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PROGRESS IN CHROMATOGRAPHY,
ELECTROPHORESIS AND
RELATED METHODS

VOLUME I

Edited by
MICHAEL LEDERER

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6$^1/_2$ × 9$^1/_2$″ xii + 276 pages 114 tables 64 illus. 1959

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VIII. THE EFFECT OF SUBSTITUENTS IN THE NAPHTHALENE NUCLEUS ON THE FLUORIMETRIC DETECTION OF TIN

J. R. A. ANDERSON*, J. L. GARNETT AND L. C. LOCK

University of New South Wales, Sydney (Australia)

(Received May 8th, 1959)

INTRODUCTION

In previous papers of this series[1-8], naphthalene derivatives have been used for the detection and determination of inorganic ions. In particular, the qualitative and quantitative applications of the substituted nitronaphthalenes as fluorimetric reagents for stannous tin have been reported[1-7]. This paper summarizes the effect of various electropositive and electronegative substituents in the nitronaphthalene nucleus upon the intensity of fluorescence in this test. The compounds investigated in this series of reactions include dinitronaphthalenes, dinitronaphthylamines, halogen substituted mononitronaphthylamines, mononitroso- and dinitronaphthols and

TABLE I

Reagents used for spraying spots of metallic salts

Reagent No.	*Reagent*
	0.1% solution in a mixture of equal volumes of 96% ethyl alcohol and 10 N HCl
1	1-nitronaphthalene
2	2-nitronaphthalene
3[a]	1,5-dinitronaphthalene
4	1,8-dinitronaphthalene
5	4-nitro-2-iodo-1-naphthylamine
6	2-nitroso-1-naphthol
7	4-nitroso-1-naphthol
8	1-nitroso-2-naphthol
9	2,4-dinitro-1-naphthol
10[b]	1,7-dinitro-2-naphthol
	0.1% solution in a mixture of 3 volumes of 96% ethyl alcohol and 1 volume 10 N HCl
11	2-nitro-4-chloro-1-naphthylamine
12	2,4-dinitro-1-naphthylamine
	0.1% aqueous solution
13	1-nitroso-2-naphthol-3,6-disulphonic acid
14	2,4-dinitro-1-naphthol-7-sulphonic acid

[a] Since 1,5-dinitronaphthalene was soluble in alcohol to less than 0.1%, a saturated alcoholic solution was employed. A 0.1% solution of the reagent in benzene was also found to be satisfactory.

[b] B.D.H. Laboratory reagent.

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* On study leave, Birkbeck College, University of London.

their sulphonic acid derivatives. The results confirm the previous conclusions that the intensity of the fluorescence depends markedly upon two factors (a) the nature of the substituent present, *i.e.* electropositive or electronegative and (b) the position of the substituent in the naphthalene ring.

EXPERIMENTAL

Reagents

All reagents used were commercially available except 2-iodo-4-nitro-1-naphthylamine and 4-chloro-2-nitro-1-naphthylamine.

2-Iodo-4-nitro-1-naphthylamine, was prepared by heating 4-nitro-2-acetoxymercuri-1-naphthylamine with iodine in aqueous potassium iodide according to the method of HODGSON AND ELLIOTT[9].

4-Chloro-2-nitro-1-naphthylamine, synthesized by the chlorination of 2-nitro-4-acetoxymercuri-1-naphthylamine dissolved in acetic acid[10].

Spot-test procedure

Experiments were performed using the same spot-test procedure as outlined in a previous communication[5].

The reagents employed are listed in Table I.

RESULTS

The results of the tests are summarized in Table II. The effect of strong hydrochloric acid upon the intensity of the fluorescence is reported in Table III.

TABLE II

Fluorescence obtained on spraying spots of ions with various reagents after treatment with 15 N NH_4OH

Ion	*Reagent number*													
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
Sn^{+2}	SF (B)	F (P)	F (P.B)	F (P.B)	WF (G.Y)	VWF (P.B)	WF (P.B)	SF (B)	WF (P.R)	WF (Br.O.G)	SF (Y.G)	F (P.R)	SF (G.B)	WF (P.R)
Sb^{+3}													WF	
[a] Ce^{+4}														WF
Mo^{+6}								WF						
W^{+6}								WF					WF	
VO^{+2}													WF	
VO_4^{-3}													WF	
ZrO^{+2}						WF								
Zr^{+4}						WF								
Ti^{+3}								WF					WF	

[a] A solution of ceric ammonium nitrate (Analar) in 3 N H_2SO_4 was used.

Fluorescence key

SF = Strong fluorescence
F = fluorescence
WF = Weak fluorescence
VWF = Very weak fluorescence

Colour key

B = Blue
G = Green
R = Red
Br = Brown
P = Purple
Y = Yellow
O = Olive.

Other ions tested included:

Be^{+2}, Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2}, Sn^{+4}, As^{+3}, As^{+5}, Bi^{+3}, Fe^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Cr^{+6}, Cu^{+2}, Co^{+2}, Ni^{+2}, Hg^{+}, Hg^{+2}, Pb^{+2}, Ag^{+}, Ce^{+3}, Cd^{+2}, Mn^{+2}, Ti^{+4}, Th^{+4}, La^{+3}, Pd^{+2}, Pt^{+2}, Pt^{+4}, Au^{+3}, Ru^{+3}, In^{+3}, Tl^{+}, Tl^{+3}, UO_2^{+2}, VO_3^{-}, Rb^{+}, Cs^{+}, Li^{+}, K^{+}, Na^{+}, Zn^{+2}.

These ions gave either no fluorescence or coloured spots with only a faint trace of fluorescence.

Ions which gave no fluorescence with the reagents were:

Fe^{+2}, Cr^{+3}, Mn^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, K^{+}, Rb^{+}, Ce^{+3}, Au^{+3}, Pd^{+2}, Tl^{+}, Tl^{+3}, VO_3^{-}, Ag^{+}.

TABLE III

Effect of HCl upon the intensity of fluorescence of spots, (0.01 ml), containing 10^{-4} g stannous tin

Reagent number in Table I	*0.1% Solution of reagent in*			
	Alcohol		*50/50 v/v Alcohol/10 N HCl*	
	B	*A*	*B*	*A*
1	VWF	F	WF	SF
2	VWF	F	WF	F
3	WF	WF	F	F
4	WF	WF	F	F
5	VWF	VWF	WF	WF
6	VWF	VWF	VWF	VWF
7	WF	WF	WF	WF
8	WF	F	WF	SF
9	VWF	WF	VWF	WF
10	VWF	WF	VWF	WF
11	VWF	F	WF	SF
12	VWF	VWF	WF	F
13			F	SF
14			VWF	WF

B = Before spraying with 15 *N* NH_4OH
A = After spraying with 15 *N* NH_4OH

The above results indicate that as previously reported for other reagents[6,7], the presence of concentrated HCl is advantageous for the fluorescent tin test.

Sensitivity tests

Sensitivity tests for stannous tin were carried out in the presence of hypophosphorous acid as previously described[1]. All the reagents tested exhibited a distinct fluorescence with stannous tin, with the exception of reagent number 6 which gave a very weakly fluorescent purple coloured spot. The fluorescence shown by the reagents was essentially blue in colour, but with some compounds yellow-green, green-blue and purplish shades were also given. Reagent numbers 1, 8, 11 and 13 gave the most intense fluorescence, followed by reagent numbers 2, 3, 4 and 12, while reagent numbers 5, 7, 9, 10 and 14 gave only weakly fluorescent spots with stannous tin. All reagents were capable of detecting 10^{-4} g stannous tin and 10^{-5} g was detected with reagent numbers 1, 3, 5 and 13. Blank tests with all reagents on spots of 2% hypophosphorous acid showed no fluorescence under the conditions of the test.

DISCUSSION

The mechanism for the stannous chloride reduction of nitro groups in naphthalene compounds has already been discussed by HODGSON[11] in terms of a conventional nucleophilic reaction. The ease of monoreduction of polynitro-compounds was shown to be dependent on the electrophilic (positive) character of the nitro group which was preferentially attacked. This theory has been confirmed by OGATA AND SUGIYAMA[12] who studied the reduction velocities of para-substituted nitrobenzenes with stannous tin. These authors showed that the larger the electron-pulling force of the substituent in the para position, the faster was the rate of reduction of the nitro group.

From the results reported in this paper for nitronaphthalene derivatives, two of the most important factors associated with the reduction appear to be:

(a) the position of the nitro group in the naphthalene nucleus, *i.e.*, whether it is α- or β- or whether it is sterically hindered and (b) the electropositive or electronegative character of *other* substituent groups present in the compound.

To summarize the relative effect of some substituents in nitronaphthalene upon the sensitivity of the stannous tin test, the reagents used in this series of reactions have been classified into the following groups in Table IV. It will be observed that each group contains different type substituents.

TABLE IV

Summary of stannous tin reduction products of reagents

Group	*Reagent No. in Table I*	*Reagent*	*Reduction product with* Sn^{+2}	*Reference to reduction*	*Fluorescence with* Sn^{+2}
A	1	1-Nitronaphthalene	1-Aminonaphthalene	13	SF
	2	2-Nitronaphthalene	2-Aminonaphthalene	13	F
B	3	1,5-Dinitronaphthalene	1,5-Diaminonaphthalene No intermediate mono-reduction product	11, 14	F
	4	1,8-Dinitronaphthalene	1,8-Diaminonaphthalene No intermediate mono-reduction product	11, 14	F
C	6	2-Nitroso-1-naphthol	2-Amino-1-naphthol	15	VWF
	7	4-Nitroso-1-naphthol	4-Amino-1-naphthol	16	WF
	8	1-Nitroso-2-naphthol	1-Amino-2-naphthol	17	SF
	13	1-Nitroso-2-naphthol-3,6-disulphonic acid	1-Amino-2-naphthol-3,6-disulphonic acid	17	SF
D	12	2,4-Dinitro-1-naphthylamine	2-Nitro-1,4-naphthalenediamine	—	F
	9	2,4-Dinitro-1-naphthol	2-Nitro-4-amino-1-naphthol	18	WF
	10	1,7-Dinitro-2-naphthol	7-Nitro-1-amino-2-naphthol	—	WF
	14	2,4-Dinitro-1-naphthol-7-sulphonic acid	2-Nitro-4-amino-1-naphthol-7-sulphonic acid	18	WF
E	5	2-Iodo-4-nitro-1-naphthylamine	2-Iodo-1,4-naphthalenediamine	10, 19	WF
	11	4-Chloro-2-nitro-1-naphthylamine	4-Chloro-1,2-naphthalenediamine	10, 19	SF

It will be seen from the above table that the stannous tin reduction products of 2,4-dinitro-1-naphthylamine and 1,7-dinitro-2-naphthol have not been reported in the literature. On the basis of HODGSON's work[11,14,22] with the monoreduction of α, β-dinitronaphthalenes, particularly 1,3-dinitronaphthalene[22], the main product expected for the reduction of 2,4-dinitro-1-naphthylamine would be 2-nitro-1,4-naphthalenediamine together with a very small amount of 4-nitro-1,2-naphthalenediamine. This conclusion is confirmed by the reduction of 2,4-dinitro-1-naphthol[18] where the main product isolated was 2-nitro-4-amino-1-naphthol. In a similar manner, the formation of 7-nitro-1-amino-2-naphthol would be expected as the major product from the stannous chloride reduction of 1,7-dinitro-2-naphthol.

Considering group A in Table IV, the relative effect of the nitro group in the α- and β-positions can be clearly seen. The observation that the α-position is the more reactive is consistent with HODGSON's theory[11,20,21] for this difference in positional reactivity. HODGSON considers that the negative inductive effect (—I) of the second nucleus must be considered, for, in this manner, the α-nitro group will be rendered more electropositive in character than the β-nitro group. Furthermore, since it is at the end of a conjugate chain in two of the three resonating structures which naphthalene can assume (Diagram I), it will be more prone to attack by the reducing medium present in acid stannous chloride solutions.

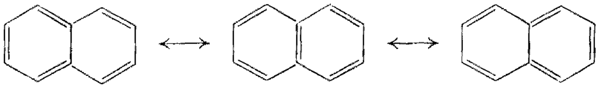

Diagram I

In group B, the effect of two α-nitro groups is shown to be equivalent to the reactivity exhibited by β-nitronaphthalene. Both compounds in group B are α, α-dinitronaphthalenes and no intermediate mononitronaphthylamine has been observed during the stannous chloride reductions of these reagents, irrespective as to whether an excess or deficit of reducing agent was used[14]. Only in the catalytic reduction[23,24] selectivity has been experienced. According to HODGSON[11], the two α-positions in each of the 1,5- and 1,8-dinitronaphthalenes are identical in situation and are attacked simultaneously by the acid reducing agent to form the respective diamines. This follows from the fact that, even if a deficiency of reducing agent is employed, the surplus dinitronaphthalene is found mixed with the diamine.

The trend of results with the compounds in group C is very similar to the reactivity of the corresponding nitro-naphthol series[7]. This is to be expected when it is realised that the nitroso derivatives are intermediates during the tin reduction of nitro compounds in strongly acid solution[25] (Diagram II).

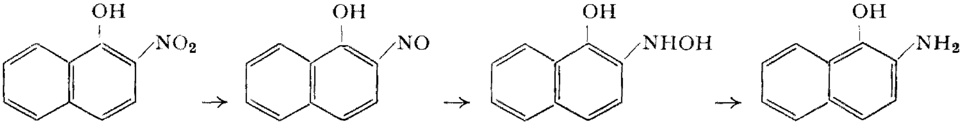

Diagram II

As with the nitronaphthols, a nitroso group in the β-position is less reactive than a nitroso group in the corresponding α-position, so that 2-nitroso-1-naphthol yields the least intense fluorescence of the four compounds listed, whereas 1-nitroso-2-naphthol is the most reactive reagent. This accentuated difference in positional reactivity in passing from the nitro to nitrosonaphthols could be readily explained if nitroso formation were the rate-determining step in the actual reduction of the nitro group. This is true for the catalytic reduction of nitro groups[23,24], but equivalent data is not yet complete for acid stannous tin reductions, although present indications[12,25–27] are that the same result will be achieved in the latter case.

In Group D, the behaviour of the dinitro compounds, especially the naphthol derivatives, is very similar to that of the parent nitronaphthols. The presence of a second nitro group in the naphthalene nucleus tends to quench the intensity of the fluorescence, so that α, β-dinitronaphthols yield a less intense fluorescence than the corresponding α- or β-mononitronaphthols. In this respect, the compounds in this group are similar in behaviour to the compounds in Group B.

The function of the sulphonic acid group in these reagents is also of interest and is indicated by the comparative properties of 1-nitroso-2-naphthol and 1-nitroso-2-naphthol-3,6-disulphonic acid in Group C. Both exhibit the same reactivity in test, a result which is to be expected in view of the postulate[5] that the function of the sulphonic acid group is essentially one of solvolysis of the parent compound towards polar solvents.

With Group E, the marked difference in reactivity between 2-iodo-4-nitro-1-naphthylamine and 4-chloro-2-nitro-1-naphthylamine is difficult to interpret without a more detailed knowledge of the actual influence of substituents on the reactivity of aromatic systems. In particular, the evaluation of the relative properties of the two compounds in Group E is more complicated than with the compounds in the Groups (A to D) due to the difficulty associated with the estimation of the relative inductive and mesomeric effects in these two systems. It is hoped to clarify this point when the results of an investigation at present being performed in this field, are available[28].

In conclusion, it may be said that any naphthalene compounds containing a nitro group would appear to be potential fluorimetric reagents for stannous tin. The potency of such reagents in this spot test will depend largely on the polar nature of other substituents. Such factors as hydrogen bonding involving the nitro group will impair the ease of reduction and consequently, the sensitivity of the reagent in test. Until more results of research into the relative effects of the inductive and mesomeric moments in naphthalene derivatives are available, it does not appear possible at this time to predict, on theoretical grounds, the structure of a nitronaphthalene derivative which will yield maximum sensitivity of analytical test with stannous tin.

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SUMMARY

Fourteen substituted nitronaphthalene derivatives have been examined as reagents for the fluorimetric detection of tin. The compounds investigated included dinitronaphthalenes, dinitronaphthylamines, halogen substituted mononitronaphthylamines, mononitroso- and dinitronaphthols and their sulphonic acid derivatives. Four of these reagents have been found to exhibit strong fluorescence and another four to give moderate fluorescence with stannous tin. All reagents are capable of detecting 10^{-4} g stannous tin and with four of them, 10^{-5} g is capable of detection in 0.01 ml of solution. The results indicate that two of the most important factors relating structure of reagent to intensity of fluorescence are (a) the position of the nitro group in the naphthalene nucleus, *i.e.*, whether it is α- or β- or whether it is sterically hindered and (b) the electropositive or electronegative character of *other* substituent groups in the reagent.

RÉSUMÉ

Quatorze dérivés de substitution du nitronaphtalène ont été examinés en vue de leur utilisation comme réactifs fluorimétriques pour l'identification de l'étain. Les résultats obtenus montrent que l'intensité de la fluorescence dépend principalement des deux facteurs suivants: (a) la position du groupe nitro dans le naphtalène; (b) le caractère électropositif ou électronégatif des autres groupes substitués.

ZUSAMMENFASSUNG

14 substituierte Nitronaphthaline wurden auf ihre Eignung als fluorimetrisches Reagenz zum Nachweis von Zinn untersucht. Es konnte gezeigt werden, dass die Intensität der Fluoreszenz von 2 Faktoren bestimmt wird: 1. von der Stellung der Nitrogruppe (α oder β). 2. dem elektro-positiven oder elektro-negativen Charakter der anderen Substituenten.

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A NEW CRYOSCOPIC MICRO-METHOD FOR THE DETERMINATION OF MOLECULAR WEIGHTS

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INTRODUCTION

The known cryoscopic methods for the determination of molecular weights are based on the determination of initial freezing or final melting points. These methods may give reliable results if solute and solvent form no solid solutions, the heat of dilution is negligible and solid and liquid are physically stable near the melting point. But there is little or no information given as to whether these conditions are fulfilled or not.

The method described in this paper is based on the determination of a temperature–heat content curve (melting curve). This curve permits the calculation of molecular weights even when *mixed crystals* occur and the heat of dilution is not negligible. Further, it yields information as to whether the various equilibrium conditions are sufficiently approached.

The method permits extrapolation to infinite dilution and is less open to experimental errors than the known methods.

The determination of a temperature-heat content curve presents no serious difficulty. With the aid of a simple apparatus[1] the curve can be obtained within two hours. Only 200–300 mg of solvent and 1–3 mg of solute are required.

Briefly, the method is as follows. A heating curve permits the determination of the equilibrium temperature of solid and liquid as a function of the fraction of heat of melting consumed. This fraction is nearly equal to the fraction which is molten. (This approximation is not actually introduced in our theoretical considerations and serves only for the preliminary picture.)

The substance of which the molecular weight is to be determined is distributed between the solid and the liquid phase of the solvent. (When no mixed crystals occur the solute is entirely dissolved in the liquid phase of the solvent.)

As the melting proceeds a series of concentrations of the solute and the pertaining depressions is obtained. This series permits extrapolation to zero concentration.

As will be shown in the theoretical part it is more exact to plot amounts of heat consumed as a function of the depression.

THEORETICAL PART

The molecules of a polar substance when dissolved in a solvent may show a strong tendency to mutual association. This mutual association may be largely prevented when solvents showing association with the solute are applied. Association with the *excess* solvent hardly effects the molecular ratio of solvent and solute; moreover its effect on the depression of the melting point may be eliminated by extrapolation to infinite dilution. However, when (owing to the choice of the solvent) mutual association of the solute may be neglected, heats of dilution (owing to solute-solvent interaction) may be important and have to be accounted for.

Therefore the following equation is used as a starting-point for further considerations:

$$\int_{T_O}^{T_S} \frac{Q}{T^2}\,\mathrm{d}T - \int_{T_O}^{T_S} \frac{\Delta\overline{W}_L}{T^2}\,\mathrm{d}T + \int_{T_O}^{T_S} \frac{\Delta\overline{W}_S}{T^2}\,\mathrm{d}T = R\ln(1 - X_L) - R\ln(1 - X_S) \quad \text{. . (1)}$$

where Q = molar heat of melting of pure solvent at any temperature; Q_O = molar heat of melting of pure solvent at the melting point; ΔW_L and ΔW_S = partial molar heats of dilution of the liquid and the solid phase, respectively; T_S = any temperature where liquid and solid are in equilibrium (°K); T_O = melting temperature of pure solvent (°K); $\Delta T = T_S - T_O$; X_L, X_S = mol fraction of solute in the liquid and solid phase respectively; ΔC_P = difference of molar specific heats of liquid and solid phase; R = gas constant.

Assuming that $Q = Q_O + \Delta C_p \Delta T$ and that ΔW_L and ΔW_S do not depend on temperature, equation (1) may be integrated:

$$\frac{Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S}{T_O T_S}\,\Delta T + \frac{\Delta C_P}{2T_S^2}(\Delta T)^2 = R\ln\left(\frac{1 - X_L}{1 - X_S}\right) \quad \text{. . . . . (2)}$$

At low and moderate values of X_L and X_S, equation (2) can be simplified to:

$$\frac{Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S}{T_O T_S}\,\Delta T + \frac{\Delta C_P}{2T_S^2}(\Delta T)^2 = -R(X_L - X_S) \quad \text{. . . . . (3)}$$

This approximation introduces an error not exceeding 1.5% at the maximum concentrations* ($X_L < 0.03$) applied in this method; moreover, extrapolation to zero concentration largely eliminates this error.

Suppose that from a sample with a total concentration X, a mol fraction y has been melted.

Thus,

$$y X_L + (1 - y)X_S = X \text{ and } (X_L - X_S) = \frac{X - X_S}{y}$$

Substituting this in equation (3) yields

$$\frac{y(Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S)_y}{T_O T_S}\,\Delta T + \frac{y\,\Delta C_P(\Delta T)^2}{2T_S^2} = -R(X - X_S) \quad \text{. . . . . . . (4)}$$

---

* X is limited to about 0.003. $X_S < X$ unless elevation of the melting point occurs. The smallest fraction molten that is considered amounts to 10%, thus $X_L \leqslant 10\,X$.

When a mol fraction y has been melted the fraction of the total heat of melting supplied, f_y, is approximately equal to

$$\frac{y(Q_O + \overline{\Delta W}_L - \overline{\Delta W}_S)_y}{(Q_O + \overline{\Delta W}_L - \overline{\Delta W}_S)_{y=1}}$$

(At $y = 1$ the approximation is complete).

Substituting the approximate value of f_y in equation 4 results in:

$$f_y \Delta T + \frac{y \Delta C_P (\Delta T)^2 T_O T_S}{2 T_S^2 (Q_O + \overline{\Delta W}_L - \overline{\Delta W}_S)_{y=1}} = \frac{R(X - X_S) T_O T_S}{(Q_O + \overline{\Delta W}_L - \overline{\Delta W}_S)_{y=1}} \quad \ldots\ldots (5)$$

Equation (5) contains no variable values of ΔW_L and ΔW_S which may become important at large values of X_L.

When the solvents used have a heat of fusion of about 4000 cal/mol and $X < 0.003$, $(\overline{\Delta W}_L - \Delta W_S)_{y=1}$ can certainly be neglected. If only the range $0.1 < y < 1$ is considered and if ΔC_p is assumed equal to 3R or 6 cal/mol, the correction containing ΔC_p may be estimated at about 0.2% of $f_y \Delta T$. Moreover this correction term approaches zero when extrapolation to $\Delta T = 0$ is made.

Therefore it is permissible to simplify equation (5) to:

$$f_y \Delta T = -\frac{R T_O T_S}{Q_O} (X - X_S) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Now, in many cases X_S appears to be a linear function of the temperature at low values of X_S ($X_S < X$) so that $X_S = k\Delta T$.

Substitution in (6) yields

$$f_y \Delta T = -\frac{R T_O T_S}{Q_O} X + \frac{k R T_O T_S}{Q_O} \Delta T \quad \ldots\ldots\ldots\ldots\ldots (7)$$

According to equation (7) a determination of a molecular weight may be performed in the following way.

A temperature–heat content curve (melting curve) of a solvent containing about 0.003 mol solute per mol is determined.

Corresponding values of f_y and ΔT are evaluated from the melting curve. Then $f_y \Delta T$ is plotted as a function of ΔT. According to equation (7) this plot should be an approximately straight line. When extrapolated to $\Delta T = 0$ the ordinate is intersected at

$$(f_y \Delta T)_{\Delta T=0} = -\frac{R T_O^2}{Q_O} X$$

The angle of intersection is determined by $\dfrac{k R T_O^2}{Q_O}$

The value of $(f_y \Delta T)_{\Delta T=0}$ being known, the molecular weight of the solute may be calculated (see "experimental procedure").

EXPERIMENTAL PROCEDURE

Apparatus

The apparatus for the determination of temperature-heat content curves[1,2] permits a constant amount of heat per unit time to be supplied to the sample. The rate of heating of the solid is chosen as 0.2–0.6°/min. Under the prevailing conditions the melting process takes about 60 min. The temperature is recorded from 20° below the melting point of the solvent up to about 5° above the melting point.

The thermometers used are shortened stem thermometers with a range of at least 50° subdivided in 0.1°, so that readings can be taken with an accuracy of ± 0.01°. Temperature readings are taken at intervals of 1 min.

For further details concerning the determination of temperature–heat content curves reference is made to the literature[1,2].

Preparation of the sample

1–3 mg of substance (depending on the molecular weight is weighed in the measuring vessel[1]. A weighed amount of about 300 mg of solvent is added. Then the sample is heated to 5–10° above the melting point of the solvent and stirred thoroughly until the substance has completely dissolved.

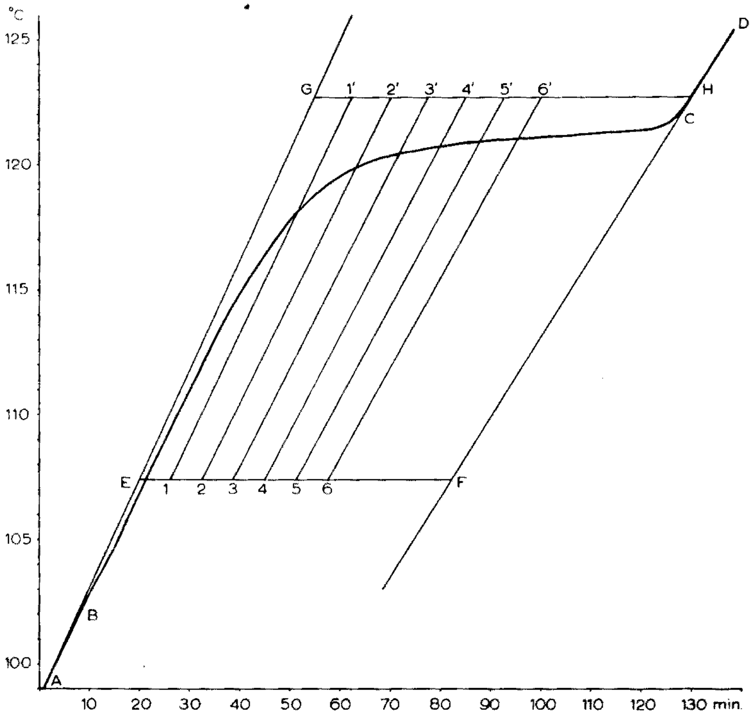

Fig. 1. Melting curve of benzoic acid + naphthalene.

The solution obtained is cooled rapidly. In order to prevent segregation, solidification should be completed within two min.

To eliminate crystal imperfections the sample is kept for 30 min at about 10° below the melting point. The sample is then ready for the determination of a melting curve.

Evaluation of f_y and ΔT

Melting curves of both the sample and the pure solvent are determined.

The general appearance of a melting curve is shown in Fig. 1. The section A B represents the heating of the solid (and the measuring vessel). At B the process of melting starts and it is completed at C. The straight line C D represents the heating of the molten sample. The amount of heat consumed between B and C is the sum of the heat of fusion, and the amounts of specific heat consumed between B and C.

The equivalent of the total heat of fusion at a certain temperature is found by extrapolating the lines A B and C D at the temperature desired. The temperatures corresponding to distinct values of f_y are derived in the following way: the lines E F and G H are drawn and each line is divided into ten equal fractions. The lines 1–1′, 2–2′, 3–3′ etc. are drawn. The temperature at which the line 1–1′ intersects the melting curve corresponds to $f_y = 0.1$, the intersection of 2–2′ corresponds to $f_y = 0.2$ etc.

The difference ΔT of the temperatures of the pure solvent and the solution at the same value of f_y is determined.

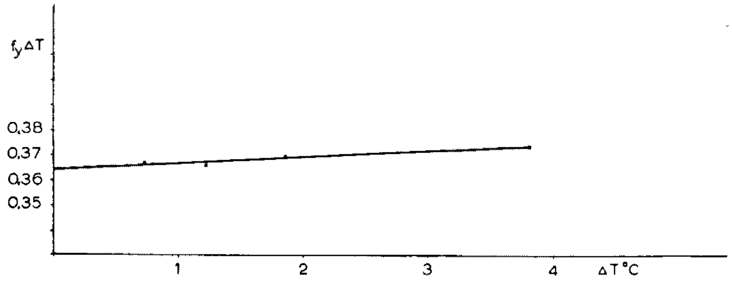

Fig. 2. Plot of $f_y \Delta T$ *versus* ΔT of benzoic acid + naphthalene.

Calculation of the molecular weight

The product $f_y \Delta T$ is plotted as a function of ΔT (see Fig. 2). A straight line is drawn through the points obtained and extrapolated to $\Delta T = 0$.

$(f_y \Delta T)_{\Delta T = 0}$ is read from the ordinate and the molecular weight m is calculated according the following equation:

$$m = \frac{1}{(f_y \Delta T)_{\Delta T=0}} \cdot \frac{gRT_0^2}{q}$$

where g = concentration in g/g solvent, and q = heat of melting of solvent per g.

NOTES

Correction for eutectic melting

If the melting curve shows an isothermal part owing to the melting of the eutecticum the following procedure is advisable. First $f_y \Delta T$ is determined in the ordinary way at $f_y = 0.5$. (When the isothermal process is still present near $f_y = 0.5$ a new melting curve should be determined with a sample containing less solute.) Then $\Delta T'$ is determined at a temperature T' slightly higher than the eutectic temperature.

The value of f_y' corresponding to $\Delta T'$ is calculated:

$$f'_y = \frac{(f_y\,\Delta T)_{y=0.5}}{\Delta T'}$$

A horizontal line through T' is drawn. On this line two fixed values of f_y' occur *viz.* f_y' (at the intersection with the melting curve) and $f_y = 1$ (at the intersection with CD).

With the aid of these two points a point is determined where f_y should be equal to zero. Through this point a new line A′B′ is drawn parallel to AB. The curve is now further treated as if A′B′ actually represented the heating of the solid. This yields a new series of values of f_y which is considered as the correct one.

If the curve shows no isothermal part it may be assumed that the eutectic melting occurs below the starting temperature. Yet the heat consumed before the first recording of temperature must be corrected for. At the lowest temperature recorded (say $\Delta T' = 20°$) a fixed value f_y' is determined by

$$f'_y = \frac{(f_y\,\Delta T)_{y=0.5}}{\Delta T'}$$

The correction procedure then followed is analogous to that described above. The correction thus introduced is relatively small (about 1%). When the correction is omitted it introduces an error of about 1% in the found molecular weight; this is not eliminated by extrapolation to $\Delta T = 0$.

When mixed crystals occur the correction is not permissible. Thus in the rare cases where a very slight partial miscibility in the solid phase occurs, an error of about 1% may be introduced.

Correction for emergent stem of the thermometer

Although the determination of the molecular weight is based on the measurement of temperature differences, the correction for the emergent stem of the thermometer can not be neglected when the cryoscopic constant has been calculated from calorimetric data.

The correction Δ to be added to the temperature difference ΔT amounts to

$$\Delta = 1.6(t_2 + t_3 - t_1)\Delta T \cdot 10^{-4}\,°\mathrm{C}$$

where t_1 = room temperature, t_2 = length of emergent stem in °C, and t_3 = melting point of the solvent in °C.

If for example, benzoic acid is used this correction may be more than 1%.

Solid solutions

When solid solutions occur equilibrium between solid and liquid is less easily approached owing to low diffusion rates in the solid phase. Lack of equilibration was found during the determination of the molecular weight of phenanthrene with diphenyl as solvent. In the first determination the plot of $f_y\Delta T$ *versus* ΔT deviated strongly from a straight line. During a second experiment heat was supplied at intervals and the sample was kept under adiabatic conditions for a sufficiently long time after each supply of heat. The plot was then a straight line and the correct molecular weight was found.

