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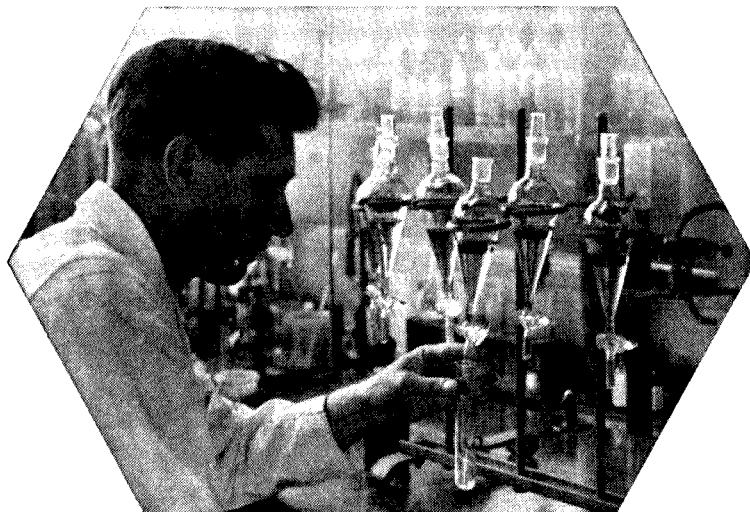
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Incidental information No.13

Items of interest from our laboratory notebooks

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

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

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

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

▶ Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-N,N-diacetic acid,** described by Belcher, Leonard and West (*Talanta,* 2 (1959) 92). This important reagent is already available from stock.
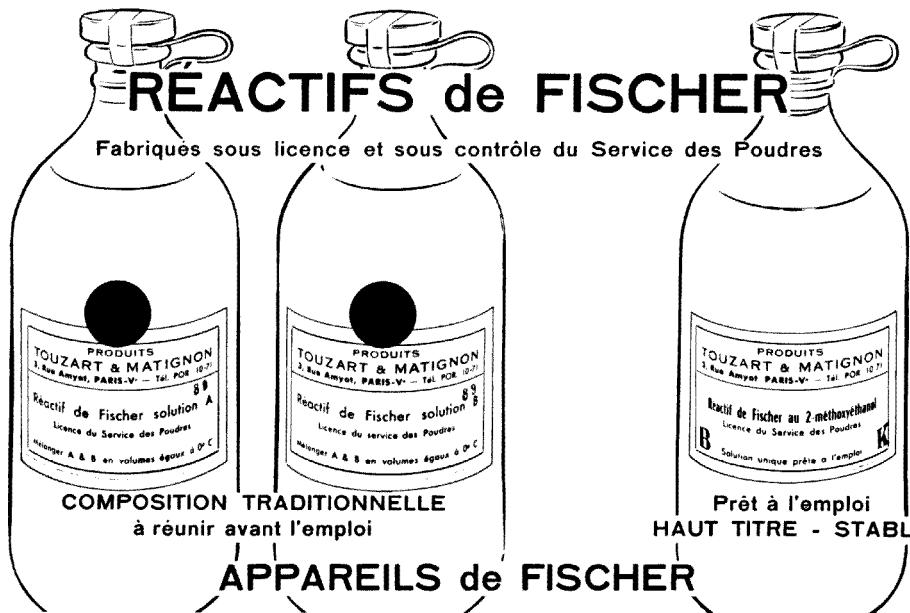
pHmètre à pile

une seule pile de 1,5 volts
1500 heures de marche

Equipé d'un oscillateur à *transistor*, le pHmètre PRO-LABO type Pl (breveté) emprunte à *une seule pile* de 1,5 volts toute l'énergie nécessaire à son fonctionnement. L'appareil fonctionne au moins 1500 heures avant de devoir échanger la pile. Les mesures de pH sont faites par lecture directe, à l'électrode de verre.

L'alimentation par une seule pile banale de longue durée apporte une *solution vraiment nouvelle* au problème du pH-mètre portatif.
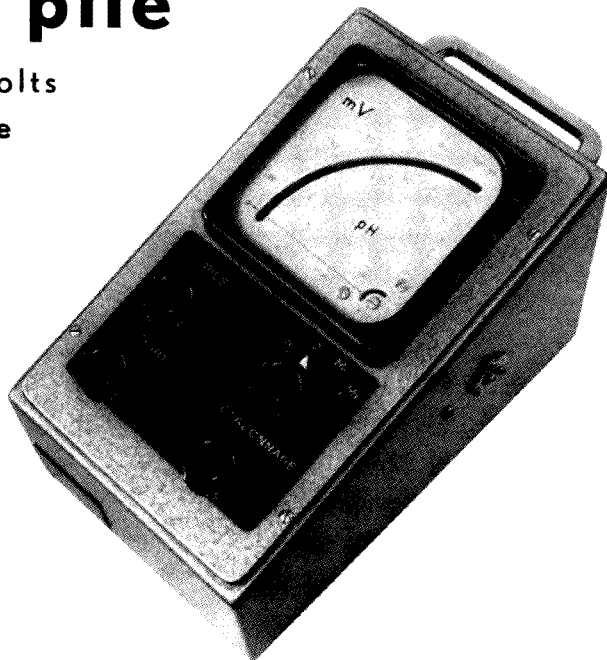
● Les pHmètres alimentés par piles sèches ont pour avantage bien connu de fonctionner avec une grande *stabilité* car leur bonne marche n'est pas sous la dépendance des fluctuations du secteur électrique. *Autonomes*, ces appareils se transportent facilement et fonctionnent en tout lieu.

● Pour que l'emploi de ces pHmètres à piles soit vraiment avantageux, il faut encore que la pile fasse un long usage, et que le modèle de piles utilisé soit facile à trouver dans le commerce. Le pHmètre PROLABO type Pl répond à ces conditions: sa consommation est très faible et la pile dure plus de 1500 heures; le voltage de cette pile, 1,5 volts est l'un des plus courants qui soient.

● L'appareil est contenu dans un boitier métallique en forme de pupitre, muni d'une poignée de transport. Le cadran de lecture, divisé en 1/10 de pH et en mV, est disposé de manière à obtenir une échelle de grand développement pour un encombrement aussi faible que possible. Sur le côté droit se trouvent les prises de connexion aux électrodes; sur le dessus, les boutons de réglage, en nombre minimum: contacteur, réglage de la pile, zéro, et étalonnage de l'électrode de verre.

