a shunting resistance S. The latter is adjusted to allow a galvo deflection 'X' when the micro-conductimetric tube T is filled with distilled water. For the galvo employed the shunt required was 45 Ohms.

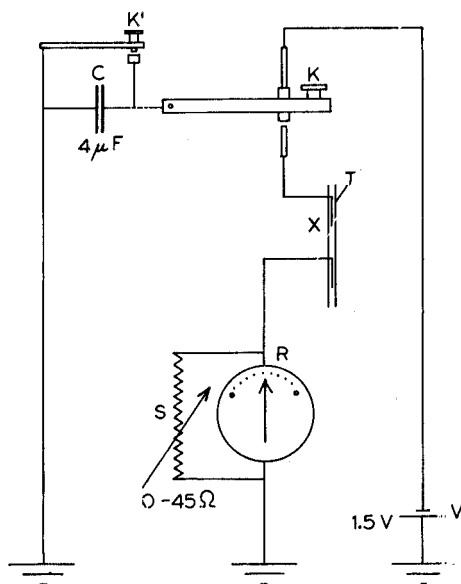


Fig. 1. Circuit diagram illustrating Blake's electrostatic discharge method for rapid zone content estimations. When a 1.5-V charging battery is employed a reflecting galvanometer is used. An ordinary micro-ammeter can take its place but in that case the charging voltage required will be higher.

For distilled water $X = 1.7$ cm on the galvo scale. K and K' are two well insulated keys of the type used for morse signalling. Key K when in the position depicted charges a $4 \mu\text{F}$ condenser C from a 1.5-V dry cell V.

X in the figure is a narrow glass tube into which samples of the liquids are drawn. The complete conductimetric tube T is illustrated in Fig. 2.

When key K' is depressed, condenser C is discharged through the liquid content of the tube X and a galvo swing is recorded. In order to ensure that the residual charge of the condenser shall not interfere with the readings, as soon as the return swing of the galvanometer has commenced the condenser is earthed by means of key 2.

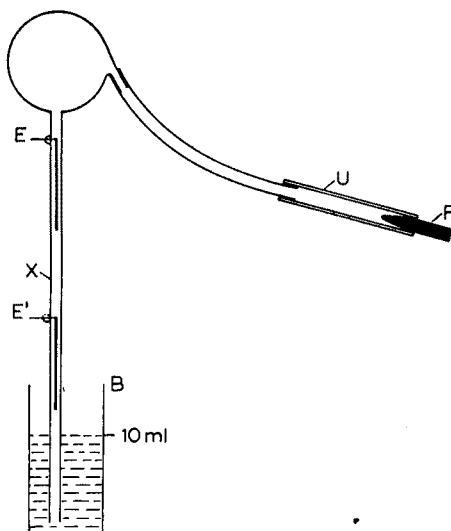


Fig. 2. This figure shows the micro-conductimetric tube employed for working with very small volumes of solution.

Conductimetric tube

The conductimetric tube² is made of pyrex glass (see Fig. 2). It has an internal diameter of 3 mm. The electrodes E and E' are each 3 cm long and are separated by 3 cm. B is the solution container for a volume of 10 ml. When working with smaller volumes a proportionately smaller container is employed. A short length of rubber gas tubing as shown makes an excellent hand pressure syringe.

Instead of using an air inlet valve³ the far end of this tube is plugged by a short length of glass rod P which can be withdrawn and replaced when it is desired to empty the conductimetric tube and to bubble air through the solution to stir it.

Before recording each galvo reading the tube should be emptied and refilled several times as the smallest amount of residue from a previous filling will affect the next measurement.

The extreme sensitivity of the apparatus provides also a most useful method for ensuring that the tube is perfectly clean before work is commenced.

Concentration vs. galvo swing graph

Fig. 3, plotted on ordinary squared paper shows a series of dilutions of CuCl_2 in distilled water ranging from $N/500$ to $N/4000$ plotted against their respective galvo swings.

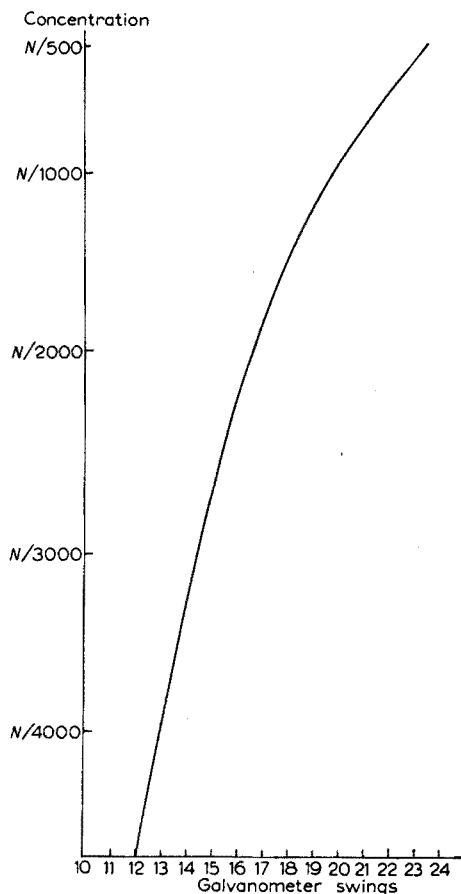


Fig. 3. This is a graph showing a series of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentrations plotted against galvanometer swings on ordinary squared paper (ambient temperature 24°).

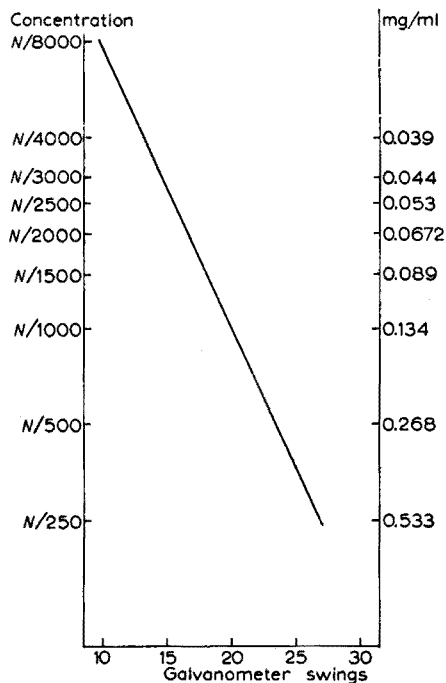


Fig. 4. This graph shows the same series of concentrations as in Fig. 3 plotted on log paper. The resultant linear graph enables both the solution concentrations and the mg content to be estimated. This chart used in conjunction with the electrostatic discharge circuit can be employed also when it is desired to make up a stock solution to any particular concentration. Spot content = mg/ml volume of solution in which it is dissolved.

Log of concentration vs. galvo swing graph

Fig. 4 shows the same series plotted on log paper. The column on the right gives the approximate milligram content of the spot or zone per cubic centimetre. To evaluate the content of a spot or zone after location it is excised and its solute is dissolved in a small measured volume X of water. Next its galvo swing is ascertained.

By reference to the log graph Fig. 4 both its concentration and its approximate mg content can be found.

Similar charts are easily prepared from N/I solutions of any solute so long as the nature and molecular weight is known.

Other suggested applications

The above static discharge method provides a rapid test for the purity of water and other liquids.

For example distilled water (once distilled) gave a galvanometer swing of 1.7 on the galvo scale whilst the swing for tap water was 18.2.

No swing was observable for benzol or ether.

A simple method for dispensing in micro-quantities

Having noted how completely chromatograph spots travel away from their starting place, so completely in fact that not the slightest trace is detectable either by R.Rf. or by static discharge methods the following scheme occurred to the writer.

Firstly, a sheet of Whatman's No. 1 filter paper was soaked in a N/I solution. When this was dry numerous small discs each 5 mm in diameter were punched from the paper.*

A series of these discs were added in succession to 10 ml of distilled water and a graph was plotted showing the relation 'No. of discs vs. galvo swings' for the various concentrations.

This graph took the form of an exceptionally even curve and showed that accurate dispensing could be carried out with such discs.

SUMMARY

This paper describes further applications of electrostatic discharge currents in paper chromatography. The swing of a mirror galvanometer due to the discharge of a condenser through various solution concentrations is employed to obtain rapid approximate determinations of the milligram content of spots and zones. The circuit is illustrated together with details of the micro-conductimetric tube. A chart is given also showing the relationship between galvo deflections and the content of any spot. It is suggested that the circuit provides a rapid method for ascertaining the purity of water, alcohol and other liquids. Finally a new method for dispensing micro quantities of any solute is described.

RÉSUMÉ

L'auteur décrit de nouvelles applications des courants de décharges électrostatiques en chromatographie sur papier. Cette technique peut être utilisée en particulier pour la détermination de la pureté de l'eau et d'autres liquides.

ZUSAMMENFASSUNG

Bei der beschriebenen Anwendung elektrostatischer Entladungsströme in der Papierchromatographie werden die Ausschläge eines Spiegelgalvanometers, die durch die Entladung eines Kondensators durch verschieden konzentrierte Lösungen hervorgerufen werden, zur Messung der Konzentration der gelösten Stoffe in den Flecken und Zonen verwendet. Anwendung zur Reinheitsbestimmung von Wasser und anderen Flüssigkeiten.

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* An ordinary office file-punch stamps out two suitable discs at a time.

DETERMINATION OF GASES IN PLUTONIUM, URANIUM AND ZIRCONIUM BY VACUUM FUSION

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INTRODUCTION

Procedures and apparatus suitable for the routine analysis of gases in stable and radioactive metals with particular emphasis on zirconium, uranium, and plutonium were desired at the Hanford Atomic Power Operation Facilities. Due to the cost, scarcity and radioactivity of the samples, it was necessary to minimize the quantity used for analysis. That requirement was fulfilled by utilizing a sensitive method in which all the gas present in the sample is released and analyzed at one time, *i.e.*, vacuum fusion.

The metallic sample is fused with carbon in a high vacuum, and any oxygen, nitrogen, and hydrogen present are evolved¹, oxygen as carbon monoxide and nitrogen and hydrogen as elements. The method permits a simultaneous and quantitative determination of total oxygen, nitrogen, and hydrogen regardless of the form in which these elements may be present. The released gases are collected in a known volume, the total pressure measured, and the gas mixture analyzed. Although a common scheme of analysis is based on fractional freezing², mass spectrometric analysis was chosen here instead for several reasons: it permits detection of trace amounts of gases, nitrogen is determined directly and not by difference, and the analysis of the gas mixture can be carried out independently of the fusion apparatus.

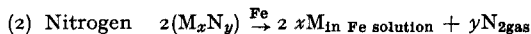
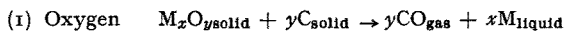
The essential condition for successfully analyzing gases in metals by vacuum fusion techniques is that the sample be brought into intimate contact with carbon at an elevated temperature and a low pressure. These conditions are satisfied if the sample is dropped *in vacuo* into a metal bath in which an adequate amount of carbon is dissolved. In practice, because of vapor pressure, melting point, carbon solubility, and carbide formation considerations iron or platinum is used for the bath material. One of the major difficulties encountered in the iron bath technique is the great increase in viscosity of the bath with time due to its increased carbon content³. Within two hours, the iron melt becomes so viscous that additional samples cannot be analyzed in that particular bath. Thus the increase in viscosity seriously hampers the possibility of using vacuum fusion as a method for routine analyses. In the present work, the radioactive samples were added to the iron bath one after the

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other, waiting only for all the gas to be collected in a known volume and the pressure measured. The mass spectrometric analyses were performed after the melting operation was completed.

For non-radioactive samples, a platinum bath is preferred since it does not become viscous and thus imposes no time limitations. A large platinum inventory is required because the sample-to-weight ratio should not exceed 3%. However, the platinum may be reclaimed at a nominal price so that the cost per analysis is reasonable. On the other hand, platinum used as a bath for radioactive samples must be discarded, making iron the preferred choice for radioactive samples.

The most generally accepted mechanisms explaining the quantitative release of oxygen, nitrogen, and hydrogen, respectively⁴, are:



It should be noted that carbon does not enter into the second and third reactions and that the metal bath is not required for the last reaction, which is merely a thermal decomposition. When only a hydrogen determination is desired, it may be obtained by merely heating the sample in a vacuum and measuring the amount of hydrogen liberated, a procedure known as vacuum extraction⁵.

EXPERIMENTAL

Apparatus

The vacuum system designed for the present work may be divided into three main sections: a furnace assembly in which gases are evolved by heating or fusing the samples, a gas collecting system where the evolved gases are pumped into a known

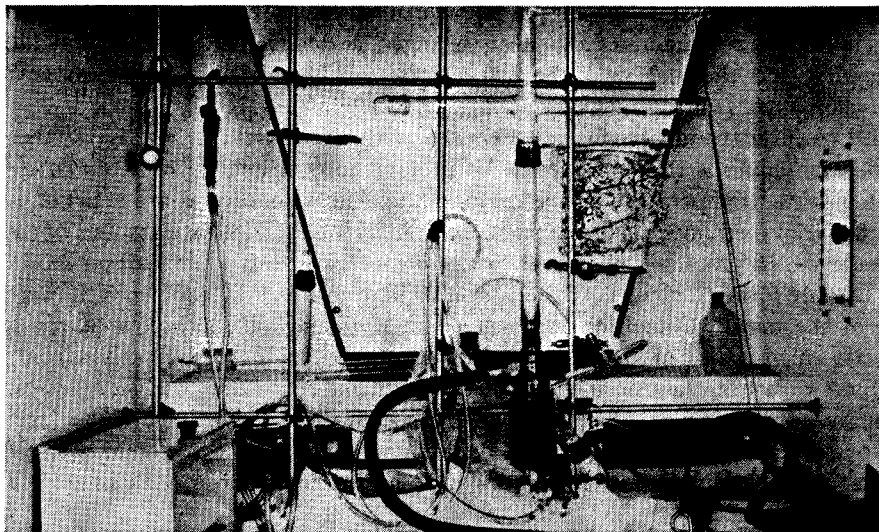


Fig. 1. Furnace assembly.

volume and their pressure measured, and a sampling manifold where the gases are transferred into bulbs which are taken to a mass spectrometer for analysis.