Solvents used

Preferably solvents are used which melt within 0.1° between $f_y = 0.1$ and $f_y = 0.5$ and which have a heat of melting of about 4000 cal/mol.

Succesfully applied solvents were:
benzoic acid (m.p. 122.4°, heat of melting 33.9 cal/g) diphenyl (m.p. 69.0°, heat of melting 28.8 cal/g) phenylacetic acid (m.p. 77°, heat of melting 41.2 cal/g) tetrachlorobenzene (m.p. 140°, heat of melting 27.1 cal/g).

Other solvents may also be useful. Solvents showing polymorphism near the melting point should be avoided.

EXPERIMENTAL RESULTS

Tables I and II show results of molecular weight determinations in benzoic acid and diphenyl respectively.

TABLE I

Solvent used is benzoic acid

compound	*mol. weight*	*mol. weight found*	*conc. weight %*	*error %*	*system*
naphthalene	128	129	1.0[a]	+0.8	no solid sol.
adipinic acid	146	146	0.6[a]	0	no solid sol.
diphenyl	154	155	1.0	+0.7	no solid sol.
antipyrine	188	187	0.6	—0.5	no solid sol.
antraquinone	208	207	0.4	—0.5	no solid sol.
tetraphenylethane	334	336	0.6	+0.6	no solid sol.
k-aglycone[3]	506	507[b]	1.0	+0.2	no solid sol.
bromophenol blue	670	670	1.2	0	no solid sol.
edible fat	864[a]	859	1.1	—0.6	no solid sol.

[a] determined by titration.
[b] mean of two determinations differing respectively +1% and —1% from the correct value.

TABLE II

Solvent used is diphenyl

compound	*mol. weight*	*mol. weight found*	*conc. weight %*	*error %*	*system*
phenanthrene	178	180	1.2	+1.1	solid sol.
anthraquinone	208	208	0.5	0	no solid sol.
edible fat	864	857	1.0	+0.8	no solid sol.

In some of the determinations mentioned in Table I the actual concentration of the solute taken is more than 3 mol %, nevertheless the error in the results is smaller than 1%.

A preliminary investigation has been made concerning the application of the method to polymers. So far, it has not been possible to obtain high polymers with known molecular weights. We restricted our investigation to polymers of the polyester type with molecular weights up to 2000. The molecular weights found tallied with those determined by a chemical method. Dependent on the degree of polymerization, solutions of polymers show deviations from equation (7).

Flory[4] and Huggins[5] discussed the influence of interaction on the activity of polymers. With the aid of the method described in this paper heats of dilution are accounted for. Since the method gives a series of data pertaining to different concentrations, it provides an easy means of discerning other effects of interaction and it may be possible to determine entropy effects arising from the dilution of a polymer solution.

In case the entropy effects are important a simple linear extrapolation to zero concentration is not permissible. Development of a suitable extrapolation method will be a matter of further investigation.

Discussion

The results presented above have not been selected and were obtained by a single experiment unless stated otherwise. The deviations from the theoretical molecular weight never exceeded 1% when no solid solutions were present.

The molecular weight determination of phenanthrene in diphenyl, which showed a rather large miscibility in the solid phase, deviated only 1.1%. If another cryoscopic method had been applied to the same system, the error would have been 50%. A determination of the molecular weight of benzoic acid in diphenyl failed. The plot of $f_y \Delta T$ *versus* ΔT showed a strong curvature and the values of $f_y \Delta T$ corresponded to nearly twice the theoretical molecular weight. With phenylacetic acid as solvent the correct molecular weight of benzoic acid was found. This experience illustrates the views presented in the theoretical part, *viz.* a solute-solvent association may prevent mutual association of the molecules of the solute.

With respect to the known cryoscopic methods the determination of melting curves has the following advantages. Owing to the fact that heat fractions are determined the influence of the heats of dilution is minimized. Polymorphic behaviour of the solvent which may cause unknown deviations in the heat of melting and in the cryoscopic constant may be recognized. Although the method is a micro method it is not based on the inaccurate micro-melting point determination and consequently solvents with a large cryoscopic constant (small heat of melting) are not required.

ACKNOWLEDGEMENT

We wish to thank the director of the Institute for Cellulose Research of the A.K.U. for providing us with some polymer samples of which the molecular weight had been determined by chemical means in his Institute.

SUMMARY

A method is described for molecular weight determination based on a temperature–heat content curve. About 2 mg of substance is required. The method is applicable even when solute and solvent form mixed crystals. A wide variety of solvents may be used. The method may yield good results in the polymer field.

The accuracy obtained is better than 1%. The new method appears to be more reliable and accurate than known cryoscopic methods.

RÉSUMÉ

Une méthode cryoscopique est proposée pour la détermination des poids moléculaires; elle est basée sur la courbe température-enthalphie, fournie par un appareil simple.

Cette méthode permet une accuratesse de 1% obtenue avec des échantillons de 2 mg environ.

ZUSAMMENFASSUNG

Es wird eine kryoskopische mikro Methode (Substanz Menge etwa 2 mg) zur Bestimmung von Molekulargewichten beschrieben, die auf der Aufstellung und Auswertung von Schmelzkurven beruht. Die Genauigkeit der Methode beträgt 1%.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

III[1]. THE IMPORTANCE OF THE IONISATION OF THE WEAK ACID OR BASE IN BUFFER MEDIA CALCULATIONS

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When buffer solutions prepared to give a specific pH value are checked by measurement, it often happens that the measured pH differs from the expected pH[2], being greater with acid buffers and less with basic buffers than expected, and the difference increases with increasing dilution of the solution and with increasing ionisation constant of the weak acid or base. Similar discrepancies arise in comparing theoretical and experimental titration curves involving weak and strong components. Study of such phenomena reveals that hydrogen ion buffers are in-

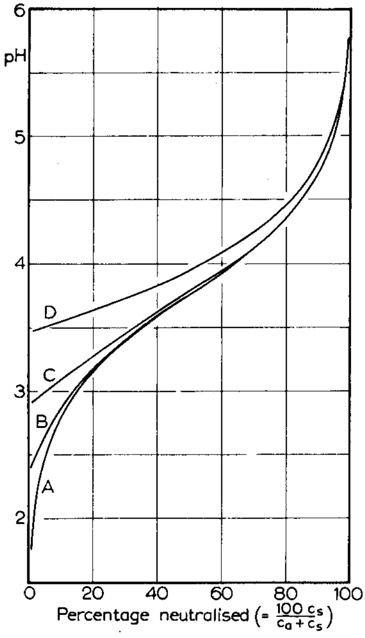

Fig. 1. pH of formic acid–formate buffer solutions: $K_a = 1.76 \cdot 10^{-4}$. Curve A: calculated from the simple equation (1). Curves B to D: calculated from the exact cubic equation[3]:

$$[H^+]^3 + (c_s + K_a)[H^+]^2 - (K_w + K_a c_a)[H^+] - K_a K_w = 0$$

Buffer concentration $(c_a + c_s)$ in Curve B, 0.1 M; in Curve C, 0.01 M; in Curve D, 0.001 M.

variably more efficient in resisting change of pH than is expected (Fig. 1). The discrepancies arise because the assumptions upon which the derivation of the simple buffer equations in common use are based are no longer valid. Whilst it is generally realised that corrections have to be applied to these equations when working at extremes of the buffer range, it is not generally appreciated how severe are the limitations, particularly in respect to ionisation of the weak acid or base, of the simple equations.

In the case of *acid buffers*, derivation of the simple equation (1) assumes that the concentration of anions furnished by the salt, of concentration c_s, adequately suppresses ionisation of the weak acid, so that the concentration of HA can be written equal to c_a the total concentration of acid present. When this assumption is no longer valid, the ionisation of the weak acid can be taken into account[3] by use of the more precise quadratic equation (2).

$$[\mathrm{H}^+] = \frac{c_a}{c_s} K_a \quad \text{. . . . .} \quad (1)$$

$$[\mathrm{H}^+] = \tfrac{1}{2}\left[\left\{(c_s + K_a)^2 + 4\,K_a c_a\right\}^{\frac{1}{2}} - (c_s + K_a)\right] \quad \text{. . . . .} \quad (2)$$

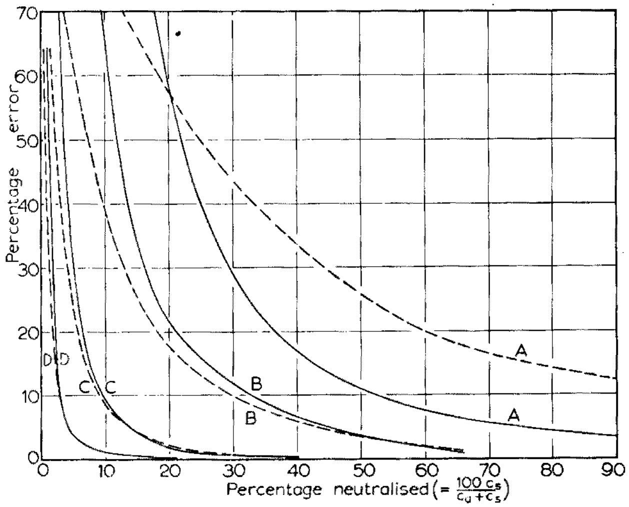

Fig. 2. The error incurred in buffer solution calculations by ignoring the ionisation of the weak acid or weak base. Full lines: acid buffers. Broken lines: basic buffers.

Curves A

Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-1}	1.0 M
10^{-2}	0.1 M
10^{-3}	0.01 M
10^{-4}	0.001 M

Curves B

Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-2}	1.0 M
10^{-3}	0.1 M
10^{-4}	0.01 M
10^{-5}	0.001 M

Curves C

Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-3}	1.0 M
10^{-4}	0.1 M
10^{-5}	0.01 M
10^{-6}	0.001 M

Curves D

Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-4}	1.0 M
10^{-5}	0.1 M
10^{-6}	0.01 M
10^{-7}	0.001 M

The relative error E incurred by the use of the simple equation is then given by

$$E = \frac{\text{simple value of } [\mathrm{H}^+] - \text{corrected value of } [\mathrm{H}^+]}{\text{corrected value of } [\mathrm{H}^+]} \quad \ldots\ldots\ldots \quad (3)$$

from which the percentage error is obtained by multiplication by 100.

Substitution of the values from (1) and (2) in (3) gives the master discriminant[1] (4),

$$c_a K_a + c_s K_a(1 + E) - E c_s^2(1 + E) = 0 \quad \ldots\ldots\ldots\ldots \quad (4)$$

Solution of the master discriminant for E[1] gives the results shown in Fig. 2, indicating that the error rises sharply as the ionisation constant K_a increases above 10^{-7} and as the concentration of the buffer solution falls.

For *basic buffers*, the effect is even more pronounced. In this case the simple equation (5) is

$$[\mathrm{H}^+] = \frac{c_s}{c_b} \frac{K_w}{K_b} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Corrected for ionisation of the weak base[3], this becomes

$$[\mathrm{H}^+] = \frac{1}{2c_b K_b}\left[K_w(K_b + c_s) + \left\{K_w^2(K_b + c_s)^2 + 4K_b c_b K_w^2\right\}^{\frac{1}{2}}\right] \quad \ldots\ldots \quad (6)$$

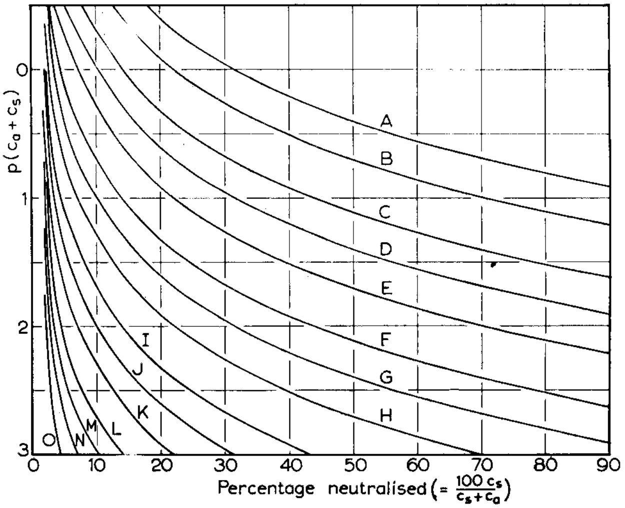

Fig. 3. The relationship between total buffer concentration and degree of neutralisation for given errors and ionisation constants.

Curve A, $K = 10^{-3}$, error = 1%
Curve B, $K = 10^{-3}$, error = 2%
Curve C, $K = 10^{-3}$, error = 5%
Curve D, $K = 10^{-4}$, error = 1%
Curve E, $K = 10^{-4}$, error = 2%
Curve F, $K = 10^{-4}$, error = 5%
Curve G, $K = 10^{-5}$, error = 1%
Curve H, $K = 10^{-5}$, error = 2%
Curve I, $K = 10^{-5}$, error = 5%
Curve J, $K = 10^{-6}$, error = 1%
Curve K, $K = 10^{-6}$, error = 2%
Curve L, $K = 10^{-6}$, error = 5%
Curve M, $K = 10^{-7}$, error = 1%
Curve N, $K = 10^{-7}$, error = 2%
Curve O, $K = 10^{-7}$, error = 5%

and the master discriminant[1] is

$$Ec_s^2 + (1 + E)c_sK_b + (1 + E)^2c_bK_b = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

which on solution for E^1 gives the results included in Fig. 2.

Examination of Fig. 2 shows that quite serious errors can arise through neglect of the ionisation of the weak acid or base. Indeed, if the maximum permissible relative error is E, the simple equations are completely invalid when the ionisation constant of acid or base exceeds Ec_s. In calculating the pH of buffer media, it is therefore necessary to consider whether correction for ionisation of the weak acid or base will make a significant difference, particularly when the ionisation constant exceeds 10^{-7} and the total buffer concentration is less than 0.1 M. This is particularly the case when dealing with media in which the acid concentration exceeds the salt concentration and in the calculations for displacement titrations.

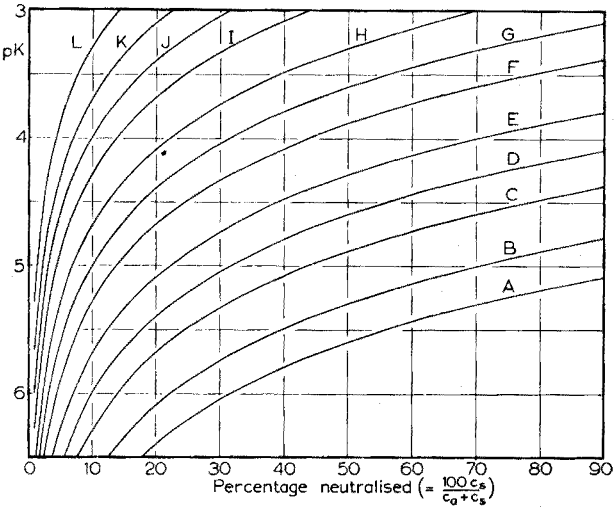

Fig. 4. The relationship between ionisation constant and degree of neutralisation for given errors and buffer concentrations.

Curve A, $c_a + c_s = 0.001$ M, error = 1%
Curve B, $c_a + c_s = 0.001$ M, error = 2%
Curve C, $c_a + c_s = 0.001$ M, error = 5%

Curve D, $c_a + c_s = 0.01$ M, error = 1%
Curve E, $c_a + c_s = 0.01$ M, error = 2%
Curve F, $c_a + c_s = 0.01$ M, error = 5%

Curve G, $c_a + c_s = 0.1$ M, error = 1%
Curve H, $c_a + c_s = 0.1$ M, error = 2%
Curve I, $c_a + c_s = 0.1$ M, error = 5%

Curve J, $c_a + c_s = 1.0$ M, error = 1%
Curve K, $c_a + c_s = 1.0$ M, error = 2%
Curve L, $c_a + c_s = 1.0$ M, error = 5%

To facilitate the assessment of conditions under which such correction becomes necessary, data calculated from particular discriminants[1] derived from the master discriminants (4) and (7) are presented in graphical form in Figs. 3 and 4, in which the degree of neutralisation is related to total buffer concentration for various values of ionisation constant and allowable error, or to ionisation exponent for various total buffer concentrations and allowable errors.

In Fig. 3, the area above a particular curve defines the conditions under which the simple equation (1) is valid. For example, if the total buffer concentration is 0.1 M, and the permissible error is 2%, then if the weak acid has an ionisation constant of 10^{-4} the simple equation is valid when more than 22.5% of the acid has been neutralised (*i.e.* $c_a/c_s \leqslant 3.45$). Similarly, if the ionisation constant is 10^{-5}, the permissible error is 1% and equal amounts of acid and salt are present (*i.e.*, 50% neutralised) then the simple equation is valid if the total buffer concentration exceeds 0.004 M. In Fig. 4, the area below a particular curve defines the conditions under which the simple equation is valid. For example, if equal amounts of acid and salt are present, the total concentration is 0.01 M and the permissible error is 2%, then the

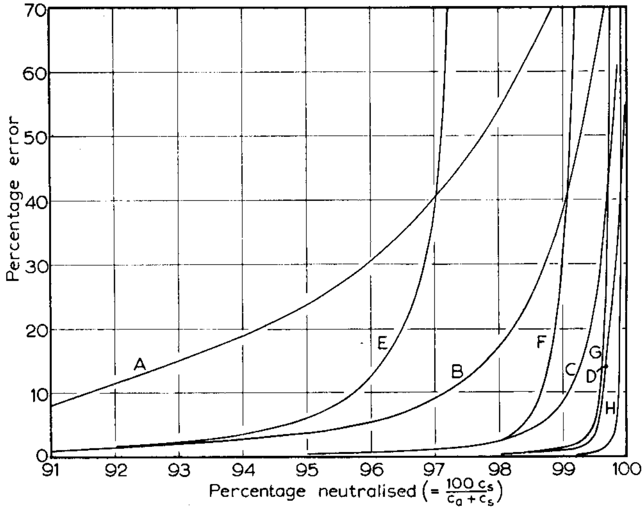

Fig. 5. The error incurred in buffer solution calculations by ignoring the hydrolysis of the salt Curves A to D: acid buffers.

Curve A

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-11}	1.0 M
10^{-10}	0.1 M
10^{-9}	0.01 M
10^{-8}	0.001 M

Curve B

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-10}	1.0 M
10^{-9}	0.1 M
10^{-8}	0.01 M
10^{-7}	0.001 M

Curve C

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-9}	1.0 M
10^{-8}	0.1 M
10^{-7}	0.01 M
10^{-6}	0.001 M

Curve D

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-8}	1.0 M
10^{-7}	0.1 M
10^{-6}	0.01 M
10^{-5}	0.001 M

Curves E to H: basic buffers. Total buffer concentration, $c_s + c_a = 0.1\ M$.

E, $K_b = 10^{-9}$; F, $K_b = 10^{-8}$; G, $K_b = 10^{-7}$; H, $K_b = 10^{-6}$.

Note: In the case of basic buffers, the progression is different from that in the other sets of curves shown. As the buffer concentration falls, the error increases so rapidly that for constants less than 10^{-7}, and buffer concentrations less than 0.1 M, the curves could not be illustrated even on a 0–100 percentage neutralised ordinate. Curves for only a single concentration are therefore given.

simple equation is valid when the ionisation constant of the acid is less than $5 \cdot 10^{-5}$. Similarly, for an acid of ionisation constant 10^{-5}, a total buffer concentration of 0.01 M and an error of 1%, more than 31.5% of the acid must be neutralised before the simple equation becomes valid.

Although the particular discriminants[1] for basic buffers[1] differ from those for acid buffer, the difference is small, and the curves in Figs. 3 and 4 will serve equally well for basic buffers.

Calculation of titration curves

Disturbances due to ionisation of the weak acid or base are important in buffer solution and displacement titration calculations, but unless the ionisation constant exceeds about 10^{-4}, this effect is not important in calculations for ordinary acid-base titrations. In the region of particular interest in the immediate vicinity of the equivalence point, it is the second assumption made in deriving equations (1) and (5) which breaks down, *viz.*, that loss of anions of weak acid or of cations of weak base by hydrolysis is so small that the anion or cation concentration can be written equal to the total salt concentration c_s. In this case, loss of anions in acid buffers can be taken into account[3] by use of the quadratic equation (8) embodying the hydrolysis correction,

$$[\mathrm{H}^+] = \frac{1}{2c_s}\left[\left\{(c_aK_a + K_w)^2 + 4K_aK_wc_s\right\}^{\frac{1}{2}} + (c_aK_a + K_w)\right] \tag{8}$$

By substitution of the values from (1) and (8) in (3), the master discriminant (9) follows,

$$(1 - E)^2c_sK_w + (1 - E)c_aK_w - Ec_a{}^2K_a = 0 \tag{9}$$

solution of which for E^1 gives the results shown in Fig. 5.

In the case of basic buffers, correction for loss of cation by hydrolysis[3] gives,

$$[\mathrm{H}^+] = \frac{1}{2K_b}\left[\left\{(K_bc_b + K_w)^2 + 4K_wK_bc_s\right\}^{\frac{1}{2}} - (K_bc_b + K_w)\right] \tag{10}$$

From (5) and (10), the master discriminant (11) follows,

$$E(1 + E)K_bc_b{}^2 - (1 + E)K_wc_b - c_sK_w = 0 \tag{11}$$

which, on solution for E^1 gives the results included in Fig. 5.

Study of Fig. 5 shows that this effect, though profound in the equivalence point region of titrations, does not extend far into the range of buffer solutions except at high dilution and very low ionisation constants, such as are not common in practice.

CONCLUSIONS

Though equations (1) and (5) indicate that the pH values of buffer solutions are independent of absolute concentration and should not alter on dilution, the effects of ionisation of the weak acid or base and of hydrolysis of the salt are strongly concentration dependent, and where these come into play pH is affected by dilution. Examination of these factors indicates that for best results, buffers should be chosen from acids or bases (better acids to avoid the temperature dependence of basic buffers on K_w) whose ionisation constant lies between 10^{-5} and 10^{-8}, and used at concentrations higher than 0.01 M. When stronger acids or bases are necessarily employed, the concentration should be increased still further. Though the buffering effect as measured by the slope of the pH – neutralisation curve increases with decreasing concentration of the solution (*cf.* Fig. 1), this is considerably offset by increasing sensitivity to dilution and decreasing buffer capacity.

ACKNOWLEDGEMENT

Thanks are due to Dr. W. B. JEPSON for his help in checking the mathematics and confirming the conclusions in this study.

SUMMARY

The limitations of the simple expressions for the hydrogen ion concentration of buffer solutions are examined. The necessity for taking into account the ionisation of the weak acid or base is greater than is generally appreciated, and neglect of this factor can lead to surprisingly large errors which increase rapidly on dilution of the solution. Graphical data are presented to facilitate definition of conditions under which this correction becomes necessary.

RÉSUMÉ

L'auteur examine le cas du calcul de la concentration en ions hydrogène des solutions tampon et montre la nécessité de tenir compte de l'ionisation de l'acide ou de la base faible. Négliger ce facteur peut conduire à des erreurs étonnament grandes, augmentant rapidement avec la dilution.

ZUSAMMENFASSUNG

Der Einfluss der Ionisation schwacher Säuren oder Basen bei der Berechnung der Wasserstoffionenkonzentration in Pufferlösungen wurde untersucht. Es hat sich ergeben, dass die Vernachlässigung dieses Faktors beim Verdünnen der Lösungen zu grossen Fehlern führen kann.

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A NEW SPOT TEST FOR PALLADIUM*

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A new test for palladium is proposed based upon the formation of a stable orange-yellow chelate of palladium(II) with phenyl-α-pyridyl ketoxime[1]. Palladium phenyl-α-pyridyl ketoximate shows maximum light absorption at 410 mμ and the chelate is highly soluble in chloroform. It can be completely extracted in a single pass from the aqueous solution between pH 5 and 11.

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EXPERIMENTAL

Reagent solution

Phenyl-α-pyridyl ketoxime was prepared at this laboratory[1] and a 1% solution of it in 95% ethanol was used as the reagent solution.

Standard palladium solution

The palladium solution was prepared from palladium(II) chloride and was 4 *M* with respect to hydrochloric acid. It was standardized gravimetrically by precipitating palladium with dimethylglyoxime. The solutions for other cations were prepared from their sulfates, nitrate and chlorides.

PROCEDURE

One drop of the weakly acidic or neutral solution is placed into the depression of a white spot plate and is treated with one drop of the reagent solution. When the test solution is strongly acidic, a few drops of 0.5 *M* sodium carbonate solution are added after the addition of the reagent solution. A yellow color indicates the presence of palladium.

Effects of other ions

The following ions do not interfere with the test: Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, NH_4^+, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, Al^{+3}, Ga^{+2}, Ce^{+3}, Ce^{+4}, Tl^+, Ti^{+4}, Zr^{+4}, Sn^{+2}, Pb^{+2}, Th^{+4}, As^{+3}, Cr^{+3}, Sb^{+3}, Bi^{+3}, Mn^{+2}, Fe^{+3}, BO_2^-, $B_4O_7^{-2}$, SiO_3^{-2}, GeO_3^{-2}, NO_2^-, NO_3^-, HPO_4^{-2}, $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2}, SeO_3^{-2}, SeO_4^{-2}, F^-, Cl^-, Br^-, ClO_3^-, ClO_4^-, BrO_3, IO_3^-, MoO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, WO_4^{-2}, VO_2^{+2}, VO_4^{-2}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, CNS^-, acetate, oxalate, malonate, succinate, tartrate, citrate, sulfosalicylate, salicylate and formate.

The other platinum metal ions, CrO_4^{-2}, $Fe(CN)_6^{-3}$, MnO_4^-, interfere with the test due to the color of these ions; Hg_2^{+2} and Hg^{+2} interfere due to the precipitation of the black oxide. These interferences can be eliminated by extracting the palladium chelate with chloroform. Copper(II), Fe^{+2}, Co^{+2}, Ni^{+2} also form colored complexes with the reagent, soluble in chloroform. Their interference is prevented by masking with EDTA (disodium salt). Gold(III) reacts with the reagent to form an orange-yellow chelate[2,3], soluble in chloroform. Interference by gold(III) can be eliminated by reducing the gold with ascorbic acid. Organic masking agents like glycol and mannitol are without adverse effect. Cyanide and pyridine render the test useless and must be destroyed before performing the test.

Detection of palladium in presence of other platinum metals, mercury(I), mercury(II), chromate, permanganate, and ferricyanide ions

One drop of the weakly acidic solution of Pd(II) and other platinum metals is taken into a 5-ml beaker and treated with one drop of the reagent solution and ten drops of water. When the mixture is too acidic, it is neutralized by adding a few drops of 0.5 *M* Na_2CO_3 solution. To the mixture is then added 0.5 to 1 ml of chloroform. The phases are then intimately mixed with an extraction pipet[4] and allowed to separate. The presence of palladium is shown by the yellow color of the chloroform extract.

Detection of palladium in presence of copper(II), iron(II), cobalt(II), nickel(II)

A drop of weakly acidic or neutral test solution is treated in a 5-ml beaker with

10 drops of 0.1 M EDTA solution, one drop of the reagent solution and 0.5 to 1 ml of chloroform. The palladium chelate is extracted, separated and observed as described above.

Detection of palladium in presence of gold

A drop of weakly acidic or neutral test solution is treated with one drop of the reagent solution and 10 drops of water and a few drops of 0.5 M Na_2CO_3 solution. At the mixture is then added a pinch of ascorbic acid and the mixture is warmed. The gold chelate is reduced to the metallic state. The palladium chelate is then extracted from the mixture and observed as described before.

Sensitivity

In aqueous solution: limit of identification = 1 μg and the dilution limit = 1 : 1,000,000.

In chloroform: limit of identification = 0.5 μg dilution limit = 1 : 1,100,000.

ACKNOWLEDGEMENT

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SUMMARY

A new spot test for palladium is based upon the formation of an orange-yellow chelate with phenyl-α-pyridyl ketoxime. Interference by the metals usually associated with palladium can be easily and completely prevented. Limit of identification: 0.5 μg Pd.

RÉSUMÉ

Une nouvelle réaction à la touche est proposée pour l'identification du palladium. Elle est basée sur la formation du chélate jaune orange, obtenu avec la phényl-α-pyridylcétoxime.

ZUSAMMENFASSUNG

Palladium reagiert mit Phenyl-α-pyridylketoxim unter Bildung eines orangegelb gefärbten Chelates. Diese Reaktion kann als Tüpfelprobe für Palladium verwendet werden.

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SEPARATION OF NIOBIUM AND TANTALUM FROM ZIRCONIUM WITH SALICYLHYDROXAMIC ACID

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The determination of niobium or tantalum in the presence of zirconium is difficult, because zirconium almost always coprecipitates. The potassium carbonate fusion method[1] allows the separation of niobium and zirconium within certain limits, but the separation from tantalum is less satisfactory. SCHOELLER's[2,3] pyrosulfate–tannin method proved to be inadequate when a small quantity of zirconium was present with a large amount of earth acids. ALIMARIN AND FRID[4] recommended the use of pyrogallol as a sequestering agent to keep titanium and zirconium in solution and thus to separate them from niobium and tantalum. Salicylhydroxamic acid[5-7] proved effective for the estimation of zirconium[8] at a pH between 2.5 and 6.5; the interference of titanium was avoided by complexation with hydrogen peroxide.

Salicylhydroxamic acid has recently been found to be applicable for the separation and determination of zirconium in presence of niobium, which is not precipitated from sulphuric acid-hydrogen peroxide solution at any pH. The separation of zirconium from tantalum is not satisfactory as tantalum always coprecipitates even when double precipitation is used.

EXPERIMENTAL

The chemicals used were all of reagent grade; pH adjustments were made with the aid of indicator papers.

Standard solutions of niobium and tantalum: A weighed quantity (0.1–0.2 g) of niobium or tantalum pentoxide (Specpure, Johnson and Matthey) was fused in a silica crucible with ten times its weight of potassium bisulfate, extracted with a mixture of 140 ml of water, 50 ml of hydrogen peroxide (20 vol) and 10 ml of conc. sulphuric acid and made up to a definite volume. The niobium or tantalum content was determined in an aliquot by the cupferron method[10] after the removal of hydrogen peroxide by boiling.

A weighed quantity of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) was dissolved in water containing a little hydrochloric acid and made up to a definite volume with water. The zirconium content of the solution was determined in an aliquot as the oxide.

Salicylhydroxamic acid, m.p. 168–170°, was prepared by the procedure of BHADURI[6]. A freshly prepared 1% solution of the reagent in hot water was used as the precipitant.

Procedure

To a solution of niobium and zirconium containing 5% (v/v) sulphuric acid and 5–10% (v/v) of hydrogen peroxide (20 vol) was added an excess of the freshly prepared reagent solution. The pH of the solution was then adjusted to above 2.5 with dilute ammonia. The zirconium precipitate was filtered and washed with a hot solution, containing 1% ammonium nitrate and 0.1% reagent. The precipitate was then ignited and weighed as ZrO_2. For reprecipitation, the ignited oxide was fused with bisulfate, extracted with sulphuric acid–hydrogen peroxide solution, and treated as above. The filtrates and washings were evaporated to about 200 ml. When all the hydrogen peroxide had decomposed, the niobium was determined either by the N-benzoyl-N-phenylhydroxylamine method[9] or by the cupferron method[10]. For the separation from tantalum the same procedure was followed.

The data in Table I indicate that the separation of zirconium from niobium is satisfactory and that the method can be conveniently applied for the analysis of zirconium–niobium alloys. In the presence of tantalum the zirconium values always have a positive error of 1–3 mg. Even redissolution and reprecipitation fail to give correct results.

TABLE I

Taken mg			*Found mg*		
ZrO_2	Nb_2O_5	Ta_2O_5	ZrO_2	Nb_2O_5	Ta_2O_5
36.0[a]	10.8[a]	—	36.0[a]	10.6[a]	—
72.0[b]	10.8[b]	—	72.3[b]	10.6[b]	—
180.0[b]	10.8[b]	—	180.6[b]	10.5[b]	—
36.0[a]	27.0[a]	—	35.7[a]	27.2[a]	—
9.0[b]	108.0[b]	—	9.4[b]	107.9[b]	—
9.0[b]	236.0[b]	—	9.3[b]	235.2[b]	—
12.0[b]	—	12.0[b]	13.4[b]	—	10.8[b]
36.0[b]	—	12.0[b]	38.1[b]	—	9.9[b]
12.0[b]	—	145.8[b]	14.8[b]	—	142.8[b]

[a] single precipitation. [b] double precipitation.