● L'éxécution d'une mesure est remarquablement simple. L'appareil une fois réglé (ce réglage est rapide et durable), les électrodes sont immergées dans la solution à mesurer, et le contacteur mis sur la position de mesure; le pH est lu directement sur le cadran au point où s'arrête l'aiguille.

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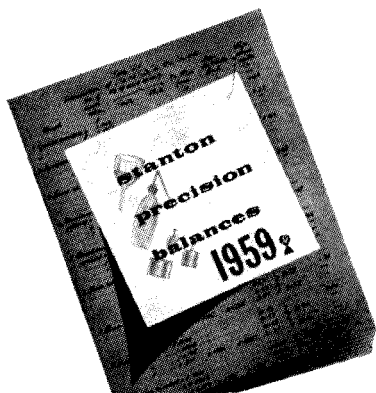
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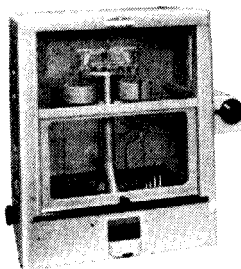
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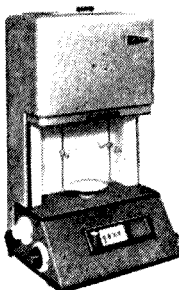
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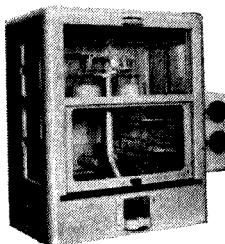
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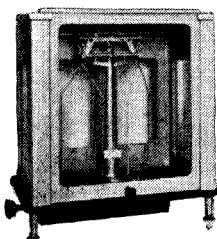
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SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. I

M. OOSTING

Analytical Research Institute T.N.O., Rijswijk (The Netherlands)

INTRODUCTION

Solvent extraction has been used for a long time but originally seemed to be of interest to organic chemists only; the quantitative treatment of the relatively simple equilibria involved in organic work is well-known and does not cause any difficulties. Although solvent extraction in inorganic chemistry has also been known for a long time, it did not become commonly used until about 1940.

The general application of solvent extraction in inorganic analysis is hindered because the complicated equilibria make quantitative treatment either too simplified or too intricate for practical use. It is our opinion that more extensive use would be made of this attractive technique if the fundamental principles could be expressed in a quantitative form which would not present undue mathematical difficulties, but which would not be so simplified that only worthless results could be obtained. We therefore developed expressions which we believe avoid both drawbacks.

Among the attractive aspects of solvent extraction in inorganic analysis are:
a) the completeness of the separations obtained,
b) the selectivity of the separations, which can often be influenced in various ways (pH, complexing agents), and
c) the fact that the residual aqueous solution can easily be used for the determination of other ions, with or without using solvent extraction.

It should be stressed that extraction is primarily a method of separation. If the extracted component is intensely coloured, a quantitative determination can be done but this should not be the criterion of the usefulness of an extraction. However, among the increasing number of articles on solvent extraction, relatively few deal with the extraction of colourless compounds as a separation prior to some appropriate method of determination.

As a rule, the description of extraction phenomena is only incidental and far from complete. Often the essential data are missing, such as the reagent concentration, the volumes of the aqueous and solvent phases, and the number of successive extractions. In this respect, many of the published data appear to be conflicting. Table I which shows some data collected from papers dealing with extraction with oxine and chloroform may serve as an example.

Some quantitative considerations on extraction equilibria have already been published, but these have not yet led to a satisfactory understanding of the functions of all the important factors.

TABLE I

Element	Complete extraction	pH at which incomplete extraction is said to take place	No extraction	References
Al	6.6 ± 0.2		2.8	1
	8.9			2
	4.3 – 4.6	2.5 – 4.3; 4.6 – 6		3
	5			4
Bi	8.9			2
	4 – 5.3	2 – 4; > 5.3		3
Cu	2.8			1
	8.9			2
	> 2.5	1.6 – 2.5		3
	2.5			5
Ni	2.8			1
	8.9			2
	> 6.8	2.6 – 6.8		3
UO$_2$	8.9			2
	3			6
Fe	2.8			1
	8.9			2
	2 – 3	1.5 – 2; > 3.5		3
	5			4
	4.5			7

In some cases a careless use of the expressions might lead to wrong conclusions. In FLAGG[8] is given the expression:

$$\frac{MDz_2(o)}{M^{+2}(w)} = K \frac{HDz^2(o)}{(H^+)^2(w)},$$

originally published by KOLTHOFF AND SANDELL[9], in which $MDz_2(o)$ represents the concentration of a metaldithizonate and $HDz(o)$ the concentration of dithizone (both in the organic phase), $M^{+2}(w)$ the concentration of metal ions and $H^+(w)$ the concentration of hydrogen ions (both in the aqueous phase); K is a constant.

The objections to this expression are:

1. The quotient

$$\frac{MDz_2(o)}{M^{+2}(w)}$$

does not show clearly the degree of separation obtained because the volumes of both phases must be known for this purpose. It is more correct to use the ratio of both quantities, expressed in mg moles and mg ion, rather than concentrations.

2. The term $HDz(o)$ depends on the total amount of dithizone, the pH, the volumes of both phases and the organic solvent chosen.

3. The expression might lead to the wrong conclusion, *i.e.* that an extraction would be promoted by increasing $HDz(o)$. This is only true, however, if $HDz(w)$ and $Dz^-(w)$ are also increased, which means a higher total reagent concentration. With a given amount of reagent, however, it is of advantage to decrease $HDz(o)$, which can be effected by increasing the pH.

Analogous expressions have been published by FURMAN, MASON AND PECOLA[10], by SANDELL AND CUMMINGS[11] and by MORRISON AND FREISER[12].

A different expression is given by IRVING AND WILLIAMS[13], who derive the apparently simple expression:

$$x = 50(1 - \tanh 1.1513 \, n \, \varDelta \, \text{pH}),$$

where x represents the percentage of metal ion extracted and n the valency of the metal ion considered.