The furnace assembly is shown in Fig. 1. The furnace tube is made entirely of quartz and consists of a ground joint connected to 26 mm tubing which in turn is connected to a section of 52 mm tubing with the lower end rounded off to form the bottom. For vacuum fusion work, a graphite crucible surrounded by lampblack is placed in the furnace tube. The crucible is heated inductively and crucible temperatures of 2400° are obtainable while the furnace tube does not heat above 500° .

The quartz tube is sealed to a loading tree consisting of a vertical glass tube onto which are connected four horizontal arms. One arm is used to connect the tree to the rest of the vacuum system and the other arms are used to hold the samples and the

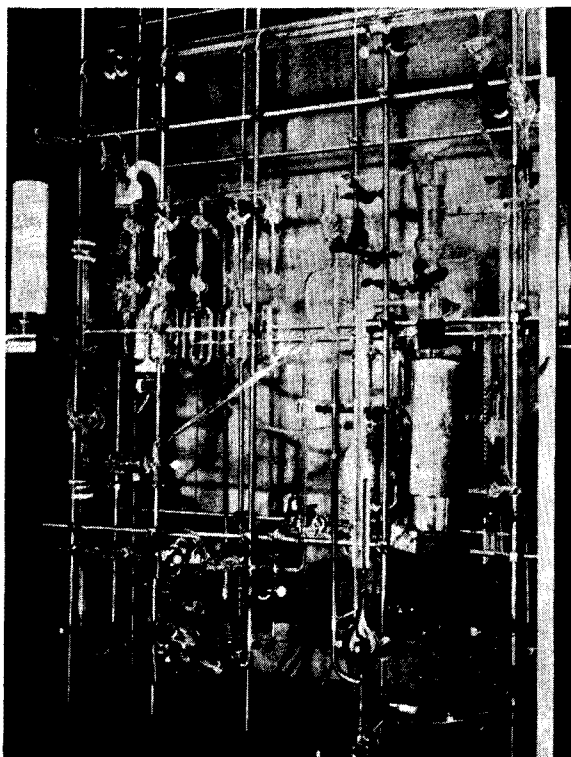


Fig. 2. Gas collecting and analyzing system.

pieces of hydrogen-fired iron used for the bath. At the upper end of the tree is a ground joint to which a cap containing an optical window is sealed. The temperature of the graphite crucible is measured with an optical pyrometer by sighting through the optical window which was constructed by sealing one end of a Beckman spectrophotometer cell to a ground joint. The loading tree and furnace tube are enclosed in a hood which is converted to a glove box during plutonium work.

An all glass high vacuum system shown in Fig. 2 is used for the gas collecting

system. Gases evolved from the furnace tube are pumped by a mercury diffusion pump into one several possible combinations of calibrated volumes where the pressure is measured by use of a McLEOD gauge. The gas is then pumped by the same mercury diffusion pump from the calibrated volumes into a sampling manifold where five sample bulbs are attached by means of standard ground joints. There is a stopcock on each bulb and one above each joint. The volume of the manifold is small in comparison to the volume of a sample bulb so the majority of the gas is collected in a bulb. The sampling bulbs are used to transfer the gas mixtures to a mass spectrometer for analyses.

Procedure

Cleaned and weighed samples are placed in one side arm of the loading tree and hydrogen-fired iron pellets are placed in a second arm. The system is evacuated and the graphite crucible outgassed at 2100° until a low rate of gas evolution is attained. The iron pellets are added to the crucible, outgassed below their melting point and then melted. The blank rate at 1900° is determined. A sample is added to the melt and the released gases collected until the blank rate is re-established. The majority of the gas is transferred to a sample bulb and the remainder is pumped out. The temperature is momentarily lowered to about 1100° while a piece of vacuum-melted tin is dropped into the crucible. The tin immediately volatilizes from the crucible and condenses on the furnace tube walls, coating them with a thin layer which covers up any reactive metal film which may have formed and thus prevents getting of gases.

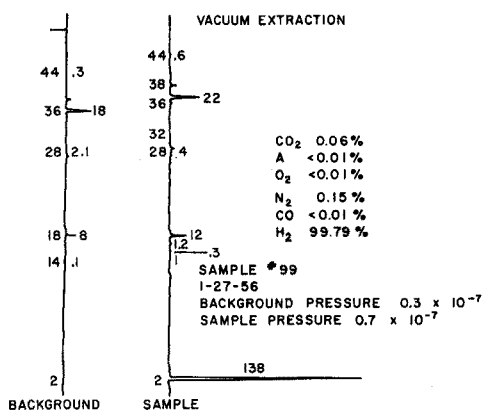


Fig. 3. Mass spectrum of gases released by vacuum extraction.

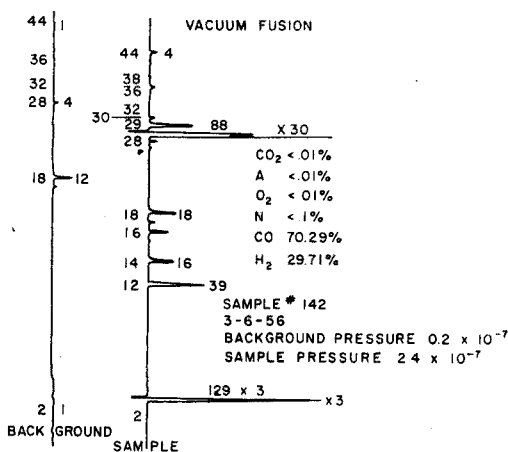


Fig. 4. Mass spectrum of gases released by vacuum fusion.

The next sample is added to the melt and the procedure is repeated until all samples have been added. The gas mixtures contained in the bulbs are taken to a mass spectrometer for analyses. From the measured pressures in known volumes, mass spectrometer results, and sample weights, the results are calculated.

The only precautions taken during work with plutonium are to convert the hood to a glove box and to use a separate furnace tube and loading tree. Only minor amounts of contamination have been spread outside the glassware, permitting the glove box to be reconverted to a hood following a plutonium run.

Results

Typical mass spectra obtained by vacuum extraction and vacuum fusion are shown in Figs. 3 and 4, respectively. The mass spectrum shown in Fig. 3, which was obtained for the gases released from a zirconium sample heated at 1300°, demonstrates that only hydrogen is evolved by this procedure. The mass spectrum obtained by vacuum fusion of a duplicate sample (Fig. 4) contains, in addition to the hydrogen contribution, peaks at masses 28, 16, 14, and 12 due to carbon monoxide and nitrogen. These two gases are quantitatively differentiated by standard techniques using the cracking patterns of the pure gases.

Oxygen, hydrogen and nitrogen values obtained using a platinum bath were compared to these obtained with an iron bath. Plutonium samples with a gas content of 150 p.p.m. oxygen, 90 p.p.m. N₂, and 60 p.p.m. H₂ were chosen for the experiment. The results agreed within 10, 6, and 3 p.p.m., respectively demonstrating that either metal may be employed.

TABLE I
RESULTS IN P.P.M. OF HYDROGEN ANALYSES OF ZIRCONIUM SAMPLES

Sample number	Calculated value	Hanford vacuum extraction	Hanford vacuum fusion	Battelle vacuum extraction
1	46.3	46 48		48
2	50.8	55 51		56
3	112	116 110		114
4		16	15 18	
5		39	45	
6		20	21 15 15	
7		18	14 23	
8	99.9	100	94	

The results of hydrogen analyses on zirconium samples are given in Table I. Samples 1 through 3 show the typical agreement obtained by vacuum extraction procedures while samples 4 through 8 compare hydrogen values obtained by vacuum extraction and vacuum fusion. Vacuum fusion yields the poorer results as is to be expected from the fact that hydrogen constitutes only a fraction of the total gas evolved during the fusion procedure.

The results of oxygen analyses of zirconium samples are presented in Table II. Samples 1 through 3 were obtained from the Bureau of Mines and the results are in excellent agreement with their values. Samples 4 through 8 were picked at random from a group of samples analyzed by the chlorine residue method and vacuum fusion. Good agreement was obtained in some cases. However, in others the results differ significantly. High vacuum fusion results are unlikely since the pressure rise is

measured until the blank rate is regained, although low values result from incomplete reaction or readsorption of the gases. Therefore, in those instances where the fusion result is the higher, it is believed to be the more accurate. Zirconium nitride, which is more stable than zirconium oxide, was not successfully determined by vacuum fusion. All gases in plutonium and uranium are readily evolved as are the oxygen and hydrogen from zirconium.

TABLE II

RESULTS IN P.P.M. OF OXYGEN ANALYSES OF ZIRCONIUM SAMPLES

<i>Sample number</i>	<i>O₂ standard</i>	<i>Vacuum fusion</i>	<i>Residue method</i>
1	1000	970, 980, 970	
2	1050	1040	
3	1100	1090, 1070	
4		920	930
5		980	990
6		930	990
7		1030	830
8		1060	750

In general, vacuum fusion techniques are reproducible and consistent with results obtained with other acceptable methods. The apparatus and techniques described provide a method whereby the gases present in five separate metallic samples may be collected in one melting operation of less than two hours duration.

ACKNOWLEDGEMENT

The author is indebted to E. P. GALBRAITH, E. W. CHRISTOPHERSON and G. J. ALKINE for their assistance in this work.

SUMMARY

A vacuum fusion system suitable for routine analysis of gases present in plutonium, uranium, and zirconium was built and acceptable results were obtained with the exception of the determination of nitrogen in zirconium. Hydrogen is evolved by heating the metal in a vacuum while all gases are released by fusing the sample at 1900° in a metal bath contained in a graphite crucible. The gases evolved from each sample are collected in individual bulbs for later mass spectrometric analyses. Hydrogen values within 5% and oxygen values within 10% are obtained on zirconium standards. The results for plutonium samples analyzed by the iron and platinum bath techniques are in satisfactory agreement. The apparatus and techniques described provide a method whereby the gases present in 5 separate metallic samples may be collected in one melting operation of less than two hours duration.

RÉSUMÉ

Un appareillage est proposé pour l'analyse en série des gaz présents dans des métaux stables et radioactifs, en particulier dans le plutonium, l'uranium et le zirconium. On procède par fusion au vide; les gaz recueillis sont ensuite analysés au spectromètre de masse. Des résultats satisfaisants ont été obtenus sauf pour le dosage de l'azote dans le zirconium.

ZUSAMMENFASSUNG

Es wird eine Apparatur beschrieben zur serienmässigen Bestimmung der Gase in Plutonium, Uran und Zirkonium nach dem Vakuum-Schmelz-Verfahren. Die Analyse des extrahierten Gasgemisches erfolgt mit dem Massenspektrographen. Das Verfahren versagt bei der Bestimmung des Stickstoffes in Zirkonium.

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THE DETERMINATION OF AMINOPHENOLS AND AMINOBENZOIC ACIDS

A STUDY OF EXTRACTION PROCEDURES APPLICABLE TO BIOLOGICAL MATERIALS

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Although sensitive colorimetric procedures exist for the determination of aminophenols and aminobenzoic acids, their direct application to biological materials, e.g. urine is beset with difficulties and most usually when concentrations are low.

Preliminary extraction appears to be a necessity, not only as an aid to concentration but to eliminate interfering substances, e.g. phenols, hydroxy-aromatic acids. The use of solvent extraction and ion-exchange resins have been studied for this purpose.

In this communication, investigations have been limited to *o*- and *p*-aminophenols, *o*- and *p*-aminobenzoic acids and 3-hydroxyanthranilic acid. Examples of typical results are shown.

EXPERIMENTAL

Analysis of extract

The following colorimetric methods were employed to assess the quantity of substance under investigation in the various extracts.

o- and *p*-aminobenzoic acids, diazotisation with nitrous acid followed by coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride^{1,2}.

p-Aminophenol, indophenol pigment formation in the presence of *o*-cresol and ammonia^{3,4} or molybdenum blue formation⁵.

3-Hydroxyanthranilic acid, indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide⁴ or molybdenum blue formation⁵.

o-aminophenol, indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide⁴ or molybdenum blue formation⁵.

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Solvent extraction

As a preliminary, the mixture rendered normal with respect to hydrochloric acid, was extracted 4 times with ether, with the intent of removing interfering substances such as phenols and hydroxy-aromatic acids. It was hoped that this process would only remove minimal quantities of the substances under investigation.

From the residual aqueous mixture, 3-hydroxyanthranilic acid and the amino-benzoic acids were extracted by ether at pH 3.0 and the aminophenols by ether at pH 7.0¹.

The substance contained in 10 ml of *N* hydrochloric acid was extracted 4 times with 40-ml quantities of ether. The extractions were carried out in 50-ml glass stoppered measuring cylinders. The mixtures were shaken vigorously for 2 min and after separation, the ether extracts were separated with a teat pipette.

Amino-benzoic acids/3-hydroxyanthranilic acid

The pH of the residual aqueous fluid was adjusted to 3.0 by the addition of saturated sodium acetate solution. The solution was then extracted 3 times with 40-ml quantities of ether as described above.

TABLE I

The recovery of *o*- and *p*-aminobenzoic acids by ether extraction (A) from *N* HCl at pH 3.0

Quantity taken μg	From <i>N</i> HCl		At pH 3.0	
	Quantity recovered μg	% recovered	Quantity recovered μg	% recovered
<i>o</i> -Aminobenzoic acid				
20	5.5	27.5	3.2	16.0
40	10.8	27.0	6.0	15.0
80	21.7	27.1	13.0	16.2
<i>p</i> -Aminobenzoic acid				
20	1.6	8.0	10.0	50.0
40	3.2	8.0	19.2	49.0
80	6.2	7.7	42.5	53.1

The recovery of 3-hydroxyanthranilic acid, *o*- and *p*-aminophenol, by ether extraction at pH 3.0

	Quantity taken μg	Quantity recovered μg	% recovered
3-Hydroxyanthranilic acid			
	10	6	60
	20	11	55
	50	27	54
	100	56	56
<i>o</i> -Aminophenol (pH 7.0)			
	12.5	11	88
	25	21	84
	50	43	86
	100	88	88
<i>p</i> -Aminophenol (pH 7.0)			
	12.5	11	88
	25	21	84
	50	46	92
	100	91	91

Note: The extractions at pH 3.0 and 7.0 followed on those from *N* HCl.