SUMMARY

Salicylhydroxamic acid can be used for the separation of zirconium from niobium above pH 2.5 in presence of hydrogen peroxide. Niobium can be precipitated from the filtrate with N-benzoyl-N-phenylhydroxylamine.

RÉSUMÉ

L'acide salicylhydroxamique est proposé comme réactif pour la séparation du zirconium d'avec le niobium. Ce dernier peut être ensuite précipité dans le filtrat par la N-benzoyl-N-phénylhydroxylamine.

ZUSAMMENFASSUNG

Salicylhydroxamsäure lässt sich zur Trennung des Zirkons von Niob verwenden. In dem Filtrat kann Niob mit N-Benzoyl-N-Phenylhydroxylamin gefällt werden.

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THE QUANTITATIVE ANALYSIS OF MIXTURES OF CORROSIVE HALOGEN GASES BY GAS–LIQUID CHROMATOGRAPHY

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INTRODUCTION

Many processes in the atomic energy industry involve volatile corrosive fluorides and their degradation products. A knowledge of the precise chemical form and the amount of each component present in a process gas stream is necessary for efficient plant control. This requirement has led to studies of non-destructive analytical techniques, with the aim of providing an on-line analyser for corrosive gas mixtures containing halogen fluorides and hydrogen fluoride.

ALLEN AND ELLIS[1] concluded that the method of fractional distillation was inapplicable to the problem, because hydrogen fluoride formed azeotropic mixtures with other halogen compounds, *e.g.* chlorine trifluoride and bromine pentafluoride. HAMER, LEECE AND BENTLEY[2] found that nuclear magnetic resonance spectrometry could not be applied to the problem, because halogen exchanges between components in a mixture caused collapse of spectra. Some success was obtained with corrosive gas mass spectrometry (BENTLEY, HAMER AND EVANS[3]) but is was concluded that the method could not be made adaptable for the rapid handling of large numbers of samples.

The first separations of halogen fluorides by gas–liquid chromatography were reported by ELLIS AND IVESON[4]. Since these separations were achieved, the work has been considerably extended and the potentialities and limitations of the technique have been more precisely defined.

EXPERIMENTAL

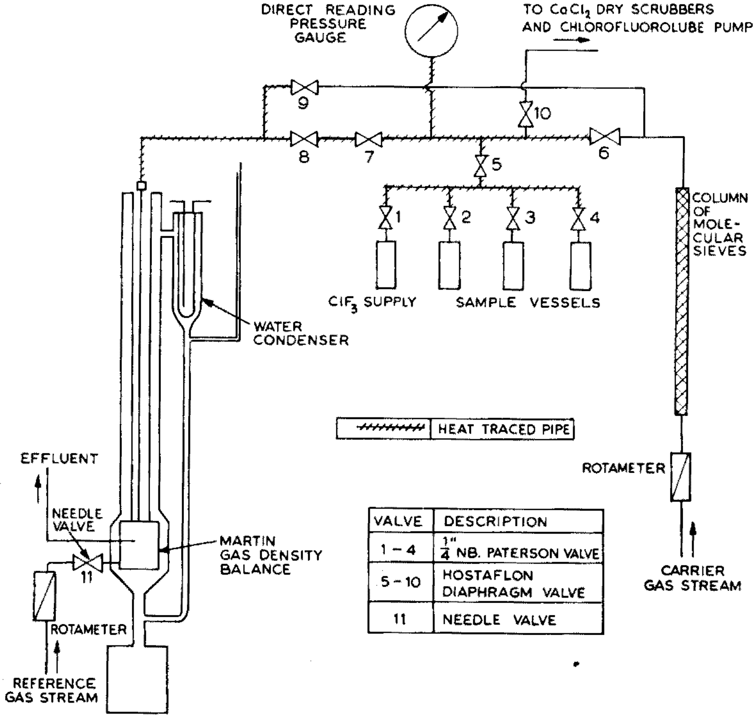
Design of apparatus

Static corrosion tests with chlorine trifluoride and hydrogen fluoride showed that the only suitable major constructional materials for the quantitative handling of corrosive halogen gases up to 60° were nickel, Monel, polytetrafluoroethylene (P.T.F.E., Fluon) and polytrifluoromonochloroethylene (Hostaflon, Kel-F).

A line diagram of the present apparatus is given in Fig. 1. The apparatus is best considered as three parts, *viz.* sample introduction system, column and detector.

Sample introduction system

All pipework in this system was of ¼ in. internal diameter nickel tubing, and all joints were either welded or brazed. Two types of valve were used. Paterson ¼ in. nominal bore chlorine valves (Paterson Eng. Co., London) were found suitable for the sample bottle manifold. At first, these were internally nickel-plated before use, but subsequent tests showed that no significant errors were introduced by using the standard commercial items with an aluminium-bronze body. For isolation of the sample volume and the remainder of the vacuum system, ⅛ in. nominal bore diaphragm valves were used. These had bodies and plugs machined from nickel, nickel-plated return springs, and diaphragms made from 1/16 in thick Hostaflon sheet. For pressure measurement a nickel diaphragm pressure transmitter was first employed, but it was found that no significant error was introduced when this was replaced by a direct-reading beryllium–copper capsule pressure gauge (0–1000 mm, Appleby & Ireland Ltd., Basingstoke) piped up to the rest of the equipment with nickel tubing. Heat tracing was extensively used in the sampling system, pipework so traced being held at 50° to enable easy manipulation *in vacuo* of uranium hexafluoride.



VALVE	DESCRIPTION
1 – 4	1/4" NB. PATERSON VALVE
5 – 10	HOSTAFLON DIAPHRAGM VALVE
11	NEEDLE VALVE

Fig. 1. Line diagram of apparatus.

Gas chromatography column

Gas–liquid chromatography columns are packed with a support phase on which a non-volatile liquid is evenly dispersed. A survey of column packing materials revealed that only polytetrafluoroethylene and polytrifluoromonochloroethylene could act as supporting solids, and Kel-F polymer oils [$(C_2ClF_3)_n$, Kellogg Corp., Jersey City, U.S.A.] were the only suitable liquids. All other materials tested reacted with the gases which were to be analysed.

Two columns were used in this work, 4ft. 6 in. and 11ft. 6 in. long, respectively, the latter being in three straight sections. The packing normally used was a 50% w/w loading of Kel-F grade '10' oil on ground Fluon powder sieved to 30–60 B.S. mesh.

Detector

The detector used in this work was a Martin gas density balance (*cf.* MARTIN AND JAMES[5,6]) which has the primary virtue of a sensing element which is never in contact with gas being analysed. It has also been shown[4] that a katharometer made from corrosion-resistant materials can be used for corrosive-gas detection. The density balance was constructed specially for this study by Dr. A. J. P. MARTIN, and differed from the model described in the literature[6] in that the drillings in the block were simulated by a skeleton of welded Monel tubing which was subsequently cast into a block of copper. Current was supplied to the anemometer heater of the density balance by a suitable bridge circuit in which a barreter (Ediswan type B.U. 280/20) operated at 2.8 A but gave a fixed heater current of 1.65 A. The output of the double thermocouple in the anemometer was led directly to a Honeywell-Brown high-speed electronic recorder with two available scales of 0–100 μV and 0–1 mV. The whole of the column and detector assembly was housed in a lagged jacket which was heated with the vapour of 1-chloro-2,2-dichlorotrifluoroethane (b.p. 48°). The need for a dummy column for the reference side of the density balance was eliminated by using a needle valve linked to a short coil of Monel pipe housed within the vapour jacket.

ANALYTICAL PROCEDURE

Carrier gas

In this work argon was normally used as carrier gas. Nitrogen was found to be satisfactory for compounds other than hydrogen fluoride. The small difference in molecular weight between nitrogen and hydrogen fluoride reduced the sensitivity of the density balance to hydrogen fluoride to about half that when argon is used. Helium was not a satisfactory carrier gas, the greater difference in molecular weight between carrier gas and eluted components being much more than offset by the reduced sensitivity of the anemometer, arising from the high thermal conductivity of helium (*cf.* MARTIN AND JAMES[6]).

Before it entered the sampling system the argon was freed from water by passing through a column 5 ft. long and 0.5 in. internal diameter, filled with Linde type 4A molecular sieves which had been activated by heating to 300° *in vacuo* for one hour. Copper pipework was used throughout the argon supply system, and suitably calibrated rotameters were used for flow measurement.

Introduction of sample

A sample of gas is introduced into the sample volume (enclosed by valves 7 and 8 on Fig. 1) from one of the vessels on the supply manifold by suitable vacuum operations. The pressure is recorded, the sample volume isolated and surplus gas is exhausted by the chlorofluorolube-filled scavenge unit which is protected by dry scrubbers containing calcium chloride. Appropriate valve operations then enable the sample to be swept into the column. Free space between the top of the column and the sampling system was packed with dry solid phase to eliminate diffusion effects, following MARTIN[7].

RESULTS

Retention times for two typical columns are given in Table I. A recorder chart speed of 2 in./min was used in compiling elution curves. The pressure drop across column A was 50 mm Hg and 140 mm Hg across column B.

The theoretical plate efficiencies of these two columns A and B to chlorine trifluoride (after KEULEMANS[8]) were approximately 100 and 220, respectively. The feasibility of analysing mixtures of many volatile inorganic fluorides by the gas chromatographic technique is immediately seen. It is also seen that certain fluorocarbon derivatives can be separated from certain corrosive gases.

Typical calibration curves for the response of the detector based on peak height measurements for various amounts of gas are given in Figs. 2 and 3. In general the more linear over-all calibrations are given by non-polar materials. Hydrogen fluoride, which appears as a negative peak (as its molecular weight is less than that of the carrier gas, argon) is the least sensitive to detection and gives the most unsymmetrical elution curves, with pronounced tailing. Peak height sensitivities for components eluted from the longer column are lower because the elution curves are all broader.

TABLE I

Compound	*Retention time (minutes) for elution peak maximum*	
	A *4ft. 6 in. column with argon rate 16.5 cm³/min*	*B* *11ft. 6 in. column with argon rate 27.5 cm³/min*
Nitrogen	1.2	2.0
Chlorine monofluoride	1.4	2.7
Hydrogen fluoride	1.7	3.4
Chlorine	2.0	5.7
Chlorine trifluoride	2.8	8.3
Uranium hexafluoride	10.5	37.5
Bromine	4.55	Not determined
Bromine pentafluoride	6.1	Not determined
Perfluoromethylcyclohexane	11.5	Not determined
Chloroundecafluorocyclohexane	17.0	Not determined

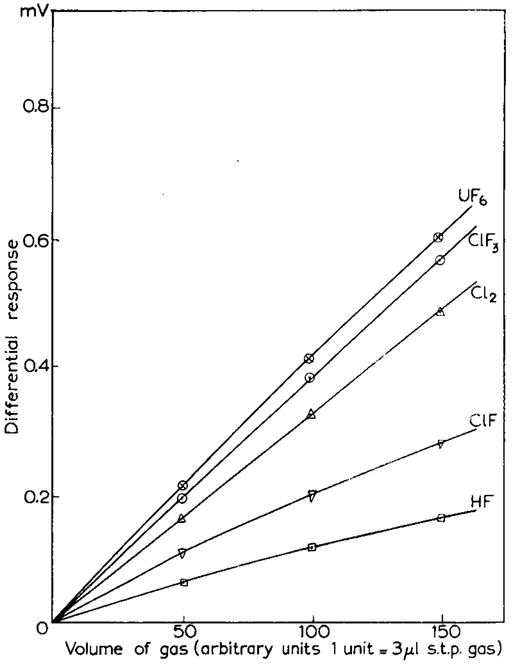


Fig. 2. Calibration curves (4ft. 6 in. column).

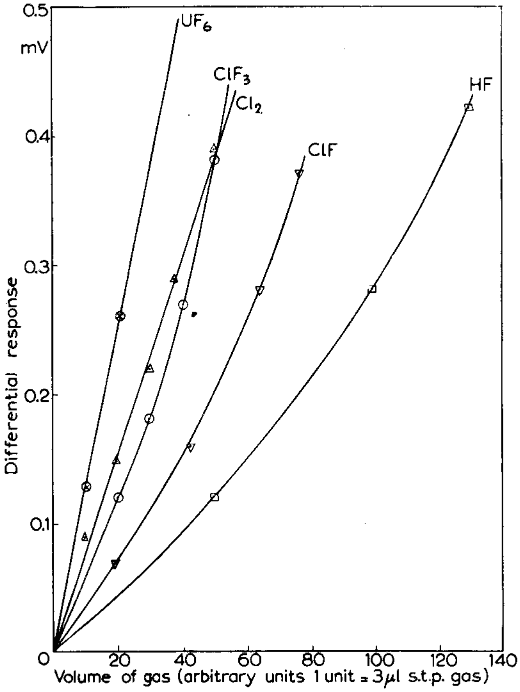


Fig. 3. Calibration curves (11ft. 6 in. column).

Using the 4ft. 6 in. column and the 100-μV scale on the recorder, the minimum reliable level of detection of chlorine trifluoride was found to be approximately 10 μl of s.t.p. gas. This gives rise to a signal of 12 μV measured on elution peak height to an accuracy of about ± 25%. For hydrogen fluoride the minimum reliable detection level was 30 μl of s.t.p. gas, giving a signal of 7 μV peak height to an accuracy of about ± 25%. Three sources contribute to inaccuracies in detection and measurement of these very small quantities of corrosive gases, namely:

a. The minute changes in input potential fed to the recorder,
b. Sluggishness of recorder response,
c. Measurement of low pressures of reactive gases.

For normal analytical work, when 150 μl of s.t.p. gas of chlorine, chlorine monofluoride, chlorine trifluoride or uranium hexafluoride are present in any gas mixture sample, the amount present can be measured to within 1% of the determined value. For hydrogen fluoride, 150-μl samples can be determined within an accuracy limitation of ± 5% of determined value. Accuracies ± 1% with hydrogen fluoride can only be achieved with quantities exceeding 500 μl.

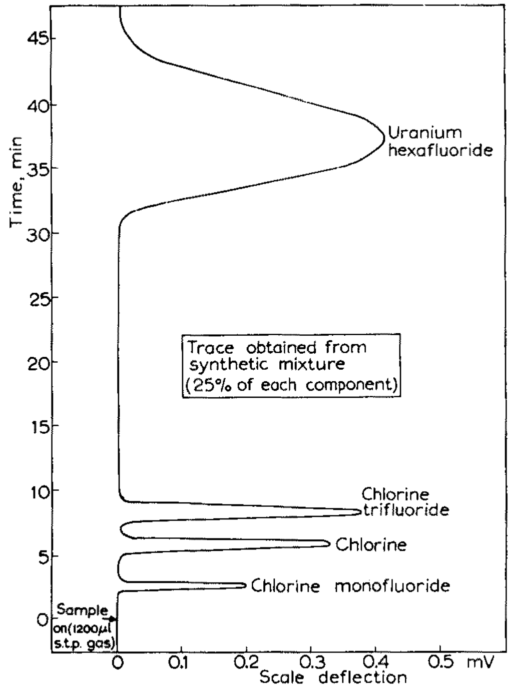


Fig. 4. Specimen trace using 11ft. 6 in. column.

The validity of results of gas chromatographic analysis of corrosive gases has been extensively checked with synthetic gas mixtures. Some of these analyses using the 4ft. 6 in. column were reported by ELLIS AND IVESON[4]. A typical set of analyses using 1200-μl samples on the 11ft. 6 in. column is given in Table II. A chromatogram from one of these is reproduced in Fig. 4.

The reproducibility of analyses of very small samples of mixtures of corrosive gases is given in Table III. Repeated samples (120 μl of s.t.p. gas) of a synthetic gas mixture were analysed by the standard technique using the 4ft. 6 in. column. The volume composition of the mixture was ClF 5%, HF 57.5%, ClF_3 27.5% and UF_6 10%.

These analyses all fall within the specific limitations of accuracy quoted in previous paragraphs.

TABLE II

REPRODUCIBILITY AND VALIDITY OF ANALYSES OF SYNTHETIC MIXTURES

	Percentage by volume							
Sample	ClF		Cl_2		ClF_3		UF_6	
	Synthetic	Found	Synthetic	Found	Synthetic	Found	Synthetic	Found
1	25	25.0	25	25.2	25	24.9	25	24.9
		25.0		25.0		24.8		25.2
2	10	10.0	30	30.2	40	40.0	20	19.8
		10.0		30.1		40.0		19.9
3	15	15.0	35	34.9	40	40.0	10	10.1
		15.1		34.8		40.2		9.9

TABLE III

REPRODUCIBILITY OF ANALYSES OF VERY SMALL SAMPLES

Sample	ClF		HF		ClF_3		UF_6	
	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)
1	7	5	11	60	38	30	9	9
2	10	8	12	66	42	33	12	12
3	7	5	12	66	42	33	9	9
4	8	6	13	72	42	33	12	12

Operation of gas chromatography unit at 24°

Table I shows that the retention times on column A of ClF, HF, Cl_2 and ClF_3 at 48° are quite close together. Tests were made at 24° with the vapour jacket of the column heated with the vapour of monofluorotrichloromethane. There was, however, virtually no change in retention time for the first three of the compounds mentioned. The retention times for ClF_3 and UF_6 increased from 2.8 to 3.1 min and 10.5 to 18.5 min, respectively. Very little is therefore to be gained by lowering the operating temperature from 48° to 24° for the particular mixtures being considered.

DISCUSSION AND CONCLUSIONS

The practical results outlined here show that gas–liquid chromatography is a satisfactory and reliable method for the analysis of highly reactive corrosive volatile halogen compounds. The Martin gas-density balance has been shown to be a suitable detector for work in this field. The principal limitation in the development of the technique for analysis of corrosive inorganic gases lies in the reactivity of the materials being analysed. The only materials which can be used as chromatographic stationary phases and supporting media without reaction with the gases being examined give rise to column packings of very low efficiency, *viz.* 20–30 theoretical plates per foot compared with 3000 theoretical plates per foot obtained by SCOTT[9] for hydrocarbon separations on packed columns.

The technique is potentially applicable to any mixture of volatile inorganic compounds and is being used both for routine analysis of process-gas streams and as a research tool in the laboratory for the investigation of the gaseous products of inorganic chemical reactions.

ACKNOWLEDGEMENT

This paper is published by permission of Sir WILLIAM COOK, Managing Director, and Dr. H. KRONBERGER, Director of Research and Development, of the U.K.A.E.A. (Development and Engineering Group).

SUMMARY

The feasibility of separating many volatile corrosive halogen compounds by gas–liquid chromatography has been demonstrated. The potentialities and limitations of the method when applied to analyses of mixtures containing uranium hexafluoride, chlorine, chlorine monofluoride, chlorine trifluoride and hydrogen fluoride are detailed. The technique appears to be applicable for use generally in process-gas analysis and in the laboratory to research studies on inorganic reactions.

RÉSUMÉ

Les auteurs proposent une méthode par chromatographie gaz–liquide pour l'analyse quantitative de mélanges de composés halogénés volatils et corrosifs. Cette technique pourrait être appliquée à l'analyse de divers mélanges de composés inorganiques volatils et pour l'examen de produits gazeux formés au cours de réactions en chimie minérale.

ZUSAMMENFASSUNG

Es wird gezeigt, dass sich die gas–flüssig Phasenchromatographie zur Trennung vieler flüchtiger, korrosiver Halogenverbindungen verwenden lässt. Die Anwendung zur Analyse von Mischungen, die Halogenfluoride und Fluorwasserstoff enthalten, wird ausführlich beschrieben. Es wird auf weitere Anwendungsmöglichkeiten hingewiesen.

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THERMOLYSIS OF SULPHIDES PRECIPITATED BY SODIUM SULPHIDE

I. SULPHIDES OF ARSENIC, MERCURY, RHENIUM, ANTIMONY AND MOLYBDENUM

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The use of sodium sulphide as a reagent for precipitating and determing sulphides in gravimetric analysis has been dealt with in a series of papers from this laboratory. Previously, many elements which were precipitated as sulphides had to be weighed in other forms because a homogenous precipitate could not be obtained. The use of sodium sulphide, however, enabled these elements not only to be precipitated as sulphide but also to be weighed in this form. The weights of the sulphides obtained corresponded in most cases to the usual formulae. A systematic study by thermolysis of all the sulphides precipitated by sodium sulphide in gravimetric analysis is desirable in order to obtain fuller information about the behaviour of the precipitates and the correct conditions for weighing.

It has been pointed out[1] that if the sodium sulphide reagent is prepared below 5° there is no appreciable oxidation of the reagent and the precipitates obtained are largely free from sulphur. The thermolysis of such precipitates may therefore give different results from those obtained with sulphides precipitated by other methods. Precipitates which are free from sulphur may be expected to begin to lose weight at a higher temperature than those contaminated with sulphur and this has actually been found in some cases in the present investigation.

EXPERIMENTAL

The reagents used and the methods followed in preparing the precipitates were the same as reported in earlier papers dealing with the estimations of the metals as sulphides. The precipitates taken for thermolysis were in exactly the same condition as the corresponding precipitates just before they are weighed in the estimations of the sulphides.

The thermobalance used was the standard Stanton thermobalance. It was not possible to attain true programme control below 120°. To obtain a linear rate of heating with time automatically the high/low switches were preset, high at 2, low at 1, because the maximum temperature used for the observation was 800°. The rate of heating was 5.3 ± 0.2° per min. As the slope altered abruptly at the change-over point it was necessary to start the cam motor 8–9 min after the furnace was switched on. The thermograms shown in this paper were obtained by plotting different points of the original graph on X and Y axes.

Arsenic pentasulphide. The oven-dried arsenic pentasulphide[2] gave a horizontal level up to 270°. Above this temperature, it began to sublime and at 550° the crucible was empty except for a trace of residue which did not change in weight.

Mercuric sulphide. The oven-dried sample of mercuric sulphide[3] gave a horizontal up to 300°. Dissociation then began from 300–310° and at 500°, the crucible was empty.

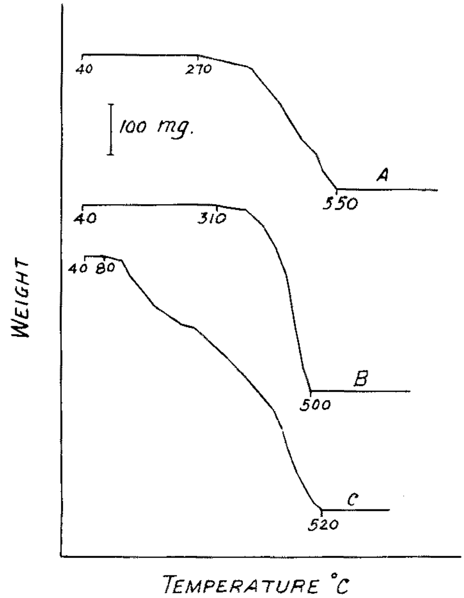

Fig. 1. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent. A. Arsenic pentasulphide, B. Mercuric sulphide, C. Rhenium heptasulphide.

Rhenium heptasulphide. Air-dried rhenium heptasulphide[3] started to lose weight at 80–90° and at 520° the crucible was empty.

Antimony trisulphide. Oven-dried antimony trisulphide[4] gave a horizontal up to 310°. On further heating it oxidized to Sb_2O_3; complete conversion to Sb_2O_3 was indicated by the horizontal at 530–580°. From 580–610° there was a gain in weight corresponding to the conversion of Sb_2O_3 to Sb_2O_4. The horizontal level after 610° corresponded to Sb_2O_4.

Antimony pentasulphide. An oven-dried sample of Sb_2S_5[5] lost weight continuously between 190° and 410°. From 410–570° there was a horizontal corresponding nearly to Sb_2O_4. From 570° there was again a slight loss and the horizontal from 590° onwards corresponded to Sb_2O_4.

Molybdenum trisulphide ($MoS_3 \cdot 2H_2O$). Air-dried molybdenum trisulphide[6] lost 1–2% of its weight at about 80°. There was then a horizontal level up to 170°. From 170°

to 290° the loss in weight corresponded to two molecules of water. From 290–390° the horizontal level corresponded to the anhydrous sulphide. A rapid loss occurred between 390° and 430° after which a horizontal level corresponded to MoO_3 which begins to volatilize at 800°.

In the case of As_2S_5, HgS and Re_2S_7, the precipitate sublimed at a particular temperature while in the case of Sb_2S_3, Sb_2S_5 and $MoS_3{\cdot}2H_2O$ it was converted to another compound which was stable up to 800°. The weights calculated and those actually obtained on heating the last three compounds are given in the following table. The divergence of the actual weights of MoS_3 and MoO_3 from the calculated weights is greater than in the case of antimony.

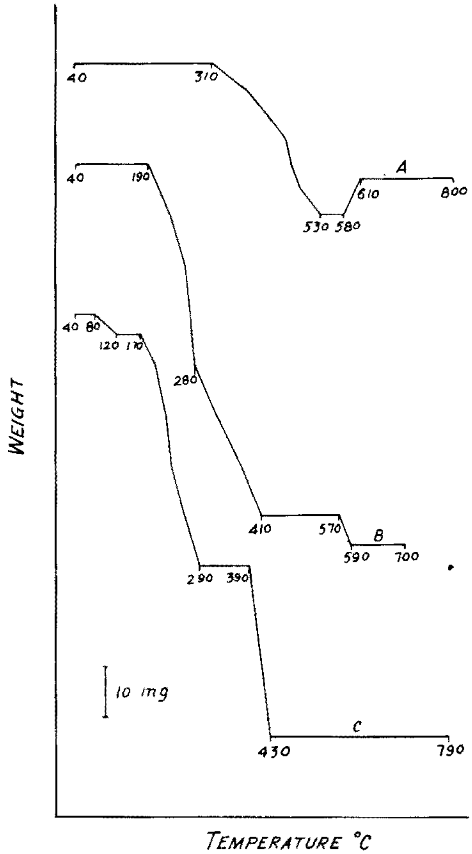

Fig. 2. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent. A. Antimony trisulphide, B. Antimony pentasulphide, C. Molybdenum trisulphide ($MoS_3{\cdot}2H_2O$).

TABLE I

Weight of Sb_2S_3 taken	*Weight of Sb_2O_3 calculated (530–580°)*	*Weight of Sb_2O_3 from graph (530–580°)*	*Weight of Sb_2O_4 calculated (610–800°)*	*Weight of Sb_2O_4 from graph (610–800°)*
258 mg	221 mg	227 mg	233 mg	236 mg
221 mg	190 mg	197 mg	200 mg	202 mg

Weight of Sb_2S_5 taken	*Weight of Sb_2O_4 calculated (590–800°)*	*Weight of Sb_2O_4 from graph (590–800°)*
331 mg	251 mg	256 mg
425 mg	323 mg	324 mg

Weight of $MoS_3 \cdot 2H_2O$ taken	*Weight of MoS_3 calculated (290–390°)*	*Weight of MoS_3 from graph (290–300°)*	*Weight of MoO_3 calculated (430–790°)*	*Weight of MoO_3 from graph (430–790°)*
267 mg	224 mg	217 mg	168 mg	183 mg
266 mg	223 mg	214 mg	168 mg	180 mg

SUMMARY

Thermolysis of the sulphides precipitated by sodium sulphide for direct determination in gravimetric analysis has been studied. It has been shown that the methods used for drying and weighing the precipitated sulphides of arsenic, mercury, rhenium, antimony and molybdenum are reliable.

RÉSUMÉ

Les auteurs ont entrepris une étude de la thermolyse des sulfures précipités par le sulfure de sodium; on a pu ainsi vérifier que les conditions de séchage et de pesée des sulfures d'arsenic, de mercure, de rhénium, d'antimoine et de molybdène convenaient à leur dosage gravimétrique.

ZUSAMMENFASSUNG

Durch Thermolyse der mit Natriumsulfid gefällten Sulfide konnte gezeigt werden, dass die üblichen Methoden der Trocknung und Wägung der Sulfide von Arsen, Quecksilber, Rhenium, Antimon und Molybdän keine Fehlresultate verursachen.

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ELECTROSTATIC METHODS OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

V. A CHROMATOGRAPH HUMIDISER

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(Received June 26th, 1959)

The 'humidiser' or chromatograph conditioner described in this paper was designed for use in conjunction with BLAKE's automatic zone locator as used to underline each conductive spot as the chromatograph travels across the electrodes[1]. Its employment makes it possible to locate and underline spots which are only very slightly conductive or which contain weakly conductive solutes*.

The 'humidiser' can be used in conjunction with either Rectified Radio-frequency (R.Rf.) or Electrostatic Discharge (Es.D.) methods of zone location.

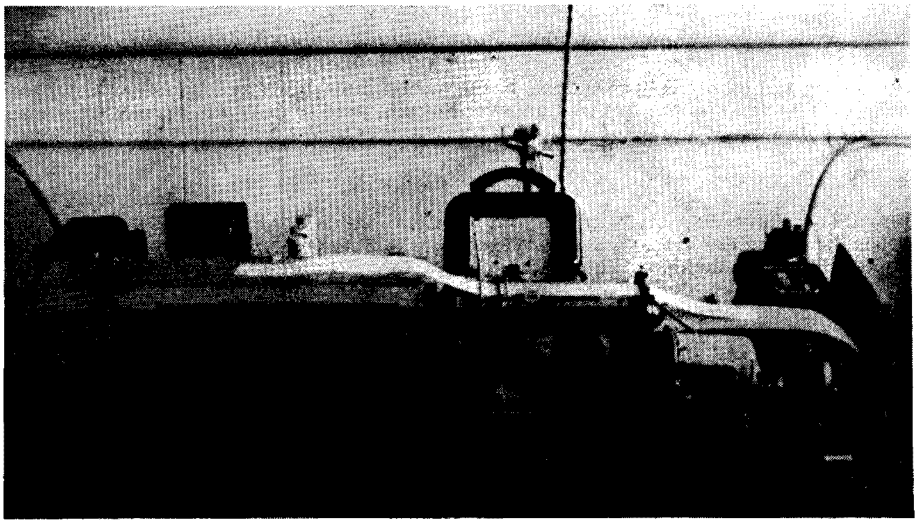

Fig 1. BLAKE's automatic chromatograph zone locator. (The humidiser is seen standing on two wooden blocks to the left of the picture).

Fig. 1 is a photograph of the underlining apparatus[1]. The operational current is supplied from a power pack seen in the background on the left. In the centre there is a relay which controls the magnet (in the centre also). The latter causes a pencil attached to the free end of the magnet's armature to mark the underside of the

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* No staining is required and it is not necessary for the spots to be visible.

chromatograph as it is drawn across by means of the small electric motor on the right of the photograph.

This automatic apparatus worked quite reliably in the rather damp laboratory situated in the basement of the old chemistry building, however when it was moved to an air-conditioned laboratory in the new chemistry building the atmosphere was often too dry, and on those occasions it was found necessary to condition the chromatographs by passing them through steam or enclosing them in a humidor immediately before commencing zone location[1,2].

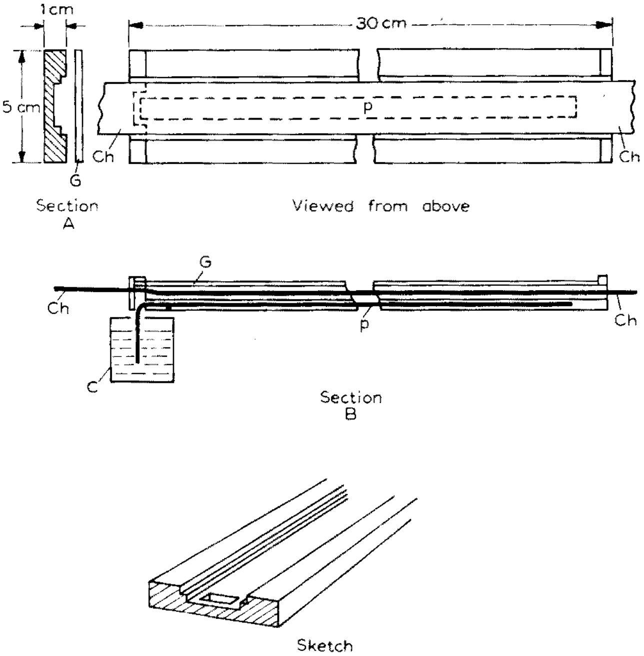

Fig. 2. This is a diagram showing the construction of the "humidiser" made of polystyrene and grooved as indicated. The water container is seen under it on the left.

Realising that a better method was needed the writer devised the "humidiser" described in this paper. This keeps the chromatograph sufficiently moist, and renders automatic zone location reliable under all the varying atmospheric conditions.