$\varDelta$ pH represents pH – pH$\frac{1}{2}$, in which pH is the actual pH considered and pH$\frac{1}{2}$ is the pH value at which 50% of the metal ion is extracted. This pH$\frac{1}{2}$ is only constant as long as the concentration of the reagent and the volumes of both phases are kept constant.

In this paper, we shall describe the qualitative pattern of the reactions involved in solvent extraction, and elaborate that pattern quantitatively after making some restrictions as to the universal validity of the resulting expressions.

During the extraction of a metal ion M^+ with an organic reagent HR and a non-miscible solvent, the following reactions have to be considered. (For the sake of simplicity the metal ion is first taken as monovalent.)

1. The reagent dissociates: $HR \rightleftarrows H^+ + R^-$, as determined by a dissociation constant K^a_{HR}.
2. The metal ion reacts with the reagent anion: $M^+ + R^- \rightleftarrows MR$, in an amount determined by the solubility product L_{MR}.
3. The "chelate" is extracted by the immiscible solvent, $MR_w \rightleftarrows MR_o$, in an amount determined by a distribution coefficient E_{MR}.

   The following reactions work against extraction:
4. The undissociated reagent is extracted by the solvent $HR_w \rightleftarrows HR_o$, in an amount determined by a distribution coefficient E_{HR}.
5. The reagent can also react otherwise than in reaction 1, e.g. $HR + H_2O \rightleftarrows H_2R^+ + OH^-$, which is determined by a dissociation constant K^b_{HR}. This applies, for example, to oxine, where the dissociation
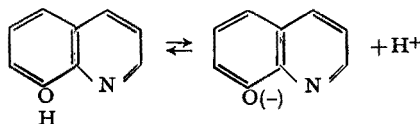
occurs as well as the reaction
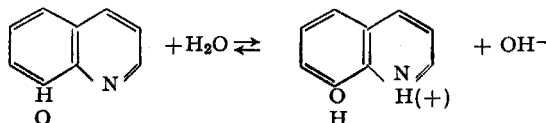
which becomes more important in acid solutions.

6. The metal ion can be fixed by other ions besides R^-, (e.g. by hydroxyl, fluoride, or tartrate ions etc.), in amounts determined by the complex constants. This

is the most important reaction when dealing with diethyldithiocarbamate (pH always above 5, often in the presence of tartrate, cyanide, EDTA).

Schematically:

$$MX \underset{\rightleftarrows}{\overset{K_c}{}} X^- + M^+ + R^- \underset{\rightleftarrows}{\overset{L_{MR}}{}} MR_w \underset{\rightleftarrows}{\overset{E_{MR}}{}} MR_o$$

$$+ H^+$$

$$\uparrow\downarrow K^a_{HR}$$

$$OH^- + H_2R^+ \underset{\rightleftarrows}{\overset{K^b_{HR}}{}} HR_w + H_2O$$

$$\uparrow\downarrow E_{HR}$$

$$HR_o$$

The problem can be split into two parts:

1. Under definite conditions what is the concentration of R^- in the aqueous phase?
2. How much of the metal ion M^+ remains in the aqueous phase when it contains the amount of R^- found under 1?

The following restrictions and assumptions will be made:

1. No complexes are formed (the reaction $M^+ + X^- \rightleftarrows MX$ does not take place).
2. A large excess of reagent is used.
3. Only those systems where the compound MR is soluble in the solvent used but almost insoluble in water will be considered.

It is well-known that free ions are not extracted to a measurable extent.

THE CALCULATION OF R^-

The problem

An aqueous solution of volume V_w contains a mg ion of a metal ion. Its concentration a/V_w is written as A.

An organic reagent HR (b mg moles) is added, the concentration of which, b/V_w is written as B. It is assumed that $B \gg A$. The reagent is amphoteric, and the dissociation constants are K^a_{HR} (dissociation as an acid) and K^b_{HR} (dissociation as a base). It is considered as a monovalent acid or base.

V_o ml of immiscible solvent, in which MR and possibly undissociated HR are soluble, is used for extraction. The quotient V_w/V_o is represented by f. The distribution coefficient E_{HR} is defined as

$$E_{HR} = \frac{HR_o}{HR_w} = \frac{\text{concn. undiss. HR org. phase}}{\text{concn. undiss. HR aq. phase}}.$$

Resolution

An excess of reagent $= b$ mg moles is present in 4 forms:

1. HR_w, the undissociated reagent in the aqueous phase,
2. HR_o, the undissociated reagent in the organic phase,
3. H_2R^+, reagent dissociated as a base (in the aqueous phase),
4. R^-, reagent, dissociated as an acid (in the aqueous phase).

The equations are:

$$K_{HR}^{a} = \frac{H^+ \cdot R^-}{HR_w} \quad \dots \dots \dots \dots \quad (1)$$

$$K_{HR}^{b} = \frac{OH^- \cdot H_2R^+}{HR_w} \quad \dots \dots \dots \dots \quad (2)$$

$$E_{HR} = \frac{HR_o}{HR_w} \quad \dots \dots \dots \dots \dots \quad (3)$$

Now of course:

$$b = [HR_w] + [HR_o] + [H_2R^+] + [R^-] \quad \dots \dots \dots \quad (4)*$$

and, as $B = b/V_w$:

$$B = HR_w + \frac{E_{HR}}{f} \cdot HR_w + H_2R^+ + R^- \dots \dots \dots \quad (4a)$$

Using equations (1) to (3), all terms can be expressed as a function of R^-.

$$B = \frac{H^+}{K_{HR}^a} \cdot R^- + \frac{E_{HR}}{f} \cdot \frac{H^+}{K_{HR}^a} \cdot R^- + \frac{K_{HR}^b}{OH^-} \cdot \frac{H^+}{K_{HR}^a} \cdot R^- + R^-$$

$$\text{or } B = R^- \left\{ \frac{H^+ \cdot f \cdot OH^- + E_{HR} \cdot H^+ \cdot OH^- + f K_{HR}^b \cdot H^+ + K_{HR}^a \cdot f \cdot OH^-}{K_{HR}^a \cdot f \cdot OH^-} \right\} \quad \dots \dots \quad (5)$$

or, multiplying the numerator and denominator by H^+ and resolving R^-, since $H^+ \cdot OH^- = K_w$

$$R^- = \frac{K_{HR}^a \cdot f \cdot K_w \cdot B}{H^+ K_w (f + E_{HR}) + f \left\{ K_{HR}^b (H^+)^2 + K_{HR}^a \cdot K_w \right\}} \quad \dots \dots \dots \quad (6)$$