Aminophenols

The pH of the residual aqueous fluid was adjusted to 7.0 by the addition of solid sodium bicarbonate. The solution was then extracted 3 times with 40-ml quantities of ether as described above.

Ether extracts were evaporated to dryness in an all glass vacuum still.

Typical results are shown in Table I.

Although 3-hydroxyanthranilic acid is not extracted from aqueous solution by ether at pH 7.0, the aminophenols are partially extracted by ether from aqueous solution at pH 3.0. Extracts containing 3-hydroxyanthranilic acid may therefore be contaminated with aminophenols if such are present in the aqueous phase. Interference tends to occur in the determination of 3-hydroxyanthranilic acid when aminophenols are present.

The following differential solvent extraction procedure appears to be satisfactory and may be applied to an extract obtained from an ion-exchange resin.

The pH of 1 ml of an aqueous solution, normal with respect to hydrochloric acid, was adjusted to 7 by the addition of 8% sodium bicarbonate solution. The solution was extracted 3 times with 40-ml quantities of ether. These combined ether extracts may be used for the determination of aminophenols. 1 ml of 10 *N* hydrochloric acid was added to the aqueous residue, the pH of which was then adjusted to 3 by the

TABLE II

The recovery of *o*- and *p*-aminophenols and 3-hydroxy-anthranilic acid by ether extraction

	Quantity taken μg	Quantity recovered μg	% recovered
<i>o</i> -Aminophenol (pH 7)			
	25	23	92
	50	48	96
	100	93	93
<i>p</i> -Aminophenol (pH 7)			
	25	22	88
	50	47	94
	100	94	94
3-Hydroxyanthranilic acid (pH 3.0), following extraction at pH 7.0			
A.	50	43	86
	100	87	87
	200	192	96
B. in the presence of 200 μg <i>o</i> -aminophenol			
	50	42	87
	100	92	92
	200	190	95
C. in the presence of 200 μg <i>p</i> -aminophenol			
	50	43	86
	100	92	92
	200	194	97

addition of a saturated solution of sodium acetate. This solution was extracted 3 times with 40-ml quantities of ether. These combined ether extracts were then used for the determination of 3-hydroxyanthranilic acid, after evaporation to dryness.

Some typical results are shown in Table II.

ION-EXCHANGE RESINS

Examinations were limited to the use of the ion-exchange resin Dowex 50 (H⁺). The technique employed was very similar to that used by BROWN AND PRICE⁶ in an examination of metabolites of tryptophan in urine.

Preparation of the column

The resin (200–400 mesh) was contained in a glass tube fitted with a sintered glass base (Quickfit and Quartz Ltd.). The dimensions of the operational column were: height/70 mm; diameter/10 mm. Flow rate was controlled at 30 ml/h.

Before use the column was washed with 80 ml of 8 N hydrochloric acid followed by 200 ml of water. Immediately before use, the column was washed with 25 ml of 0.1 N hydrochloric acid.

Operation of the column

The substance under examination was applied to the column in 100 ml of 0.1 N hydrochloric acid. Elutions were carried out with 80 ml of 0.5 N, N, 2.5 N and 5 N hydrochloric acid respectively. All fluids that had passed through the column were collected and evaporated to dryness in an all glass still. The residues were dissolved in 10 ml of water.

Some typical results are shown in Table III.

TABLE III

THE ELUTION BY HYDROCHLORIC ACID OF *o*- AND *p*-AMINOBENZOIC ACIDS, 3-HYDROXYANTHRANILIC ACID, *o*- AND *p*-AMINOPHENOLS

The figures refer to the % of the original quantity determined in the respective eluate

Quantity in μg	Concentration of hydrochloric acid				
	0.1 N	0.5 N	N	2.5 N	5 N
<i>o</i> -Aminobenzoic acid					
1000	—	—	1.5	99.5	0.5
500	—	—	0.6	90.0	9.5
250	—	—	1.5	97.0	2.0
150	—	—	2.3	93.0	5.7
<i>p</i> -Aminobenzoic acid					
1000	—	—	1.3	78.0	22.0
500	—	—	1.6	85.0	15.0
200	—	—	0.8	64.7	37.5
100	—	—	5.3	87.1	9.6
3-Hydroxyanthranilic acid					
1000	—	0.8	35.0	50.5	2.8
500	—	0.6	16.3	75.4	1.2
250	—	0.1	36.3	64.6	0.3
<i>o</i> -Aminophenol					
1000	—	1.9	48.3	41.6	6.4
500	—	2.6	50.4	39.4	7.6
250	—	3.2	52.6	38.6	3.6
<i>p</i> -Aminophenol					
1000	—	2.1	31.6	66.2	3.2
500	—	1.9	29.2	64.6	4.4
250	—	1.7	32.9	60.2	3.8

RESULTS AND DISCUSSION

Determinations of many substances in biological materials must be preceded by a preliminary separation in order to increase concentration or to eliminate interfering substances. More than one stage may be necessary especially if there is interference from substances mutually separated.

The aminophenols appear to be separated equally efficiently by ion-exchange resin or by solvent extraction at pH 7. When solvent extraction at pH 7 is preceded by ether extraction at pH < 1, slight losses are encountered but these are proportional within the range examined. Such losses may be countered by submitting standards to the same treatment or by the use of a pre-determined correction factor. Examination of eluates from ion-exchange columns requires the use of the combined *N* and 2.5 *N* HCl extracts. The percentage found in the other extracts is low and such may be countered by the use of standards submitted to the same treatment or by the use of a pre-determined correction factor. Eluates from columns would contain 3-hydroxyanthranilic acid if present. Such may be eliminated by using the solvent extraction technique at pH 7.

Separation of 3-hydroxyanthranilic acid by ether at pH 3.0 following on ether extraction at pH < 1 does result in losses. Within the range examined these losses appear to be proportional hence an appropriate correction factor may be employed. Separation of 3-hydroxyanthranilic acid by ion-exchange resins (*N* and 2.5 *N* hydrochloric acid eluates) results in negligible losses. The latter would appear to be the preferable procedure. Separation of 3-hydroxyanthranilic acid from aminophenols would appear to be a quantitative procedure and probably most generally applicable to eluates from ion-exchange columns.

Separation of aminobenzoic acids from biological fluids by solvent extracted is best effected at pH 3 following ether extraction at pH < 1 to remove interfering substances. This procedure involves losses which are much higher in the case of the *ortho* compound. Percentage recoveries at pH 3 are linear over the range examined in the case of both compounds. Standards prepared under similar conditions are a necessity. Separation of the aminobenzoic acids by ion-exchange resins (2.5 *N* and 5 *N* hydrochloric acid eluates) results in negligible losses. The latter would appear to be the preferable procedure.

The procedures described have been found to be applicable to biological fluids, *e.g.* urine.

In the present investigation, the use of ion-exchange resins has been limited to the use of a fixed volume of eluting agent and also a limited number of eluates. The range of such could no doubt be greatly extended.

SUMMARY

Extraction procedures (solvent and ion-exchange resin) have been studied with regard to their potential use in the determination of aminophenols, aminobenzoic acids and 3-hydroxyanthranilic acid in biological materials.

RÉSUMÉ

Des procédés d'extraction (par solvant et par résine d'échange d'ions) ont été examinés en vue d'une application des dosages d'aminophénols, d'acides aminobenzoïques et de l'acide hydroxy-3-anthranilique dans des substances biologiques.

ZUSAMMENFASSUNG

Es wird die Anwendungsmöglichkeit von Extraktionsverfahren (Lösungsmittel und Jonen-References p. 560

austauscherharze) bei der Bestimmung von Aminophenolen, Aminobenzoesäuren und 3-Hydroxyanthranilsäure in biologischen Substanzen untersucht.

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DETERMINATION OF FREE ACID IN URANIUM(VI) SOLUTIONS BY MEANS OF CATION EXCHANGERS

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INTRODUCTION

The usual titration with a standard base cannot be used for the determination of free acid in uranium(VI) solutions, owing to hydrolysis effects. In early methods this interference was prevented by precipitating uranium as peroxide or ferrocyanide and its subsequent removal by filtration¹. It can also be eliminated by adding a complexing agent, e.g. oxalate² or fluoride³⁻⁷, which inactivates the uranyl ion. The effect of some other hydrolyzable ions, e.g. aluminium⁸ or thorium⁹ can be eliminated in the same way. The neutralization point in the subsequent titration can be determined visually, potentiometrically⁶ or conductometrically^{2,5}. Another possibility for the determination of the free acid can be based on the fact that the pH value of a nearly neutral uranyl nitrate solution is a sensitive indication of its free acid content. The acid should first be neutralized by a standard alkali so that its concentration does not exceed 0.1 N. After determining the pH, the acid content can be found from curves for known uranyl nitrate concentrations. To obtain the free acid, this content is to be corrected for the neutralized acid^{10,11}.

In this paper an ion-exchange method for free acid determination is described. It requires very little solution, and is suitable for wide range of uranium and free acid concentrations. The solutions are passed through a column of the cation exchanger in the hydrogen form. To determine the free acid, it is necessary to titrate the total acid in the effluent and to subtract the amount equivalent to uranium. The amount of uranium is determined on a separate sample.

It should be noted that SAMUELSON¹² used same principle to determine the total amount of ions in salt solutions, and BHATNAGAR¹³ to estimate the free nitric acid in uranyl nitrate.

EXPERIMENTAL

Apparatus and reagents

Unicam Spectrophotometer SP 500, glass cells 1 cm. Magnetic stirrer with polythene-covered stirring bar. Ion-exchange column: 2 g of air-dried Dowex 50, 8% cross-linked, H-form, 100-150 mesh; capacity 3.6 mequivs./g; column dimensions 100 mm high, 8 mm diameter.

Uranyl nitrate hexahydrate, B.D.H., Lab. reagent. Uranyl sulphate obtained from the nitrate by metathesis on Dowex 50.

Distilled water, freshly prepared, and showing no traces of acidity when filtered through the hydrogen-saturated ion exchanger¹².

Procedure

Pass a sample of the solution through the column of Dowex 50 resin in the hydrogen form at a flow rate of approximately 1 ml/min into a 50-ml Erlenmeyer flask. Wash the column with water until neutral and titrate the combined effluent and wash-water with standard 0.1 *N* sodium hydroxide against methylorange. Separately determine the uranium content of the solution. Subtract the quantity of acid equivalent to uranium from that obtained by titration. The column is easily regenerated with 6 *N* hydrochloric acid, and after washing with water until neutral, can be used again.

Note: If, for any reason, it is not desirable to determine uranium in the original solution, the uranium can be eluted from the column.

RESULTS

The procedure was tested with nitric acid solutions of uranyl nitrate. In these solutions the uranium/free acid ratio (in equivs.) was varied from 1:25 to 52:1, and the acid concentrations from 0.02 to 7.6 *N*. Uranium was determined spectrophotometrically by the thioglycolate method¹⁴. Some results are presented in Table I.

TABLE I
DETERMINATION OF FREE NITRIC ACID IN SOLUTIONS OF URANYL NITRATE

Sample, ml	Taken		Mequivs. U	Found mequivs. HNO ₃	Error %
	Mequivs. U	Mequivs. HNO ₃	mequivs. HNO ₃		
1.00	0.830	0.016	52:1	0.019	+18.75
0.50	0.247	0.025	10:1	0.024	- 4.00
0.50	0.255	0.051	5:1	0.050	- 1.96
2.00	0.503	0.148	3.4:1	0.146	- 1.35
0.50	0.086	0.429	1:5	0.421	- 1.86
0.50	0.228	2.285	1:10	2.313	+ 1.22
0.50	0.152	3.796	1:25	3.779	- 0.45
2.00	2.991	4.273	1:1.4	4.282	+ 0.21
1.00	0.457	4.570	1:10	4.587	+ 0.37
2.00	2.991	8.200	1:2.8	incomplete adsorption	

When the quantity of uranium equals half the resin capacity, it is possible to use 2 ml of the 2.5 *N* nitric acid solution. At a greater acid concentration, the adsorption of uranium is incomplete. The uranium/free acid ratio has only a slight effect on

the results. For instance, at a ratio of 1:20, the maximum deviation is $\pm 2.0\%$, and at 10:1, with the same acid concentration, the deviation is $\pm 2.3\%$.

To find out the minimum quantity of acid which can be determined with reasonable accuracy, solutions with various acid concentrations were analyzed. In the most unfavourable case, *viz.* an aliquot of 0.0080 mequivs. of acid (100 λ) with a uranium/free acid ratio of 7:1 and a free acid concentration of 0.080 *N*, the value of 0.0081 \pm 0.0005 mequivs. was found (101 \pm 6.3%). For these investigations smaller columns containing approximately 0.5 g of resin were used (resin beds 50 \times 5 mm).

The proposed procedure can also be used for solutions of hydrolyzable cations other than uranium. The solutions may contain more than one hydrolyzable cation, if these can be determined simply and with a sufficient accuracy. In Table II free acid contents are given for solutions containing both uranium and aluminium. Uranium and aluminium were determined spectrophotometrically in original solutions: uranium as above, and aluminium with aluminon in acid medium¹⁵. The direct determination was possible as both methods are insensitive to foreign cations. At greater uranium concentrations, aluminium can be determined by the same method, but in alkaline medium?

TABLE II

DETERMINATION OF FREE NITRIC ACID IN SOLUTIONS OF URANYL NITRATE AND ALUMINIUM NITRATE

Uranium	Taken (mequivs.)		Found nitric acid mequivs.	Error %
	Aluminium	Nitric acid		
0.140	0.405	2.068	2.093	+1.21
0.132	0.448	2.098	2.076	-1.05
0.355	0.448	2.098	2.106	+0.38

The same procedure can be used to determine free sulphuric acid in uranyl sulphate solutions (Table III). Columns with resin beds of 50 \times 5 mm were used. Uranyl ion has a greater tendency to form negatively charged complexes in sulphuric acid than in nitric acid medium, which restricts the use of concentrated sulphuric acid solutions. It is, however, always possible to dilute the solution to the acidity at which the adsorption of uranium is quantitative.