The humidiser is attached to the top of the zone locator and as close to the electrodes as possible. It consists of a strip of polystyrene, groved as indicated in Fig. 2. Section 'A'. In the centre of the figure Section 'B' there is a container 'C' filled with water, into which dips the end of a narrow strip of wet filterpaper 'P'. This lies along the bottom of the deepest groove.

The chromatograph 'Ch' rests comfortably across the upper groove and is thus prevented from touching the wet paper below it; above the chromatograph is placed a removable sheet of glass which seals the chamber.

Evaporation from the wet paper is sufficiently rapid to allow the chromatograph to be pulled through the humidiser for zone location only a few seconds after it has been placed therein. The humidiser can be employed also in conjunction with BLAKE's R.Rf. zone localizer when that instrument is required only for locating the zones, before they are excised and their content is dissolved[3].

While testing the possibilities of using the humidiser for R.Rf. work the following phenomenon was observed.

The spot edge effect

The needle of a 60–0–60 micro-ammeter was set by zero-shunt at 0 for the clean portions of a strip of filter-paper which was spotted with N cobalt chloride. The strip was unconditioned* and the atmospheric humidity at the time was 66%.

When the spot was passed across the electrodes it was noticed that the zero reading for the paper extended right up the edge of the spot, at both front and back edges of the latter, and at that point the meter deflections (at both edges) read 1.5 μA.

The strip was then placed in the humidiser for 2.5 min; this increased the meter reading (on both edges of the spot) to 13 μA. It was observed that the zero position had shifted very slightly towards the negative side of the 0 in the scale of the meter.

After a further 5 min exposure to moisture in the humidiser the zero had shifted back further to —1 μA, and the meter reading for the spot had increased to 37 μA.

After a further 20 min in the humidiser the zero had shifted back to —3 μA, and the meter reading for the spot edges had increased to 90 μA.

From these observations it would appear that the spot being more hygroscopic than the filter-paper absorbed moisture more rapidly. Not only did it obtain water from the atmosphere but it also robbed moisture from the paper in its vicinity, suggesting a steady influx of moisture all round the spot. This phenomenon may provide a satisfactory explanation for the slight irregularity of the base line on solute distribution by current graphs.

SUMMARY

This paper describes a "humidiser" or conditioner employed to sensitise chromatographic spots of weakly conductive solute. It may be used with BLAKE's R.Rf. or his Es.D. methods. Special reference is made to its use in conjunction with automatic zone location. A photograph of this apparatus is reproduced. 'The spot edge effect' is recorded. (A phenomenon observed during spot localization).

RÉSUMÉ

L'auteur décrit un dispositif „humidificateur" permettant de sensibiliser les spots chromatographiques de solutes peu conducteurs. Il peut être utilisé conjointement avec l'appareil automatique de localisation des zones.

ZUSAMMENFASSUNG

Es wird eine als „Humidiser" bezeichnete Einrichtung beschrieben, die erlaubt, Flecken von schlecht leitenden Substanzen besser zu lokalisieren. Die Vorrichtung kann in Verbindung mit einem Apparat zur automatischen Festlegung der Zonen verwendet werden.

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* "Unconditioned" implies that the spot had been allowed to dry in the air over night, and was passed through the localizer just as it was.

RÉACTIONS COLORÉES DE STÉROÏDES

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(Reçu le 27 mai 1959)

Les réactions colorées des substances stéroïdiques sont fort nombreuses. Quoique de très légères modifications (fonctionnelles ou spatiales) du noyau stéroïdique puissent influencer sensiblement le comportement réactionnel des composés envisagés, ceux-ci demeurent difficiles à caractériser par des moyens simples et rapides quand il s'agit de produits proches parents. Nous proposons ici quelques réactions colorées de certaines substances qui présentent (dans un squelette relativement important) de faibles modifications structurales.

PARTIE EXPÉRIMENTALE

Réactions sulfuriques

L'action de l'acide sulfurique seul est généralement négligeable, cependant on observe quelques colorations et surtout le développement de fluorescences. Si l'addition d'acide acétique à l'acide sulfurique modifie parfois la réaction, c'est cependant l'addition d'un oxydant qui s'avère surtout favorable.

Les réactions que nous avons décrites antérieurement pour les A^+ ont été reprises pour les stéroïdes et les résultats obtenus ont été consignés dans le Tableau I.

Il ressort de ce tableau que ce sont surtout les dérivés hydroxy-3,Δ5 qui réagissent avec les divers oxydants. La méthyltestostérone pourtant s'avère positive alors que la testostérone fournit une réaction négative.

Parmi les oxydants, il faut surtout signaler l'acide periodique, le sélénite, le perborate et le persulfate. Une mention spéciale revient au molybdate qui, en présence d'acide acétique, réagit avec de nombreux stéroïdes.

Réactions molybdiques

Si l'on utilise un réactif acétique d'acide molybdique (contenant un peu d'acide sulfurique), on constate qu'on obtient des réactions positives avec un grand nombre d'hormones, de stéroïdes et de façon générale de substances à noyau phénanthrénique. Toutefois la cinétique de la réaction diffère; les dérivés non saturés réagissent plus rapidement et plus facilement. La position d'une ou de plusieurs doubles liaisons (parfois de la fonction OH) paraît fréquemment influencer le développement de la coloration. L'action de la chaleur amenuise les écarts et on obtient dès lors des résultats similaires pour des substances de nature différente. (Tableau II)

L'ergostérol (doubles liaisons) réagit donc aisément. Une mention spéciale revient à l'acide abiétique*. La réaction est fortement positive avec le réactif molybdique.

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* La réaction est fournie par l'acide abiétique mais reste négative avec l'acide déhydroabiétique (éther méthylique). Nous remercions le Prof. Dr. SANDERMANN, du Bundesforschungsanstalt für Forst u. Holzwirtschaft (Reinbek/Hamburg) pour l'envoi de ces 2 échantillons.

TABLEAU I

Stéroïdes	*Ac. sulfurique + ac. acétique*[a]		*chlorure de fer (III)*[a]	*sélénite de sodium*	*ac. periodique*	*perborate de sodium*	*sulfate de cerium (IV)*	*persulfate de sodium*	*molybdate de sodium*
	(a)	*(b)*							
cortisone acétate			—	—	—	—	—		bleu
prégnènolone			rouge	rouge					bleu
prednisolone		c	trace rouge	—	—	—	—		bleu
prednisone			—	—	—	—	—		bleu
progestérone			—	—	—	—	—		bleu
hydrocortisone acétate			—	—	—	—	—	—	bleu
folliculine			—	brun	—	brun	—	—	bleu
dipronionate de méthylandrostènediol	trace violet	brun	bleu- violet	rouge violet	violet	violet intense	trace violet	violet	bleu
méthylandrostènediol	trace violet	brun	bleu violet	rouge violet	violet	violet intense	trace violet	violet	bleu
désoxycorticostérone acétate	jaune	vert	—	—	—	—	—	—	bleu
monobenzoate d'oestradiol	vert	brun	—	vert	—	—	—	—	—
méthyltestostérone	vert	brun	—	rouge	rouge	rouge	trace rouge	—	bleu
testostérone propionate	—	trace brun	—	—	—	—	—	—	bleu
testostérone			—[b]		—	—	—	—	

(a) = réaction annulaire. (b) = après mélange des solutions.

[a] Colonne 2 et suivantes ont trait à des réactions annulaires.

[b] Après 24 heures, belle coloration verte de tout le mélange et bande spectroscopique.

[c] La prednisolone peut être déterminée en présence de prednisone. Le produit dissous dans l'acide acétique (contenant 15% d'acide sulfurique en volume) développe à chaud (sans addition d'oxydant) une belle coloration violette. La prednisone ne donne pas cette réaction. L'acide sulfurique sans acide acétique conduit au charbonnement.

On obtient également une réaction positive avec les résines renfermant cet acide (colophane, etc.).

TABLEAU II

Substance	*Quantité de substance nécessaire (en µg) pour obtenir D.O. = 1 (10 mm, 650 mµ)*	
	à froid[a]	*après 10 min au bain-marie bouillant*
Strophantine	340	40
Ouabaïne	∞	44
Acide abiétique	54	27
Cholate de sodium	1800	51
Cholestérol [b]	26	21
Ergostérol	30	12

[a] Substance dissoute dans 2 ml d'acide acétique p.a. On ajoute 0.5 ml réactif molybdique (0.5 ml de solution aqueuse de molybdate de sodium à 50% dans 25 ml d'acide acétique) et 0.5 ml d'acide acétique contenant 15% d'acide sulfurique en volume. Après 3 h on ajoute encore 5 ml d'acide acétique.

[b] Nous avons déterminé le cholestérol dans le sérum sanguin par cette méthode (0.01 ml). Les résultats sont cependant parfois plus élevés que ceux obtenus par les méthodes classiques.

Réaction des „corticostéroïdes"

Nous avons finalement traité les divers stéroïdes par une solution acétique de molybdate de sodium, sans acide sulfurique, et constaté qu'on obtient des réactions positives avec la prednisone et la prednisolone. La réaction n'est cependant pas due à la présence de 2 doubles liaisons Δ_{1-4}, puisque la Δ_{1-4} androstadiène, 17β-ol,3-one, fournit une réaction négative.

testostérone	—	desoxycorticostérone acétate	—
testostérone propionate	—	hydrocortisone acétate	—
dipropionate de testostérone	—	cortisone acétate	—
méthyltestostérone	—	prednisolone	+
folliculine	—	prednisone	+
monobenzoate d'oestradiol	—	androstane 3α,17β-diol	—
pregnènolone	—	androstane 3β,17β-diol	—
progestérone	—	androstène diol 3β,17α	—
*trans*déhydro-androstérone	—	androstène 3β,17β-diol	—
*epi*déhydro-androstérone	—	alloprégnane 3β,20α-diol	—
méthylandrostènediol	—	Δ_5-prégnène 3β,20α-diol	—
dipropion. de méthylandrostène diol	—	Δ_{1-4} androstadiène 17β-ol,3-one	—
		acide 3β-hydroxy Δ_5 étiocholénique*	—

Il ressort de ce tableau que ni les 17-OH ni les 3-OH ou =O, ni même les 2 doubles liaisons Δ_{1-4} sont responsables d'une réaction positive. Les réactions négatives que nous avons obtenues au début avec la cortisone et l'hydrocortisone étaient dues au fait que ces dernières se présentent sous leurs formes acétylées. Il est donc possible de déterminer la cortisone ou l'hydrocortisone libre en présence de leurs dérivés éthérifiés. Toutefois la desoxycorticostérone libre fournit également une réaction positive.

Cette réaction n'a cependant rien de commun avec la réaction molybdique de HEARD ET SOBEL[1] ou celle de SCHWARZ[2] puisque ces réactions sont positives avec les dérivés dits γ-cétols ou α,β,3-cétoniques non saturés.

Dans notre cas, seul le groupement „corticostéroïde" réducteur développe la

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* Nous remercions la firme Roussel-Uclaf pour l'envoi de cet échantillon.

réaction et des substances telles que la progestérone ou la testostérone par exemple (positives dans les réactions de Heard et Sobel ou Schwarz) ne réagissent pas*.

Dosage de la cortisone libre: La cortisone est dissoute dans l'acide acétique. On porte à 3 ml avec de l'acide acétique et l'on ajoute 4 ml de réactif (réactif molybdique: à 0.5 ml de solution aqueuse de molybdate de sodium à 25% on ajoute 40 ml d'acide acétique). Après 2 heures on mesure à 650 mμ.

Prise d'essai (µg)	*D.O. (10 mm)*	*D.O./10 µg*
25	0.077	0.031
50	0.140	0.028
100	0.280	0.028
150	0.450	0.030
200	0.600	0.030
250	0.720	0.029
300	0.890	0.030
100 µg cortisone libre	0.297	
100 µg cortisone libre + 2500 µg acétate de cortisone	0.307	
200 µg cortisone libre	0.565	
200 µg cortisone libre + 2500 µg acétate de cortisone	0.595	
2500 µg acétate de cortisone	0.002	
100 µg hydrocortisone libre	0.207	
100 µg hydrocortisone libre + 2500 µg acétate d'hydrocortisone	0.217	
200 µg hydrocortisone libre	0.425	
200 µg hydrocortisone libre + 2500 µg acétate d'hydrocortisone	0.445	
2500 µg acétate d'hydrocortisone	0.003	

Réaction des Δ_5-stéroïdes

Par addition d'un oxydant à l'acide sulfurique on obtient surtout des réactions positives avec les Δ_5-stéroïdes, tel qu'il ressort du Tableau I. Nous avons tenté d'utiliser d'autres acides. En remplaçant l'acide sulfurique par l'acide perchlorique (70%, $d = 1.67$) nous conjuguons l'action de l'acide à celle de l'oxydant. Les résultats sont cependant peu encourageants. L'addition d'un oxydant s'avère utile. Surtout l'acide iodique et le chlorate de potassium produisent de belles réactions. Toutefois le sélénite de sodium développe la réaction la plus intense. Cette réaction rappelle quelque peu certaines réactions décrites par d'autres auteurs telles que les réactions de Pontius[3] pour les stéroïdes à noyau aromatique, et surtout celle de Witten et Stone[4] pour les 3-OH Δ_5-stéroïdes (effectuée sur chromatogramme). Rappelons que le chromatogramme est soumis à l'action du phénol, du molybdate de sodium et de l'acide perchlorique, et porté à une température de 75°.

Dans notre cas, la réaction effectuée en tube à essai peut avoir lieu sans addition de phénol, quoique la présence de phénol soit favorable. Le remplacement du molybdate par le sélénite nous permet d'obtenir une réaction à température ordinaire et de toutes façons quelque soit la réaction effectuée (sur chromatogramme ou par voie humide) le remplacement du molybdate par le sélénite augmente la sensibilité de la réaction. L'*épi*- et la *trans*déhydroandrostérone ainsi que le méthylandrostène-

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* Les réactions du type formazane (rouge ou bleu de tétrazolium), quoique fort différentes, présentent quelque analogie.

diol fournissent des réactions positives. La méthyltestostérone contrairement à la testostérone est également positive.

Dosage du méthylandrostènediol: On dissout le méthylandrostènediol dans 1 ml de solution alcoolique de phénol à 50%. On ajoute 0.10 ml de réactif (1 g de sélénite de sodium dans 5 ml d'eau), puis 2.5 ml d'acide perchlorique. Après 3 heures on mesure à 610 mμ (Beckmann, 10 mm).

μg	*D.O.*	*D.O./10 μg*
12.5	0.112	0.091
25	0.237	0.094
50	0.475	0.095
100	0.960	0.096
150	1.370	0.092

Dosage de l'épidéhydroandrostérone: On dissout la prise d'essai dans 2 ml de solution phénolique à 50% dans l'alcool. On ajoute 0.40 ml de réactif (1 g de sélénite de sodium dans 5 ml d'eau), puis 5 ml d'acide perchlorique. Après 30 min on mesure à 510 mμ (Bausch et Lomb, tube de 12 mm ø).

μg	*D.O.*	*D.O./10 μg*
10	0.070	0.070
15	0.100	0.066
20	0.140	0.070
40	0.265	0.066
80	0.550	0.068
120	0.810	0.067
160	1.100	0.069

La réaction au brome

L'action d'un oxydant en présence de phénol rappelle la réaction classique de Halphen[5] utilisée pour l'identification des acides résineux dans les cires, résines, savons, etc. (présence de colophane, acide abiétique).

Rappelons que la substance est dissoute dans une solution phénolique de tétrachlorure de carbone (phénol 1, CCl_4 4). En présence d'acides résineux la solution acquiert une belle coloration violette.

Cette réaction appliquée aux stéroïdes s'est avérée négative (ou négligeable) pour toute une gamme de stéroïdes.

Nous avons préalablement examiné le comportement de dérivés phénoliques autre que le benzophènol.

phénol	++	2,4-dichlorophénol	±
p-chlorophénol	++	2,4,5-trichlorophénol	±
m-crésol	+	α-naphtol	±
m-aminophénol	—	β-naphtol	±
p-bromophénol	+	*p*-nitrophénol	—
o-chlorophénol	+		

Seuls le *p*-chlorophénol (surtout), le *p*-bromophénol et l'*o*-chlorophénol ont fourni des résultats intéressants. Ils ne présentent cependant pas d'avantage marqué par rapport au benzophénol ordinaire.

Seul le méthylandrostènediol développe une belle coloration verte. L'*épi-* et la *trans*déhydroandrostérone demeurent négatifs. La spécificité s'en trouve accrue.

Ici également l'acide abiétique fait exception et fournit une réaction positive. L'acide déhydroabiétique reste négative.

*trans*déhydroandrostérone	—	cortisone acétate	—
*epi*déhydroandrostérone	—	prednisolone	—
méthylandrostènediol	+	prednisone	—
acide abiétique	+	hydrocortisone acétate	—
colophane	+	folliculine	—
ac. déhydroabiétique	—	monobenzoate d'oestradiol	—
androstane $3\beta,17\beta$-diol	—	testostérone propionate	—
androstane $3\alpha,17\beta$-diol	—	testostérone	—
androstène $3\beta,17\beta$-diol	trace	progestérone	trace
androstènediol $3\beta,17\alpha$-diol	trace	désoxycorticostérone acét.	trace
Δ_5-pregnène $3\beta,20\alpha$-diol	trace	méthyltestostérone	trace
alloprégnane $3\beta,20\alpha$-diol	—	cholestérol	trace
épiandrostérone	—	ergostérol	trace

Réaction aldéhydique

Quelques réactions de stéroïdes avec certains aldéhydes ont été décrites; ces réactions sont toutefois peu sensibles. Nous avons utilisé le pipéronal, la vanilline et la *p*-diméthylaminobenzaldéhyde. Leur action est peu marquée. Par contre l'*o*-dialdéhyde phtalique s'est avérée favorable.

folliculine	jaune	alloprégnane $3\beta,20\alpha$-diol	—
épiandrostérone	—	monobenzoate d'oestradiol	—
prednisone	—	testostérone propionate	—
progestérone	—	testostérone	—
hydrocortisone	—	pregnénolone	trace
hydrocortisone acétate	—	méthylandrostènediol	violet
désoxycortisone acétate	—	transdéhydroandrostérone	violet
		épidéhydroandrostérone	violet

On obtient des réactions positives avec les déhydroandrostérones et le méthylandrostènediol (la testostérone est négative)*.

Dosage de la folliculine: On ajoute à la prise d'essai (substance sèche) 0.25 ml de réactif (50 mg d'*o*-dialdéhyde phtalique dans 5 ml d'alcool), ensuite 7 ml d'acide chlorhydrique conc. ($d = 1.19$). On mesure à 360 mμ après 2 à 5 min (spectrophotomètre Bausch et Lomb, tubes de 12 mm ø).

μg	*D.O.*	*D.O./10 μg*
2.5	0.038	0.152
5	0.075	0.150
10	0.150	0.150
20	0.280	0.140
40	0.580	0.145
60	0.850	0.141

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* La pregnénolone est également positive (la coloration violette produite dans l'essai à blanc peut être attenuée par addition d'acide acétique).

Dosage de l'épidéhydroandrostérone: La substance est additionnée de 0.20 ml réactif (200 mg d'*o*-dialdéhyde phtalique dans 5 ml d'alcool) et de 5 ml d'acide chlorhydrique conc. ($d = 1.19$). Après 30 min on ajoute 5 ml d'acide acétique p.a. et on mesure à 535 $m\mu$ (spectrophotomètre Bausch et Lomb, tubes de 12 mm ø).

μg	*D.O.*	*D.O./10 μg*
12.5	0.033	0.026
25	0.068	0.027
50	0.132	0.026
100	0.263	0.026
150	0.390	0.026
200	0.530	0.026
250	0.680	0.027

La réaction est 12 fois plus sensible que celle à la *p*-diméthylaminobenzaldéhyde.

Réactions d'hétéropolyacides

Sur chromatogramme: Le chromatogramme est traité par une solution alcoolique d'acide silicotungstique et on examine tel quel ou après action de la chaleur:

à froid, apparaissent

- dipropionate de méthylandrostènediol
- transdéhydroandrostérone
- méthylandrostènediol
- méthyltestostérone
- acide abiétique
- prégnènolone
- ergostérol

à chaud, se développent

- dihydrocholestérol
- stigmastérol
- cholestérol
- prednisolone
- folliculine

Ces réactions ont été décrites par divers auteurs.

Anhydride acétique: Après action de l'acide silicotungstique, on vaporise de l'anhydride acétique. On obtient à peu près les mêmes spots colorés. Toutefois la coloration est généralement plus intense et déjà à froid, les produits suivants fournissent une réaction positive:

- dihydrocholestérol
- stigmastérol
- cholestérol
- testostérone
- propionate de testostérone
- folliculine
- progestérone

Incontestablement l'anhydride acétique excerce donc une action favorable. Cette modification oriente la réaction dans une direction nouvelle. D'autres substances pourront être caractérisées et surtout des déterminations quantitatives pourront être effectuées sur des stéroïdes en solution.

En solution: Le stéroïde dissous dans l'anhydride acétique est additionné d'acide silicotungstique. La solution est portée à 100°.

	coloration	*fluorescence*
méthylandrostènediol	verte	+
transdéhydroandrostérone	violet-intense	
épidéhydroandrostérone	violette	
androstènediol $3\beta,17\alpha$	jaunâtre	verte + +
androstènediol $3\beta,17\beta$	jaune foncé	verte + +
androstane $3\alpha,17\beta$-diol	nég.	
Δ_5-pregnène $3\beta,20\alpha$-diol	jaunâtre	jaune
androstane $3\beta,17\beta$-diol	nég.	
folliculine	rouge	rouge
testostérone	verdâtre évoluant vers jaune brun	
cortisone	jaune intense	
progestérone	jaune	

a. Dosage de l'épidéhydroandrostérone

La prise d'essai (résidu sec) est additionnée d'une goutte de réactif (1 g d'acide phosphotungstique dans 1.5 ml d'acide acétique; 1 goutte = ± 0.016 ml = ± 10 mg), puis de 0.25 ml d'anhydride acétique. Après 1 h 3/4 de contact on ajoute 10 ml d'anhydride acétique. On mesure alors immédiatement à 570 mμ (Bausch et Lomb, tube de 12 mm ø).

µg	*D.O.*	*D.O./10 µg*
12.5	0.062	0.050
25	0.125	0.050
50	0.240	0.048
100	0.480	0.048

b. Dosage de la folliculine

La prise d'essai (résidu sec) est additionnée d'une goutte de réactif (1.5 g d'acide phosphotungstique dans 2 ml d'acide acétique; 1 goutte = ± 0.016 ml = ± 12 mg), puis de 0.25 ml d'anhydride acétique. Après 1 h 1/2 de contact, on ajoute 10 ml d'anhydride acétique. On mesure alors immédiatement à 560 mμ (Beckmann, 10 mm).

µg	*D.O.*	*D.O./10 µg**
50	0.162	0.032
100	0.330	0.033
150	0.474	0.031

On constate donc que des corps proches parents tels que le transdéhydroandrostérone ou l'épidéhydroandrostérone d'une part et l'androstanediol et les androstènediols d'autre part se comportent de façon différente. Fréquemment, il semble exister un certain parallèlisme avec la réaction de LIEBERMANN**.

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* Les résultats sont donc moins favorables que pour l'épidéhydroandrostérone. On peut obtenir des erreurs relatives de 4–6%.

** Réaction fortement positive pour la méthyltestostérone, négative avec la testostérone.

DISCUSSION

Si nous avons tenté successivement de remplacer le chlorure de fer(III) par d'autres oxydants, et l'acide sulfurique par l'acide perchlorique, nous avons cependant essayé de circonscrire davantage encore le problème en pourvoyant systématiquement au remplacement d'un des solvants ou d'une des substances réagissantes.

Dans la réaction de HALPHEN, on peut substituer de l'acide chlorhydrique ou bromhydrique au brome. Il est donc vraisemblable que c'est l'acide bromhydrique, produit par action du brome sur le phénol, qui déclanche la réaction. Quant au tétrachlorure de carbone, il s'avère également facultatif. On peut obtenir des réactions positives avec le méthylandrostènediol en dissolvant ce produit dans l'acide tri-, di- ou monochloracétique. Si l'acide acétique seul ne fournit point de réaction, celle-ci peut cependant devenir positive par addition d'un oxydant, un peu de chlorure de fer(III) par exemple (bain-marie, repris par chloroforme, coloration bleue).

On peut se passer du chlorure de fer(III) en ajoutant du chlorure de zinc à la solution acétique (réactions au bain-marie). Le solvant acétique peut lui-même être remplacé par de l'alcool octylique par exemple. Enfin, on peut substituer au chlorure de zinc de l'anhydride phosphorique.

Nous croyons donc pouvoir conclure qu'un grand nombre de réactions de stéroïdes, enserrées dans un réseau étroit de conditions opératoires ne présentent de spécificité que pour autant que ces conditions soient respectées. Nous estimons que ce sont avant tout les liquides lyophobes et l'action d'un oxydant qui contribuent au développement des diverses réactions.

RÉSUMÉ

Diverses réactions colorées peuvent servir à l'identification et au dosage de stéroïdes. L'acide molybdique en solution acétique constitue un réactif d'α-cétols libres. Les Δ_5-stéroïdes peuvent être dosés par un réactif au sélénite. La réaction d'HALPHEN et l'o-dialdéhyde phtalique ont servi à l'identification et au dosage de certains stéroïdes. Les hétéropolyacides peuvent servir à des fins qualitatives et quantitatives pour autant que ces hétéropolyacides soient utilisées en présence d'anhydride acétique.

SUMMARY

A number of colour reactions for the identification and determination of steroids are described.

ZUSAMMENFASSUNG

Es werden eine Anzahl Farbreaktionen zum Nachweis und zur Bestimmung von Steroiden beschrieben.

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SPOT TESTS FOR THE IDENTIFICATION OF TITANIUM ALLOYS AND THEIR DIFFERENTIATION FROM ZIRCONIUM AND ITS ALLOYS

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INTRODUCTION

During manufacture of the various titanium alloys every precaution is taken to ensure that they retain their identity. Zirconium bearing materials are manufactured in an entirely independent plant and, at this stage, the probability of mixing these with titanium alloys is almost impossible. There are, however, occasions when users of these materials have sought an additional safeguard against inadvertent mixing during fabrication, and it is then desirable to be able to apply a simple confirmatory spot test which will classify these various alloys.

EXPERIMENTAL

Chemical spot tests on metal surfaces are usually based on a preliminary attack of the metal with a drop of a suitable solvent, such as hydrochloric or nitric acid. Titanium, zirconium and their alloys do not readily respond to acid attack in this way, but it has been shown that fluoboric and hydrofluoric acids are both relatively good solvents for these metals[1]. Unfortunately, the presence of fluoride, excess acid, and the preponderance of parent metal in the resulting solution, precludes a straightforward application of many specific cationic reactions. Modifications to known chemical reactions were therefore investigated, with preference for tests incorporating characteristic colour reactions. No attempt was made to develop tests which would differentiate between alloys containing the same alloying metals in different amounts, and a separate test for the identification of aluminium was not investigated, because alloys containing this metal can be more easily identified by a positive reaction given by other metals that normally accompany aluminium, for example tin in Ti/Al/Sn and vanadium in Ti/Al/V alloys.

In the following experimental tests the surface of the metal under test was freshly abraded with fine emery cloth before applying the solvent acid, which was either fluoboric or hydrofluoric acid.

IDENTIFICATION OF TITANIUM ALLOYS

Under the following headings, reactions of the various titanium alloys were considered and relevant factors in the development of suitable tests are outlined. The tests finally recommended have been subjected to extensive trials and the author is satisfied that they serve adequately to differentiate the alloys in question.

The reactions of a particular alloy are quite distinct from those of titanium or any of the other titanium alloys mentioned.

Titanium–aluminium–tin alloy

Three coloured complexes, resulting from reaction with special reagents, are used as a means of detecting tin. They are the so-called 'molybdenum blue' colour, produced by reduction of molybdates and phosphomolybdates[2-4], the violet colour formed with cacotheline[5] and the magenta coloured reaction product with toluene-3,4-dithiol (dithiol)[6].

These reactions were examined, but it was not possible, by simple modification, to overcome interference by titanium in the 'molybdenum blue' and cacotheline reactions. No characteristic colour was produced on the addition of dithiol solution to a Ti/Al/Sn alloy, following initial attack with fluoboric acid, but a pale red colour was formed with dithiol, characteristic of tin, after nitric acid was added to the drop of fluoboric acid solution. The nitric acid appears to dissolve the tin, which darkens the metal surface when only fluoboric acid is used as solvent. Addition of thioglycollic acid to the dithiol solution produced a more distinct pale red colour and delayed formation of a brown colour which appeared on standing.

Titanium–aluminium–manganese alloy

The most suitable test for detecting manganese depends on the formation of permanganic acid by oxidants, such as potassium periodate or sodium bismuthate, in nitric acid solution. After initial attack of the prepared surface with the recommended solvent, the solution was oxidised with nitric acid and solid sodium bismuthate was added, but under these conditions formation of permanganic acid was transient, due to reduction by nitrous acid. Addition of urea, however, to decompose nitrous acid, stabilised the characteristic colour. If the drop was disturbed after addition of sodium bismuthate, the permanganic acid colour faded; the addition of too much sodium bismuthate produced a similar effect.

Titanium–aluminium–vanadium alloy

Several well-known reactions for the qualitative identification of vanadium were tried, following initial attack of the metal surface, but none was entirely satisfactory. The preliminary tests included reduction of ferric iron in the presence of an indicator[7], reaction with α-benzoinoxime[8] and sodium tungstate[9]. It was observed, however, that when a solution of potassium ferrocyanide was added to the test solution a reddish-brown precipitate was obtained, and this was easily differentiated from coloured precipitates produced with titanium or with other titanium alloys.

Titanium–copper alloy

Application of the well-known sodium diethyldithiocarbamate reaction[10] in ammoniacal solution, following initial attack of the metal with fluoboric acid and nitric acid, was entirely satisfactory for identifying copper in titanium–copper alloy.

Titanium–molybdenum alloy

Molybdenum-bearing alloys are more soluble in hydrofluoric acid than in fluoboric acid, and a mixture of hydrofluoric and nitric acids was used as a solvent in the development of a suitable test. Of the tests applied for detecting molybdenum, that based on the formation of molybdenyl thiocyanate[11] proved most satisfactory. The intensity of the red colour produced depended on the concentration of nitric acid present in the solvent and the duration of the initial acid attack. If the nitric acid concentration was greater than (1 + 1), thiocyanate was decomposed, and if less than (1 + 4), the concentration of acid was not sufficient to dissolve molybdenum in the sample. A compromise was a solvent containing 10 ml hydrofluoric acid (1 + 9) and 6 ml conc. nitric acid ($d = 1.42$). This solvent, which must be stored in a polythene container, was stable for at least 24 h. The ammonium thiocyanate–stannous chloride reagent was also stable for a similar period.

IDENTIFICATION OF ZIRCONIUM IN THE PRESENCE OF TITANIUM AND ITS ALLOYS

Three reagents known to give characteristic reactions with either titanium or zirconium are hydrogen peroxide[12], alizarin red S (sodium alizarin sulphonate)[13] and solochrome cyanine R 200[14]. Fluoride was known to interfere with two of the reactions under specified conditions, but the extent of its interference with solochrome cyanine R 200 was uncertain. Titanium reacts with hydrogen peroxide in acid solution to form yellow pertitanic acid; vanadium and molybdenum also produce yellow colours under similar conditions. Fluoride suppresses these colour formations, particularly that produced by titanium.

After initial attack of titanium and titanium alloys with fluoboric acid, a drop of hydrogen peroxide (20 vol) immediately produced a yellow colour, which persisted for several min, and no colour was obtained when the same test was applied to zirconium, zirconium–tin alloy and Zircaloy 2. The test, therefore, clearly distinguishes titanium and its alloys from zirconium and the zirconium alloys mentioned. Very dilute solutions of hydrogen peroxide in the presence of titanium gave either a very transient yellow colour or no colour at all. Some difficulty was experienced in dissolving Ti–Mo alloy in fluoboric acid (10%) but an addition of 1 ml of hydrofluoric acid (40%) to 10 ml of the fluoboric acid solution was effective.

Solochrome cyanine R 200 is a water soluble dye and yields lakes with some metals. An aqueous solution (0.1%), which is blood-red in colour, first turned orange when applied to zirconium and its alloys, but after about 5 min the red colour was restored. With titanium and titanium alloys the drop of reagent decolourised almost immediately.