This is the most general expression for R^-. Sometimes, this expression can be simplified. For example, if the reagent is not amphoteric, $K_{HR}^b = 0$, and accordingly:

$$R^- = \frac{K_{HR}^a \cdot f \cdot B}{H^+(f + E_{HR}) + f K_{HR}^a}.$$

If the reagent is also a very weak acid, or if we consider strongly acid solutions ($K_{HR}^a \ll H^+$), then, because $(f + E_{HR}) \leqslant f$,

$$R^- = \frac{K_{HR}^a \cdot f \cdot B}{H^+(f + E_{HR})}.$$

THE CALCULATION OF THE EXTRACTION ERROR

It is assumed that extraction of a metal chelate can only take place if a certain amount of undissociated metal chelate is formed in the aqueous phase. The compound MR should be dissociated incompletely and accordingly there is a dissociation constant:

$$K_{MR} = \frac{M^+ \cdot R^-}{MR_w}.$$

_____

* Square brackets refer to quantities (in mg moles or mg ion), the other symbols to concentrations.

In the presence of solid MR, the aqueous and the organic phase are both saturated, hence for the partition coefficient:

$$E_{MR} = \frac{MR_o \text{ sat.}}{MR_w \text{ sat.}} . \text{ But as } E_{MR} = \frac{MR_o \text{ unsat.}}{MR_w \text{ unsat.}}$$

it follows that

$$\frac{MR_o \text{ sat.}}{MR_w \text{ sat.}} = \frac{MR_o \text{ unsat.}}{MR_w \text{ unsat.}} \quad \ldots \ldots \ldots \ldots \quad (7)*$$

Consider the extraction of a metal ion M^+ in the presence of a definite amount of R^-. In an aqueous solution saturated with regard to MR:

$$K_{MR} = \frac{M^+ \cdot R^-}{MR_w \text{ sat.}} \text{ and } M^+ \cdot R^- = L_{MR}.$$

K_{MR} is readily seen to be $K_{MR} = L_{MR}/MR_w$ sat.

Now, in most extractions the aqueous phase is unsaturated with regard to MR, hence in the aqueous phase:

$$K_{MR} = \frac{M^+ \cdot R^-}{MR_w \text{ unsat.}},$$

$$\text{or } M^+ \cdot R^- = K_{MR} \cdot MR_w \text{ unsat.} = L_{MR} \cdot \frac{MR_w \text{ unsat.}}{MR_w \text{ sat.}}$$

or substituting (7):

$$M^+ \cdot R^- = L_{MR} \cdot \frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}}$$

$$\text{or } M^+ = \frac{1}{R^-} \cdot L_{MR} \frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}} \quad \ldots \ldots \ldots \ldots \quad (8)$$

In precipitation reactions $M^+ \cdot R^- = L_{MR}$ and thus:

$$M^+ = \frac{1}{R^-} \cdot L_{MR} \quad \ldots \ldots \ldots \ldots \ldots \quad (9)$$

From equations (8) and (9), it can be seen that an ion is more completely removed from a solution by extraction than by precipitation because

$$\frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}} < 1.$$

Strictly speaking, the amount of metal ion which is not removed by precipitation is:

$$M^+ + MR_w \text{ sat.} = \frac{1}{R^-} \cdot L_{MR} + MR_w \text{ sat.}$$

The amount of ion which is not removed by extraction is $M^+ + MR_w$ unsat., and this can be written as:

$$\frac{1}{R^-} \cdot L_{MR} \cdot \frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}} + MR_w \text{ sat.} \frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}} \text{ or}$$

$$\left\{ \frac{1}{R^-} \cdot L_{MR} + MR_w \text{ sat.} \right\} \frac{MR_o \text{ unsat.}}{MR_o \text{ sat.}}.$$

---

* As a rule MR_o sat. is not large. For oxinates in chloroform we found values of $10^{-3} - 10^{-2}$, so we may regard the saturated solutions as dilute ones to which the corresponding laws apply unrestrictedly.

Thus the conclusion concerning more complete removal by extraction still applies. In the following part it is assumed that MR_w is always negligible compared to M^+. KOLTHOFF AND SANDELL[9] also use this supposition. IRVING AND WILLIAMS[13] object to it, but use a neglection which on further consideration turns out to be based on the same supposition. The good agreement found by IRVING AND WILLIAMS between the calculated and the experimentally found extractions proves the validity of this neglection at least for the systems investigated.

The concentration of the unextracted metal ion M^+ was found to be

$$M^+ = \frac{L_{MR} \cdot MR_o \text{ unsat.}}{R^- \cdot MR_o \text{ sat.}} \quad \cdots \cdots \cdots \cdots \quad (8)$$

If the term m^+ res. (idual) is introduced for the number of mg ions of metal that are not extracted, then m^+ res. $= V_w M^+$.

$$m^+ \text{ res.} = \frac{V_w \cdot L_{MR} \cdot MR_o \text{ unsat.}}{R^- \cdot MR_o \text{ sat.}} \quad \cdots \cdots \cdots \cdots \quad (10)$$

$$\text{Now } MR_o \text{ unsat.} = \frac{a - m^+ \text{ res.}}{V_o} \quad \cdots \cdots \cdots \cdots \quad (11)$$

and substituting (11) in (10):

$$m^+ \text{ res.} = \frac{V_w \cdot L_{MR} (a - m^+ \text{ res.})}{V_o R^- \cdot MR_o \text{ sat.}} = \frac{fL_{MR} \cdot a}{R^- \cdot MR_o \text{ sat.}} - \frac{fL_{MR} \cdot m^+ \text{ res.}}{R^- \cdot MR_o \text{ sat.}}$$

$$\text{or } m^+ \text{ res.} \left\{ 1 + \frac{fL_{MR}}{R^- \cdot MR_o \text{ sat.}} \right\} = \frac{f \cdot a \cdot L_{MR}}{R^- \cdot MR_o \text{ sat.}}$$

Hence, for the unextracted fraction of the metal ion or "extraction error":

$$\frac{m^+ \text{ res.}}{a} = \frac{fL_{MR}}{R^- \cdot MR_o \text{ sat.} + fL_{MR}} \quad \cdots \cdots \cdots \cdots \quad (12)$$

This equation, together with (6) completely describes the extraction equilibria. Substitution of R^- from eq. (6) in (12) leads to a very complicated form. It will be shown in a later paper that this substitution is not necessary. For n-valent metal-ions, we can derive in exactly the same way:

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL_{MR_n}}{(R^-)^n \cdot MR_{no} \text{ sat.} + fL_{MR_n}} \quad \cdots \cdots \cdots \quad (12a)$$

SUMMARY

Two equations are derived, showing the quantitative relationship between the course of a solvent extraction and the factors involved. These equations only contain independent variables.