TABLE III

DETERMINATION OF FREE SULPHURIC ACID IN SOLUTIONS OF URANYL SULPHATE

Sample, ml	Taken		Mequivs. U	Found mequivs. H ₂ SO ₄	Error %
	Mequivs. U	Mequivs. H ₂ SO ₄	Mequivs. H ₂ SO ₄		
1.00	0.246	0.340	1: 1.4	0.340	± 0.00
1.00	0.246	1.263	1: 5.1	1.264	+0.05
1.00	0.246	2.836	1: 11.5	incomplete adsorption	
2.00	0.246	2.836	1: 11.5	2.822	-0.49

SUMMARY

An ion-exchange method for the determination of free acid in solutions containing uranium(VI) is described. The solution is passed through a cation exchanger in the hydrogen form and the total acidity is determined as well as the uranium content of the original solution; the free acid is then calculated. The method is also applicable to solutions containing other hydrolyzable cations.

RÉSUMÉ

Une méthode par échange d'ions est proposée pour le dosage de l'acide libre dans des solutions d'uranium(VI). Elle peut être également appliquée à d'autres solutions de cations hydrolysables.

ZUSAMMENFASSUNG

Freie Säure in Uran(VI) Lösungen kann nach Behandlung der Lösung mit einem Kationenaustauscher in der H-Form durch Titration des Eluates bestimmt werden. Anwendungsmöglichkeiten für andere hydrolysierbare Verbindungen werden erwähnt.

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RESORCINOL AS A REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF FERRIC IRON

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In a recent communication the use of resorcinol as a reagent for the spectrophotometric determination of uranium has been reported¹. Resorcinol gives a violet colour with ferric ions, which is unaffected by ferrous ions. In contrast to existing methods²⁻⁵ the preparation of the reagent is simple. The use of resorcinol as a reagent for the spectrophotometric determination of ferric iron is described in this paper.

EXPERIMENTAL

Absorption measurements were made on Coleman's Universal Spectrophotometer, Model 14. A Marconi pH meter was employed for pH measurements. A freshly prepared solution of resorcinol (Merck's pure quality) was used for the measurements. Solutions of ferric chloride (AnalaR) were freshly prepared and the iron content was determined gravimetrically as Fe_2O_3 . Suitable AnalaR salts were used for testing the interference of cations and anions.

DISCUSSION

The absorption spectra of the coloured species (0.004 *M* ferric chloride and 0.4 *M* resorcinol, Curve A, and 0.008 *M* ferric chloride and 0.08 *M* resorcinol, Curve B, in aqueous media) in presence of excess of resorcinol is shown in Fig. 1 along with that of the pure reagent of the same concentration, Curve C. The coloured product has an appreciable absorption at 450 $m\mu$ while the reagent has negligible absorption. The wavelength $m\mu$ was selected to study the various factors described below.

Colour intensity and pH

The pH of the solution has a considerable effect on the colour intensity. Solutions containing the same amounts of ferric chloride and resorcinol (in excess) were prepared at different pH values and their absorption was measured. The results (Fig. 2) indicate that the colour intensity reaches a maximum at pH 2.9. Excess of reagent, even more than a ten-fold excess, has no influence on the colour intensity.

Stability of the colour and the sensitivity of the reagent

The solution attains its maximum intensity immediately after the addition of reagent. The colour is stable for about five hours at room temperature and then fades slowly. The reagent solution is initially slightly brown and slowly darkens on

standing for several days. On heating, the colour decreases appreciably and disappears completely at about 75°. The corrected optical densities of solutions containing 0.5, 0.8, 1.0 and 2.0 p.p.m. of ferric chloride showed that the smallest amount of ferric ion that can be detected is 1.0 p.p.m.

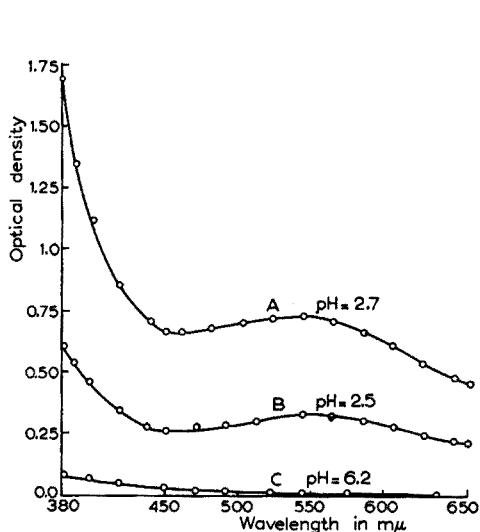


Fig. 1. Curve C: absorption of an aqueous solution of resorcinol (0.04 *M*). Curve B: absorption of a mixture of ferric chloride (0.008 *M*) and resorcinol (0.08 *M*). Curve A: absorption of a mixture of ferric chloride (0.004 *M*) and resorcinol (0.04 *M*).

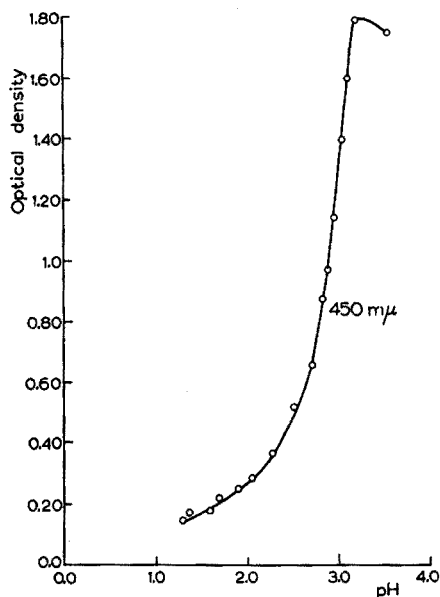


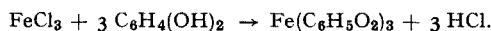
Fig. 2. Variation of optical density with pH of a mixture of ferric chloride (0.004 *M*) and resorcinol (0.04 *M*).

Composition

The composition of the coloured product was determined by following Job's continuous variation method⁶ as modified by VOSBURGH AND COOPER⁷. Solutions of *M*/60 ferric chloride and *M*/30 resorcinol were mixed in different proportions in a total volume of 20 ml. The optical densities at different wavelengths, *e.g.* 450 and 540 *mμ*, were plotted against the composition of the solution, *i.e.*,

$$\frac{[\text{R}]}{[\text{R}] + [\text{Fe}^{3+}]}$$

(Fig. 3). Both curves show maxima at a composition corresponding to 0.75, thus indicating the formation of a 1:3 product between ferric ion and resorcinol:



An attempt to determine the composition by conductivity and pH titration methods failed to give conclusive results possibly because one of the reaction products is a free acid.

Beer's law

The validity of Beer's law for the system was investigated by the usual method at 450 $m\mu$ (Fig. 4). The system obeys Beer's law in the concentration range $0.25 \cdot 10^{-3} M$ to $1.416 \cdot 10^{-3} M$.

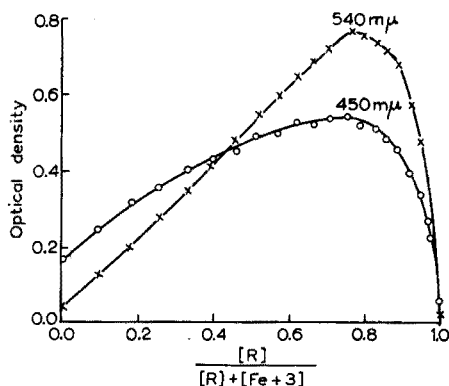


Fig. 3. Curves showing the composition of the coloured product formed from ferric chloride and resorcinol at 450 $m\mu$ and 540 $m\mu$.

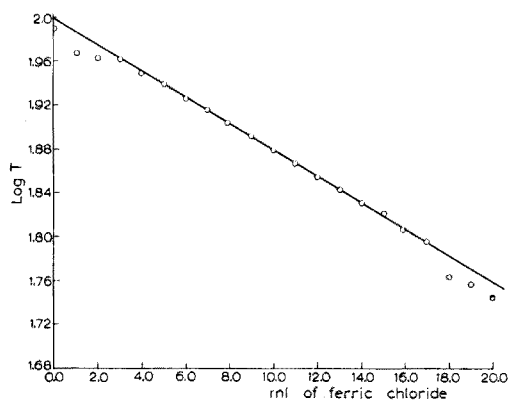


Fig. 4. Curve showing the validity of Beer's law for the system ferric chloride-resorcinol.

Interference of other ions

The effect of certain ions that are likely to interfere with the estimation of ferric iron was tested (Table I). The amount of an ion (in p.p.m.) that will produce a $\pm 2\%$ change in optical density was taken as the tolerance limit.

TABLE I
EFFECT OF SOME CATIONS AND ANIONS

Ferric ion $0.00125 M$ (69.8 p.p.m.) and resorcinol $0.0125 M$. Temp. $25-27^\circ$

Salts	Ions	p.p.m.	% Change	Tolerance limit p.p.m.
KCl	Cl^-	10,000	-2.2	10,000
KNO ₃	NO_3^-	12,400	no change	large excess
K ₂ SO ₄	SO_4^{2-}	4,800	-2.0	4,800
NaF	F^-	1,900	-58.5	
		30	-23.5	
KBr	Br^-	8,000	+2.0	8,000
KI	I^-	6,350	-1.8	6,500
KClO ₃	ClO_3^-	835	+2.3	835
KBrO ₃	BrO_3^-	320	+3.2	
		200	+1.8	200
KIO ₃	IO_3^-	12	+7	
NaNO ₂	NO_2^-	1	+89	
Na ₂ S ₂ O ₃	$S_2O_3^{2-}$	280	-2	280

TABLE I (continued)

<i>Salts</i>	<i>Ions</i>	<i>p.p.m.</i>	<i>% Change</i>	<i>Tolerance limit p.p.m.</i>
K ₂ S ₂ O ₈	S ₂ O ₈ ⁻²	192	-17	
		10	+22	2
		2	+2.5	
Na ₂ CO ₃	CO ₃ ⁻²	10	+30	
KCNS	CNS ⁻	2	+12	
KMnO ₄	MnO ₄ ⁻	2	+56	
K ₂ CrO ₄	CrO ₄ ⁻²	6	+65.5	
K ₂ Cr ₂ O ₇	Cr ₂ O ₇ ⁻²	5	+45.6	
K ₃ Fe(CN) ₆	Fe(CN) ₆ ⁻³	4	+82.3	
K ₄ Fe(CN) ₆	Fe(CN) ₆ ⁻⁴	1	+18.5	
Na ₂ HAsO ₄	AsO ₄ ⁻³	11	+9	
KH ₂ PO ₄	PO ₄ ⁻³	72	-37.5	
		24	-12	
		2	-1.3	2
(NH ₄) ₂ MoO ₄	MoO ₄ ⁻²	6	+23	
		3	-22.0	3
K ₄ Sb ₂ O ₇	Sb ₂ O ₇ ⁻⁴	1	+2.5	1
Na ₂ WO ₄	WO ₄ ⁻²	5	+3	
		2	+2.1	2
		11	+20	
K-formate	HCOO ⁻	150	-2.8	150
Na-acetate	CH ₃ COO ⁻	3	+5.7	
Na-oxalate	C ₂ O ₄ ⁻²	37	+40	
Na-K-tartrate	C ₆ H ₄ O ₆ ⁻²	3	+5.7	
Na-succinate	C ₄ H ₄ O ₄ ⁻²	65	+30	
		22	+17.6	
		5	+1.9	5
Na-salicylate	C ₆ H ₄ (OH)COO ⁻	3	+60	
Na-citrate	C ₆ H ₅ O ₇ ⁻³	6	+2.0	6
AgNO ₃	Ag ⁺	1	+20.7	
CuSO ₄	Cu ⁺²	3	+3.4	
		2	+2.3	2
		50	+4	
HgCl ₂	Hg ⁺²	59	-8	
SnCl ₄	Sn ⁺⁴	2	+51.3	
BiCl ₃	Bi ⁺³	224	+4	
CdCl ₂	Cd ⁺²	112	+3.1	
		56	+2.4	50
		63	-2.3	63
Al ₂ (SO ₄) ₃	Al ⁺³	13	+10	
CrCl ₃	Cr ⁺³	5	+4	
		3	+1.9	3
		2	+3	
Co(NO ₃) ₂	Co ⁺²	1	+1.5	1
NiCl ₂	Ni ⁺²	2	+7	
		1	+3.1	1
		1	+3	1
Ce(NO ₃) ₃	Ce ⁺³	2	+2.0	2
BeSO ₄	Be ⁺²	7	+8	
Th(NO ₃) ₄	Th ⁺⁴	1	+1.7	1

ACKNOWLEDGEMENT

The author expresses his grateful thanks to Prof. A. K. BHATTACHARYA for his kind interest in the present work, and to Mr. P. C. JAIN for his valuable assistance.

SUMMARY

A spectrophotometric method for a rapid determination of ferric iron with resorcinol is described. Ferrous iron has no effect.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage rapide du fer(III), au moyen de résorcine. Le fer(II) ne gêne pas.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Schnellmethode zur Bestimmung von Eisen(III) neben Eisen(II) mit Hilfe von Resorcin beschrieben.

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SCHNELLE PAPIERCHROMATOGRAPHISCHE TRENNUNG VON Ba, Ca, Sr UND Mg

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EINLEITUNG

In der systematischen qualitativen Analyse der Kationen mittels Trennungen auf nassem Wege bietet bekanntlich die Gruppe der Erdalkalimetalle Schwierigkeiten, die durch die grosse Ähnlichkeit im chemischen Verhalten dieser Ionen verursacht werden. Eine sorgfältige Analyse dieser Gruppe erfordert denn auch relativ grossen Aufwand an Zeit und Mühe. Namentlich die Trennung von Ca und Sr ist gewöhnlich unbefriedigend. Für die bezüglichen Arbeitsmethoden sei auf die zahlreichen Bücher über qualitative Analyse verwiesen.