Alizarin red S is a well-known water soluble dye used for detecting zirconium and several other metals. The aqueous solution produces a red colour with zirconium salts, and this is stable at relatively high acidities, but the zirconium lake is decolourised by fluorides and silico fluorides. When a drop of the aqueous solution was added, after the initial fluoboric acid attack, no colour was observed at first, but a pale red colour developed gradually on standing in the presence of zirconium and its alloys. If the acid drop was allowed to react with the metal surface for about 2 min, before applying the reagent, a pale red colour was formed immediately. It appears that the reduction in acidity, brought about by solution of the metal, together with the relatively high concentration of zirconium in solution, was sufficient to prevent interference by the amount of fluoride present; the colour was stable for at least 20 min.

During the initial acid attack a black spot appeared on the surface of some of the zirconium–tin alloys tested, and this was probably due to the presence of tin. The pale red colour was not so easily seen, and it was prone to fading. With titanium and its alloys, the colour produced was in striking contrast, being dark-blue or green-blue. Alizarin red S is considered to be the most satisfactory reagent.

METHOD

It is advisable, in applying the following differentiating spot tests, to use control samples of known composition.

Before applying any of the tests, abrade the surface of the specimen with fine emery cloth; the surface of the metal must be bright and clean. Apply the acid solvent and reagents by means of a thin glass rod.

Reference to 'other titanium alloys' refers to the titanium alloys on pages 50–52, and reference to zirconium alloys refers to the zirconium alloys on pages 52–53.

(a) IDENTIFICATION OF TITANIUM ALLOYS

Solvents

Fluoboric acid solution. To 280 ml of hydrofluoric acid (40%) (maintained at 10°) add, in small quantities, 130 g of boric acid. Store in a polythene bottle. Dilute 10 ml of this solution with 10 ml of water before use.

Hydrofluoric acid–nitric acid solution. Dilute 5 ml of hydrofluoric acid (40%) to 50 ml with water. Add 30 ml of nitric acid ($d = 1.42$) and store in a polythene container. This reagent must not be kept for more than a few days.

TIN

Special reagents

Dithiol solution. Dissolve 0.2 g of toluene-3,4-dithiol (dithiol) in 100 ml sodium hydroxide solution (1%) and add a few drops of thioglycollic acid. This solution is unstable and must be freshly prepared.

Nitric acid solution (Approx. 2 N). Dilute 15 ml of nitric acid ($d = 1.42$) to 100 ml with water.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add a drop of nitric acid solution (approx. 2 *N*), then one drop of dithiol solution. A pale red colour develops with Ti–Al–Sn alloy. No colour is formed with titanium and other titanium alloys except Ti–Al–V and Ti–Al–Mn, which produce a brown coloured spot after standing for 3–4 min.

MANGANESE

Special reagents

Nitric acid ($d = 1.42$). Add 0.5–1.0 g of urea to about 10 ml of nitric acid ($d = 1.42$) before use, *i.e.* sufficient urea to provide a layer of undissolved solid.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add one drop of nitric acid ($d = 1.42$). Moisten a very thin glass rod and dip into sodium bismuthate powder so that a little solid adheres to the tip of the rod. Transfer the adhering powder to the test drop but *do not stir.* A pink colour develops in 1–2 min in the presence of manganese. If in doubt, view the spot with a hand lens; any pink colouration will be seen at the boundary of the sodium bismuthate. The sodium bismuthate must be added immediately after the addition of nitric acid. No colour is produced with titanium and other titanium alloys.

VANADIUM

Special reagents

Dilute fluoboric acid solution. Mix 20 ml of fluoboric acid solution (see 'Solvents') with 50 ml of water before use.

Potassium ferrocyanide solution (10%). Dissolve 10 g of potassium ferrocyanide in water and dilute to 100 ml.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add one drop of potassium ferrocyanide solution (10%). A reddish brown precipitate is formed if vanadium is present.

Titanium and other titanium alloys give either a green, yellow-green or yellow-brown precipitate.

COPPER

Special reagents

Dilute fluoboric acid solution. Mix 20 ml of fluoboric acid solution (see 'Solvents') with 50 ml of water before use.

Nitric acid solution (1 + 1).

Sodium diethyldithiocarbamate solution (0.2%). Dissolve 0.2 g of sodium diethyldithiocarbamate and 5 g of ammonium citrate in 60 ml of water. Add 10 ml of ammonia solution ($d = 0.940$) and dilute to 100 ml.

Procedure

Apply one drop of the dilute fluoboric acid solution. After 3 min add one drop of nitric acid solution (1 + 1). After a further 2 min add one drop of sodium diethyldithiocarbamate solution (0.2%). A yellow colour develops in the presence of copper.

With Ti–Al–Sn and Ti–Al–Mn alloys, a light brown colour develops in the spot about 2 min after addition of the sodium diethyldithiocarbamate reagent.

MOLYBDENUM

Special reagents

Ammonium thiocyanate–stannous chloride solution. Dissolve 20 g of ammonium thiocyanate in water and dilute to 50 ml.

Dissolve 20 g of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 50 ml of hydrochloric acid (1 + 1). Mix the two solutions. This reagent must be prepared daily.

Procedure

Apply a drop of hydrofluoric acid–nitric acid solution (see 'Solvents'). After 3 min add one drop of the ammonium thiocyanate–stannous chloride solution. A brilliant red colour is formed in the presence of molybdenum. This colour fades after about 30 sec.

Titanium, Ti–Al–V, Ti–Al–Mn, Ti–Al–Sn and Ti–Cu alloys give a yellow colour

(b) IDENTIFICATION OF ZIRCONIUM IN THE PRESENCE OF TITANIUM AND ITS ALLOYS

Solvent

Fluoboric acid solution. To 280 ml of hydrofluoric acid (40%) (maintained at 10°) add, in small quantities, 130 g of boric acid. Store in a polythene bottle. Dilute 10 ml to 100 ml with water before use.

Special reagents

Alizarin red S solution (0.1%). Dissolve 10 mg of alizarin red S in 10 ml of water.

Procedure

Apply a drop of dilute fluoboric acid solution. After 1–2 min add one drop of alizarin red S solution.

A red colour forms with zirconium and zirconium alloys. Titanium and titanium alloys react with the reagent to give a dark blue or green-blue spot, and a pink edge develops in the drop on long standing.

ACKNOWLEDGEMENT

Acknowledgement is made to Mr. W. T. ELWELL, Division Chief Analyst, for his interest in this investigation, and for assistance in the preparation of this paper, and to MISS J. HEWSON for practical assistance.

SUMMARY

During manufacture every precaution is taken to safeguard against inadvertent mixing of titanium and zirconium alloys. There are, however, occasions when confirmation of identity is desirable. Simple spot tests are described for the rapid differentiation of a range of titanium alloys and for distinguishing these materials from zirconium and its alloys. After a preliminary attack of the abraded metal surface with either fluoboric or hydrofluoric acid, characteristic coloured reaction products are formed with well known reagents, and these tests serve to classify the material.

RÉSUMÉ

Des réactions à la touche sont décrites pour identifier des alliages de titane et pour les distinguer du zirconium et de ses alliages. Le métal à examiner est attaqué superficiellement soit par l'acide fluoborique, soit par l'acide fluorhydrique.

ZUSAMMENFASSUNG

Titanlegierungen lassen sich von Zirkonium und seinen Legierungen durch Tüpfelproben der auf Oberfläche der Legierungen nach Anätzen mit Fluoroborsäure oder Fluorwasserstoffsäure unterscheiden.

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SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF INDIUM IN URANIUM AND THORIUM METALS AND THEIR SALTS

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A method has been developed for the spectrophotometric determination of indium in uranium and thorium metals and their salts in the range 0.1 to 10 p.p.m.

According to SANDELL[1], indium can be separated by oxine–chloroform extraction at pH 3.5, but elements such as gallium, aluminium, cobalt, nickel, thallium, tin, molybdenum, iron, vanadium and bismuth interfere by giving coloured extracts.

A method has been described by MAY AND HOFFMAN[1] in which indium and other metals listed above are first extracted with oxine–chloroform solution at pH 4 in presence of ammonium citrate. After the oxinates have been decomposed, indium, aluminium, gallium, thallium and bismuth are extracted with chloroform from an aqueous citrate–cyanide solution at pH 8.5 in presence of cupferron and dithizone. The metals are then transferred to the aqueous solution by shaking the extracts with 1% nitric acid. Finally, indium is determined in alkaline solution containing potassium cyanide and ammonium cyanide with dithizone–chloroform. It is possible to determine 10 μg of indium in presence of 10 mg of copper, zinc and lead; bismuth, tin and thallium interfere.

The oxine–chloroform method cannot be used to separate indium from uranium and thorium at pH 4; the recovery is not quantitative. Recently, REYNOLDS AND SHALGOSKY[2] tried to recover indium from 1 g of zinc by this separation but they were also unsuccessful.

LUKE AND CAMPBELL[3] determined indium in residues from germanium chloride distillation by extraction with dithizone–chloroform from an alkaline solution containing citrate and cyanide, and developing the colour with oxine–chloroform after the decomposition of dithizonates. However, photometric measurement of indium as oxinate in chloroform at 420 mμ showed that it was not sensitive enough for less than 10 μg in 20 ml of oxine–chloroform solution.

Principle

From an alkaline solution containing ammonium citrate and potassium cyanide indium is extracted along with lead, bismuth, thallium and tin[4] by a solution of dithizone in chloroform. The optimum pH of extraction is 8.3–9.6[1]. Bismuth if present in large amounts can be removed by prior extraction with dithizone-chloroform at pH 3.5–4. Stannic tin is not extracted along with indium[3,4].

Indium along with lead and thallium is then extracted back to 1% nitric acid.

Indium alone is then extracted with dithizone–carbon tetrachloride solution at pH 5 to 6 in presence of sodium thiosulphate to complex lead and bismuth[5]. Thallium is not extracted at this pH. The indium content of the sample is determined by measuring the optical density of the organic phase at 510 mμ.

EXPERIMENTAL

Reagents

Distilled water redistilled in glass apparatus was used for preparing all reagents.

Indium solution. 0.5 g of indium metal (spec. pure) was dissolved in a few ml of nitric acid and diluted with water to give solutions containing 0.1, 1, 10 and 100 μg/ml. The first two solutions were prepared as required from the stock solution.

Ammonium citrate solution 50%. 100 g of ammonium citrate were dissolved in 200 ml of water. Dilute ammonia was then added till the solution was blue to thymol blue indicator and impurities were removed by shaking with 0.02% dithizone in chloroform; dithizone was removed by washing with chloroform.

If ammonium citrate is not available then 432 g of citric acid monohydrate (E. Merck) are dissolved in 100 ml of water and about 500 ml of conc. ammonia ($d = 0.91$) is added slowly to the cold solution till just alkaline to litmus. This is diluted to 1 l and treated as above.

10% Ammonium citrate. 20 ml of 50% ammonium citrate solution were diluted to 100 ml with water.

2N Sodium acetate solution. 27.22 g of crystalline sodium acetate (A.R.) were dissolved in water and made up to 100 ml. It was purified by treating with dithizone as above.

Acetate–Acetic acid buffer (pH 5.5). 18 ml of 2 *N* sodium acetate solution and 20 ml of 0.2 *N* acetic acid were mixed and diluted to 200 ml and was then purified by shaking with dithizone carbon tetrachloride until the organic layer was distinctly green. It was then washed with carbon tetrachloride to remove dithizone.

10% Potassium cyanide. 10 g of potassium cyanide (E. Merck) were dissolved in 100 ml of water. The required aliquot was treated with dithizone–chloroform just before use.

1% Nitric acid (v/v). 1 ml of E. Merck G. R. grade nitric acid and 99 ml of water were mixed.

0.02% Dithizone in chloroform. 40 mg of dithizone (E. Merck) were dissolved in 200 ml of chloroform and the solution was shaken in a separating funnel with 10 ml of strong ammonia and 100 ml of water. The organic phase was rejected and the aqueous layer was washed with 50 ml of chloroform. The organic layer was again rejected. The aqueous layer was cooled and acidified with hydrochloric acid. The dithizone liberated was then extracted with 75 ml of chloroform and aqueous phase rejected. The chloroform layer was once again washed with 100 ml of water. The organic layer was diluted to 200 ml with chloroform and stored in an amber bottle in a cold place.

0.02% Dithizone in carbon tetrachloride. It was prepared as above using carbon tetrachloride instead of chloroform.

0.002% Dithizone in carbon tetrachloride. A fresh solution was prepared as required by diluting 10 ml of the above solution to 100 ml with carbon tetrachloride.

20% Hydroxylamine hydrochloride. 20 g of hydroxylamine hydrochloride were dissolved in 60 ml of water. A few drops of meta-cresol purple were added and the solution was neutralized with ammonia. An excess of a 4% solution of sodium diethyldithiocarbonate was added and extracted with chloroform until no yellow colour was obtained with copper solution. Hydrochloric acid was then added until the solution turned pink. The solution was then diluted to 100 ml with water.

20% Sodium thiosulphate. It was freshly prepared by dissolving 20 g of sodium thiosulphate (A.R.) in 100 ml water and was purified by shaking with dithizone–carbon tetrachloride solution.

PRELIMINARY EXPERIMENTS

The optimum pH of extraction of indium as dithizonate from an aqueous solution containing sodium thiosulphate (2 ml of 20%) was found to be 5 to 6 and the optimum wavelength 510 mμ in agreement with the data of SANDELL for indium dithizonate in the absence of sodium thiosulphate.

PROCEDURE

Standard curve

Indium standards containing 0.25 to 10 μg were prepared and the standard curve was obtained as described below.

Aliquots of standard solution were transferred to 100-ml separating funnels and diluted to 20 ml with water. 10 ml of 10% ammonium citrate were added and the pH was adjusted with dilute nitric acid to 3.5 to 4 using indicator paper. 5 ml of 0.02% dithizone in chloroform were added and shaken for 1 minute. The extraction was repeated 2–3 times until the organic phase remained distinctly green. The organic phases were discarded and the aqueous layer was washed with chloroform.

To the aqueous phase 2 ml of 10% potassium cyanide and 0.2 ml of the hydroxylamine reagent were added. The pH of the solution was adjusted to about 9 with a few drops of ammonia using universal indicator paper. 5 ml of 0.02% dithizone in chloroform were added and the solution shaken for 2 min. The organic phase was transferred to another 100-ml separating funnel. The extraction was repeated 3–4 times. All the organic extracts were collected together in a 100-ml separating funnel and shaken with 20 ml of distilled water for 30 sec. The aqueous layer was rejected. Two more washings were given to remove excess alkali. 20 ml of 1% nitric acid were added to the organic phase and shaken for 2 min to back-extract indium into the aqueous phase. The organic layer was rejected and the acid was washed with carbon tetrachloride to remove all chloroform.

To the acid solution 13 ml of 2 *N* sodium acetate and 2 ml of 20% sodium thiosulphate were added. The pH of the solution was about 5.5. 10 ml of 0.002% dithizone in carbon tetrachloride were added from a 10-ml pipette and the solutions were shaken for 2 min. The first few ml of the carbon tetrachloride layer were rejected, which also served to wash the stem of the funnel. The remaining organic layer was directly transferred to a 1-cm pyrex cell which had been rinsed with the organic phase. The optical density of the solutions was measured with a Beckman DU Spectrophotometer at 510 mμ against water.

The optical densities of the standards taken directly at pH 5 to 6 using sodium acetate–acetic acid buffer with or without thiosulphate agreed with the optical densities of the standards following the complete procedure.

Beer's law was obeyed from 0.25 to 10 μg of indium (Table I).

TABLE I

THE OPTICAL DENSITIES OF STANDARD SOLUTIONS OF INDIUM

With 10 ml of 0.002% dithizone–carbon tetrachloride at 510 mμ

Indium taken μg	*Optical density*	
	I	*II*
0.25	0.015	0.015
0.50	0.028	0.030
1.00	0.055	0.060
2.00	0.120	0.120
3.00	0.190	0.183
4.00	0.235	0.240
5.00	0.300	0.310
10.00	0.615	0.610

Recoveries of indium added to uranium and thorium

Uranium and thorium nitrate equivalent to nearly 5 g of uranyl oxide or thorium oxide was dissolved in the minimum amount of nitric acid and taken to a syrupy state on a water bath. Samples of uranium oxide were treated similarly. Thorium oxide was dissolved in the minimum amount of nitric acid by adding a few drops of 1% hydrofluoric acid to aid the dissolution. Hydrofluoric acid was removed by repeated evaporation with nitric acid.

In the case of uranium and thorium metals, the metal was rinsed with ether and then with water; it was then dried and dissolved in a few ml of nitric acid and taken to a syrupy state on a water bath. 0.25 to 10.0 µg of standard indium were added to the uranyl nitrate or thorium nitrate solutions. The total volume was made up to 20 ml and indium determined as described above.

TABLE II

RECOVERIES OF INDIUM ADDED TO URANYL NITRATE

No.	*Amounts of sample taken* (*U_3O_8*) *in g*	*Indium*		*Remarks*
		µg added	*µg recovered*	
1	1.000	Nil	Nil	No indium was indicated
2	1.000	0.25	0.25	
3	1.000	0.50	0.50	
4	1.000	1.00	0.93, 0.97	
5	1.000	2.00	2.00	
6	1.000	3.00	2.92	
7	1.000	5.00	5.00	
8	1.000	10.00	10.00	
9	1.000	5.00	5.00, 5.00*	
10 a	5.000	Nil	Nil**	
10 b	5.000	5.00	5.08**	
11 a	5.000	Nil	Nil***	
11 b	5.000	5.00	4.92***	

No. 9: The following impurities (in µg) were added to one of the samples: Lead 10; Zinc 10; Iron 10; Copper 20; Cobalt 20; Silver 10; Gold 25; Nickel 20; Bismuth 10; Chromium 10.

No. 10 a and b**: The sample contained the following impurities in p.p.m.: Boron 0.2 ± 0.02; Cadmium < 0.05; Nickel < 1; Cobalt < 1; Copper < 1; Iron = 5.5; $As_2O_3 < 1$; Beryllium < 1; Manganese < 1; Chromium < 5; Tin < 1; Zinc < 20; Cerium = 11.5; Gadolanium = 1.5; Dysprosium = 0.58; Erbium = 1.

No. 11 a and b***: The sample contained the following impurities in p.p.m.: Boron 0.35; $As_2O_3 < 1$; Beryllium < 1; Tin < 1; Iron = 9; Cadmium < 0.05; Nickel < 1; Cobalt < 1; Copper < 1; Zinc < 20; Cerium = 0.92; Dysprosium < 0.1; Erbium < 0.1.

When a 5-g sample was taken, 20 ml of 50% ammonium citrate were added instead of 10 ml. Tables II and III show the recoveries of indium added to uranium and thorium. In some of the experiments ions likely to give dithizonates were added to the uranium and thorium salts. These added impurities when taken through the whole process did not show any indium while added indium was recovered as shown in Expts. 9–11 of Table II and Expt. 8 of Table III.

TABLE III

RECOVERIES OF INDIUM ADDED TO THORIUM NITRATE

No.	*Amounts of sample taken* (ThO_2) *in g*	*Indium*		*Remarks*
		µg added	*µg recovered*	
1	1.000	—	—	No indium was indicated
2	1.000	0.25	0.25	
3	1.000	0.50	0.50	
4	1.000	1.00	0.93	
5	1.000	2.00	0.200	
6	1.000	3.00	3.00	
7	1.000	5.00	5.00	
8a*	5.000	Nil	Nil	No indium was indicated
8b*	5.000	5.00	4.92	

No. 8 a and b*: The following impurities (in µg) were added: Lead 10; Zinc 10; Iron 10; Copper 20; Cobalt 20; Silver 10; Gold 25; Nickel 20; Bismuth 10; Chromium 10.

SUMMARY

A method based on dithizone extraction and determination of indium in the range of 0.1 to 10 p.p.m. in reactor grade uranium and thorium samples is described. Sodium thiosulphate is used as a complexing agent for removing interference by lead and bismuth.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage de microquantités d'indium dans des échantillons d'uranium et de thorium. Elle est basée sur une extraction à la dithizone.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Mikromengen von Indium in Uran- und Thorium Proben. Sie beruht auf einer Extraktion mit Dithizon.

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DETERMINATION OF LOW SULFUR CONCENTRATIONS IN OILS AND ORGANIC SOLIDS

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INTRODUCTION

The petroleum industry has long recognized sulfur as one of the most troublesome contaminants in petroleum streams. It deactivates some catalysts and usually imparts an offensive odor to products; thus, it is important to know and control the sulfur concentration in feeds and product. Recently, the need arose for knowing sulfur concentrations below 200 p.p.m. in waxes and heavy gas oils. Traditional high temperature combustion methods are inadequate at this concentration because of the relatively insensitive titrimetric finishing techniques employed. Lamp sulfur procedures which are normally employed in this range are not applicable to these types of samples; thus, it became necessary to develop a new method.

The first method investigated was based on combustion-nephelometry and involved precipitation of sulfur as barium sulfate. However, poor precision was experienced with this technique. A survey of the literature revealed a colorimetric method by WEST AND GAEKE[1] for measuring sulfur dioxide in air. This method was adapted to a combustion procedure by removing sulfur dioxide from the combustion products by scrubbing through a solution of sodium tetrachloromercurate.

The method is based on the oxidation of sulfur to sulfur dioxide by combustion in a two-furnace apparatus. The evolved sulfur dioxide forms stable, non-volatile disulfitomercurate(II) ion. A red-violet color develops when disulfitomercurate, *p*-rosaniline, hydrochloric acid, and formaldehyde are mixed. The absorption of the solution is measured at 560 mμ and is directly proportional to sulfur concentration.

Sample combustion was carried out in two furnaces at two different temperatures (Fig. 1). Although the analysis can be done with a single furnace, the two-stage method

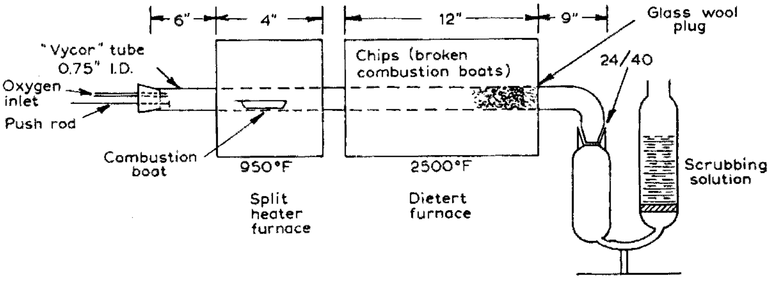

Fig. 1. Two-furnace combustion apparatus.

Anal. Chim. Acta, 22 (1960) 61–65

offers several advantages[2], the most important being improved control of the pyrolysis of the sample. This feature is particularly useful when samples varying in volatility are analyzed.

This procedure has been applied to pure organic solids, waxes, gas oils and residua. As described herein, the procedure is applicable in the range 10–300 p.p.m. sulfur. By reducing the volume of solutions, increasing amount of sample, and/or using wider absorption cells, the minimum level can be lowered substantially. The upper level can be raised by conventional dilution techniques.

EXPERIMENTAL

It is known that when sulfur is burned, an equilibrium $SO_2 \rightleftarrows SO_3$ is set up[3]. This equilibrium is temperature dependent, increasing temperature increasing the percentage of SO_2 present. It is necessary that the temperature used must be such that the percentage of SO_2 formed is independent of small temperature fluctuations in the furnace temperature. By burning known weights of sulfur (as dibenzothiophene) calibration curves at different furnace temperatures were obtained. The results are shown in Fig. 2. This indicates that a temperature of at least 2500°F is desirable. An even higher temperature would be an advantage, but the service factor on the furnaces decreases significantly at higher temperatures. Precision results are shown in Table I.

Results were obtained over a period of several days. This indicated that there was no appreciable day-to-day variation of results.

Blank

A blank is obtained by burning an empty boat in the normal manner, scrubbing and analyzing the combustion products. The main components of the blank are (a)

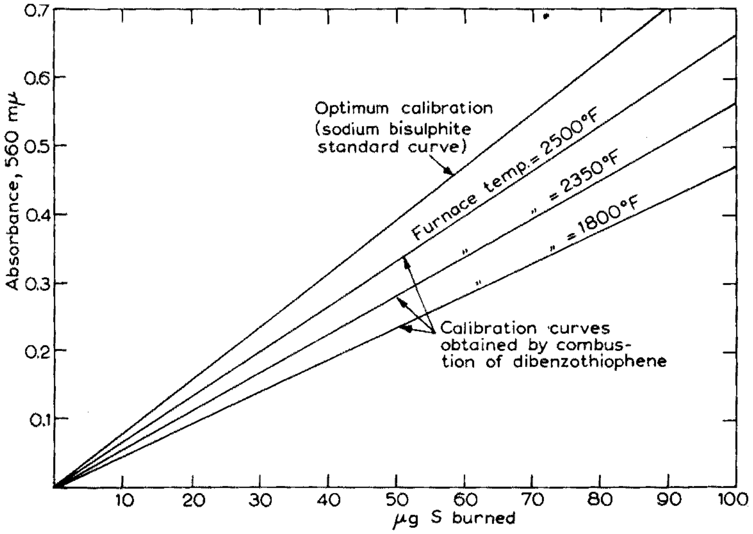

Fig. 2. Slope of calibration curve *vs.* temperature of flame.

TABLE I

PRECISION RESULTS

Sulfur added µg	*Sulfur determined* µg
10	9, 8, 12.5, 10, 12.5, 13, 11, 13 12, 5 Precision: $2\sigma = 3.7$
20	17, 18, 23
30	31, 35
40	37
50	50, 48
70	65, 66
80	78
90	86, 85, 87, 90, 91.5, 93, 92, 90 Precision: $2\sigma = 5.9$
100	101, 104

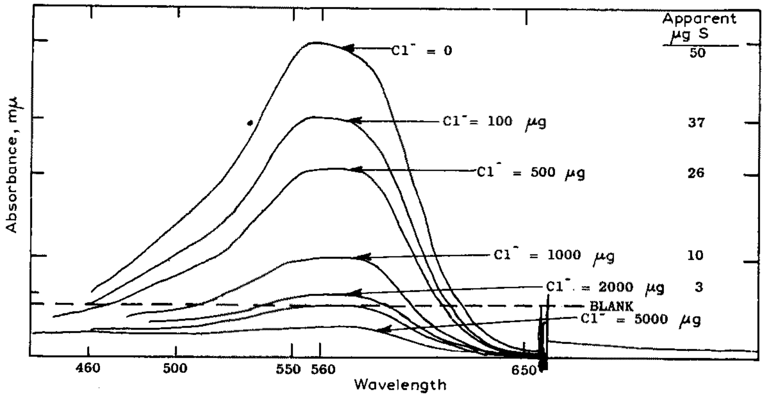

Fig. 3. Interference due to chloride. All samples contain 50 g of S plus various amounts of added chloride. Absorbancy trace obtained on a Cary spectrophotometer.

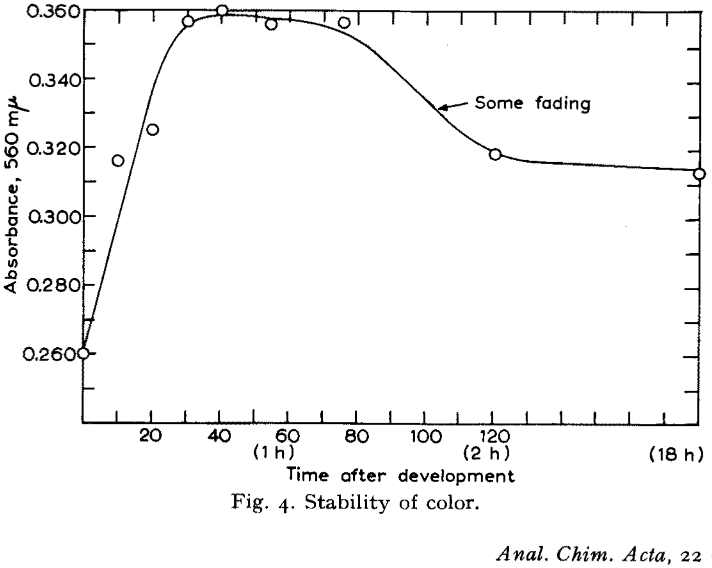

Fig. 4. Stability of color.

sulfur in the oxygen stream, (b) sulfur in the boats, and (c) the color developed from the reagents alone. Results indicate that (a) sulfur in the oxygen stream was negligible, (b) the boats should be burned off at 2500°F and kept in a vacuum desiccator prior to use, and (c) the reagent blank was considerable, but constant for a set of reagents.

Interferences

The effect of the presence of nitrogen or chloride in the sample was determined. This was done by adding known amounts of pure compounds to sulfur samples at the 50 p.p.m. S level. The results as shown by Figs. 3 and 4 indicated that chloride interfered at all levels and nitrogen interfered if present in quantities greater than 100 μg, *i.e.*, 0.01% on a 1-g sample. Both elements bleached the color and seemed to act as oxidizing agents. Experiment showed that inorganic chloride (HCl) and organic chloride (CCl_4) gave similar results.

RECOMMENDED PROCEDURE

Reagents

Sodium tetrachloromercurate solution, 0.1 *M*: Dissolve 20.2 g of reagent grade mercuric(II) chloride and 11.7 g of reagent grade sodium chloride in water and dilute to 1 l.

Hydrochloric acid-bleached para-rosaniline, 0.04%: Mix 40 m of a 1% aqueous solution of *para*-rosaniline hydrochloride and 60 ml of conc. hydrochloric acid; dilute to 1 l.

Formaldehyde, 0.2%: Dilute 5 ml of 40% formaldehyde to 1 l with distilled water.

Sodium bisulfite, reagent grade and *oxygen* (cylinder).

Apparatus

Beckman Model B Spectrophotometer, 1-cm cells (Other suitable spectrophotometers are available).

Furnace, tube type, 4 inch length capable of operation at 1000°F.

Furnace, tube type, 12 inches length capable of operation at 2500°F.

Combustion tube, 0.75 inch ID × 31 inches length, Zirconia.

Assemble the combustion apparatus as shown in Fig. 1. Regulate 4-inch furnace to 950°F and 12-inch furnace to 2500°F. Adjust oxygen rate to 3 l per min. Pour 50-60 ml of sodium tetrachloromercurate solution in scrubber. Depending upon sulfur concentration, weigh up to 1 g of sample into combustion boat. Position boat in center of 950°F furnace and leave it there until the initial burning subsides (2-5 min). Push boat into 2500°F furnace and let it remain there 15 min.

Quantitatively transfer the scrubbing solution to a 100-ml volumetric flask. To the flask add 10.0 ml of acidic *p*-rosaniline solution and 10.0 ml of formaldehyde solution. Fill to mark with sodium tetrachloromercurate solution. Allow to stand 20-30 min for full color development. The color is stable for 1 h. Determine absorbancy of the sample solution at 560 mμ. Read concentration of sulfur from calibration curve (Fig. 2), which has been previously prepared by using fresh standard solutions of sodium bisulfite in sodium tetrachloromercurate solution. The curve should cover the range 0-100 mμ sulfur.

A combination combustion-reagent blank is determined by the same procedure as described in the first paragraph, except the sample is omitted.

Sulfur oxidized to sulfur trioxide is not measured; therefore, the equilibrium amounts of sulfur trioxide formed during combustion must be determined on a pure compound and the necessary correction applied in the calculations. Alternatively, the calibration curve can be determined by burning various size samples of a pure organic sulfur compound. The resulting values will not include the sulfur trioxide formed and a correction factor will not be necessary.

CONCLUSIONS

The method is rapid (30 min per analysis when a group is analyzed), accurate, and precise. Accuracy and precision data obtained on a synthetic sample of 4,4'-thio*bis*-(6-*tert.*-butyl-*m*-cresol) in alcohol are given in Table I. The short term standard deviation is 5.9 p.p.m. sulfur at the 90 p.p.m. sulfur level, and 3.6 p.p.m. S at the 10 p.p.m. level. Chloride interferes at all levels; nitrogen interferes if present in quantities greater than 0.01% for a 1-g sample.

ACKNOWLEDGEMENT

The authors wish to thank C. R. TESSIER who carried out much of the experimental work, and Esso Standard Oil Company for permission to publish this work.

SUMMARY

A rapid and reasonably precise method was needed for determining low sulfur concentrations (<200 p.p.m.) in organic solids, gas oils, and heavier liquids. This level of sulfur is below the useful range of conventional procedures; therefore, the development of a new method became necessary and a satisfactory combustion–colorimetric method was developed. The method is based on the oxidation of sulfur to sulfur dioxide by combustion and the subsequent formation of stable, non-volatile disulfitomercurate(II) ion. A red-violet color develops when disulfitomercurate, *p*-rosaniline, hydrochloric acid, and formaldehyde are mixed. The absorption of the solution is measured at 560 mμ and is directly proportional to sulfur concentration.