RÉSUMÉ

Par deux équations dérivées, l'auteur donne une interprétation quantitative d'une extraction par solvant, en fonction des différents facteurs qui peuvent intervenir.

ZUSAMMENFASSUNG

Es wird gezeigt, dass der Einfluss bestimmter Faktoren auf den quantitativen Verlauf einer Extraktion mit Lösungsmitteln durch zwei Gleichungen ausgedrückt werden kann.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM USING 4-METHYL-1,2-CYCLOHEXANEDIONEDIOXIME*

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INTRODUCTION

Many reagents have been proposed for the spectrophotometric determination of palladium. The reducing properties of mercury(I) chloride have been used to determine submicrogram quantities of palladium by observing the color and opaqueness of the palladium metal deposited on the mercury(I) chloride[1,2]. Palladium has also been determined by estimating its catalytic effect on the reduction of nickel(II) by sodium hypophosphite[3]. Hydrobromic acid[4], iodide[5-8], tin(II) chloride[9], and thiocyanate[10,11] have also been suggested as colorimetric reagents.

Some of the organic reagents which have been reported for the determination of palladium are: 4-nitrosoresorcinol[12], *p*-dimethylaminobenzylidenerhodanine[13,14], compounds containing the *p*-nitrosoamino groups[15-17], 2-mercapto-4,5-dimethylthiazol[18], 1-nitroso-2-naphthol[19], 2-nitroso-1-naphthol[20], rubeanic acid[21], ethylenediaminetetraacetic acid (EDTA)[22], thiourea[23], and substituted acetylenes[24]. Various oximes have also been reported for the colorimetric determination of palladium[25-27].

Many of the reagents mentioned above do not possess all the desired properties of an ideal colorimetric reagent[28]. SOGANI AND BHATTACHARYYA[29] have proposed 3-hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine as a colorimetric reagent for palladium, and they report it to be better and more ideal than any of the reagents mentioned previously in the literature. Recently MAJUMDAR AND CHAKRABARTTY suggested 2,5-dimercapto-1,3,4-thiodiazole (Bismuthiol I)[30] and 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolone-2 (Bismuthiol II)[31] as new reagents for the determination.

KODAMA[32] used *o*-nitrosoresorcinol monomethyl ether as a colorimetric reagent for palladium and rhodium. Palladium is heated with perchloric or sulfuric acid until fumes are evolved. The solution is transferred to a separatory funnel and extracted with chloroform. The absorbance of the chloroform phase is measured at 420 mμ.

A procedure employing nickel or potassium dialkyl- and diaryldithiophosphates for the determination of palladium was published by BUSEV AND IVANIUTIN[33]. The complex formed is insoluble in strong acids such as hydrochloric or sulfuric, but can be extracted with chloroform or carbon tetrachloride. The maximum absorption of the complex in carbon tetrachloride is at 295 mμ and is used for spectrophotometric determinations in the range of 0.014–0.090 mg Pd/25 ml; however, the absorbance of more concentrated solutions (0.16–1.1 mg Pd/25 ml) is measured spectrophotometrically at 340 mμ.

Although the reactions of palladium with *vic*-dioximes have been known for a long time, very few colorimetric methods have been published employing them. Those dioximes which have been used are methylglyoxime[25,26,34], dimethylglyoxime[35], and α-furildioxime[36].

4-Methyl-1,2-cyclohexanedionedioxime (4-methylnioxime) can be easily prepared[37] and has been reported to be an excellent gravimetric reagent for palladium[38]. The purpose of this study was to determine the merits of this compound as a colorimetric reagent.

APPARATUS AND REAGENTS

Absorbance measurements were made with a Beckman Model DU spectrophotometer using 1-cm silica cells. A Cary Model 12 recording spectrophotometer was used to scan the spectra of the complexes and reagents. A Beckman Model G pH meter was used for pH studies. The volumetric glassware employed was Kimble Normax and Pyrex class "A". 4-Methyl-1,2-cyclo-hexanedionedioxime: this compound was prepared in this laboratory[37] and a saturated aqueous solution was used. Standard palladium solution: a solution was prepared by dissolving 0.8236 g of reagent-grade palladium chloride in hydrochloric acid and diluting to 2 l. This solution was standardized gravimetrically using 1,2-cyclohexanedionedioxime according to the procedure of VOTER, BANKS, AND DIEHL[39]. The concentration of palladium was found to be 2.11·10^{-3} moles/l.

Buffer solution: a hydrochloric acid–potassium chloride buffer solution was prepared by mixing 5.30 ml of 0.2 N HCl and 25 ml of 0.2 N KCl solutions and diluting to 100 ml.

Other chemicals used were reagent-grade quality.

EXPERIMENTAL WORK

HOOKER[40] found that palladium could be determined by the suspension–spectrophotometric method proposed by FERGUSON AND BANKS[41] for the determination of nickel. Gum arabic is added to the solution to stabilize the suspension of the precipitate. Highly colored ions seriously interfere in this method. However, if gum arabic is omitted and the precipitate allowed to form and then extracted, a very sensitive method results.

The precipitate of bis (4-methylnioximato-*N,N'*) palladium(II) was found to be soluble in chloroform and to have an absorption band at 280 mμ. Neither 4-methylnioxime nor chloroform shows appreciable absorption at this wavelength.

For optimum extraction the pH of the aqueous phase should be between 0.7 and 5.0. The solution should be prepared 60 min prior to extraction.