Die Möglichkeit einer papierchromatographischen Trennung wurde bereits von mehreren Autoren gezeigt. Die verschiedenen Arbeitsweisen unterscheiden sich *u.a.* mit Bezug auf die Papiersorte, das geradlinige oder radiale Laufen der mobilen Phase, die Zusammensetzung dieser Phase, die Zeitdauer vom Akklimatisieren des Papiers, die Dauer des Flüssigkeitsstromes und die Wahl der Nachweisreagenzien.

Auf der Suche nach einer Arbeitsweise die sich sowohl zum Unterrichtspraktikum als zu allgemeinen analytischen Zwecken eignen würde, stellten wir der zu wählenden

Methode folgende Anforderungen: leichte Durchführbarkeit mit einfachen Hilfsmitteln; kurze Dauer; gute Reproduzierbarkeit; genügend empfindlicher Nachweis jedes Ions auch neben relativ grossen Mengen der anderen, z.B. im Verhältnis 1:100. Keine der uns aus der Literatur bekannten Arbeitsweisen genügte all diesen Anforderungen gleichzeitig.

Im Laufe einer langen Reihe von Versuchen haben wir vielleicht alle in der Literatur empfohlenen Flüssigkeitsgemische, sowie die lineare und die zirkulare Chromatographie miteinander verglichen. Letztere Ausführungsform führte am schnellsten zum Ziel, und von den Laufmitteln ergaben die Gemische von Methylalkohol und Salzsäure¹, noch besser unter Zufügung von Tetrahydrofuran² weitaus die beste Kombination von schnellem Laufen und weiter, gleichmässiger Trennung der Zonen.

Das von uns benutzte Gemisch hatte die Zusammensetzung: 70% Salzsäure (8N), 20% Methylalkohol und 10% Tetrahydrofuran (Vol. %).

Die im Folgenden beschriebene Arbeitsweise entspricht dem oben genannten Zwecke.

ARBEITSWEISE

Aus dem Filtrat der Schwefelammongruppe werden die Erdalkalien einschliesslich Mg mittels Glühen mit Oxalsäure und Behandeln mit Ammonkarbonat nach SCHEINKMANN^{3,4} als Karbonate erhalten, das Mg wohl zum Teil als Hydroxyd.

Nach Ausziehen der Alkaligruppe mit Wasser werden die Erdalkalikalcarbonate in der gerade benötigten Menge HCl 2 N gelöst (Lösung A); von dieser Lösung wird mittels einer Mikropipette 1 μ l auf eine Filterscheibe (S und S nr. 589²) gebracht (Fig. 1, Punkt A). Der Rest der Lösung wird zur Trockne eingedampft und das Salz in einer äusserst geringen Menge Wasser (eventuell nur teilweise) zu einer möglichst grossen Konzentration gelöst (Lösung C). Auch von dieser Lösung, die also konzentrierter ist als A, wird 1 μ l auf das Papier gebracht (Punkt C).

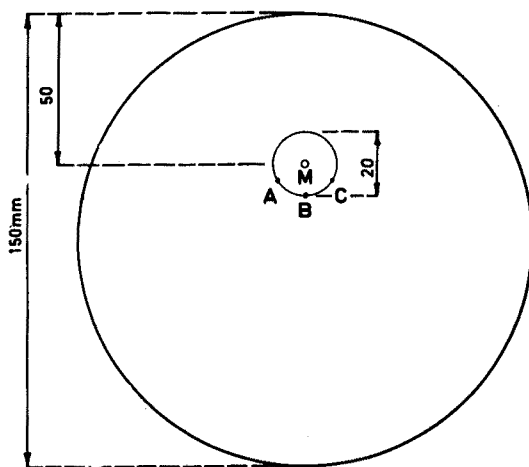


Fig. 1. Das Papier mit den Flecken.

A und C = Probelösung. B = Vergleichslösung. M = Loch mit Docht.

Die Anwendung von zwei verschiedenen Konzentrationen derselben Substanz hat den Vorteil dass in der verdünnteren Lösung die überwiegenden Komponenten keine zu breite Zonen bilden, während in der konzentrierteren der Nachweis der geringeren Komponenten verbessert wird.

Von einer Vergleichslösung, die die Chloride von Mg, Ca, Sr und Ba in einer Konzentration von $20\ \mu\text{g}$ jedes Kations im μl enthält, wird gleichfalls $1\ \mu\text{l}$ auf das Papier gebracht (Punkt B).

Die Punkte A, B und C liegen auf einem Kreise. Die Stellen und Abmessungen sind in der Fig. 1 ersichtlich. Im Mittelpunkt M des Kreises steckt ein Docht in einem Loch von 2 bis 3 mm Durchmesser; der Docht wird aus einem quadratischen Stückchen ($15 \times 15\ \text{mm}^2$) derselben Papiersorte gewickelt. Bekanntlich wird das Ergebnis des Versuches von der Dicke des Dochtes, also von der Intensität des Flüssigkeitsstromes, beeinflusst.

Das benötigte Gefäss ist äusserst einfach und wird aus drei Petrischalen zusammengestellt, wie aus Fig. 2 ersichtlich ist. In der abgebildeten schrägen Stellung der Schalen findet die Equilibrierung des Papiers statt; dies erfordert eine halbe Stunde, wonach das Ganze horizontal gestellt wird und das Chromatographieren anfängt, das $\frac{3}{4}$ Stunden dauert. Dann wird die Papierscheibe an der Luft, am besten mit Hilfe von Lampe oder Föhn, gut getrocknet.

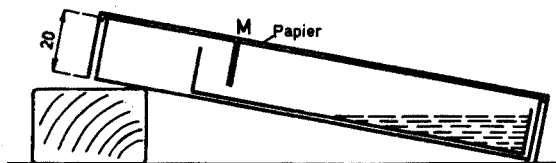


Fig. 2. Die Apparatur.

Zum Nachweis der Kationen ist der mobilen Phase von vornherein Oxin zugegeben ($0.1\ \text{g}$ in $100\ \text{ml}$); dieser Zusatz ist ohne einfluss auf die R -Werte. Die Zonen werden mit grüner oder bläulich grüner Fluoreszenz sichtbar wenn das getrocknete Chromatogramm auf eine Schale mit konzentriertem NH_3 gelegt und unter der Ultraviolettlampe beobachtet wird. Die einfache Philips Nr. HP 125 W genügt dem Zwecke ebenso gut wie eine Heraeus Analysenquarzlampe.

ERGEBNISSE

In der Reihenfolge Mg, Ca, Sr, Ba wurden für $100 R_e$ nachstehende Werte gefunden: 38–44, 54–60, 64–72 und 81–85. Diese Zahlen beziehen sich auf die Mitten der Zonen, deren Tiefe bei grosser Konzentration bis $10\ \text{mm}$ gehen kann. Die erzielte Gleichmässigkeit der Trennung stellt eine Bedingung für eine befriedigende Untersuchung der Gruppe dar: anders könnte von zwei relativ nahe aneinanderliegenden Zonen die schwächere leicht überdeckt werden.

Da die Werte von R_e , ausser von der Zusammensetzung der laufenden Flüssigkeit, auch von der Art des Papiers abhängig sind, ist es empfehlenswert bei Gebrauch

einer anderen Papiersorte den gleichmässigen Verlauf der R_f Werte im voraus zu prüfen und nötigenfalls die Zusammensetzung der mobilen Phase anzupassen.

Die Anwendung der Vergleichslösung im mittleren Sektor erhöht die Sicherheit der Beobachtung schwacher Zonen und bietet auch einen Anhalt zur groben Schätzung der Mengen.

Die erreichten Empfindlichkeiten waren für Mg, Ca, Sr und Ba, in dieser Reihenfolge und bei direkter Verwendung von $1 \mu\text{l}$ Versuchslösung, also ohne vorhergehende Behandlung mit Oxalsäure und Ammonkarbonat:

1. beim Chromatographieren jedes Kations einzeln: 0.25, 1, 1 und $1 \mu\text{g}$; 2. neben 100 μg irgendeines der andern drei Ionen: 0.25, 1, 1 und $1 \mu\text{g}$; 3. neben je 50 μg von zwei der andern Ionen: 0.25, 1, 1 und $1 \mu\text{g}$; 4. in gesättigter Lösung von MgCl_2 , d.h. neben 120 μg Mg: —, 1, 1 und $1 \mu\text{g}$; 5. in gesättigter Lösung von CaCl_2 , d.h. neben 220 μg Ca: 1, —, 2 und $2 \mu\text{g}$.

Die oben beschriebene papierchromatographische Arbeitsweise erlaubt also die Trennung und den Nachweis der Erdalkalitionen von Mg bis Ba mit guter Empfindlichkeit unter Verwendung einfacher Hilfsmittel und innerhalb einer Arbeitszeit.

Schliesslich sei noch erwähnt dass das Laufmittel am besten wöchentlich frisch bereitet wird. Mit älterer Flüssigkeit bekommen die Chromatogramme manchmal einen grün fluoreszierenden Hintergrund, der die Empfindlichkeiten wesentlich beeinträchtigt.

ZUSAMMENFASSUNG

Es wird eine zirkulare papierchromatographische Methode beschrieben zur schnellen Trennung und Identifizierung der Erdalkalien. Die mobile Phase besteht aus einem Gemisch von Methylalkohol, Salzsäure und Tetrahydrofuran, woran das Reagens Oxin zugefügt wird. Mit dieser Methode kann $1 \mu\text{g}$ jedwedes Kations in Gegenwart von insgesamt hundertfacher Menge der anderen drei Kationen nachgewiesen werden. Bei Mg ist die Empfindlichkeit $0.25 \mu\text{g}$.

SUMMARY

A method for a rapid separation and sensitive detection of the alkaline earth cations by means of circular paper chromatography is described.

RÉSUMÉ

Une méthode est décrite pour la séparation rapide et pour l'identification sensible des cations alcalino-terreux, au moyen de la chromatographie circulaire sur papier.

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Eingegangen den 9. Mai, 1959

DETERMINATION OF PORPHYRINS IN CRUDE PETROLEUM

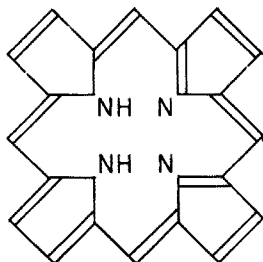
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INTRODUCTION

The undesirability of certain trace metals and all nitrogenous compounds in petroleum fractions that are to be catalytically refined is well known. Metals deactivate cracking and other catalysts¹, and nitrogen compounds impair both the activity of catalysts² and the stability of refined products³. Certain metals are known to be bound, at least in part, to the nitrogens in the large porphyrin molecules in crude oil. Such stable metal porphyrins as those of vanadium and nickel have also been found in distillates. In view of the relationship of porphyrins to these problems, a rapid method for determining porphyrin content would be useful. It would also be helpful in studies of the origin of petroleum.

Porphyrins are a class of compounds consisting of four condensed pyrrol rings having the general structure:



The different porphyrins are formed by the substitution of different organic side-chains on the periphery of the large ring. Their spectra all show similar absorption maxima in the visible region. A chloroform solution of porphyrins shows a maximum absorption peak at 500 $m\mu$, which provides a convenient basis for a quantitative spectrophotometric method for determining porphyrins.

Although the general techniques were established earlier by TREIBS⁴, only one method has been published for the quantitative determination of porphyrins in crude petroleum. In the method of GROENNINGS⁵ the porphyrins are freed from their metal complexes by treatment, in sealed ampoules for four days, with glacial acetic acid saturated with hydrogen bromide. Oil impurities are removed from the diluted acid-porphyrin solution by repeated transfer between ether and 7% hydrochloric acid. Quantitative colorimetric measurement of the porphyrins is made in chloroform solution.

A shorter, simpler, and more accurate procedure has been developed for determining porphyrins in crude petroleum. The acid reagent and the petroleum are reacted in an open flask, as used in extracting metals from petroleum distillates⁶. The crude porphyrins are purified by a simple and rapid filtration and recovered quantitatively.

METHOD

The reagents are conventional, except for an acetic acid-hydrogen bromide reagent, which may be purchased or prepared by saturating glacial acetic acid at 0° with anhydrous hydrogen bromide. The procedure for extracting and measuring the porphyrins is as follows:

Conduct the extraction in a hood using the apparatus shown in Fig. 1. Dilute 50 g of crude petroleum with an equal volume of benzene, and transfer into the extraction flask. Add a volume of glacial acetic acid-hydrogen bromide reagent equal to that

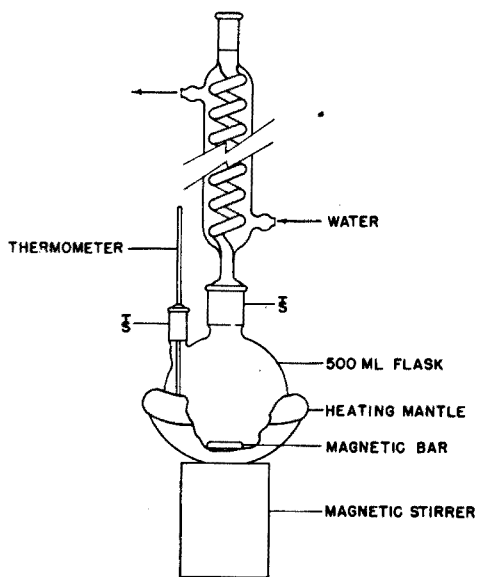


Fig. 1. Apparatus for the extraction of porphyrins from crude oil.