The method is rapid, accurate and precise. The short-term 2-sigma precision limits are 5.9 p.p.m. sulfur at the 90 p.p.m. level and 3.6 p.p.m. at the 10 p.p.m. level. Two samples can be analyzed per hour. The succes of the method is due in part to the use of two furnaces at different temperatures during the combustion step. This arrangement affords good control of the combustion and is particularly useful where various types of samples are to be analyzed.

RÉSUMÉ

Une méthode rapide et précise est proposée pour le dosage du soufre en très faibles concentrations dans des huiles et des substances organiques solides. Elle est basée sur l'oxydation du soufre en anhydride sulfureux par combustion et sur la formation de disulfitomercurate stable non volatil; ce dernier réagit avec la *p*-rosaniline, l'acide chlorhydrique et le formaldéhyde pour donner une coloration violette. L'absorption de cette solution est mesurée à 560 mμ; elle est directement proportionnelle à la teneur en soufre.

ZUSAMMENFASSUNG

Es wird eine rasche und genaue Methode beschrieben zur Bestimmung sehr kleiner Mengen von Schwefel (<200 p.p.m.) in organischen Substanzen, Gasölen etc. Die Methode beruht auf der Oxydation des Schwefels zu Schwefeldioxyd und Überführung in das stabile, nicht-flüchtige Disulfitomercurat Ion, das mit *p*-Rosanilin, Salzsäure und Formaldehyd gemischt eine rotviolette Färbung ergibt. Die bei 560 mμ gemessene Absorption ist direkt proportional dem Schwefelgehalt.

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SUR LES RÉACTIONS DES IONS DU PLUTONIUM AVEC L'ACIDE ÉTHYLÈNEDIAMINOTÉTRACÉTIQUE

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Le plutonium et le trilon B (sel disodique de l'acide éthylènediaminotétracétique) forment un complexe non ionique, soluble, permettant d'éliminer le plutonium (ainsi que Am et Pb) de l'organisme vivant, où il se trouve probablement, sous forme de plutonium (IV)[1,2]. D'après MILLNER ET WOODHEAD[3], on peut déterminer les ions Pu^{+3} par titrage avec une solution de trilon B (pH = 2,5).

Les complexes du trilon B avec Pu(VI), comme ceux de U(VI)[4,5] et avec Pu(V), comme ceux des ions Me^{+}[6,7], peuvent être utilisés pour la séparation du plutonium d'avec plusieurs éléments, dont les complexes sont plus stables, ainsi que pour la séparation de Pu(IV), Pu(V) et Pu(VI).

PARTIE EXPÉRIMENTALE

Nous avons opéré en solutions perchloriques, les ions ClO_4^- ne formant pas de complexes avec le plutonium[8].

Reactifs

Solutions de $PuO_2(ClO_4)_2$, préparées par oxydations répétées de $Pu(NO_3)_4$ ou $PuCl_4$ (contenant moins de 0.1% de matières étrangères) par l'acide perchlorique à 72%, à l'ébullition; on évapore à sec pour chasser l'excès d'acide perchlorique, et on reprend le résidu par une solution $HClO_4$ 0.5*M* + $NaClO_4$ 0.5 *M* ou par une solution $NaClO_4$ 1.0 *M*. On vérifie que l'oxydation soit complète par spectre d'absorption. La concentration en plutonium est déterminée en comptant le nombre des particules α ($\pm$1–2%).

Solution de trilon B 0.01 *M* (recristallisée plusieurs fois) standardisée à l'aide d'une solution de nitrate de plomb 0.01002 *M*.[9]

Appareillage

La densité optique a été mesurée au spectrophotomètre Beckman DU avec des cuves de 10.0 mm (mesures reproductibles à 0.001–0.005). Les courbes des titrages conductimétriques ont été faites à l'aide du pont de Wheatstone, à température constante (25 ± 0.1)° et fréquence 1000 Hz. Le pH des solutions a été mesuré au potentiomètre LP – 4 à électrode de verre.

1. *Pu(VI) en milieu acide*

Le spectre d'absorption des solutions de $PuO_2(ClO_4)_2$ (0.002–0.017 *M*) + $HClO_4$ 0.5 *M* + $NaClO_4$ 0.5 *M* est identique à celui obtenu en présence de trilon B 0.01 *M*.

Ainsi, dans les solutions, où $\mu = 1$ et $[H^+] = 0.5\,M$, Pu(VI) ne forme pas de complexes avec EDTA, ou bien, si ces complexes existent, ils sont très peu stables.

2. *Pu(VI) à pH* = 3-5

(a) Solutions avec $\mu = 1$

Après addition d'un fort excès de trilon B à nos solutions, nous avons observé un changement de coloration; en quelques minutes, la solution incolore ou faiblement rose devient jaune citron, et, quelques minutes après elle redevient incolore; au bout de quelques jours, elle reprend une coloration jaune orange, stable. La vitesse des changements de coloration dépend de la quantité de trilon ajoutée.

Tous ces changements ont été suivis par mesures spectrophotométriques; d'après l'abaissement de la densité optique à $\lambda = 835$ mμ, on a pu calculer la diminution de la concentration de PuO_2^{+2} (Fig. 1).

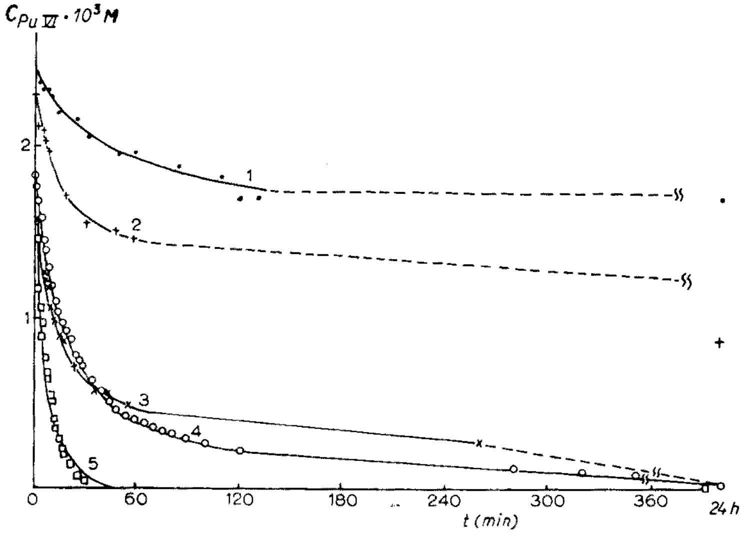


Fig. 1. Changements de concentration de PuO_2^{+2} en présence de trilon B. Solution initiale: $PuO_2(ClO_4)_2$ 0.0029 *M* + $NaClO_4$ 1 *M*, pH = 5; trilon B: courbe 1 = 0.000218 *M*; courbe 2 = 0.000334 *M*; courbe 3 = 0.000435 *M*; courbe 4 = 0.000724 *M*; courbe 5 = 0.00101 *M*.

Il est évident, que: 1) la vitesse de diminution de $[PuO_2^{+2}]$ dépend de la concentration en trilon B; 2) si cette concentration est assez élevée, tous les ions PuO_2^{+2} passent dans un état nouveau, dont l'absorption est différente de celle des solutions de $PuO_2(ClO_4)_2$; 3) dans le cas d'une faible concentration en trilon B, il se produit un équilibre entre les ions ordinaires PuO_2^{+2} et un état nouveau du plutonium; cet équilibre s'établit en 24–48 h.

Les spectres d'absorption des solutions obtenues sont identiques pour toutes les concentrations de trilon B, à condition qu'elles soient assez élevées. On peut voir dans la Fig. 2 un de ces spectres; il diffère fortement du spectre d'absorption de la solution initiale de $PuO_2(ClO_4)_2$ (courbe 1, Fig. 3) et il est tout à fait identique au spectre de la solution obtenue par réduction de PuO_2^{+2} avec l'hydroxylamine (courbe 2, Fig. 3). On sait que celle-ci, dans les conditions citées, réduit quantitativement Pu(VI) en Pu(V)[10].

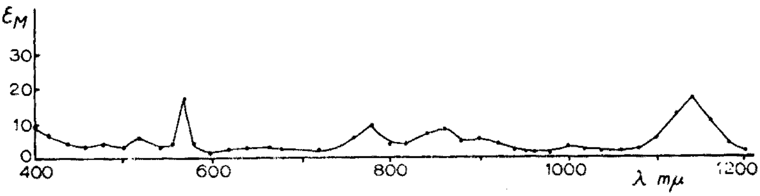


Fig. 2. Spectre d'absorption de la solution obtenue par l'action du trilon sur $PuO_2(ClO_4)_2$ en 24 h.

$$\frac{\text{Concn. trilon B}}{\text{Concn. Pu}} = 0.25$$

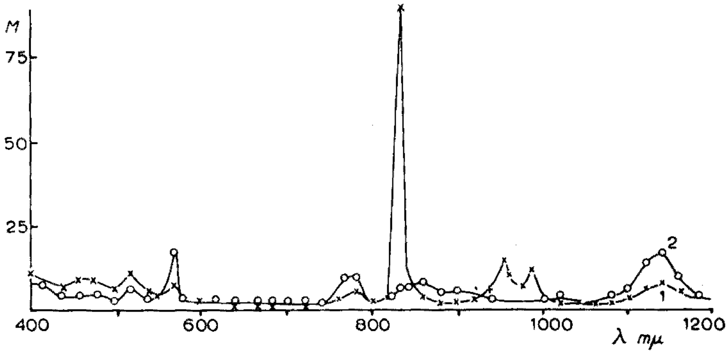


Fig. 3. Spectres d'absorption des solutions: 1. $PuO_2(ClO_4)_2$ 0.0029 *M*, $NaClO_4$ 1.0 *M*. 2. PuO_2ClO_4 0.0029 *M*, $NaClO_4$ 1.0 *M*.

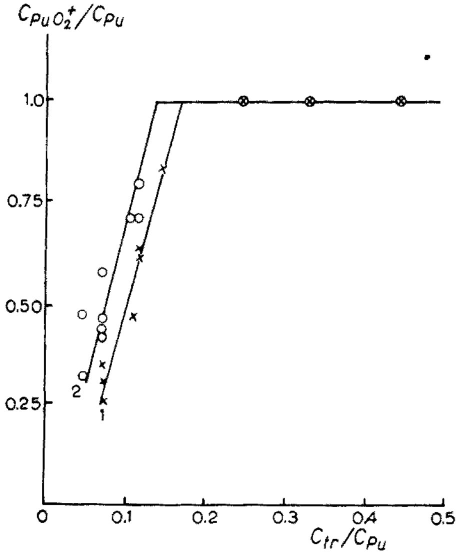


Fig. 4. Degré de réduction de Pu(VI) à (concn. trilon B: concn. Pu) divers. Solution initiale $NaClO_4$ 1 *M*, $PuO_2(ClO_4)_2$ 2.9 . 10^{-3} *M*. courbe 1, $[PuO_2^{+2}]$, $\lambda = 955$ mμ. courbe 2, $\lambda = 835$ mμ.

On peut en conclure que le trilon B, en solution $NaClO_4$ *M*, (pH = 3–5), réduit Pu(VI) en Pu(V); la réaction s'effectue en proportions stoechiométriques.

La Fig. 4 nous montre que, pour une réduction complète de PuO_2^{+2} en PuO_2^{+}, il est nécessaire, que la concentration molaire du trilon B soit égale à 0.17 par rapport à la concentration molaire du plutonium, mesurée à $\lambda = 955$ mμ; et 0.14 à $\lambda = 835$ mμ soit en moyenne: 0.155. Par conséquent, une molécule de trilon B réduit six atomes de plutonium(VI).

Le second changement de coloration, incolore à jaune orange peut être accéléré en chauffant. Le spectre d'absorption de la solution ainsi obtenu est représenté par la courbe 1, Fig. 5. En la comparant avec celle de Pu(V) (Fig. 2), on constate que le plutonium a passé à un nouvel état. La courbe 1 (Fig. 5) représente un spectre d'absorption du complexe Pu(IV, -trilon B, (ressemblance avec spectre de Pu(IV) en présence du trilon B) (courbe 2, Fig. 5).

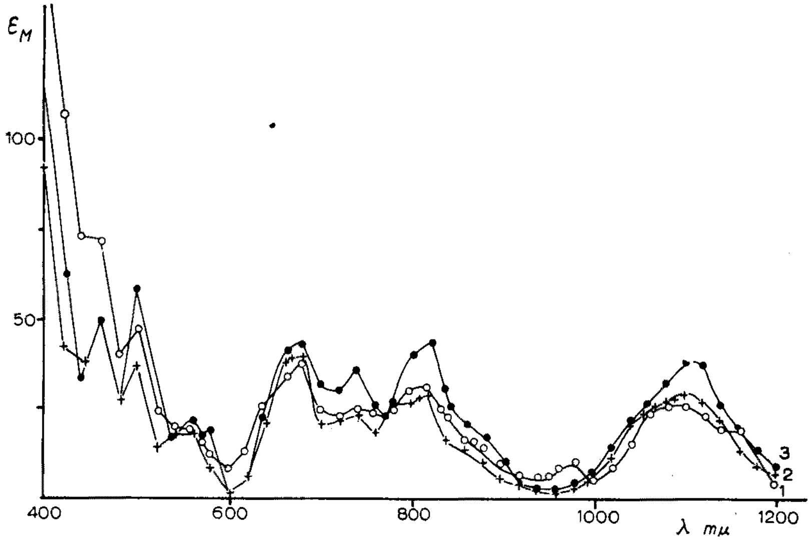


Fig. 5. Spectres d'absorption: 1. Solution Pu(VI) 0.0026 *M* + trilon B 0.0035 *M* + $NaClO_4$ 1 *M*, chauffée 4 h à 80–90° et refroidie; pH = 5. 2. $Pu(NO_3)_4$ 0.0117 *M* + trilon B 0.0148 *M*; pH = 1.35. 3. Pu(VI) 0.0080 *M* + trilon B 0.10 *M*, un mois après préparation; pH = 5.

L'apparition de Pu(IV) est confirmée aussi par la formation d'un précipité de $Pu(OH)_4$, dans le cas où le trilon B est ajouté en quantités insuffisantes (moins qu'équimolaires) pour former le complexe, soluble à pH 3–5.

Il faut remarquer que la réaction de PuO_2^{+2} avec le trilon B est toujours accompagnée d'un abaissement de pH.

(*b*) *Solutions aqueuses sans électrolyte étranger*

En mesurant le changement d'absorption à $\lambda = 835$ mμ, nous avons pu déterminer la vitesse de réduction de Pu(VI) par le trilon B dans la solution aqueuse de $PuO_2(ClO_4)_2$ sans $NaClO_4$ (Fig. 6).

Pour faire une comparaison, nous avons tracé la courbe 1 obtenue dans la solution de $NaClO_4$ 1 *M*.

Dans la solution de trilon B 0.1 *M* et de Pu(VI) 0.008 *M* la réduction de Pu(VI) en Pu(V) s'effectue instantanément, on peut observer un accroissement visible de la concentration de Pu(IV) avec une apparition de la coloration jaune orange. Pour observer le cours du processus (Fig. 7), on a choisi une bande d'absorption à λ = 500 mμ, due à l'ion complexe, formé par Pu(IV) et trilon B.

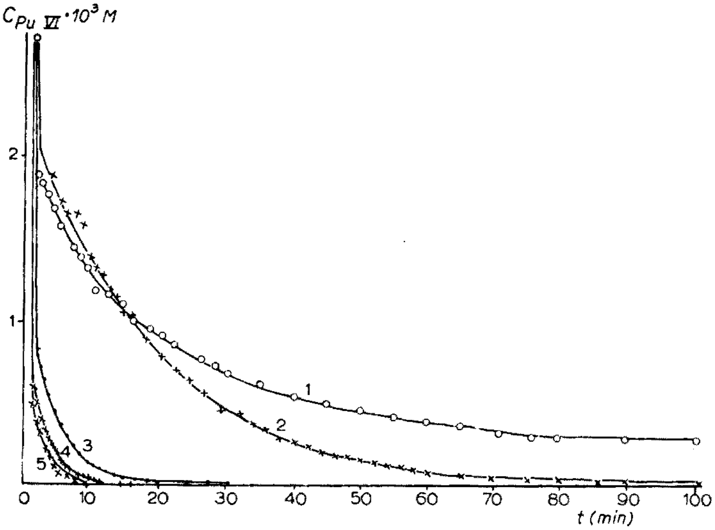


Fig. 6. Changement de concentration de Pu(VI) en présence de trilon B, en fonction du temps. Courbe 1, Pu(VI) 0.0029 *M* + trilon B 0.00072 *M* + $NaClO_4$ 1 *M*. Courbe 2, Pu(VI) 0.0033 *M* + trilon B 0.00094 *M*. Les courbes 3, 4 et 5 Pu(VI) 0.0033 *M* + trilon B 0.0035 *M*; pH = 4.

Après quatre jours la valeur d'absorption change peu.

En absence de $NaClO_4$, on a constaté la même augmentation d'acidité des solutions pendant la réaction entre PuO_2^{+2} et trilon B.

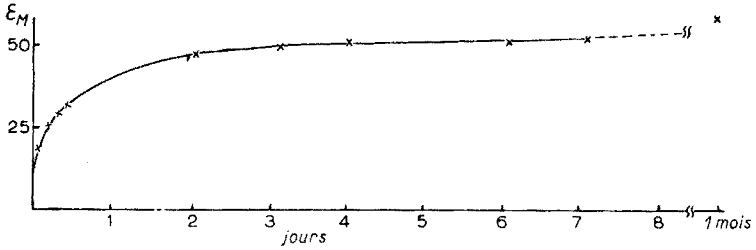


Fig. 7. Changement de coefficient molaire de l'absorption en fonction du temps pour une solution contenant Pu(V) 0.0080 *M* + trilon B 0.10 *M*; pH = 5; λ = 500 mμ.

3. *Réaction entre Pu(V) et trilon B*

On a étudié la formation du complexe Pu(V)-trilon B dans les solutions de PuO_2ClO_4, obtenues par réduction de $PuO_2(ClO_4)_2$ avec l'hydroxylamine.

Différentes quantités de trilon B ont été ajoutées à la solution contenant PuO_2ClO_4 + $NaClO_4$ 1 *M*. En mesurant ensuite pendant deux ou trois heures la densité optique des solutions à $\lambda = 1140$ mμ, 570 mμ et 400 mμ.
On a constaté qu'elle ne variait pas.

Au cours de ces mesures, les solutions sont restées incolores; devenant cependant jaune orange en trois jours, après leur préparation.

L'addition d'un grand excès de trilon $\mathrm{B}(C_{tr} : C_{Pu} = 0.6 \div 4.7)$ à la solution ne change pas, pendant deux heures, le degré d'absorption de la lumière par ce dernier.

Les ions incolores[6,11] forment avec le trilon B des complexes incolores. Ainsi, le comportement de Pu(V), dans la solution contenant le trilon B, a été étudié par titrage conductimétrique. Lors de la première série d'essais, on a titré la solution aqueuse de $PuO_2(ClO_4)_2$ 0.0080 *M*, de pH 3–4.5, par le trilon B.

Dans la Fig. 8 sont représentés les résultats obtenus.

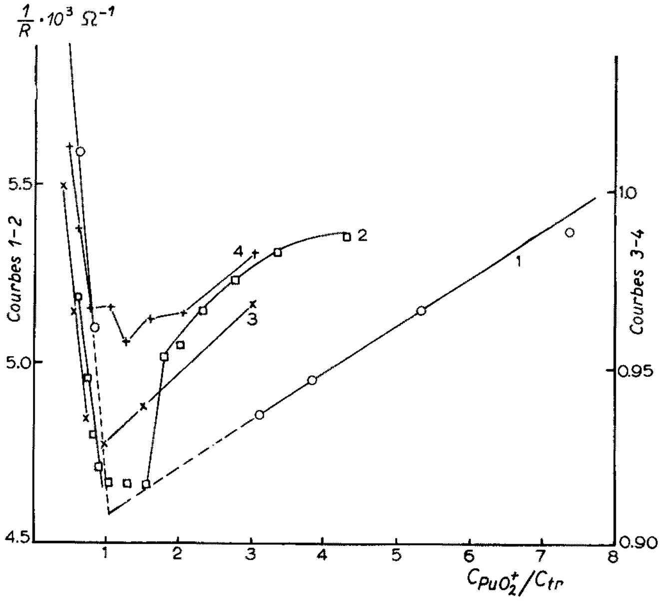


Fig. 8. Titrage conductimétrique de la solution aqueuse de $PuO_2(ClO_4)_2$ par le trilon B. Courbe 1, PuO_2^{+2} 0.0080 *M* et trilon B 0.060 *M*. Courbe 2, PuO_2^{+2} 0.0081 *M* et trilon B 0.162 *M*. Les courbes 3 et 4, PuO_2^{+} 0.00066 *M* et trilon B 0.0435 *M*.

Le titrage est d'une durée telle (60 à 100 min), qu'au moment d'arriver à la solution équimolaire du plutonium et du trilon B pratiquement tout le plutonium est à l'état de Pu(V). Les courbes montrent que la conductibilité électrique est minimum dans la région de formation de la solution équimolaire.

On a pu obtenir des résultats plus exacts par titrage conductimétrique rapide, au moyen de trilon B, de la solution $\mathrm{PuO_2ClO_4}$ 0.00066 *M* (pH étant 2.4), obtenue par réduction de la solution $\mathrm{PuO_2(ClO_4)_2}$ avec l'hydroxylamine.

Avant, ainsi que vers la fin du titrage conductimétrique, la solution de plutonium(V) a été analysée spectrophotométriquement, pour vérifier l'absence du plutonium à d'autres valences.

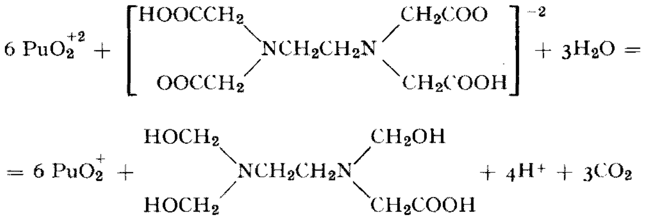
Les courbes 3 et 4 (Fig. 8) confirment que, dans ce cas, dès que le mélange équimolaire $\mathrm{PuO_2^+}$ et trilon B est obtenu, la conductibilité électrique devient également minimum.

Les résultats du titrage conductimétrique indiquent que la formation du complexe trilon B–$\mathrm{PuO_2^+}$ s'effectue dans le rapport 1:1.

DISCUSSION

Nous avons examiné d'une manière plus détaillée la réduction de Pu(VI) en Pu(V).

On sait qu'une molécule de trilon B réduit six ions $\mathrm{PuO_2^{+2}}$ avec formation d'ions hydrogène. Par conséquent, on peut admettre* la possibilité de la réaction suivante**.



$$6\,\mathrm{PuO}_2^{+2} + \left[\begin{array}{ccc} \mathrm{HOOCCH_2} & & \mathrm{CH_2COO} \\ & \diagdown\mathrm{NCH_2CH_2N}\diagup & \\ & \diagup\quad\quad\diagdown & \\ \mathrm{OOCCH_2} & & \mathrm{CH_2COOH} \end{array}\right]^{-2} + 3\mathrm{H_2O} =$$

$$= 6\,\mathrm{PuO}_2^{+} + \begin{array}{ccc} \mathrm{HOCH_2} & & \mathrm{CH_2OH} \\ & \diagdown\mathrm{NCH_2CH_2N}\diagup & \\ & \diagup\quad\quad\diagdown & \\ \mathrm{HOCH_2} & & \mathrm{CH_2COOH} \end{array} + 4\mathrm{H^+} + 3\mathrm{CO_2} \qquad (1)$$

Nous avons essayé de déterminer l'ordre de la réaction. On peut supposer que la vitesse de la réaction(I) est proportionnelle à la concentration de $\mathrm{PuO_2^{+2}}$ ainsi qu'à celle du trilon B, c'est-à-dire:

$$\frac{-\,\mathrm{d}[\mathrm{PuO}_2^{+2}]}{\mathrm{d}t} = K\,[\mathrm{PuO}_2^{+2}]_t \cdot [\text{trilon B}]_t. \qquad (2)$$

où $\frac{\mathrm{d}[\mathrm{PuO_2^{+2}}]}{\mathrm{d}t}$ est le changement de la concentration de $\mathrm{PuO_2^{+2}}$ par unité du temps; K = la constante de la vitesse de réaction; $[\mathrm{PuO_2^{+2}}]_t$ = la concentration en $\mathrm{PuO_2^{+2}}$ au temps t; $[\text{trilon B}]_t$ = la concentration en trilon B au même moment.

On peut conclure d'après l'équation (2) que dans le cas où la concentration du trilon B est suffisante pour nous permettre d'en négliger de petites variations l'expression devient:

$$\frac{-\,\mathrm{d}[\mathrm{PuO}_2^{+2}]}{\mathrm{d}t} = K_1\,[\mathrm{PuO}_2^{+2}]_t \qquad (3)$$

où

$$K_1 = K\,[\text{trilon B}]_{t=0} \qquad (4)$$

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* Nous exprimons notre reconnaissance à A. A. NEMODRUK pour ses conseils à ce sujet.

** Au moment de la présentation de ce travail pour la publication, un article[13] a été publié consacré à l'investigation polarographique des produits d'oxydation de l'EDTA. Les essais de l'auteur apparemment ne sont pas en contradiction avec notre version du mécanisme de la réaction.

Les données expérimentales sur le changement de la vitesse de réaction en fonction de la concentration en PuO_2^{+2} dans des solutions, renfermant du trilon B (en quantité six fois celle nécessaire à la réduction complète du plutonium (VI)), sont représentées par les courbes 1–3 (Fig. 9).

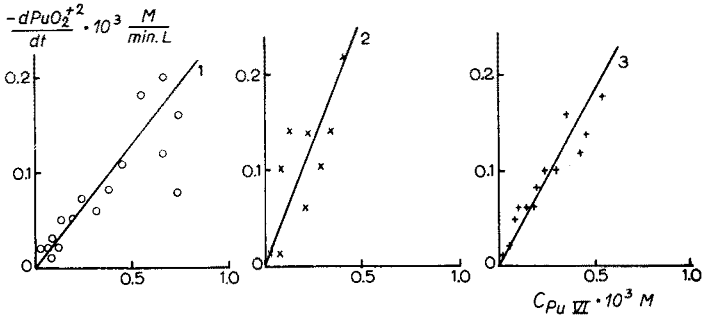

Fig. 9. Vitesses de réduction de Pu(VI) par le trilon B en excès. Concn. Pu = 0.0029 M; concn. trilon = 0.0035 M.

La pente des courbes permet de calculer les valeurs de K_1. Si l'on admet que la progression est linéaire, les valeurs des constantes de la vitesse de réaction K_1, peuvent être représentées par la Table I. Les valeurs de K sont calculées d'après l'équation (4).

TABLE I

CONSTANTES DE LA VITESSE DE REACTION (1)

Trilon B en excès et $NaClO_4$ absent, conc. trilon B = $3.5 \cdot 10^{-3}$ M

No. de la courbe dans la Fig. 9	$\frac{Concn.\ trilon\ B}{Concn.\ Pu}$	$K_1 \cdot 10^1$	$K \cdot 10^{-2}$
1	1.1	0.73	2.1
2	1.1	1.1	3.1
3	1.1	1.5	4.3
	moyenne	1	3

TABLE II

CONSTANTES DE LA VITESSE DE RÉACTION (1)

Concentration en trilon B dans la solution $NaClO_4$ relativement faible
Conc. Pu = $2.9 \cdot 10^{-3}$ M

No. de la courbe dans la Fig. 10	*Concn. trilon B* $\cdot 10^3 M$	$\frac{Concn.\ trilon\ B}{Concn.\ Pu}$	$K \cdot 10^{-2}$
1	0.72	0.25	1.0
2	0.43	0.15	3.6
3	0.33	0.11	1.4
		moyenne	2

Lorsque la concentration en trilon B n'est pas suffisante, la vitesse de la réaction varie, elle est alors proportionnelle au produit de la concentration de PuO_2^{+2} par la concentration en trilon B. Dans ce cas les données expérimentales ont été calculées d'après les courbes des Fig. 1 et 6, elles sont représentées par la Fig. 10 et données dans la Table II.

L'angle des courbes (Fig. 10) nous donne immédiatement la valeur de K_1.

Les Tables I et II prouvent que la réaction (1) est une réaction du premier ordre par rapport à PuO_2^{+2} et trilon B; les valeurs des constantes sont très proches; elles ne dépendent pas du milieu (eau ou solution de $NaClO_4$ M).

La valeur moyenne de la constante est de $(2.5 \pm 1.0)\ 10^2\ M^{-1} \cdot l \cdot min^{-1}$.

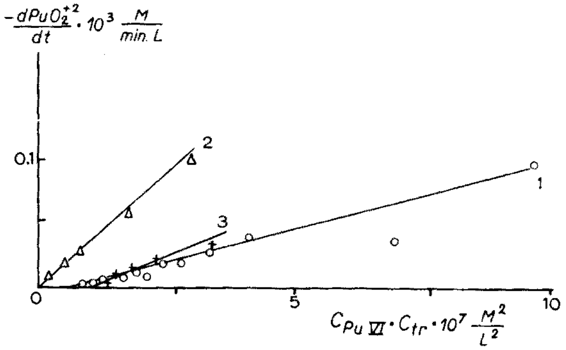

Fig. 10. Vitesses de réduction de Pu(VI) par le trilon B, (en quantités réduites). Concn. Pu = 0.0029 M. Courbe 1, concn. trilon B = 0.00072 M; courbe 2, concn. trilon B = 0.00043 M; courbe 3, concn. trilon B = 0.00033 M.

Le fait que la réaction de réduction de Pu(V) en Pu(IV) ne s'accomplit que lentement nous fait supposer que Pu(IV) ne se forme pas par réduction immédiate de Pu(V) avec le trilon B, mais plutôt par l'intermédiaire de la réaction de dismutation de Pu(V).

Pu(IV), ainsi obtenu, forme un complexe avec le trilon B, ce qui augmente considérablement la vitesse de dismutation. Il faut noter, que la vitesse de réduction de Pu(VI) par les produits d'irradiation α de l'eau[12] est beaucoup plus faible que les vitesses de réduction de PuO_2^{+2} par le trilon B, calculées ci-dessus. Pour une application analytique des ions complexes de Pu(V) et de Pu(IV) avec l'acide éthylènediaminotétracétique, il serait intéressant de faire une étude quantitative des complexes en question. Nous espérons la réaliser dans un travail ultérieur.

CONCLUSIONS

1. Dans les solutions de pH 3 à 5, le trilon B réduit Pu(VI) en Pu(V). Une molécule de trilon B réduit six ions PuO_2^{+2}.

2. La vitesse de la réaction de réduction de PuO_2^{+2} en Pu(V) par le trilon B est proportionnelle aux concentrations de PuO_2^{+2} et de trilon B; la réaction produit des ions H^+. La constante de la vitesse de réaction dans l'eau pure ainsi que dans la solution de $NaClO_4$ M à la température ordinaire est égale à $(2.5 \pm 1.0) 10^2 M^{-1} \cdot l \cdot min^{-1}$.

3. Les courbes du titrage conductimétrique des solutions de PuO_2ClO_4 par le

trilon B prouvent la formation du complexe, peu dissocié, de Pu(V) avec le trilon B, dans un rapport 1:1; cependant, le spectre d'absorption ne change pas.

4. La présence de trilon B dans la solution de Pu(V) produit une formation lente de Pu(IV).

5. Le spectre d'absorption de la solution du complexe de Pu(IV) avec le trilon B diffère du spectre de l'ion de Pu(IV) non complexé, qui existe dans des solutions plus acides.

RÉSUMÉ

Nous avons étudié les réactions des ions du plutonium dans les solutions de trilon B. Des mesures de densité optique ont montré qu'à pH = 3 à 5, Pu(VI) est réduit en Pu(V) par le trilon B. Le titrage conductimétrique d'une solution de plutonium(V) par le trilon B montre qu'il y a formation d'un complexe Pu(V)-trilon B (1:1). Pu(V) en solution, avec un excès de trilon B, passe en quelques jours à l'état d'un complexe Pu(IV)-trilon B.