It was observed that the chloroform phase was stable for only 3 h after being equilibrated with an aqueous phase which was adjusted to pH 2 with hydrochloric acid. However, if the aqueous phase is adjusted to pH 2 with a hydrochloric acid–potassium chloride buffer, the chloroform phase remains stable for more than 24 h.

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GENERAL PROCEDURE

An aqueous phase containing 2.5–250 μg of palladium is transferred to a 125-ml beaker and adjusted to approximately pH 2 using the hydrochloric acid–potassium chloride buffer. The solution is then transferred to a 125-ml separatory funnel, one ml of the saturated solution of 4-methylnioxime is added, and the solution allowed to stand for 1 h. The aqueous phase is then extracted with three 7-ml portions of chloroform. The extracts are combined, transferred to a 25-ml volumetric flask, and diluted to volume with chloroform. As a drying agent, 0.5 g of anhydrous sodium sulfate is added. The absorbance of the chloroform phase is measured against chloroform at 280 mμ using 1-cm silica cells. The amount of palladium is determined by reference to a calibration curve.

INTERFERENCES

The extraction–spectrophotometric method eliminates the interference of many of the highly colored ions which cause trouble in the suspension–spectrophotometric method. However, as in the case of the suspension–spectrophotometric method, the following ions were found to interfere when present: ruthenium(III), copper(II), cobalt(II), iron(II), and iron(III). Successful masking agents were found in all cases except ruthenium. Microgram but not milligram quantities of copper(II) may be masked with thioglycolic acid. Interference from cobalt can be eliminated by conversion to the hexacyanocobaltate(III) complex. Iron(II) can be oxidized to iron(III) and complexed with either tartrate, phosphate, or fluoride; fluoride was found to be the most effective masking agent.

DISCUSSION

One of the outstanding properties of the substituted nioximes is the high solubility in chloroform of the bis (*vic*-dioximato-N,N′)metal(II) complexes containing palladium and nickel. Therefore, the quantitative extraction of these complexes into chloroform and a subsequent spectrophotometric determination is possible. 4-Methylnioxime has several advantages over other reagents for the spectrophotometric determination. The pH at which the complex is formed and extracted is not critical, the complex is readily extracted into chloroform, the chloroform solution is stable for more than 24 h, and great sensitivity can be achieved. Interference by highly colored, extractable ions is easily avoided by using readily available masking agents; only ruthenium must be absent when palladium is determined.

The molar absorptivity of the bis(4-methylnioximato-N,N′)palladium(II) complex was calculated from the calibration curve and found to be $1.51 \cdot 10^4$ l/moles-cm in chloroform at 280 mμ.

SUMMARY

A procedure for the determination of palladium with 4-methyl-1,2-cyclohexanedionedioxime by an extraction–spectrophotometric method has been developed. Interference by copper(II), cobalt(II), iron(II), or iron(III) can be eliminated by suitable masking agents. Ruthenium(III) must be absent or separated prior to the determination of palladium. The molar absorptivity of the bis(4-methyl-1,2-cyclohexanedionedioximato-N,N′) palladium(II) complex has been calculated and found to be $1.51 \cdot 10^4$ l/moles-cm in chloroform at 280 mμ.

RÉSUMÉ

Une méthode par extraction et par spectrophotométrie est proposée pour le dosage du palladium. On emploie comme réactif la méthyl-4-cyclohexanedionedioxime-1,2.

ZUSAMMENFASSUNG

Es wird eine kombinierte Extraktions–spektrophotometrische Methode zur Bestimmung von Palladium mit Hilfe von Methyl-4-cyclohexandion-dioxim-1,2 beschrieben.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR CATIONS AND ANIONS

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A procedure has been evolved for the complete analysis of a mixture for its cations and anions. An extensive study of the behaviour of salts of the common elements towards sodium hydroxide and sodium carbonate has led to a procedure which can be used for the simultaneous detection of basic and acid radicals; most of the basic-forming elements when boiled with sodium hydroxide and sodium carbonate behave as acids.

The most important facts which are either already well-known or have come to light are: (a) metals like lead, arsenic, antimony, tin, aluminum and zinc form soluble salts when boiled with sodium hydroxide which are not affected by subsequent treatment with sodium carbonate. (b) Substances like Prussian blue, Turnbull's blue, zinc or copper ferrocyanide, silver ferro- and ferri-cyanides, fused lead chromate, chromium chloride (violet), which are said by some authors to be insoluble in the systematic scheme for basic radicals, are decomposed either with the precipitation of the metal as hydroxide or its conversion to soluble salts, whereas the acid constituent is invariably converted to the soluble sodium salt. (c) Silver, copper, bismuth, cadmium, iron, manganese, nickel and cobalt are completely precipitated as oxides, hydrated oxides or hydroxides. (d) Trivalent chromium salts are converted to $Cr(OH)_3$, which is amphoteric and is partially converted to soluble sodium chromite, which again precipitates $Cr(OH)_3$ on boiling. (e) A fact, which has not hitherto been reported is the behaviour of mercury salts towards sodium hydroxide and sodium carbonate. The precipitation of mercury by sodium hydroxide or sodium carbonate is never complete; mercury is always found in appreciable quantities in the filtrate. (f) The behaviour of the alkaline earths towards sodium hydroxide is already well known. The filtrate obtained after boiling the mixture containing the alkaline earth with sodium hydroxide, contains appreciable amounts of barium and traces of strontium and calcium; the quantity of magnesium depends on the presence of ammonium salts. Unless ammonium salts are completely removed by boiling with a sufficient excess of sodium hydroxide for a fairly long time appreciable amount of magnesium pass into the filtrate. But all the alkaline earths are completely precipitated on further boiling with sodium carbonate. (g) The most important feature of the proposed scheme is the detection of certain metals in the form of anions. These elements are not found in the systematic analysis of the mixture for basic radicals. For example, aluminium and zinc are always converted to their soluble sodium salts, except strongly ignited aluminium oxide, which is

treated under insolubles. Lead salts are also completely dissolved by sodium hydroxide, except for lead sulphate which is only partly soluble. Thus provision has to be made for its detection in the scheme for basic radicals, and as an insoluble. Similarly, the sulphides of arsenic, tin and antimony are converted by boiling with sodium hydroxide solution to their soluble thiosalts. However, a very small amount of arsenic and antimony is transformed to the oxides, which are soluble in the subsequent acid treatment for the detection of basic radicals. The behaviour of mercuric sulphide is peculiar; it is partly dissolved on boiling with sodium hydroxide but most of it remains insoluble. This provides a twofold check for the detection of these elements.