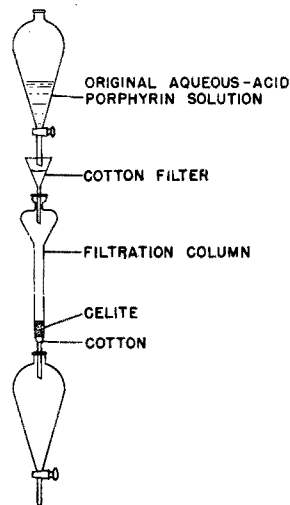


Fig. 2. Apparatus for the removal of oil impurities from acid-porphyrin solution.

of the oil. Stir the mixture for six hours at 45° and then transfer it to a separatory funnel containing about 75 g of crushed ice. Rinse the extraction flask with small amounts of benzene, and add the rinsings to the separatory funnel. Without shaking, let the mixture stand until the oil and aqueous phases have distinctly separated.

As diagrammed in Fig. 2, filter the red aqueous-acid phase through cotton directly into the filtration column. Shake the oil phase gently with 25 ml of 20% hydrochloric acid to extract any remaining porphyrins. Pass the acid wash through the cotton filter, and discard the oil. Wash the cotton free of porphyrin solution with a small amount of 20% hydrochloric acid. Hasten the filtration of the combined acid-

porphyrin solution through the Celite by applying slight air pressure, and receive the filtrate in a separatory funnel. (Mesh size of the Celite is immaterial, but it must be washed thoroughly with 20% hydrochloric acid before use.) Wash the bed of Celite free of red porphyrin solution with small amounts of 20% hydrochloric acid, and combine the washings with the acid-porphyrin solution.

Extract the porphyrins from the combined acid solutions with 25-ml portions of reagent-grade chloroform. Continue the extractions until the extract shows no red color. Use a pocket spectroscope to check either the acid or chloroform phases for completeness of extraction.

Remove all traces of acid from the chloroform extract by washing five times with an equal volume of distilled water. To remove traces of water, filter the chloroform solution through cotton wetted with chloroform. Receive the filtrate in a 500-ml volumetric flask, and dilute to volume.

Measure the absorbance at 500 $m\mu$ of the porphyrin solution against chloroform as a blank in a suitable spectrophotometer with a tungsten light source. Determine the concentration of porphyrin from a calibration curve.

Prepare the calibration curve from porphyrins isolated from crude petroleum. Because the porphyrin content of a given crude petroleum may be unknown, continue thorough extractions of quantities of the petroleum until enough porphyrins have been obtained for preparing standard solutions to establish a calibration curve; a stock solution of 20 mg of porphyrins in 100 ml of chloroform is sufficient. Combine the chloroform solutions and distill off the chloroform. To purify the residue of crude porphyrins, dissolve it in a minimum volume of chloroform and precipitate it with five volumes of 95% methanol⁵. Repeat this process until a non-sticky product is obtained (about 10 times). Estimate the purity of the porphyrins by comparing the elemental analysis with the per cent composition of desoxyphyllerythro-etio-porphyrin, $C_{32}H_{36}N_4$, the predominant porphyrin in petroleum⁴. Further aids to the estimation of purity are melting point, and a study of the absorptivity of the porphyrins in chloroform solution. Apply the purity correction to the concentrations of the standard solutions, and plot their absorbances *vs.* concentration to establish the linear calibration curve.

No study was made of the necessity of preparing the calibration curve from crystalline porphyrins, and a valid curve could probably be obtained from a noncrystalline product. The numerous recrystallizations required to obtain a non-sticky product would be eliminated, and the resulting calibration curve would be more representative of the porphyrins being measured.

TABLE I
EFFECT OF TIME ON FLASK EXTRACTION OF PORPHYRINS

Extraction time, h	Porphyrins p.p.m.
4	284
5	291
6	312
6	302
7	305
24	312
96	304

DEVELOPMENT OF METHOD

Development of the present method resulted from a detailed investigation of previously published techniques^{4,5} for determining porphyrins. Lagunillas (Venezuela) crude petroleum was used in these studies.

Determination of porphyrins in this petroleum by the GROENNINGS⁵ method showed a content of 303 p.p.m. With the sole modification of the extraction flask for the ampoule in the GROENNINGS' method, the same amount of porphyrins was extracted and the extraction was completed in six hours, as shown in Table I. Although the extraction time in the ampoule method could also be shortened, the flask is far more convenient than the sealed ampoule. A shorter reaction time in the ampoule has been recently confirmed⁷.

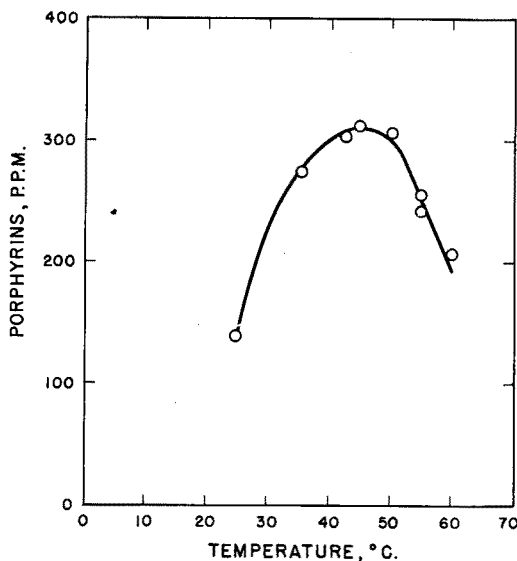


Fig. 3. Effect of temperature on flask extraction of porphyrins. (Extraction time: 6-8 h).

The extraction temperature in the flask method is critical, however, and Fig. 3 shows that about 45° is optimum. Decomposition or volatilization may account for the decreased recovery at higher temperatures.

Oil impurities in the aqueous acid-porphyrin solution are removed in the latter stages of purification in the GROENNINGS' method by transferring the porphyrins twice between 7% hydrochloric acid and ether. As expected⁹ absorption spectra of the ether solutions from which porphyrins were extracted by 7% hydrochloric acid showed that not all of the porphyrins are removed. Higher concentrations of hydrochloric acid, however, extract porphyrins from ether solution quantitatively^{8,9}. Data in Table II show the additional amounts of porphyrins extracted by 20% hydrochloric acid. Thus, in the case of Lagunillas crude, purification of the porphyrins by transfer between 7% hydrochloric acid and ether loses about 39 p.p.m. of the porphyrins, or about 13% remains in the ether solutions.

TABLE II
 PORPHYRINS LEFT IN ETHER BY 7% HCl, BUT EXTRACTED BY 20% HCl,
 p.p.m.

<i>1st Ether solution</i>	<i>2nd Ether solution</i>	<i>Total</i>
26	7	33
11	11	22
32	17	49
36	8	44
31	14	45
	Average	39

The tedious and time-consuming transfers between acid and ether are eliminated in the present method by direct filtration of the original acid solution through a column of Celite. This technique recovers all of the porphyrins and removes oil impurities more conveniently. Quadruplicate determinations of the porphyrin content of Lagunillas crude petroleum by the present method showed 347, 355, 322, and 336 p.p.m., with an average of 340 p.p.m. The results show a standard deviation of 12 p.p.m. When the 39 p.p.m. of porphyrins in the ether which is not extracted by 7% hydrochloric acid (Table II) is added to the 303 p.p.m. measured by the GROENNINGS' procedure, the results are in excellent agreement with the present method.

The need for complete removal of acid from the final chloroform solution of the porphyrins was revealed in a study of the spectra of the chloroform solution at different stages of washing. Except for a shift to higher wavelengths, the absorption spec-

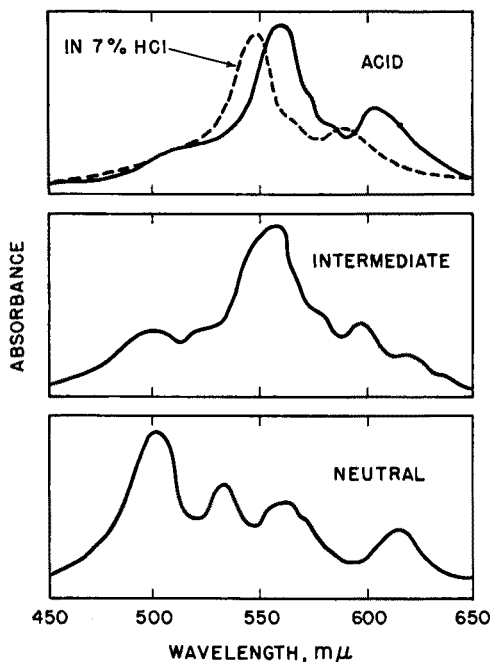
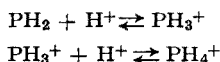


Fig. 4. Spectra of porphyrins in chloroform.

trum of the unwashed chloroform solution showed the two absorption peaks exhibited by acid solutions of porphyrins¹⁰. Thorough water-washing of the chloroform solution results in a characteristic four-peaked spectrum¹¹. The changes in absorption spectra, illustrated in Fig. 4, are reversible simply by the addition or removal of acid. The center absorption curve represents an intermediate spectrum between the acid and neutral forms. Over a two-week period, the absorbance of a chloroform solution of porphyrins washed 10 times decreased from 0.400 to 0.359. The decrease in absorbance probably results from the presence of hydrogen chloride produced by the decomposition of chloroform. The spectral changes result from shifts in the equilibrium between the neutral and protonated forms of the porphyrin molecules and are separate and distinct from changes in spectra resulting from chemical decomposition of the porphyrins^{8,12}. If PH_2 is considered as the neutral porphyrin molecule, the equilibria may be represented as:



The four nitrogens in the porphyrin ring have been shown to participate in a series of acid-base equilibria¹³. Solutions of porphyrins in varying concentrations of hydrochloric acid up to 20% showed no change in absorbance. To insure that no significant decrease in absorbance occurs in the chloroform solution washed five times in the routine method, the porphyrins should be stored in the filtered acid solution if optical measurements can not be made within a day.

TABLE III
EFFECT OF IMPURITIES ON THE DETERMINATION OF PORPHYRINS IN ACID SOLUTION

Purification	Porphyrins <i>p.p.m.</i>	
	Acid	CHCl_3
Groennings' method	374	324
	383	331
Present method	414	347
	400	322
	399	336

The existence of a suitable absorption peak in the spectrum of acid solutions of porphyrins suggested the possibility of further shortening the present method, by eliminating the transfer of the porphyrins into chloroform and the subsequent water washing of the chloroform solution. Table III shows, however, that purification of porphyrins by either the GROENNINGS' method or the present method resulted in higher apparent concentrations of porphyrins when measured in acid solution than when measured in chloroform. The discrepancy is believed due to an impurity in the acid phase. Until the nature of the impurity and a convenient method for removing it are found, the porphyrins must be transferred into chloroform for accurate determination.

CONCLUSION

Because of its simplicity, the present method lends itself to multiple routine analysis. Although this investigation was limited to Lagunillas crude petroleum, the

method may be applicable to many other crudes, reduced crudes, and petroleum fractions, as well as to other fields of study where quantitative knowledge of porphyrins is needed.

SUMMARY

The method of GROENNINGS for determining porphyrins in crude petroleum, based on extraction with glacial acetic acid-HBr, has been simplified, shortened, and improved in precision and accuracy. Porphyrins are extracted at atmospheric pressure, and the extract is purified by filtration through Celite. Extraction and spectrophotometric determination of the porphyrins can be completed in a single day. The method has a standard deviation of 12 p.p.m. in the 300 p.p.m. range. The normal four-peaked spectrum of porphyrins in chloroform is converted in time to the two-peaked acid spectrum. The change is reversible and results from a shift in the equilibrium between the free base and the protonated porphyrin molecule. This behavior is distinct from changes brought about by decomposition of the porphyrin.

RÉSUMÉ

L'auteur propose une modification de la méthode de GROENNINGS pour le dosage des porphyrines dans le pétrole. Cette nouvelle technique est plus simple, plus rapide et permet d'obtenir une précision meilleure. On procède à une extraction au moyen du mélange acide acétique-acide bromhydrique, puis à une extraction dans le chloroforme et finalement au dosage spectrophotométrique de la porphyrine extraite.

ZUSAMMENFASSUNG

Es wird eine vereinfachte, kürzere und mit grösserer Genauigkeit arbeitende Modifikation der Methode von GROENNINGS zur Bestimmung der Porphyrine im Erdöl beschrieben. Die Porphyrine werden mit einem Bromwasserstoff-Eisessig Gemisch extrahiert und in Chloroform spektrophotometrisch bestimmt.

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A SYSTEM FOR THE ANALYSIS OF NITRATES AND OXIDES OF NITROGEN*

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In this laboratory, it has been necessary to construct a system for the analysis of oxides of nitrogen in a study concerning the decomposition of metal nitrates and the interaction of NO_2 with metal oxides. With this system it is possible to determine the absolute amounts of NO_2 , N_2O_3 , NO , and of either N_2O or mixture of N_2 and O_2 , simultaneously present in the gas phase. It is also possible, by prior thermal decomposition, to analyze the nonvolatile metal nitrates and nitrites.

The design is partially based upon work by MEYER AND VOOGEL¹ in which it was reported that metallic nickel at moderate temperatures retains the oxygen component in the oxides of nitrogen. It has been possible to adapt and modify the procedure of MEYER AND VOOGEL to yield quantitative results.

The method of analysis

The system consists of five major parts: the reaction chamber, the nickel-nickel oxide tube, the pumping and manometering section, and two purification sections. The sample to be analyzed is placed in the reaction chamber (Y) of Fig. 1. The entire system is then evacuated to a pressure of 10^{-6} mm of Hg. This eliminates the possibility of analyzing compounds that are volatile at room temperature. The sample is then thermally decomposed. For materials that tend to volatilize preceding decomposition, a heated silver or platinum gauze was placed in the mouth of the reaction chamber. This insures that decomposition of the metal nitrate is complete. Precautions must then be taken to remove the oxide coating on the gauze. The decomposition products now pass toward cold trap (G). By cooling this trap with liquid nitrogen, it is possible to separate the NO_2 - N_2O_3 components from the more volatile NO (present only if originally in excess of NO_2), and the N_2O or N_2 - O_2 mixture. The latter gases now pass to the tube H, which consists of nickel supported upon asbestos.