SUMMARY

The behaviour of plutonium ions in a solution of trilon B was investigated. At pH 3-5 plutonium(VI) is reduced to plutonium(V) and a (1:1) complex of plutonium(V) and trilon B is formed. With excess trilon B a plutonium(IV)-trilon B complex is formed after some time.

ZUSAMMENFASSUNG

Es wurde das Verhalten von Plutonium-Ionen in einer Lösung von Trilon B untersucht: Bei pH 3-5 wird Plutonium(VI) zu Plutonium(V) reduziert und ein Komplex von Plutonium(V)-Trilon B (1:1) gebildet. Mit einem Ueberschuss von Trilon B bildet sich nach einiger Zeit ein Komplex von Plutonium(IV)-Trilon B.

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AMPEROMETRIC TITRATION OF BORON WITH FRUCTOSE

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The current use of boron as a key component in many synthetic preparations has increased the need of reliable methods for its determination. Although it is easy to convert boron to the borate form, it is often difficult to measure the borate ion concentration. Direct alkalimetric titration methods are not applicable because boric acid has such a low ionization constant. Direct gravimetric methods cannot be employed because there are no reagents that will selectively and quantitatively precipitate the borate ion.

The more or less classical method that is generally used for determining borate in aqueous solutions is based on complexing the borate with a polyhydric alcohol[1]. In this method the acidity of the solution is adjusted to pH 4 and a large excess of a polyhydric alcohol such as mannitol is added. The alcohol complexes the borate and releases an equivalent quantity of hydronium ions. The liberated hydronium ions are then titrated with standard alkali. This method when properly applied is accurate and features simplicity in technique. However, the method is not applicable in the presence of weak acids or bases. It is limited in that several milligrams of boron are required for a reasonably accurate titration.

The more recent developments have for the most part been modifications of the classical method or the development of new colorimetric procedures. The colorimetric methods although very sensitive are often subject to involved manipulations to offset such factors as unstable reagents, time dependent color development, contamination by trace impurities, etc.

HEYROVSKÝ AND SMOLEŘ[2] found that fructose gives a well defined polarographic wave with the DME in a 0.1 *M* lithium chloride solution in both a neutral and an alkaline medium.

JAMBOR AND KISBAN[3] demonstrated that boric acid depresses the polarographic wave height of glucazone without affecting its half wave potential. A similar effect was noticed in the polarography of fructose. In this case the wave height of the fructose itself was depressed by the presence of borate. Since fructose exhibits a well defined polarographic wave, an investigation has been made to see if this phenomenon could be utilized as a basis for a quantitative method to determine boron. It was found that the amount that the wave is depressed is related to the concentration of boron but the relationship is not directly proportional. However, if the borate is titrated amperometrically with standard fructose to a preestablished current value the relationship between the titer and boron concentration is a direct proportion. The method described is based upon this amperometric technique.

APPARATUS

Leeds and Northrup Electro-Chemograph Type E, was used in this study. Any other polarographic instrument capable of applying a potential of —2.05 V and measuring current in the μA range might be used.

The polarographic Cell Assembly shown in Fig. 1 was employed. It was equipped with a micro buret graduated in units of 0.002 ml. A silver–silver chloride reference electrode and a dropping mercury electrode were used. The constant temperature bath maintained the temperature within ± 0.1°.

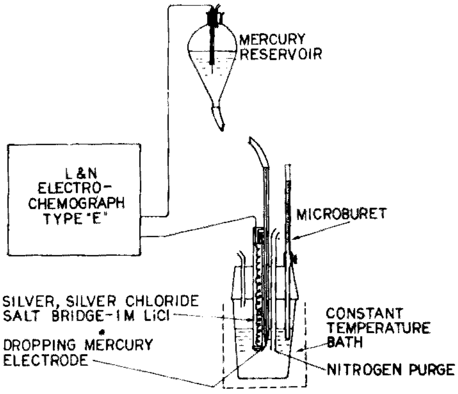

Fig. 1. Polarographic assembly.

PREPARATION OF REAGENTS

Fructose (0.1 *M*): dissolve 18.012 g of reagent grade D(-)levulose in water and dilute to one l. Standard borate (0.2 mg of boron per ml): dissolve 1.142 g of boric acid in water and dilute to one l. Lithium chloride–lithium hydroxide (1.0 *M* and 0.1 *N*): dissolve 42.4 g of lithium chloride and 4.2 g of lithium hydroxide mono-hydrate in water and dilute to one l. Lithium hydroxide (0.1 *N*): dissolve 4.2 g of lithium hydroxide monohydrate in water and dilute to one l. Hydrochloric acid (0.1 *N*): dilute 8.3 ml of conc. hydrochloric acid to one l with water. Phenolphthalein indicator: dissolve 1 g of indicator in 50 ml of ethyl alcohol and add 50 ml of water.

CALIBRATION CURVE

To a series of 25-ml volumetric flasks add the following volumes of standard borate solution, 0, 1, 2, 3, 4, 5 ml. Treat each solution in the following manner:

Add 1 drop of phenolphthalein indicator solution and neutralize by the dropwise addition of 0.1 *N* lithium hydroxide. Add 2.5 ml of the lithium chloride–lithium hydroxide electrolyte and dilute to the mark with water. Pipet 20 ml of the solution into a polarographic cell and measure the pH with a pH meter using the glass– calomel electrode system. If the pH differs from 12 by more than 0.1 units, adjust to that value by the addition of either 0.1 *N* hydrochloric acid or lithium hydroxide, from a 1 ml Mohr pipet. Record the exact volume of solution used in making this adjustment. Attach the cell to the polarographic assembly and purge with nitrogen for a period of 5 min. Record the height of the mercury column and the cell temperature. The calibration curve will be valid only for these conditions of temperature and mercury height. Set the current sensitivity dial so that full scale deflection corresponds to three μA and with an applied potential of —2.05 V, record the value of current flowing through the circuit. Add a series of small increments of 0.1 M fructose from the buret, purging with nitrogen for 1 min between each addition, and record the corrected current values corresponding to each incremental addition. All observed current values after the initial reading must be corrected because of dilution by the following equation:

$$I_{\text{corr.}} = \frac{(I_{\text{obs.}})\,(V_N + V_t)}{20}$$

where $I_{\text{corr.}}$ = corrected current (μA), $I_{\text{obs.}}$ = observed current (μA), V_N = volume of solution required to adjust pH (ml), V_t = volume of titrant added (ml).

Make a plot of diffusion current against volume of titrant and record the value of titrant corresponding to a current increase of 1.5 μA as the end-point of the titration.

Subtract the volume of titrant corresponding to the end-point of the blank (solution containing no boron) from the end-point values of the other solutions. Prepare the calibration curve by plotting the titration differences against the mg of boron in each standard solution.

PROCEDURE

In a 25-ml volumetric flask, neutralize to a phenolphthalein end-point a solution containing from 0.1 to 2 mg of boron by the addition of 0.1 N lithium hydroxide or hydrochloric acid. If the volume of sample solution is too great, make the solution alkaline with lithium hydroxide and evaporate in boron free glassware to a volume of about 15 ml and transfer to a 25-ml volumetric flask. Add 2.5 ml of the lithium chloride–lithium hydroxide electrolyte and dilute to the mark with water. Pipet 20 ml of the resulting solution into a polarographic cell and follow the procedure described for titrating the standard solutions used in the preparation of the calibration curve. Determine a reagent blank for each set of samples. Using the difference in titer between the sample and reagent blank, determine the boron concentration from the calibration curve. Calculate the percent boron in the sample with the following equation:

$$X = \frac{(M)\,(100)}{(1000)\,(W)}$$

Where X = % boron in sample. M = mg of boron from the calibration curve. W = weight of sample analyzed.

RESULTS AND DISCUSSION

A polarogram of fructose at 30° in a 0.1 N lithium chloride adjusted to a pH of 12 with lithium hydroxide is shown in Fig. 2. The fructose wave starts in the vicinity of -1.80 V and reaches a limiting current at -2.05 V. The value of the limiting current increases with pH and at pH values greater than 9.5 is directly proportional to the fructose concentration. A plot of limiting current against concentration at pH 12 is shown in Fig. 3. These results show that both temperature and pH must be controlled in this system.

It was found that the presence of the borate ion depresses the limiting current of the fructose wave without significantly effecting the half wave potential. Fig. 4 shows the depression of the polarographic wave of a $6.6 \cdot 10^{-4}$ molar solution of

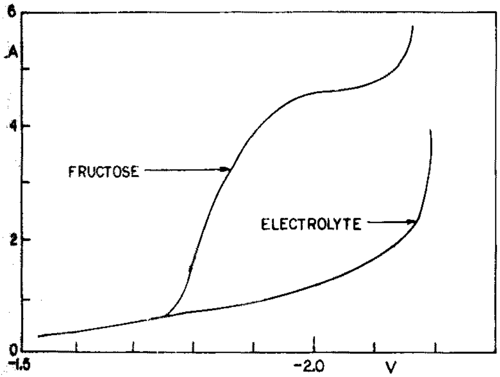

Fig. 2. Polarogram of fructose.

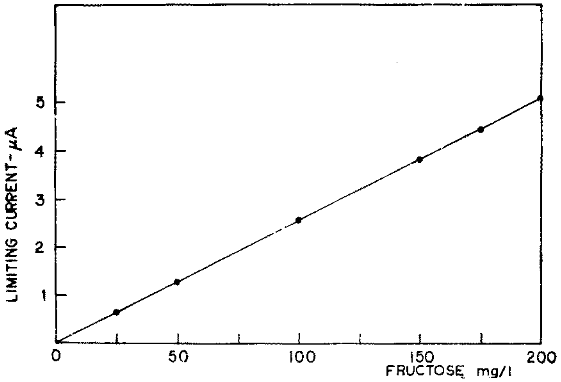

Fig. 3. Relationship of fructose concn. to limiting current.

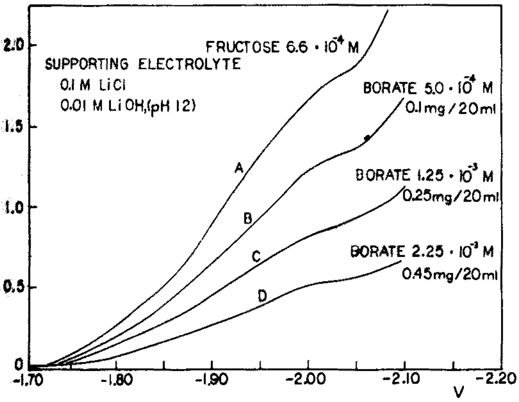

Fig. 4. Effect of borate on the fructose polarogram. Polarogram A $6.6 \cdot 10^{-4}$ *M* fructose. Polarogram B $6.6 \cdot 10^{-4}$ *M* fructose, $5 \cdot 10^{-4}$ *M* borate. Polarogram C $6.6 \cdot 10^{-4}$ *M* fructose, $1.25 \cdot 10^{-3}$ *M* borate. Polarogram D $6.6 \cdot 10^{-4}$ *M* fructose, $2.25 \cdot 10^{-3}$ *M* borate.

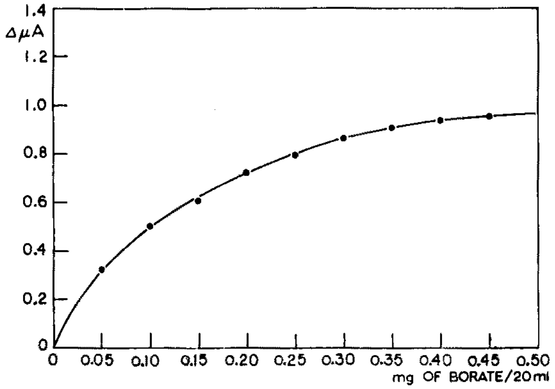

Fig. 5. Change in limiting current *vs.* borate concentration.

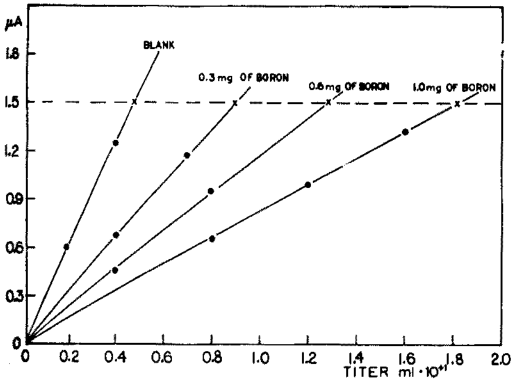

Fig. 6. Amperometric titrations of borate solutions with 0.1 *M* fructose at —2.05 V.

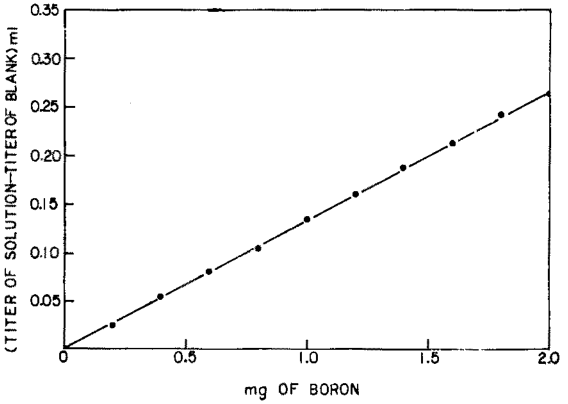

Fig. 7. Typical calibration curve (net titer *vs.* mg of boron).

fructose at pH 12 caused by the presence of various amounts of boron. The amount of depression is not directly proportional to the boron concentration. A plot of this relationship is shown in Fig. 5. An analytical method developed with this relationship as its basis would have a limited range in that at higher concentrations the sensitivity is decreased. To offset this condition one would have to make tedious dilutions, readjustments of pH, etc.

In order to examine the amperometric technique a series of solutions was prepared containing known amounts of boron in a 0.1 *N* lithium chloride solution adjusted to a pH of 12 with lithium hydroxide. Each solution was placed in a polarographic cell and titrated amperometrically with a 0.1 *N* fructose solution at a potential of —2.05 V. After correcting for the volume of titrant added, a plot of current against ml of titrant was made, Fig. 6. For each titration the plot of current against titrant is a straight line differing only by its respective slope. It is noted that at a constant current value such as 1.5 μA that the difference between the volume of titrant corresponding to the blank and of the standard is directly proportional to the concentration of boron. This proportionality is shown in the plot of Fig. 7.

Since the amperometric titration is carried out at an applied potential of —2.05 V, all polarographically active cations present in even small concentrations with the exception of lithium will interfere. The interference is due to the reduction of the cations at more positive potentials than the fructose causing a considerable quantity of current to flow through the circuit. This makes the measurement of the current due to the fructose highly inaccurate. However this interference may be removed very conveniently by passing the sample through the hydrogen form of a cation-exchange resin. The ion-exchange procedure has been described in detail by MARTIN AND HAYES[4]. The applicability of this procedure was tested by preparing several standard boron solutions containing various polarographically active cations and passing them through the exchange resin before making the amperometric titrations. The results are shown in Table I.

Commonly occurring anions such as chloride, iodide, bromide, phosphate, and carbonate do not interfere. Bromate and iodate ions do interfere because they are reduced at more positive potentials than fructose. Interference from these anions may be eliminated by passing sulfur dioxide gas through the sample while in the alkaline form, thus reducing the anions to bromide and iodide respectively.

The method has been used successfully in our laboratories to determine the boron content of new synthetic preparations of compounds such as BPI_2 and adducts from the reaction of tripropyl phosphine and diborane. The general procedure consisted of decomposing the sample by sodium peroxide fusion and passing the resulting solution through a cation-exchange resin to remove the sodium. An aliquot of the eluant was tested by the proposed method. In the case of BPI_2 a portion of the iodide was oxidized to the iodate state during the fusion process. This necessitated reducing the iodate to iodide by purging with sulfur dioxide prior to the amperometric titration.

In order to obtain an idea of the accuracy of the method a series of solutions were prepared containing known quantities of boron. These solutions were analyzed over a period of a month using the above procedure and the same calibration curve. The results of the analysis indicating an accuracy of about ± 0.01 mg are listed in Table II.

TABLE I

ACCURACY OF THE ANALYSIS AFTER TREATMENT BY ION EXCHANGE

Cations originally present mg/25 ml	*Boron present mg/25 ml*	*Boron found mg/25 ml*
Na^+ (40)	1.00	1.02
Na^+ (40)	0.50	0.49
Zn^{+2} (20)	1.00	1.00
Mg^{+2} (20)	1.00	0.98
Ca^{+2} (20)	1.00	1.01
Cu^{+2} (20)	1.00	1.00
Cu^{+2} (40)	0.50	0.51

TABLE II

ACCURACY OF TITRIMETRIC PROCEDURE

Boron present mg/25 ml	*Boron found mg/25 ml*	*Deviation*
0.05	0.05	—
0.10	0.09	−0.01
0.35	0.36	+0.01
0.49	0.50	+0.01
0.74	0.74	—
0.98	0.98	—
1.10	1.12	+0.02
1.42	1.42	—
1.67	1.66	−0.01
1.80	1.81	+0.01
1.90	1.90	—
2.00	1.98	−0.02
	S D. ± 0.007	

Although we have not tested it, the method should be applicable to those procedures requiring that the boron be distilled from a sulfuric acid–methyl alcohol solution as methyl borate. The distillate would be collected in a lithium hydroxide solution and titrated directly.

SUMMARY

Aqueous solutions of borate can be titrated amperometrically with standard fructose solutions. This procedure may be used to determine the boron content of various types of samples after conversion of the boron to the borate form. The method is based upon the observation that the polarographic wave of fructose in a 0.1 *M* LiCl, 0.01 *N* LiOH solution is depressed by the presence of borate ions. Under the prescribed conditions the method is sensitive to a few hundredths of a milligram of boron. The few commonly occurring interferences can be conveniently removed prior to the titration.

RÉSUMÉ

Les auteurs proposent une méthode de titrage ampérométrique des borates au moyen d'une solution étalon de fructose. Elle est basée sur la réduction de l'onde polarographique du fructose par addition d'un borate. On peut ainsi déterminer la teneur en bore de divers types d'échantillon après transformation en borate.

ZUSAMMENFASSUNG

Borate können amperometrisch mit Standard-Fructoselösungen titriert werden. Die Methode beruht auf der Beobachtung, dass die polarographische Kurve von Fructose durch Borat-Ionen abgeflacht wird.

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THE DETERMINATION OF URANIUM BY CATHODE-RAY POLAROGRAPHY

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INTRODUCTION

The determination of uranium by conventional polarography is an accepted and widely used technique as may be seen from the numerous papers on the subject in recent years[1]. Recently MILNER AND NUNN[2] made a study of this determination using a square wave polarograph, but the only published application of cathode-ray polarography to this determination appears to be that of TUCKER[3].

In view of the inherently greater sensitivity, speed of operation, and discrimination against interfering reductions of the C.R. polarograph as compared with conventional instruments, it was decided to develop a method applicable to the C.R. instrument.

THEORETICAL

In contrast to normal polarography in which a steady or average diffusion current is measured, the C.R. polarograph indicates the change in current, produced by the application to the dropping mercury electrode of a fairly rapid potential sweep, linear with respect to time.

The complexity of the reactions occurring at the dropping mercury electrode during the polarography of uranium solutions is such that in view of the different mode of operation of the two polarographs, the method for the determination of uranium described by SHALGOSKY[4] is inapplicable to the latter instrument.

The formal potentials of the various oxidation states of uranium in 1 M perchloric acid at 25° are[5,6].

$$U \overset{-1.80\text{ V}}{\text{————}} U^{+3} \overset{-0.63\text{ V}}{\text{————}} \underbrace{U^{+4} \overset{+0.58\text{ V}}{\text{————}} UO_2^{+} \overset{+0.063\text{ V}}{\text{————}} UO_2^{+2}}_{+0.32\text{ V}}$$

Experimentally it is found that the U(IV)/U(III) and U(VI)/U(V) couples are reversible, whilst the U(V)/U(IV) and U(VI)/U(IV) couples are irreversible. This is in agreement with a criterion for reversibility that no covalent metal-oxygen bonds are formed or broken during reduction-oxidation.

Apart from the complexity of polarograms resulting from the possible production of the three waves corresponding to U(VI) → U(V), U(V) → U(IV), and U(IV) → U(III), the primary reduction product U(V) is capable of disproportionation *viz.:*

$UO_2^{+} + H^{+} \longrightarrow UOOH^{+2}$

$UO_2^{+} + UOOH^{+2} \longrightarrow UO_2^{+2} + UOOH^{+}$ (Rate determining step)

$UOOH^{+} \longrightarrow$ Stable U(IV) species.

Although this mechanism, proposed by KERN AND ORLEMANN[7], involving a proton transfer has been challenged as a result of the work of DUKE AND PINKERTON[8], the rate of disproportionation is first order with respect to the hydrogen ion concentration and second order with respect to the U(V) concentration. Additionally, the rate of disproportionation is greatly increased in the presence of anions which form strong complexes with U(IV) species (*e.g.* SO_4^{-2} and F^-)[9].

Using an ordinary polarograph, the method described by SHALGOSKY[4], in which a perchloric–sulphuric–tartrate supporting electrolyte is used, yields *n* values of about 1.8 down to a uranium concentration of approximately 10^{-4} *M*. The drop time of the electrode is sufficiently long for conditions of apparent equilibrium to be obtained and for *n* to approach the value of 2 for the U(VI) → U(IV) reduction.

In the case of the C.R. polarograph the criterion for the production of a well defined wave is that the reduction should be rapid and reversible, and, in the case of a reduction followed by a chemical reaction leading to further reduction, that the rate of the chemical reaction must be very rapid in comparison with the rate of potential sweep applied to the dropping mercury electrode. From the ill-defined shape of the wave on the C.R. polarograph this latter condition does not appear to be fulfilled in the case of the disproportionation of U(V) in the sulphuric–tartrate base mentioned above.

However, in the presence of fluoride ions, the rate of disproportionation of U(V) is very fast[9], and on the C.R. instrument the wave height thus obtained is about 80% greater than that expected for a one electron reduction, but owing to the deleterious effect of fluoride ions on the dropping mercury electrode, and the failure hitherto to produce a permanent electrode in plastic, the method is of little use in practice.

In order therefore to avoid the complications and difficulties arising from complex formation in the supporting electrolyte, a study was made of the behaviour of uranium in a relatively non-complexing base solution, *viz.* perchloric acid, using both a conventional and a C.R. polarograph.

EXPERIMENTAL

Apparatus, reagents and experimental conditions

Cambridge Instrument Co. pen recording polarograph. Maximum sensitivity $2.5 \cdot 10^{-3}$ $\mu A \cdot mm^{-1}$. Capillary characteristic 1.92 $mg^{\frac{2}{3}} \cdot sec^{-\frac{1}{2}}$ in 1 *M* potassium chloride with no applied potential. Cathode Ray polarograph. Capillary characteristic. Weight of one drop (W) = 6.0 mg in 1 *M* potassium chloride with no applied potential.

Half wave potentials refer to the mercury pool anode, unless specified against the saturated calomel electrode (S.C.E.). In the latter case they were measured between the dropping mercury electrode and the S.C.E. via a $NaClO_4$–agar salt bridge under conditions in which "no current" was drawn in the measuring circuit.

Solutions were deoxygenated with high purity ("white spot") nitrogen, and polarographed at 25 ± 0.1° using a mercury pool as anode.

A standard uranium solution was prepared by dissolving the pure metal in nitric acid and evaporating to fuming after the addition of perchloric acid. The final solution was 0.100 *M* with respect to uranium, and 1 *M* with respect to perchloric acid. Additional uranium solutions were prepared by dilution of this standard with perchloric acid, such that the acidity was maintained at 1 *M*.

When required, a 0.1% solution of B.D.H. peptone, containing 0.2% of redistilled phenol as preservative was used as a "maximum suppressor", this solution being diluted 100 fold in use.

Reagents were of AnalaR or equivalent quality, and in particular the perchloric and hydrochloric acids used in the preparation of the more dilute ($\leqslant 4 \cdot 10^{-5}$ *M*) uranium solutions were "lead free" (Pb $\ngtr$ 0.005 p.p.m.).

Redistilled water was used throughout.

Effects of uranium concentration and of acidity

In the initial experiments the effects of variations in the concentrations of uranium and acidity were examined. Except for Series 1 and 2, the ionic strength was maintained at 1.0 by the addition of sodium perchlorate.

The results of these experiments are given in Table I.

In considering alternative acid supporting electrolytes, sulphuric acid is, as already mentioned, unsatisfactory for use with the C.R. instrument. The use of nitric or hydrochloric acids involves control of the acidity or, more specifically, control of the concentration of nitrate or chloride ion, because of their effect on the rate of disproportionation of U(V) owing to their complexing of U(IV) species.

TABLE I

EFFECT OF URANIUM CONCENTRATION AND ACIDITY

Series	*Concentration of U in mM/l*	*Concentration of H^+ in moles/l*	*Step height in mm*[a]	
			Pen recording polarograph	*C.R. polarograph*
1	4.00	5.0	7420	13,500
	0.40		660	1,050
	0.040		54	105
2	4.00	2.0	6750	10,000
	0.40		600	1,070
	0.040		50	97
3	4.00	1.0	6100	10,000
	0.40		520	1,000
	0.040		50	100
4	4.00	0.50	5700	10,000
	0.40		510	950
	0.040		50	100
5	4.00	0.10	5250	10,000
	0.40		517	1,000
	0.040		42	95
6	4.00	$1.26 \cdot 10^{-2}$	5170	9,500
	0.40		510	975
	0.040		41	85
7	4.00	$1.0 \cdot 10^{-3}$	5170	9,500
	0.40		480	1,000
	0.040		42	105

[a] The step heights are those which would be obtained (a) using the maximum sensitivity of the Cambridge instrument (b) using 1/20 of the maximum sensitivity of the C.R. instrument.

Interferences

Copper, lead, antimony, arsenic, tin, molybdenum, bismuth and vanadium were noted as possible interfering elements in the determination of uranium, and their behaviour in 1:1 ratio to uranium in a N $HClO_4$ – 0.01 N HCl supporting electrolyte was examined.

Mo causes serious interference and must be removed. Sb and V caused slight interference by distortion of the base of the uranium wave.

Bi when present as bismuth perchlorate, caused no interference, but the addition of bismuth in the form of a solution in hydrochloric acid produced interference. This is attributable to the complexing of bismuth by chloride ion and the reduction of this complex at a more negative potential than that of the bismuthyl ion. Pb, As, Sn caused no interference, their reduction waves occurring well after that due to uranium.

Cu caused no interference, the reduction wave preceded the uranium wave by a substantial amount.

Following the observation by LEWIS AND OVERTON[10] "that uranium gives a wave in acid tartrate solution which is removed from the copper wave" it may have been inferred by other workers that the addition of tartrate was necessary to separate the uranium and copper waves in other media.

Measurements were therefore made of the half-wave potentials of uranium, copper and lead in the proposed supporting electrolyte and following the addition of tartrate. The results of these measurements are shown in Table II.

TABLE II

HALF-WAVE POTENTIALS

Element	*Medium*	$E_{\frac{1}{2}}$ *V vs. S.C.E.*
Uranium	(a) 1 *N* $HClO_4$ 0.01 *N* HCl	— 0.200
		± 0.005
	(b) 1 *N* $HClO_4$ 0.01 *N* HCl 0.05 *M* Sodium tartrate	— 0.195
Copper	as in (a) above	— 0.010
		± 0.005
	as in (b) above	— 0.000
Lead	as in (a) above	— 0.420
		± 0.005
	as in (b) above	— 0.420

Calibration curves were prepared over the range $2\cdot10^{-6}$–$4\cdot10^{-3}$ *M* uranium in the case of the C.R. instrument and $4\cdot10^{-5}$–$4\cdot10^{-3}$ *M* for the pen recorder, and checks made of the precision of the proposed procedure, which in common with most methods for the determination of uranium is best applied after a preliminary separation.

DISCUSSION

From the results shown in Table I, it is apparent that the height of the uranium wave is relatively insensitive to changes in acidity around the 1 *M* level, and this is of great practical convenience. At pH values greater than 1 the results on the Cathode Ray instrument were often unsatisfactory owing to the splitting of the wave into two parts.

In order to establish a stable and reproducible anode potential it is customary to add chloride ions to the supporting electrolyte, and the addition of hydrochloric acid to give a concentration of 0.01 *M* fulfils this requirement.

Whilst the suggested concentration is uncritical to say ± 100%, it should not be permitted to reach 0.1 *M*, or higher, since for example in the presence of copper the stabilisation of cuprous ions by chloride complexing will result in the copper reduction proceeding in two steps and to the reduction potential becoming sufficiently negative to interfere with the uranium wave. A similar situation arises in the presence of bismuth.

In solutions containing these larger amounts of chloride, this interference can be overcome by lowering the acidity to pH 1–2 and adding tartrate. Since the reaction between cupric and tartrate ions is considered to involve the replacement of hydroxyl group hydrogens[11,12] as well possibly as attachment through carboxylate groupings, the degree of complex formation will obviously be very pH-dependent. It is not surprising therefore that, (as is shown in Table II) the addition of tartrate has an insignificant effect on the values of the half-wave potential at an acidity of 1 *M*.

The two acids are available in a state of high purity. Alternatively they can readily be further purified by distillation, and in the case of hydrochloric acid the isopiestic[13] method is applicable.

CONCLUSIONS

An electrolyte 1 *M* with respect to perchloric acid and 0.01 *M* with respect to hydrochloric acid forms a very satisfactory base for the determination of uranium by either conventional or cathode-ray polarography.

Accurate control of the acidity of the base solution is unnecessary.

The only element causing serious interference is molybdenum.

For the C.R. polarograph the calibration is linear over the range $2 \cdot 10^{-6}$–$4 \cdot 10^{-3}$ *M* uranium. At a uranium concentration of $4 \cdot 10^{-5}$ *M* the coefficient of variation of the results from the Cambridge Polarograph is 1.8% and that for the Cathode Ray is 1.5%. At a uranium concentration of $4 \cdot 10^{-4}$ *M* these figures are 1.8% and 1.3% respectively.

The method is particularly suited to the determination of uranium, following separation procedures such as those described by WILD[14] or MAECK *et al.*[15].

ACKNOWLEDGEMENTS

The authors wish to thank Mr. H. I. SHALGOSKY for valuable discussions, and Mrs. S. BROWN who carried out much of the experimental work.

SUMMARY

The determination of uranium in the concentration range $2 \cdot 10^{-6}$–$4 \cdot 10^{-3}$ *M* has been studied by using both conventional and cathode-ray polarography. The preferred supporting electrolyte is 1 *M* perchloric acid, molybdenum is the only element which will cause serious interference at levels of the same order as that of the uranium.

RÉSUMÉ

Une étude a été effectuée sur le dosage de l'uranium, par polarographie ordinaire et par polarographie à rayon cathodique. On propose l'acide perchlorique comme électrolyte de base.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Uran durch gewöhnliche oder Kathodenstrahlen-Polarographie in Gegenwart von Perchlorsäure.

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THE DETERMINATION OF ORGANIC NITRO, NITROSO AND AZO COMPOUNDS WITH COPPER

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INTRODUCTION

An excellent review of the various methods for the quantitative determination of nitro groups has been given by BECKER AND SHAEFER[1]. Most of these methods involve the reduction of the nitro group with a known excess of a strong reducing agent such as titanous, stannous, or chromous ion followed by back-titration, after the reaction is complete, with a standard solution of an appropriate oxidizing agent. These methods are not convenient for a single or occasional analysis since two standard solutions must be prepared; one of these, the reducing agent, is commonly oxygen sensitive and requires storage of stock solutions under an inert atmosphere and frequent standardizations.

In 1950 VANDERZEE AND EDGELL[2] proposed an indirect gravimetric method for the determination of aromatic nitro compounds which was based on the reduction of the nitro group to the amine in acidic solution with an excess of metallic tin. From the loss in weight of the tin, the amount of nitro compound could be calculated. The procedure has the advantage that no standard solutions are required and only commonly available equipment is used. Under ideal conditions the accuracy was found to be ± 0.5%. These authors, however, point out several difficulties with the procedure. Large errors result from oxidation of the metallic tin by air and by excess hydrogen ion. VANDERZEE AND EDGELL state that the initial acid concentration should be adjusted so that the final concentration, after reaction, is approximately 0.15 *M*; the concentration of alcohol solvent should be minimized to reduce errors; and sufficient nitro compound to cause reaction of *ca.* 0.7 g of tin should be used since the value of the blank is relatively large. As a result, careful attention to experimental details is required. Certain compounds, *i.e.*, *p*- and *m*-iodonitrobenzene, *m*-nitrobenzaldehyde and 1,3,5-trinitrobenzene, were found to give errors as large as 6–10% even under ideal conditions.