In the present work, only a limited number of acid and basic radicals has been selected, *i.e.* those which an elementary student is likely to encounter.

These are:

(*a*) *Acid radicals.* $[Fe(CN)_6]^{-4}$, $[Fe(CN)_6]^{-3}$, F^-, Cl^-, Br^-, I^-, SO_4^{-2}, SO_3^{-2}, S^{-2}, $S_2O_3^{-2}$, CNS^-, PO_4^{-3}, $(COO)_2^{-2}$, CH_3COO^-, NO_3^-, NO_2^-, SiO_3^{-2} and BO_3^{-3}.

(*b*) *Basic radicals.* The so-called common elements which include acid-forming elements like As, Sb, Sn, Pb, Zn, Al etc.

The details of the procedures to be followed in analyzing completely a mixture for its anions and cations are given below.

I. Boil 0.5–1 g of the mixture with 50 ml of 4 N sodium hydroxide solution for 4–5 min, add 4–5 g of solid sodium carbonate, boil and filter.

Treat the filtrate for the detection of acid radicals and the residue for basic radicals including the insolubles.

II. Test a portion of the filtrate for lead and treat the rest of the filtrate with lead carbonate (4–5 g), boil and filter. The precipitate may consist of lead carbonate, lead sulphide, mercuric sulphide, mercuric oxide and mercury. Wash with distilled water.

A black precipitate at this stage indicates the presence of sulphide.

Dissolve the precipitate in conc. hydrochloric acid and a crystal of KClO₃, boil off chlorine and treat a portion with stannous chloride solution. A white precipitate changing to grey indicates the presence of mercury.

III. Test a portion of the filtrate from II for zinc and treat the rest with 1 M zinc acetate solution until no further precipitation takes place, heat to boiling and filter. The precipitate may contain the zinc salts of $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, AsO_3^{-3}, AsO_4^{-3}, SO_3^{-2}, $C_2O_4^{-2}$, PO_4^{-3}, $B_4O_7^{-2}$, AlO_2^- and PbO_2^{-2}, but traces of lead and aluminium may also be found in the filtrate. Wash the precipitate with distilled water.

IV. Treat the precipitate from III with an excess of 5 N ammonium hydroxide, warm and filter. Wash the insoluble residue with 2 N ammonium hydroxide, followed by distilled water and analyse according to Table I.

V. Treat the filtrate from IV with 10 ml of conc. ammonia and add magnesia mixture in slight excess. Heat nearly to boiling and filter. Analyse the precipitate according to Table II.

VI. Treat the filtrate from III with 4–5 g of sodium carbonate, boil and filter. This precipitates Pb^{+2} and Zn^{+2} completely as carbonates and Al^{+3} as hydroxide. (Reject the precipitate). Concentrate the filtrate to 20–30 ml, treat with $Ca(NO_3)_2$ solution in excess and filter. The precipitate consists of $CaCO_3$ and CaF_2.

Test the precipitate for fluoride as usual. Treat the filtrate from CaF_2 with

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TABLE I

Ppt. May contain zinc salts of [Fe(CN)$_6$]$^{-4}$, AlO$_2^-$, PO$_4^{-3}$, and PbO$_2^{-2}$. Boil with 5 N HCl, filter hot and wash with hot water.

Ppt. Zinc ferrocyanide soluble in NaOH. Confirms [Fe(CN)$_6$]$^{-4}$.	Filt. Chlorides of Zn, Al and Pb, PO$_4^{-3}$. Add dil. H$_2$SO$_4$ in excess and filter. (Reject the ppt. of PbSO$_4$). Treat the filtrate with NH$_4$Cl and NH$_4$OH in slight excess and filter.	
	Ppt. (a) Test a portion for PO$_4^{-3}$ with ammonium molybdate. (b) Test a portion for Al with oxine.	Filt. Zn^{+2}. Reject.

TABLE II

Ppt. May contain the magnesium salts of AsO$_3^{-3}$, AsO$_4^{-3}$, PO$_4^{-3}$, (F$^-$), AlO$_2^-$, SnO$_3^{-2}$, SbO$_3^{-2}$ and SbO$_4^{-3}$. Treat with 4 N acetic acid (15–20 ml) and filter.

Ppt. White AlPO$_4$. Test for Al^{+3} and PO$_4^{-3}$ as usual.

Filt. (F$^-$), AsO$_3^{-3}$, AsO$_4^{-3}$, SbO$_3^{-2}$, SbO$_4^{-3}$, SnO$_3^{-2}$, SiO$_3^{-2}$ and Mg (The presence of Al^{+3} or PO$_4^{-3}$ depends on the amount present in the original mixture). Add Ca(NO$_3$)$_2$ solution in slight excess and filter.

Ppt. CaF$_2$. Confirm by SiF$_4$ test.

Filt. AsO$_3^{-3}$, AsO$_4^{-3}$, SbO$_4^{-3}$, SbO$_3^{-2}$, SnO$_3^{-2}$, SiO$_3^{-2}$, Al^{+3} (Mg+Ca). Add 2 N Na$_2$S reagent[1] in excess followed by 3–5 g of Na$_2$CO$_3$ and filter.

Ppt. PO$_4^{-3}$, Al(OH)$_3$, MgCO$_3$ and CaCO$_3$. Dissolve in dil. HCl and test for Al^{+3} and PO$_4^{-3}$ as usual.

Filt. Thiosalts of As^{+3}, As^{+5}, Sb^{+3}, Sb^{+5}, Sn^{+4} and Na$_2$SiO$_3$(Mg). Make acid with dil. HCl and filter at once.

Ppt. As$_2$S$_3$, Sb$_2$S$_3$, Sb$_2$S$_5$ and SnS$_2$. Boil with 6 N HCl and filter.

Filt. Thiosalts of As^{+5} and Na$_2$SiO$_3$. Add conc. HCl to give a final concentration of 6 N, heat to boiling and filter.

Ppt. As$_2$S$_3$. Test as usual.

Filt. Sb^{+3} and Sn^{+4}. Test as usual.