The impregnated asbestos is prepared by saturating with nickel ammine nitrate, and igniting the saturated asbestos in a nickel crucible at 800° . This powder is then packed into a vycor or quartz tube and reduced with hydrogen. In order to assure complete removal of the oxygen components from the nitrogenous gases, the nickel asbestos mixture must be heated to 800° . The resultant nitrogen now passes through

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the cold trap J which is cooled with liquid nitrogen, thence to the pump K² and to the manometer M, which is depicted in Fig. 2. The volume of the upper bulb is internally calibrated by introducing known quantities of hydrogen at given pressure and temperature. Knowing the volume, the amount of nitrogen transferred through the Toepler pump is determined from the residual pressure in the bulb.

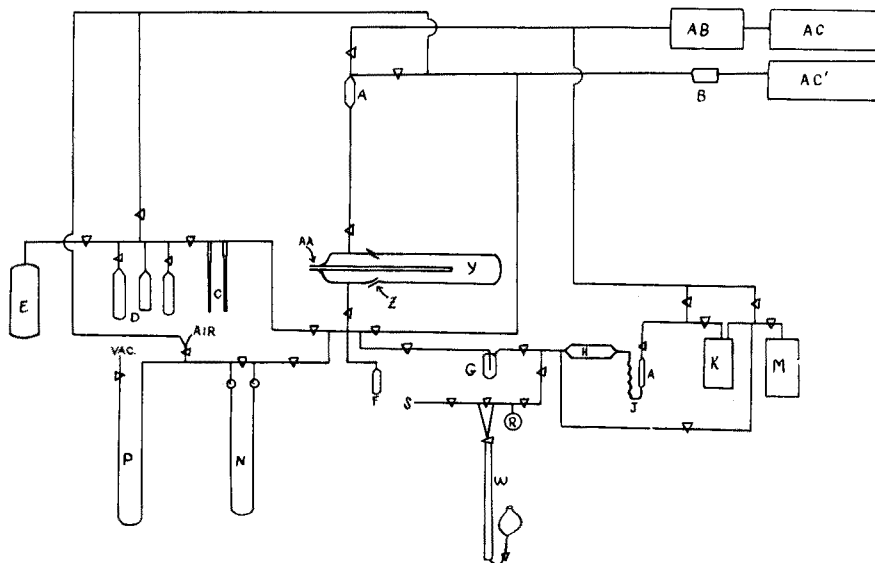


Fig. 1. Diagram of vacuum line for N-O analysis. A = Copper isolation trap, B = NO₂ catch trap, C = micro pipettes (0.1 and 1.0 ml), D = NO₂ storage - and purification, E = tank NO₂, F = finger trap, G = NO₂-N₂O separation trap, H = Ni-NiO tube, J = water trap, K = modified Toepler pump, M = volumetric manometer, N = oil manometer, P = mercury manometer, R = ballast, S = pure H₂. Pt-Pd thimble, W = volumetric H₂, Y = reaction tube, Z = 29/42 $\frac{1}{2}$ joint, AA = thermocouple well, AB = annular Jet Diffusion Pump, AC = fore pump - 10⁻³ mm, AC' = fore pump - 1 mm, ∇ = vacuum bulb stopcock 4 mm, except on NO₂ system where Teflon plug stopcocks are used.

The nitrogen sample is now removed by means of pumps AB-AC and hydrogen is admitted to the Ni-NiO mixture in tube H, maintained at 800°. The water vapor formed by reduction of NiO is trapped in J and the excess hydrogen passes to the pump K. In order to assure complete reduction, the hydrogen is circulated by means of this pump through the tube H. The hydrogen is finally transferred to M and metered. The mole quantities of N₂ and H₂ are computed and the mole quantity of O is deduced. The procedure is then repeated for nitrogen oxides condensed in trap G.

In order to purify and meter NO₂ and H₂ separate sections C-D-E, and S were constructed. NO₂ is purified by repetitive distillation and stored in D. H₂ is purified by diffusion through a heated platinum-palladium thimble and stored in S. NO₂ is metered by means of the volumetric pipettes C. H₂ is manometered into (H) by means of a burette (W) graduated in units of 1/10 ml. In employing a 50-ml gas sample, the volume is therefore determined to about 0.2%.

All gas samples pass through the tube H at a very low flow rate at moderate pressures because of the tight packing of the solid in this tube. At the temperature of operation the reduction of nitrogen oxide is quantitative under these conditions; however, the reduction of NiO by H_2 requires some care, because sufficient time must be allowed for H_2O to transfer to trap J. As will be shown later, it is desirable to circulate the H_2 repeatedly through tube H to remove all traces of moisture from the tube.

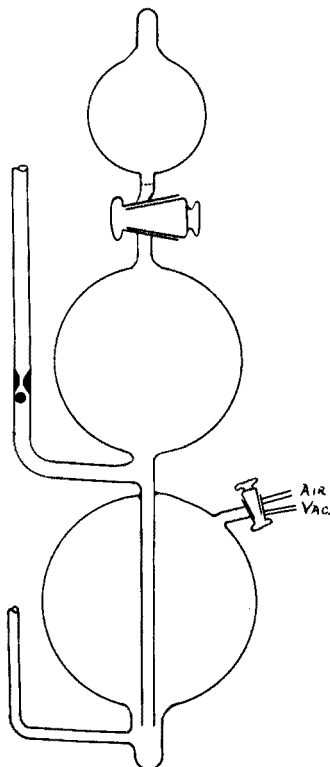


Fig. 2. Combination Toepler pump and manometer.

RESULTS AND DISCUSSION

A rather careful study of the factors affecting the analysis was carried out, using highly purified NO_2 as a test material. In order completely to reduce the nitrogen oxides, and to carry out the subsequent reduction with H_2 , it was necessary to maintain the nickel powder at 800° . Further, an excess of H_2 is required and it was necessary to await quantitative diffusion of H_2O into trap J or to circulate the H_2 gas by means of pump K. The relevant factors are summarized in Tables I and II. It is to be noted that at a temperature of 400° , less than half of the oxide was reduced. As the reduction temperature is increased, there is a progressive approach to the proper O/N ratio of two. If, at 800° , H_2 gas was allowed to pass to M without holding it at II

over an extended period of time, the result was a low O/N mole ratio (1.872). As the retention time at H was increased to 1/2 h, the O/N mole ratio exceeded 1.9, while for a 1-h period this ratio approached the proper stoichiometric value. A similar result could be obtained by circulating H₂. This method proved the most effective.

TABLE I

<i>Volume of N₂ found in cc at standard temperature and pressure</i>	<i>Ratio H/N</i>	<i>Ratio O/N</i>	<i>Temperature of reduction in °C</i>
40.413	1.616	0.81	400
23.982	2.648	1.33	450
38.777	3.26	1.63	500
15.561	3.22	1.615	550
48.197	3.795	1.897	700
49.501	3.948	1.973	800
38.739	4.124	2.062	800

TABLE II

RATIO O/N FOR VARIATION IN MODE OF REDUCTION OF NiO IN THE ANALYSIS OF NO₂
(Tube H at 800°)

<i>Volume of N₂ found in cc at standard temperature and pressure</i>	<i>Ratio H/N</i>	<i>Ratio O/N</i>	<i>Comments</i>
58.591	3.643	1.872	Hydrogen immediately passed to M
66.749	3.826	1.913	Hydrogen admitted to H and held for 1/2 h preceding pumping
25.971	4.0125	2.006	Hydrogen admitted to H and held 1 h preceding pumping
12.379	4.091	2.046	Hydrogen admitted to H and held 1 h preceding pumping
38.739	4.124	2.062	Hydrogen admitted to H and held 1 h preceding pumping
64.312	3.856	1.928	Sample circulated through H by pump K
17.139	4.019	2.009	Sample circulated through H by pump K

The decomposition of three solid nitrates was studied; Table III summarizes the results. Barium nitrate was heated to 900°; at this temperature, the nitrate is converted to BaO³ and consequently the ratios I/III and II/III should be 2 and 5. These compare favorably with the observed results. The results are slightly low due to partially adsorbed and occluded water.

Lead nitrate was decomposed at 900°. Under these conditions, it should form PbO³. If the oxide is further reduced to Pb by means of H₂, the ratios I/III and II/III should be 2 and 6 respectively. The first ratio is again slightly low, due to the presence of H₂O. The second ratio is closer to 5 due to partial reaction of PbO with the silica container, giving PbSiO₃.³ It was observed that the quartz vessel disintegrated at the conclusion of the run. Had the reaction been complete, the expected II/III ratio would have been 5.

Ammonium nitrate was decomposed at temperatures in the range 200–400°. However, to assure complete decomposition of the relatively volatile material, the gases were passed over silver gauze maintained at 700°. At higher temperatures, the silver was markedly oxidized by the N_2O gas. It was therefore necessary to include the silver in the reduction step. Quite satisfying results were obtained.

TABLE III
ANALYSIS OF NITRATES

Nitrate	I Moles (N) $\times 10^3$	II Moles (O) $\times 10^3$	III Moles nitrate $\times 10^3$	Ratio	
				I/III	II/III
Ba(NO ₃) ₂	3.242	8.030	1.623	1.936	4.949
Pb(NO ₃) ₂	3.699	9.806	1.902	1.944	5.155
NH ₄ NO ₃ ^a	2.127	1.268	1.247	1.017	1.706
NH ₄ NO ₃	2.757	1.392	1.374	2.006	1.013
NH ₄ NO ₃	3.886	1.928	1.903	2.042	1.013

^a Silver gauze oxidation not included.

The above results indicate that the procedure, under carefully controlled conditions, yields correct results and that the procedure may be applied in confidence. Further work on the thermal decomposition of metallic nitrates and studies in the interaction of NO₂ with metallic oxides are under way⁴.

ACKNOWLEDGEMENT

The author wishes to express thanks to Dr. J. M. HONIG for his constant interest in this work and to Mr. Q. CHOI for his suggestions.

Thanks are due to the National Sciences Foundation for a grant G5122 under which the testing of the equipment was completed.

SUMMARY

A system for the analysis of oxides of nitrogen and metal nitrates is presented. The factors affecting the analysis are tested by analyses of NO₂, and various nitrates.

RÉSUMÉ

Une méthode est proposée pour l'analyse des oxydes d'azote et des nitrates métalliques.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Analyse von Oxyden des Stickstoffs und Metallnitraten.

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SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM WITH 9-METHYL-2,3,7-TRIHYDROXY-6-FLUORONE

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Titanium(IV) in acid solutions forms a rose-red complex with methyl fluorone, in the same way as molybdenum(VI). The colour reaction is very sensitive; a spectrophotometric method for the determination of traces of titanium is described in this paper.

Amongst the several spectrophotometric methods¹, that using hydrogen peroxide²⁻⁴ is most favoured because of its simplicity and relative freedom from interference. Its low sensitivity, however, necessitated studies of other methods *e.g.* dihydroxymaleic acid⁵, tiron⁶ and chromotropic acid⁷. The last reagent is more sensitive than the others but is highly photosensitive and needs accurate pH control. Recently the very sensitive phenyl fluorone has been applied⁸.

The reaction of methyl fluorone with titanium is very similar to that with molybdenum⁹ and the titanium complex has the same tendency to precipitate out of the acid solution unless peptised and kept in solution by gelatin in presence of 12% ethanol. The colour formed is quite suitable for spectrophotometric measurements and shows maximum intensity between pH 1.7 and 2.1, with maximum absorption at 520 m μ . The system obeys Beer's law from 0.025 to 0.6 p.p.m. of titanium, but the optimum range is from 0.1 to 0.6 p.p.m. of titanium, where the percentage analysis error per 1% absolute photometric error is 3.1. JOB's method of continuous variation and the molar ratio method indicate that in solution the complex contains the metal and the reagent in the ratio of 1:2. The molar extinction coefficient of the complex is 60360 and the instability constant is $1.6 \cdot 10^{-12}$ determined at 20°.

EXPERIMENTAL

Apparatus and solutions

The Uvispek spectrophotometer with 10-mm quartz transmission cells, and the pH indicator were the same as in the previous work⁹.

Titanium solution: About 26.0 g of potassium titanium fluoride were fused with pure sulphuric acid and the resulting sulphate was dissolved and made up to 1 l with water. The final solution was about 5 N in sulphuric acid. The titanium content per ml of the solution was determined gravimetrically. Weaker solutions were made as required by dilution.

A 0.025% (w/v) solution of methyl fluorone, and a sodium acetate-hydrochloric acid buffer pH 2 were prepared as in the previous work. A 0.4% (w/v) solution of gelatin, and equimolecular solutions of titanium were also prepared.

Spectral transmittancy: To a 50-ml beaker were added successively an aliquot of the titanium solution, 1 ml of the gelatin solution, 3 ml of the reagent and 2 ml of absolute alcohol. The pH was adjusted to 2 with N sodium acetate and the solution transferred to a 25-ml flask; 3 ml of the buffer solution were added and the solution was made up to 25 ml with distilled water. Simi-

larly a reagent blank without titanium was prepared. The test solution contained 0.25 p.p.m. of titanium. The optical densities of the test and the blank solutions were measured against distilled water at various wavelengths from 480 to 600 $m\mu$. The spectral transmittancy curves are shown in Fig. 1. At 520 $m\mu$, the complex shows maximum absorption against the reagent blank, and this wavelength was chosen for all further work.

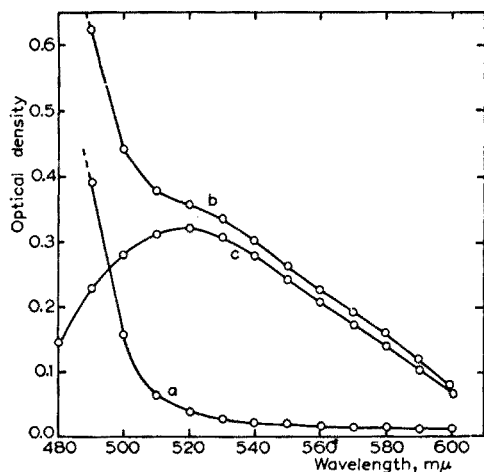


Fig. 1. Spectral transmittancy curves: (a) Reagent against water. (b) Reagent plus titanium against water. (c) Reagent plus titanium against reagent.