The procedure given below is similar, in principle, to the method of VANDERZEE AND EDGELL. However, many of the difficulties associated with the use of tin have been eliminated by the choice of a reducing metal which is not oxidized by hydrogen ion. Copper metal was chosen because of its availability in pure form and because it is not oxidized by protons. The concentrations of the acid and the organic solvent have no appreciable influence on the analytical results.

EXPERIMENTAL

Apparatus

Reactions were carried out in a 200-ml round-bottom flask fitted with a reflux condenser by means of a ground-glass joint. A two-hole rubber stopper, through which was inserted a glass tube for carbon dioxide delivery, was placed in the top of the reflux condenser. Alternatively, small pieces of "dry ice" could be added from time to time through the condenser to maintain an inert atmosphere above the reaction mixture.

Reagents

Reagent-grade absolute ethanol (U.S. Industrial Chemicals Co., New York) was used without further purification. Diethylene glycol dimethyl ether (Ether 141, Ansul Chemical Co., Marinette, Wisc.) was distilled from metallic copper. After long contact of the ether with air, destruction of peroxides by distillation from dilute sulfuric acid saturated with ferrous sulfate may be desirable. These solvents were deaerated before use by bubbling with carbon dioxide. Electrolytic copper foil (Allied Chemical and Dye Corp., New York, 0.002 in thick) was cut into pieces approximately 1 cm square. These were bent into a cylindrical form to facilitate drying. The copper was washed with dilute sulfuric acid, rinsed with deaerated water and deaerated reagent-grade acetone, dried in a filter flask under a stream of carbon dioxide, and stored under vacuum. The copper could be used for successive determinations provided air oxidation between determinations was avoided and no insoluble coating was formed on the surface during reaction. Most of the compounds determined were Eastman "white label" reagents which had been recrystallized according to standard techniques. The melting points were taken and were in close agreement with literature values.

Analytical procedure

Twenty ml of ethanol or Ether 141 and 20 ml of *ca.* 6 *N* sulfuric acid were added to the reaction flask. Deaeration of the mixture was carried out by addition of small pieces of "dry ice". Sufficient nitro compound to cause reaction of 0.5 to 1 g of copper metal was dissolved in the solvent and 6 to 15 g of clean, dry copper were added to the reaction flask. The mixture was refluxed for 1 to 2 h while a slow stream of carbon dioxide was passed through the condenser. Small pieces of "dry ice" may be added during the reflux period as a substitute for the gas, if desired.

After completion of the reaction, the liquid was decanted from the flask. Five or six rapid rinses of the copper with deaerated water were followed by three rinses with deaerated acetone. The copper was dried under vacuum and weighed. The loss in weight of copper is related to the amount of nitro compound present by the equation.

$$3Cu + ArNO_2 + 7H^+ = 3Cu^{+2} + ArNH_3^+ + 2H_2O \qquad (1)$$

Blanks were run along with the samples and varied from 1.2 to 18 mg copper depending upon care used in excluding oxygen from the reaction vessel and reagents.

RESULTS

The results obtained for several compounds are given in Table I. Accuracy and precision is of the order of 0.5%.

The reaction time given is not necessarily the shortest time required for quantitative reaction. Most reductions are complete after 1–1.5 h. Reduction generally proceeds faster in Ether 141 than in ethanol because of the higher reflux temperature. As a generalization, compounds with three nitro groups may be reduced faster than those with two, which react faster than those with one. Aliphatic nitro compounds are much more resistant to reduction than aromatic compounds and require an inconveniently long reaction time.

TABLE I

DETERMINATION OF VARIOUS NITRO, NITROSO, AND AZO COMPOUNDS

Solvent A: 20 ml ethanol, 20 ml 6 *N* H_2SO_4; Solvent B: 20 ml Ether 141, 20 ml 6 *N* H_2SO_4

Compound	*Reaction time, h*	*Solvent*	*Average % recovery and S. D.*
m-chloronitrobenzene	2	A	100.7 ± 0.3
m-nitrobenzaldehyde	2	A	101.5 ± 0.7
m-nitrobenzonitrile	2	A	100.9 ± 1.2
p-nitrobenzoic acid	2	A	100.3 ± 0.7
o-nitrophenol	2.5	A	100.8 ± 0.7
m-dinitrobenzene	2	A	100.1 ± 0.9
m-dinitro-*o*-cresol	2.5	A	100.7 ± 0.4
2,4-dinitrotoluene	1.5	B	100.4 ± 0.1
2,4,6-trinitrotoluene	1	B	100.3 ± 0.3
picric acid	1	B	99.8 ± 0.2
1,3,5-trinitrobenzene	1	B	101.1 ± 0.6
4-dimethylaminoazobenzene	2.5	A	98.7 ± 0.6
Azobenzene-4-carboxylic acid	2.5	A	99.9 ± 0.7
p-nitrosodiethylaniline	1	B	98.9 ± 0.4
tri(hydroxymethyl)nitromethane	22	A	99.8
tri(chloromethyl)nitromethane	22	A	100.3
m-iodonitrobenzene	1.5–2	A,B	104.2 ± 1.3

A series of determinations of 2,4-dinitrotoluene was made using concentrations of sulfuric acid varying from 2 to 4 *N*. Although the reaction apparently proceeds more slowly at lower acid concentrations, essentially quantitative results were obtained in each case and precise control of acid concentration is not necessary. This is a definite advantage of copper metal over tin as a reducing agent.

Two of the compounds, 1,3,5-trinitrobenzene and picric acid, caused an insoluble coating to form on the copper during the reflux period. Reduction of sample size to *ca.* 0.2 g decreased interference from this source. In the determination of styphnic acid, 2,4,6-trinitroresorcinol (not shown in the table), sufficient coating was formed with even a 0.2-g sample to lower the results to 94.5% of the theoretical value. No suitable solvent for this coating was found.

Since the performance of a nitroso compound was of interest, *p*-nitrosodiethylaniline was studied. Reduction was rapid, requiring only 1 h reflux when Ether 141 was used as the organic solvent. The result (assuming 4 equivs. per mole), corrected for a reaction mixture blank of 2.8 mg, was 98.9 ± 0.4%. The blank was determined by refluxing the amine reaction mixture with a weighed amount of copper for the same length of time used for the original reaction.

LIMITATIONS AND INTERFERENCES

Several workers have shown that reduction products other than the simple amines are formed in the reduction of α-nitronaphthalenes with titanous ion[3] and with tin[4] in the presence of hydrochloric acid. The reaction of copper metal with both 1-nitronaphthalene and 1-nitro-2-methylnaphthalene was found to give consistently low results based on the normal six equivalents per nitro group reduced. The reduction products were isolated in order to determine the presence of products other than the simple amines. After refluxing 1-nitronaphthalene for 6 h with ethanol as the organic solvent, the reaction mixture was allowed to cool. A white crystalline compound, which was the sulfate salt of 4-ethoxy-1-naphthylamine, separated.

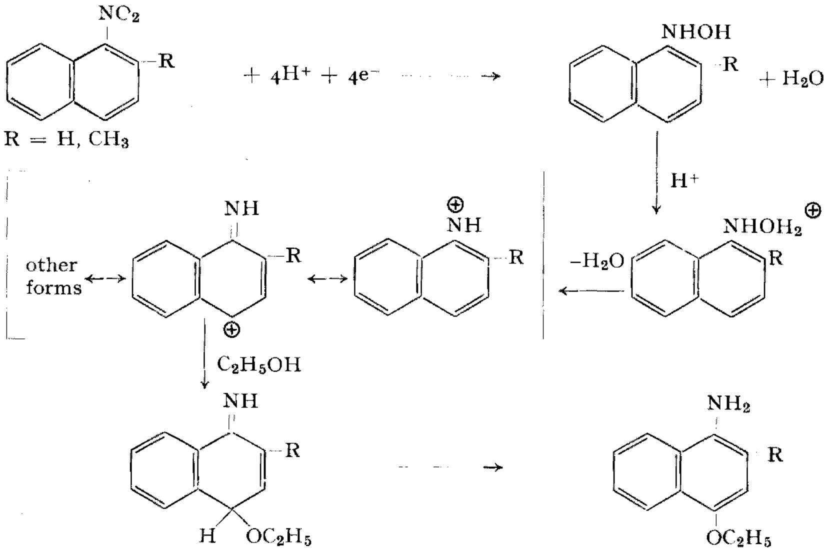
Anal.: Calculated for $(C_{12}H_{14}NO)_2SO_4$: C, 61.00%; H, 5.97%; N, 5.93%. Found: C, 61.35%; H, 5.94%; N, 5.61%.

The benzamide of the free amine melted at 213–14°. The literature[5] reports the melting point of 4-ethoxy-1-naphthylbenzamide as 214–15°.

An acidic aqueous ethanol solution of 2-methyl-1-nitronaphthalene was reduced by refluxing with copper metal for 12 h. Excess ethanol was removed by distillation, and the benzamide of the reduction product was prepared by the Schotten-Baumann method. The product was isolated by chromatography using a benzene–ether eluent with 100–200 mesh Florisil (Floridin Co., Tallahassee, Fla.). The melting point of the benzamide, 4-ethoxy-2-methyl-1-naphthylbenzamide, was 180.5–181.0°.

Anal.: Calculated for $C_{20}H_{19}NO_2$: C, 78.66%; H, 6.27%; N, 4.59%. Found: C, 78.39%; H, 5.93%; N, 4.76%.

The 4-ethoxy-1-naphthylamines are likely formed by the rearrangement of the naphthylhydroxylamines, intermediates in the reduction processes. The mechanism for this rearrangement may be similar to that of the acid rearrangement of phenylhydroxylamine[6]. The formation of both 4-ethoxy-1-naphthylamine and 4-ethoxy-2-methyl-1-naphthylamine can be represented by the following scheme:



This reaction mechanism involves 4 equivs. per mole in the reduction of the nitro compound to the amine rather than the usual 6 equivs. per mole. Results calculated on the basis of the weight of copper lost during the reaction were high (4.20 equivs. for 2-methyl-1-nitronaphthalene and 4.73 equivs. for 1-nitronaphthalene) which suggests that other reactions (*e.g.*, direct reduction to the amine) occur simultaneously.

Phenylhydrazines reduce cupric ion to copper metal according to reaction 2 and would be expected to interfere.

$$ArNHNH_2 + 2Cu^{+2} + H_2O = ArOH + 2Cu + N_2 + 4H^+ \quad . \; . \; . \; . \; . \quad (2)$$

A sample of 2,4-dinitrophenylhydrazine was analyzed by the usual technique. Colloidal copper was formed soon after reaction commenced. Attempts to retain all the colloidal copper on a medium porosity sintered-glass crucible were unsuccessful and high results were obtained.

Complexing anions, such as the halides, which stabilize the cuprous state interfere. Several runs were made with equimolar amounts of 2,4-dinitrotoluene and chloride ion. After 1.5 h reflux using Ether 141 as the organic solvent, the maximum result was 45% of theoretical based on two equivs. per mole copper or 90% based on one equiv. per mole of copper. An attempt was made to complex all the copper as the chlorocuprous ion by carrying out the reaction in 6 *N* hydrochloric acid. However, blank determinations run in this media were very large, approaching 0.1 g. It may be shown from the data given by DIEHL[7] that copper in the presence of a concentrated chloride solution is capable of being oxidized by a concentrated acid solution. Therefore blank determinations are large and the results of analysis are highly questionable.

m-Iodonitrobenzene gave results *ca.* 4% high when the reaction was run for 1.5 to 2 h using either Ether 141 or ethanol as solvent. Partial reduction of the iodo group according to reaction 3 was suspected.

$$9Cu + 2IArNO_2 + 16H^+ = 7Cu^{+2} + Cu_2I_2 + 2ArNH_3^+ + 4H_2O \quad . \; . \; . \; . \quad (3)$$

The reduction product after prolonged reaction was identified as follows. *m*-Iodonitrobenzene was refluxed for 8 h in the ethanol-acid solvent. The formation of a white precipitate, presumably cuprous iodide, in the refluxing solution was noted. The benzamide of the resulting amine was prepared by the Schotten-Baumann procedure. The sample was compared with an authentic sample of benzanilide by means of mixed melting point and infrared spectra. The reduction product was benzanilide and resulted from dehalogenation of the benzene ring. A determination of the moles of copper reacted per mole of compound gave the result 4.48 which is in excellent agreement with the value 4.50 predicted from equation 3. Thus the iodine may be quantitatively removed by prolonged reaction, but is only partially reduced during normal reaction periods. Only the nitro group in *m*-chloronitrobenzene is reduced.

Inorganic oxidizing agents which would react with copper metal (*e.g.*, nitrate or ferric ion) would interfere. Aldehydes, ketones, carboxylic acids, alcohols, phenols, amines, and nitriles are among those functional groups which do not interfere with this determination.

SUMMARY

An indirect gravimetric method for the determination of organic nitro, nitroso and azo compounds has been investigated. The amount of nitro, nitroso, and azo compound present is calculated from the loss in weight of copper metal during the reduction of the compound to the amine. Interferences are discussed in detail. No standard solutions are required and only commonly available equipment is used. Accuracy is of the order of ± 0.5%.

RÉSUMÉ

Une méthode gravimétrique indirecte a été examinée pour le dosage des nitro-, nitroso- et azocomposés organiques. Elle est basée sur la diminution de poids du cuivre métallique, utilisé pour la réduction de ces substances en amines.

ZUSAMMENFASSUNG

Beschreibung einer indirekten gravimetrischen Methode zur Bestimmung von organischen Nitro-, Nitroso- und Azoverbindungen. Sie beruht auf der Feststellung des Gewichtsverlustes des zur Reduktion verwendeten metallischen Kupfers.

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AMPEROMETRIC TITRATION OF ALBUMIN IN BLOOD SERUM BY COPPER(II)

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In a recent study in these laboratories, it has been shown that in ammoniacal buffer of pH 9.2, copper(II) reacts with bovine serum albumin in a mole ratio of one to one but does not react with human γ-globulin under similar conditions[1]. Because of the structural similarity of bovine serum albumin to human serum albumin, these results suggest that the reaction of copper(II) with albumin can be made the basis for an amperometric titration of albumin in blood serum with copper(II). This was substantiated by the titration of a sample of fractionated serum which revealed that the only substantial consumption of copper(II) occurred in the albumin fraction.

This paper reports the results of titration of some 50 samples of normal sera and

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17 samples of cancerous sera with copper(II). Facilities for routine electrophoretic analysis of blood sera were not available to us. However, it was possible to obtain independent analyses of the serum samples at the Laboratory of the University of Minnesota Hospital. These analyses were carried out by precipitation in 28% sodium sulfite solution[2, 3] which was the method then in routine use in the Hospital laboratory. While this method yields results which are quite useful for routine purposes, it is not as accurate as the electrophoretic procedure, and comparison of the copper(II) titration values with electrophoretically analyzed serum samples would be desirable.

The sulfhydryl content of each sample was also determined amperometrically[4, 5]. No simple relation between sulfhydryl and albumin content (from copper titration) was found, and the data are therefore not reported. In agreement with previous work[5] both sulfhydryl and albumin were in general lower in pathologic sera than in normal sera.

EXPERIMENTAL

Materials

Standard copper sulfate solutions were prepared by accurate dilution of a more concentrated solution which had been standardized iodometrically. Conductivity water was used in the preparation of all solutions. Solutions were deaerated with Linde nitrogen of 99.9% purity. All other chemicals used were reagent grade.

Plasma samples

Blood samples were obtained from patients at the University of Minnesota Hospital. The samples were allowed to stand at room temperature until clotting occurred and then centrifuged. The serum was drawn off with a hypodermic syringe and stored in a refrigerator at 4°.[6] Titrations were carried out the same day the samples were drawn.

Titrations

Amperometric titrations were carried out with a circuit similar to that described by LINGANE AND KOLTHOFF[7]. The platinum electrode was rotated at a constant speed of 600 or 900 r.p.m. by a Bodine synchronous motor. Potentials refer to the saturated calomel electrode. The titration vessels were 125-ml beakers fitted with rubber stoppers with holes for the indicator electrode, nitrogen inlet and outlet, salt bridge, and buret. The proper quantity of buffer (usually 25 ml of a solution 0.1 M in ammonia and 0.1 M in ammonium nitrate, pH 9.2) and one ml of blood serum were placed in the titration cell and deaerated with a stream of nitrogen which had been previously passed through buffers of the same composition. Care was taken to avoid any loss of protein through the nitrogen outlet tube because of foaming of the solution after the serum was added. Nitrogen was passed through the solution continuously during the titration. Titrants (10^{-1}–10^{-3} M) were added from a Gilmont ultramicroburet of 0.1-ml total capacity or from a semi-microburet with 0.01 ml divisions.

The titrations were carried out at a potential of —0.4 V *vs.* the saturated calomel electrode. It was found that there was a considerable tendency for the galvanometer to drift to lower values after each addition of the reagent. Accordingly, readings were taken at uniform intervals (usually one min) after each addition of titrant. End-points were found by the usual plot of current *vs.* volume of titrant added. A typical titration is shown in Fig. 1. The end-points were quite reproducible.

A sample of normal serum fractionated by starch block electrophoresis was provided by Dr. H. H. ZINNEMAN of the Minneapolis Veterans' Hospital. Both the whole serum and each individual fraction were titrated with copper(II) under the conditions described previously.

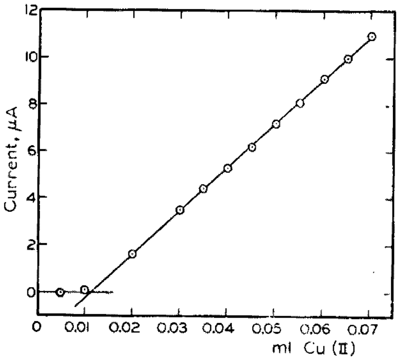

Fig. 1. Titration of blood serum with copper(II). One ml serum in 25 ml buffer, 0.1 M NH_3 + 0.1 M NH_4NO_3, pH 9.2. $CuSO_4$, $4.77 \cdot 10^{-2}$ M, Rotated platinum electrode, 900 r.p.m. —0.4 V *vs.* S. C. E.

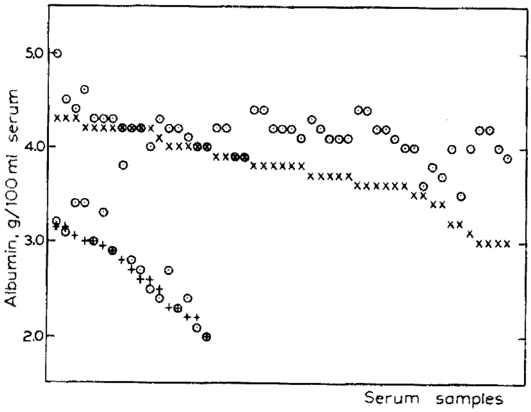

Fig. 2. Albumin content of normal and cancerous blood sera. x = Copper(II) titration values of normal sera. + = Copper(II) titration values of cancerous sera. ⊙ = Neutral salt fractionation values.

RESULTS AND DISCUSSION

The results of this investigation are shown in Fig. 2 which gives a comparison of the albumin values determined amperometrically with those determined by fractional precipitation. It can be seen that there is essential agreement between the methods, particularly for the pathologic sera. In general, the precipitation method tends to yield higher albumin values than the copper titration method, especially for the normal sera. This is attributed to the imperfect separations obtained by the salt fractionation procedure.

TABLE I

TITRATION OF BLOOD SERUM WITH Cu(II)

Medium: 0.1 M NH_3 + 0.1 M NH_4NO_3, pH 9.2; R.p.e. at 600 r.p.m., —0.4 V

Serum fraction	*Cu(II) value, as g % albumin*
Albumin	3.41
α_1-globulin	0.25
α_2-globulin	0
β-globulin	0
γ-globulin	0
Total	3.66
Whole serum, by Cu(II)	3.68
Whole serum, tyrosine	3.70

The results obtained on the sample of fractionated serum are given in Table I. While the unusually close agreement between values is certainly fortuitous, it is significant that over 93% of the copper titer of the whole serum is accounted for in the albumin fraction. The remaining 7% occurs in the α_1-globulin fraction and can be attributed to overlap of the albumin and α_1-globulin fractions. From these experiments it is concluded that under these conditions, the copper titration is specific for albumin.

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We wish to express our appreciation to the University of Minnesota Hospital staff for the blood samples and their analysis and to Dr. H. H. ZINNEMAN for the sample of fractionated blood serum. This work was supported by grants from the U.S. Public Health Service and the Louis and Maud Hill Family Foundation.

SUMMARY

Determination of the albumin content of blood serum by amperometric titration with copper(II) in ammoniacal buffer of pH 9.2 yields values in essential agreement with, but in general somewhat lower than, those obtained by precipitation in 28% sodium sulfite solution. While the amperometric titration method gives reproducible results of the right order of magnitude, comparison of results with a large number of electrophoretically analyzed samples would be desirable.

RÉSUMÉ

Les auteurs ont effectué une étude du dosage de l'albumine dans le sérum sanguin, par titrage ampérométrique au moyen de cuivre(II).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Albumin in Blutserum durch amperometrische Titration mit Kupfer(II)-Lösung.

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THE DETERMINATION OF ARSENIC IN TREATED WOOD

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INTRODUCTION

Arsenical mixtures have been used for many years as wood preservatives and more recently in the form of copper chrome arsenates and copper zinc chrome arsenates. The available methods of analysis for arsenic in wood treated with these preservatives have been examined to determine their suitability as rapid routine procedures. Any method adopted should enable the determination of 0.6 mg of arsenic pentoxide with a precision of ± 5% or better without interference from the remaining preservative compounds or phosphorus which is always present in wood frequently in amounts equivalent to the lower limits of arsenic to be determined.

Hitherto, the method which has been used in this laboratory has involved the destruction of the wood substance with mixed nitric, sulphuric and perchloric acids followed by the distillation of the arsenic as As^{+3} from hydrochloric acid using ferrous sulphate as the reducing agent[1]. The distillate was subsequently titrated with standard iodine solution. This method is somewhat tedious on a routine scale though it is known to give good results and our experience showed that one operator could carry out about ten duplicate determinations per day using two sets of distillation equipment. It was therefore hoped that any new method would materially increase the number of analyses per day.

The methods examined may be classified as follows:

I. *Colorimetric.* (a) Arsenomolybdate, (b) molybdenum blue, (c) arseno-vanado-molybdate.

II. *Turbidimetric.* Precipitation of As° by hypophosphorous acid or stannous chloride.

III. *Volumetric.* (a) Reduction to As^{+3} and titration with iodine, chloramine T, bromate or ceric sulphate. (b) Reduction to As° and titration with iodine, bromate or chloramine T.

As it was known[2] that phosphorus interfered in methods I (a) and (b), a study of the ultraviolet spectra of arseno-molybdic and phospho-molybdic acids was made to examine the possibility of a determination in this region. No satisfactory differences appeared in the absorption curves. The extraction procedures, for the removal of molybdophosphoric acid, of FARRER AND NUIR[3] and MERVEL[4] were examined as a means of overcoming the interference from phosphorus. Such procedures were found to offer little advantage in convenience compared with the old method.

The method of GULLSTROM AND MELLON[5] for the determination of arsenic as molybdo-vanado-arsenate was examined in regard to its suitability in the presence of phosphorus which is also known to form a similar heteropoly acid. Unfortunately the method was found to be less sensitive for arsenic and the contaminating phosphorus which would at times be present in excess of the arsenic seriously reduced the suitability of the method.

Turbidimetric methods based on the precipitation of arsenic as As° have been proposed by DELAVILLE AND BELIN[6] and KING AND BROWN[7] but it was found that rapid coagulation of the arsenic occurred which could not be stabilized with gelatine or silicate and the method gave erratic results.

Procedures based on the precipitation of arsenic as As° developed by EVANS[8] were examined but were found to offer no saving in time as compared with the old method. It was however noticed that hypophosphorous acid is oxidized by sulphuric acid when heated to fumes and therefore attempts were made to carry out the determination by adding slight excesses of hypophosphorous acid to the sulphuric acid solution of the arsenate and subsequently heating to fumes. The arsenic initially precipitated as the metal and subsequently redissolved to give As^{+3}. The excess hypophosphorous acid was oxidized during the fuming to dissolve the arsenic and any reduced copper present was also reoxidized to Cu^{+2}. After dilution the arsenic was titrated with ceric sulphate and the procedure gave excellently reproducible results. Unfortunately the recoveries were only of the order of 90% and the method was abandoned. Other reducing agents such as sulphide, thiosulphate and thioacetamide were tried but none of these gave good results although, in the case of the sulphide, the results were again reproducible but low.

FINAL METHOD

The method of SCHULEK AND VILLECZ[9] of reduction to As^{+3} with hydrazine sulphate was tested and found to give excellent results. Some modifications were made to the procedure. Hydrazine sulphate was added as a saturated aqueous solution and titration was with standard ceric sulphate using ferrous *o*-phenanthroline perchlorate as the indicator instead of the bromate procedure. Corrections for blank and any reducing substances present were made by a preliminary titration to the end-point without the addition of the osmic acid catalyst followed by titration of the As^{+3} after addition of the catalyst. The following method based on that of SCHULEK AND VILLECZ[9] for the determination of arsenic in treated wood was adopted.

EXPERIMENTAL

Reagents

Concentrated nitric acid, concentrated sulphuric acid, hydrazine sulphate. Saturated aqueous solution. Ceric sulphate 0.1 *N*, ceric sulphate 0.01 *N*. Osmium tetroxide 0.25% in 0.1 *N* sulphuric acid, ferrous *o*-phenanthroline perchlorate and a saturated aqueous solution.

Procedure

Transfer a weighed 1.000-g portion of treated wood ground to pass a 30-mesh sieve to a 200-ml Kjeldahl flask. Add 25 ml conc. nitric acid and 3 ml conc. sulphuric acid.

Gently heat the contents of the flask until the initial vigorous reaction has subsided and thereafter heat more strongly until strong fumes of sulphuric acid appear. Should the digest show signs of charring – the development of brown colour – several drops of nitric acid will clear the solution. It may be necessary in the case of very resinous samples to add several additional small portions of nitric acid. The final digest should be clear green.

Transfer the digested sample quantitatively to a 150-ml Erlenmeyer flask and heat to fumes of sulphuric acid again.

Cool, add 1 ml of hydrazine sulphate solution, rinsing the neck of the flask with distilled water to wash all traces of hydrazine sulphate into the acid mixture. Heat to fumes once more and fume for ten min. Cool and dilute with 40 ml of distilled water.

Add 0.5 ml of ferrous *o*-phenanthroline perchlorate indicator and titrate with standard ceric sulphate, approximately 0.01 *N* (prepared by dilution of the stock solution of 0.1 *N* reagent), using a 2-ml microburette. The titrant should be added in 0.01-ml portions and generally about 0.07 ml will be required for the titration (equivalent to about 0.004% As_2O_5). At the end-point the colour changes from orange-red to a faint green. The volume taken need not be recorded but the end-point should be stable for 15 sec. Read the burette and add 3 drops of osmium tetroxide catalyst when the colour of the reduced form of the indicator is restored and titrate with the standard ceric sulphate adding the titrant slowly as the end-point is approached.

Standardize the approximately *N*/100 ceric sulphate by titrating aliquots of standard *N*/100 arsenate solution carried through the above process or alternatively *N*/100 arsenite solution.

Notes on the method

(1) In instructions for the digestion of organic material as a preliminary to the determination of arsenic, it is often stated that charring should be avoided as this will tend to cause reduction and volatilization of the arsenic. Since any charring with the above method can occur only after boiling off of the nitric acid when all chlorides should have been volatilized and, as it is implicit in the hydrazine sulphate reduction that As^{+3} is non volatile at the temperature at which sulphuric acid fumes, it did appear that there was not much likelihood of serious loss of arsenic should slight charring occur during digestion. A test showed that after one hour's charring losses of arsenic did occur but these were not unduly high when the time of charring was taken into consideration (see Table I). Thus one can reasonably confidently assume that the occasional slight charring which occurs, if it is not unduly prolonged, is not a serious hazard in the analytical process.

TABLE I

EFFECT OF CHARRING ON As_2O_5 RECOVERIES

Not charred *mg As_2O_5*	*Charred 1 h* *mg As_2O_5*
0.58	0.54
0.59	0.54
1.18	1.13
1.17	1.13
2.41	2.36
2.41	2.34

(2) The fuming after transference to the Erlenmeyer flask is to remove the final traces of nitric acid. Should brown fumes develop on fuming then an additional dilution and fuming should be made as excess nitric acid is still present.

(3) The quantity of hydrazine sulphate solution is adequate for at least 14 mg As_2O_5.

(4) Dilute *N*/100 ceric sulphate solutions require some days standing in order to stabilize by oxidation any reducing substances in the solution and should therefore be standardized daily until the titre becomes constant.

(5) If the sample has been insufficiently fumed to destroy the excess hydrazine sulphate difficulty will be experienced in obtaining a stable end-point in the initial titration. In this case it is preferable to begin the determination again.

RESULTS

The results obtained by the method are given in Tables II and III.

Ceric sulphate standardized by 10 replicate titrations of *N*/100 arsenite at the 2.87-mg level.

DISCUSSION OF RESULTS

The results in Table II show good recoveries of added arsenic and the observation of SCHULEK AND VILLECZ[9] that low recoveries are obtained in the presence of copper is not supported. The results in Table III show excellent agreement between the old and new methods and this is especially interesting as determinations were carried out on separately weighed wood samples.

The new method represents a considerable saving in time allowing the determination of some forty samples per day as against ten per day by the old method with two distillation units in operation. The main limiting factor with the method is now the number of samples which can be digested per day.

TABLE II

TITRATIONS USING ARSENIC PENTOXIDE SOLUTIONS

10 replicates at each level

Taken mg As_2O_5	*Found*[a] mg As_2O_5	*Found*[b] mg As_2O_5
2.87	Max. 2.91	2.89
	Min. 2.88	2.85
	Mean 2.90	2.87
0.58	Max. 0.60	0.60
	Min. 0.58	0.56
	Mean 0.59	0.58

[a] Arsenic pentoxide alone.

[b] Arsenic pentoxide + 0.01 g $CuSO_4 \cdot 5H_2O$ + 0.01 g $K_2Cr_2O_7$. (To simulate working conditions)

TABLE III

COMPARISON OF RESULTS OBTAINED BY DISTILLATION AND THE HYDRAZINE SULPHATE PROCEDURES[a]

Results as % As_2O_5

Sample No.	*By distillation*	*By hydrazine sulphate*
1	0.016	0.016
2	0.026	0.027
3	0.046	0.046
4	0.051	0.047
5	0.062	0.062
6	0.071	0.069
7	0.078	0.077
8	0.128	0.127
9	0.235	0.215
10	0.274	0.265

[a] Wood samples treated with copper chrome arsenate.

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The writer is indebted to Miss P. CORTEN for carrying out many of the analyses given above and to the Director, New Zealand Forest Service for permission to publish.

SUMMARY

The SCHULEK AND VON VILLECZ method for the determination of arsenic in organic compounds has been applied to the determination of arsenic in wood. Copper and chromium do not interfere.

RÉSUMÉ

La méthode de SCHULEK ET DE VON VILLECZ pour le dosage de l'arsenic dans les composés organiques a été appliquée au dosage de l'arsenic dans des bois traités.

ZUSAMMENFASSUNG

Es wird die Anwendung der Methode zur Bestimmung von Arsen in organischen Substanzen nach SCHULEK UND VILLECZ auf die Bestimmung von Arsen in Holz beschrieben.

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Short Communication

Thermographic semiquantitative micro-determination of sulfuric acid

When concentrated sulfuric acid is placed in contact with filter paper, it readily chars the cellulose fibers of the paper. But with dilute aqueous solutions of sulfuric acid, the paper remains white. However, if the paper impregnated with sulfuric acid solutions is heated at 170° for 10 min, yellow, brown or black spots appear, the color depending on the acid concentration. This is the basis of a new technique, *thermography*, where the color development is due to heating and is made without reagents. Perchloric and phosphoric acids react similarly, and can also be determined.

Whatman No. 1 filter paper can be used for the semiquantitative determination of sulfuric acid in aqueous solutions. The following scales are used: a) 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0 μg of sulfuric acid per 2 μl. b) 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0 μg of sulfuric acid per 10 μl.

The comparison of colors obtained with unknown solutions with that of the scales showed good reproducibility. The color of the spots is permanent and the papers can be stored.

The determination of sulfate in waters after conversion to sulfuric acid with the aid of cation-exchangers is being studied.

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