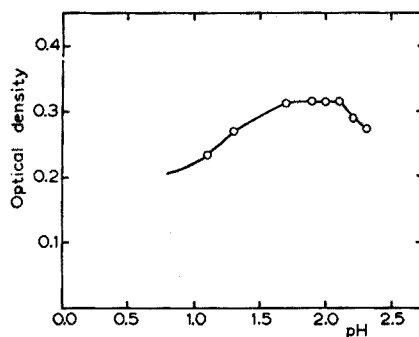


Fig. 2. Effect of pH.

Effect of pH, reagent and time

For the study of the effect of pH, the pH of the test and the reagent solutions was altered by suitable addition of *N* sodium acetate or *N* sulphuric acid. The change of absorption with respect to the reagent blank at various pH values is shown in Fig. 2. The readings were quite constant within the range 1.7–2.1 which was used for subsequent work. Above pH 2.3, the titanium complex precipitated even in presence of gelatin and alcohol.

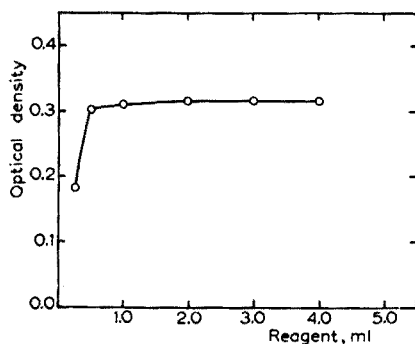


Fig. 3. Effect of reagent.

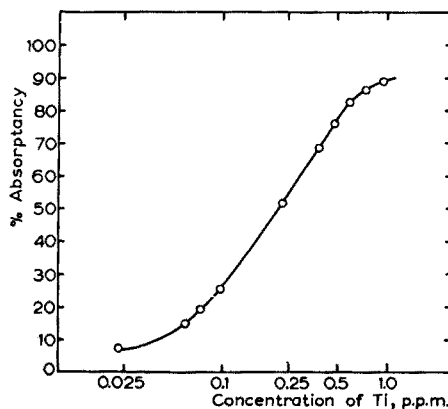


Fig. 4. Standard curve for titanium-methyl-fluorone complex.

The variation of O. D. with increasing amounts of reagent is shown in Fig. 3; 2 ml of 0.025% (w/v) reagent solution sufficed for the maximum colour intensity of 0.25 μg Ti/ml in a total volume of 25 ml.

The titanium-methyl fluorone complex is quite stable for over 24 h at room temperature and within that period shows no change in the absorption value.

Beer's law curve

The O. D.-concentration curve is a straight line passing through the origin. From 0.025 to 0.6 p.p.m. of titanium the O. D. increases linearly with concentration in accordance with Beer's law.

The optimum range and accuracy of the proposed method were determined as described earlier⁹. The optimum range (Fig. 4) is from 0.1-0.6 p.p.m. of titanium, where the relative analysis error per 1% absolute photometric error is 3.1%.

Effect of foreign ions

Chloride, nitrate, perchlorate, sulphate, acetate, ferrous, uranyl, thorium, chromium, aluminium, potassium, sodium and alkaline earths in reasonable amounts did not interfere with the determination, while fluoride, oxalate, tartrate, citrate, phosphate, ceric and cerous, ferric, vanadate and chromate interfered. Ferric and vanadate ions, if masked by ascorbic acid before the addition of the reagent, could be tolerated even up to 30 p.p.m. and 10 p.p.m. respectively.

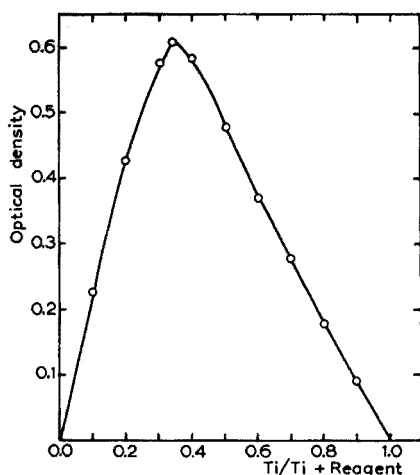


Fig. 5. Job's method of continuous variation.

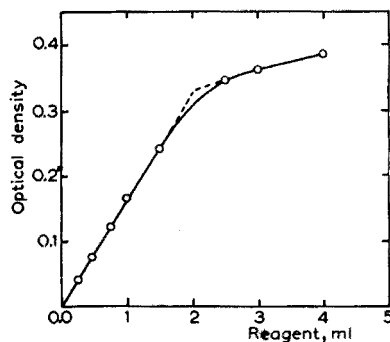


Fig. 6. Molar ratio method.

Composition of the complex

For the elucidation of the composition of the complex by Job's method the absorptions of mixtures (12 ml) of equimolar solutions ($1 \cdot 10^{-4} M$) of titanium and reagent were measured at 520 $m\mu$, the total volume being kept constant at 25 ml by water. Fig. 5 shows the corrected absorption plotted against increasing amounts of titanium; the peak of the curve indicates compound formation at the metal to reagent ratio of 1:2. The molar ratio method supports this finding (Fig. 6).

Extinction coefficient, sensitivity, degree of dissociation and instability constant

The molar extinction coefficient of the complex calculated from Beer's law is

$$\frac{0.315 \cdot 47.9 \cdot 10^8}{0.25} = 60360.$$

The sensitivity of the reaction according to SANDELL'S definition is 0.00079 $\mu\text{g}/\text{cm}^2$.

Since 1 mole of titanium reacts with 2 moles of methyl fluorone to form 1 mole of the complex, the instability constant, K , is evaluated from the equation

$$K = \frac{ac(2ac)^2}{c(1-a)} = \frac{4a^3c^2}{1-a}$$

where c is the concentration of the complex in moles per l and a is the degree of dissociation. The value of a is obtained from the relationship⁹

$$a = \frac{E_m - E_s}{E_m}.$$

The E_m and E_s values are equal to 0.315 and 0.238 respectively at a titanium concentration of $5.198 \cdot 10^{-6} M$; thus the degree of dissociation a , equals 0.2444 and K is $1.6 \cdot 10^{-12}$.

ACKNOWLEDGEMENT

The authors wish to thank the University Grants Commission, Government of India, for providing the instruments used.

SUMMARY

9-Methyl-2,3,7-trihydroxy-6-fluorone is described as a highly sensitive reagent for titanium. The rose-red complex gives maximum absorption at $520 m\mu$ and obeys Beer's law from 0.025–0.6 p.p.m. of titanium. The optimum concentration range is from 0.1–0.6 p.p.m. of titanium, where the relative error is 3.1%. The complex in solution has a metal to reagent ratio of 1:2. The molar extinction coefficient and the instability constant of the complex are about 60360 and $1.6 \cdot 10^{-12}$.

RÉSUMÉ

Les auteurs proposent la méthyl-9-trihydroxy-2,3,7-fluorone-6 pour le dosage spectrophotométrique du titane. Réactif très sensible; le complexe obtenu est rouge rose avec absorption maximum à $520 m\mu$; coefficient d'extinction moléculaire 60360.

ZUSAMMENFASSUNG

Als sehr empfindliches Reagenz zur spektrophotometrischen Bestimmung von Titan hat sich Methyl-9-trihydroxy-2,3,7-fluoron-6 erwiesen. Der gebildete rosa-rote Komplex besitzt ein Absorptionsmaximum bei $520 m\mu$ und einen molekularen Extinktionskoeffizienten von 60360.

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Short Communication

A note on the relative density of mixtures of water and *n*-butanol within the butanol rich range.

The author recently required the relative densities of mixtures of *n*-butanol and water, the composition of the samples lying within the butanol rich range. These were available only at 20° from the International Critical Tables¹ and from WAD AND GOKHALE² for 30°. Rather than interpolate values, it was decided to make fresh determinations. It was found, however, that there was a reasonable agreement between the determined and interpolated values.

n-Butanol was prepared from a commercially pure source by fractionating, using a glass column, 60 cm by 5 cm, filled with small glass rings (0.8 cm × 1.0 cm O.D.). The fraction boiling between 116° and 117° at 755 mm pressure was selected for use. A Schiff's test showed it to be substantially free from aldehydes. The water was doubly distilled from glassware then boiled, to remove dissolved gases, and cooled immediately before the mixtures were prepared. The relative densities were determined using a pycnometer with the temperature controlled to 25° ± 0.1 in a thermostat bath. The results are given in Table I.

TABLE I

<i>X</i>	<i>Y</i>	90% confidence limits of $\mu_Y(X)$
1.494	0.81144	0.00012
2.899	0.81421	0.00011
4.213	0.81672	0.00010
5.660	0.81951	0.00008
6.968	0.82198	0.00007
8.227	0.82436	0.00006
9.443	0.82658	0.00006
10.808	0.82910	0.00007
11.938	0.83130	0.00008
13.070	0.83340	0.00009
14.244	0.83577	0.00010
15.392	0.83749	0.00012

X represents the percentage by weight of water in *n*-butanol. *Y* is the relative density as determined for the solution of composition *X*.

The data obtained in the above manner was submitted to a statistical analysis along the following lines. A straight line relationship was assumed between the percentage of water by weight in *n*-butanol and the relative density of the solution at 25°. This may be represented as

$$\mu_Y(X) = a + \beta X$$

where *X* is the water content in percent, $\mu_Y(X)$ is the true value of the relative density at a particular water content and *a* and β are constants. If *Y* represents the

determined value for relative density of a solution of composition X , the deviations from the means, $x = X - \bar{X}$ and $y = Y - \bar{Y}$, may be found, and from them the constants a and b of the least-squares equation $\hat{Y} = a + bX$

where $a (= \bar{Y} - b\bar{X})$ and $b = (\sum xY / \sum x^2)$ estimate α and β respectively.

Thus \hat{Y} may be taken as the best estimate of the true relative density, $\mu_r(X)$ for the mixture of composition X . It is assumed that X is an independent variable having controlled values and Y is a normal variate.

The values of a and b found from the data in Table I were $a = 0.80879$ and $b = 0.0018831$.

To obtain the standard error of estimate, S_e , of the least-squares line, the value of $\sum Y^2 = \sum \hat{y}^2 - b \sum xy$ was calculated, where $y = Y - \hat{Y}$ and hence

$$S_e = \sqrt{\frac{\sum \hat{y}^2}{n-2}}$$

for n observation. This value was found to be 0.00012.

The 90% confidence limits of α and β were calculated from these expressions and had the values which follow them.

$$\text{for } \alpha = a \pm t_{0.1, n-2}, S_e \sqrt{\left(\frac{1}{n} + \frac{\bar{X}^2}{\sum x^2}\right)} = \pm 0.00014$$

$$\text{for } \beta = b \pm t_{0.1, n-2}, S_e / \sqrt{\sum x^2} = \pm 0.000017$$

For the above calculation t was taken as 1.812 a value obtained from DAVIES³.

The 90% confidence limits of $\mu_r(X)$ did not deviate sufficiently from the determined values to make it worth while graphing them; they are therefore shown in Table I.

The value of a ($= 0.80879$) agrees very closely with the specific gravity of pure n -butanol at 25°C/25°C, a value of 0.80878 as calculated from data in the International Critical Tables⁴.

The author's thanks are due to Mr. P. D. LARK for his generous help with the statistical work.

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¹ *International Critical Tables*, 3 (1926) 112.

² Y. D. WAD AND A. G. GOKHALE, *J. Indian Inst. Sci.*, 4 (1921) A; *C.A.*, 15 (1921) 2760¹.

³ O. L. DAVIES, Ed, *Statistical Methods in Research and Production*, Oliver and Boyd, London 1957.

⁴ *International Critical Tables*, 3 (1926) 28.

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REVUE DE LIVRE

Colorimetric methods of analysis, including photometric methods, par F. D. SNELL, C. T. SNELL et C. A. SNELL, volume II A., D. van Nostrand Company Inc. Princeton, New Jersey 1959, 793 p., 32 fig., 112 s., 6 d.

F. A. SNELL et C. T. SNELL sont les auteurs d'un traité de colorimétrie en 4 vol. Ils viennent d'en faire paraître un 5ème, le volume II A, qui complète le volume II sur l'analyse colorimétrique inorganique. Il renferme donc toutes les méthodes établies depuis la parution du volume II. Je dis toutes, car les auteurs ont fait une bibliographie extrêmement complète des années 1947 à 1956. C'est une formule très heureuse étant donné la foule considérable de travaux qui paraissent dans ce domaine. Au lieu de refondre complètement leur livre, les auteurs ont préféré le compléter, de telle sorte que les volumes II et II A forment un tout cohérent, extrêmement bien documenté, le premier volume gardant toute sa valeur, avantage qui sera apprécié de tous ceux qui s'efforcent d'avoir une bibliothèque à l'ordre du jour.

En consultant le volume II A, on se rend compte de l'importance toujours plus grande que prennent les méthodes colorimétriques dans la science moderne, grâce aux remarquables avantages qu'elles présentent. Les auteurs ont su, et la chose n'était pas facile, classer, ordonner tous ces travaux. On y trouve, non seulement les méthodes d'analyse mais aussi les mises en solutions, les séparations, l'effet des ions gênants et la façon d'éliminer ces derniers. De plus des méthodes complètes d'analyse sont proposées pour divers échantillons: alliages, liquides biologiques, minerais, silicates, etc. Chacune d'elles y est brièvement exposée mais de façon précise si bien qu'il n'est pas toujours nécessaire de recourir aux références bibliographiques. En résumé un excellent ouvrage.

D. MONNIER (Genève)

ERRATA

Analytica Chimica Acta, Vol. 20 (1959) page 337, Table I: The second equation under "Three ions present" should read:

$$(\text{Ni}) \cdot 10^5 = 11.6 A_{s640} + 4.08 A_{s440} - 4.50 A_{s385}$$

instead of:

$$(\text{Ni}) \cdot 10^5 = 11.6 A_{s640} - 4.08 A_{s440} - 4.50 A_{s385}$$

Analytica Chimica Acta, Vol. 21 (1959), page 57, in the references. Reference 4 should have as its first author FRITZ WILL instead of W. FITZ.

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