Ppt. Yellow As$_2$S$_3$. Confirms AsO$_4^{-3}$.

Filt. SiO$_3^{-2}$. Evaporate to dryness and dehydrate silica. Test for Si by SiF$_4$ test.

$Ba(NO_3)_2$ solution, heat to boiling and filter. Wash the precipitate with distilled water and analyse according to Table III.

TABLE III

Ppt. May contain $BaCrO_4$ and $BaSO_4$. Treat with dil. HCl and filter.	
Ppt. $BaSO_4$. Confirms SO_4^{-2} by carbonized match-stick test.	Filt. Ba^{+2}, CrO_4^{-2} (HCl). Add NH_4OH in excess. A yellow ppt. confirms CrO_4^{-2}.

VII. Treat the filtrate from VI with $AgNO_3$ solution in excess, warm to 70° and filter. Test the filtrate for MnO_4^- and the precipitate according to Table IV.

TABLE IV

Ppt. May contain AgCl, AgBr, AgI, AgCNS and Ag_2S.
(A black ppt. of Ag_2S at this stage indicates the presence of thiosulphate). Treat the ppt. with NH_4OH and $(NH_4)_2S$, boil to expel ammonia and filter.

Ppt. Ag_2S. Reject.	Filt. CNS^-, I^-, Br^- and Cl^- as ammonium salts. Add HNO_3 and $Fe(NO_3)_3$. Shake with CCl_4 and allow to stand for 5 min.		
	CCl_4 layer. Purple colour shows I^-.	Aqueous layer. Br^-, Cl^-, $Fe(CNS)_3$ and some iodine. Boil off iodine, cool, dilute and add $KMnO_4$ solution till a light pink colour persists. Shake with CCl_4. ($KMnO_4$ decomposes CNS^-, so that it does not interfere in the tests for Br^- and Cl^-.)	
		CCl_4 layer. Orange shows Br^-.	Aqueous layer. Boil off bromine, add $NaNO_2$ and $AgNO_3$. A white ppt. shows Cl^-.

VIII. Treat the filtrate from V with $Ca(NO_3)_2$ and $Ba(NO_3)_2$, heat to boiling and filter. Analyse the precipitate according to Table V and the filtrate according to Table VI.

IX. Treat the residue from I with 10 ml of conc. HNO_3 and evaporate to nearly 3 ml. Add 20 ml of conc. HCl and evaporate to a moist residue. Boil the residue with 20 ml of 2 N HCl and filter.

TABLE V

Ppt. May consist of CaF_2, CaC_2O_4, $BaSO_3$, $BaCrO_4$, BO_3^- and $Ba(OH)_2$. Treat with 5–10 ml of dil. CH_3COOH and filter.

Ppt. CaF_2, CaC_2O_4, $BaSO_3$ and $BaCrO_4$. Boil with a saturated solution of Na_2CO_3 for 5 min and filter. Reject the ppt. of $BaCO_3$ and $CaCO_3$. Treat the filtrate with acetic acid in slight excess and add $Ca(NO_3)_2$. Filter.			Filt. Ba^{+2} and BO_3^-. Evaporate to dryness, take up the residue with dil. HCl and test for borate as usual.
Ppt. CaF_2, CaC_2O_4. Confirm F^- and $C_2O_4^{-2}$ as usual.	Filt. SO_3^-, CrO_4^{-2} (Ca). Add bromine-water followed by HCl and $BaCl_2$.		
	Ppt. $BaSO_4$ Confirms SO_3^{-2}.	Filt. CrO_4^{-2}, Ba and HCl. Add NH_4OH in excess. A yellow ppt. confirms CrO_4^{-2}.	

(A) The insoluble residue may contain halides: $AgCl$, CaF_2; sulphates: $BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$ (anhydrous), $PbSO_4$; strongly ignited oxides: SiO_2, Sb_2O_4, SnO_2, Al_2O_3, Cr_2O_3 and $Sn_2P_2O_7$. Analyse as usual[2].

(*Note*: The treatment of the residue with $4N$ sodium hydroxide solution may be omitted here.)

TABLE VI

Filt. May contain $[Fe(CN)_6]^{-3}$, BO_3^{-3}, and traces of Sb and Sn (Ba+Ca). Add NH_4OH in slight excess, followed by 2–4 g of Na_2CO_3. Boil for 5 min and filter.

Ppt. BaCO₃ and CaCO₃. Reject.	Filt. $[Fe(CN)_6]^{-3}$, BO_3^{-3} and traces of Sb and Sn. Divide in two parts.
	Part I. Acidify with dil. HCl and test for $[Fe(CN)_6]^{-3}$ with $FeSO_4$ solution. Blue ppt. or colour confirms $[Fe(CN)_6]^{-3}$. *Part II*. Evaporate to dryness and test for borate by BF_3 test. Note: The solution need not be tested for Sn and Sb here; these elements have already been tested for in Table II.

(B) The filtrate may be tested for the following elements according to the scheme based on the decomposition of thiosalts[3]: Hg, (Pb), Bi, Cu, Cd, Ni, Co, Mn, Fe, Cr, (As), (Sb), (Sn) and alkaline earths. The elements shown in brackets are present in very small amounts.

X. *Detection of S^{-2}*. Certain sulphides are not decomposed on boiling with alkali as suggested in I. A separate portion of the original mixture must be tested for this anion.

Detection of NH_4^+. Heat a portion of the original mixture with sodium hydroxide and test for ammonia.

Detection of Na^+ and K^+. Extract a portion of the original mixture with 10–15 ml of distilled water, treat with concentrated ammonium sulphide and filter. From the filtrate remove the metals of the arsenic and tin groups by decomposing the thiosalts and filter off the precipitated sulphides. Test the filtrate for Mg^{+2}, Na^+ and K^+ as usual.

SUMMARY

The behaviour of different elements towards sodium hydroxide and sodium carbonate is reviewed. Detailed procedures for the complete analysis of a mixture containing anions and cations are given.

RÉSUMÉ

L'auteur a examiné le comportement de différents éléments vis-à-vis de l'hydroxyde et du carbonate de sodium. Une méthode d'analyse complète anions et cations est décrite.

ZUSAMMENFASSUNG

Es wurde das Verhalten verschiedener Elemente gegen Natriumhydroxyd und Natriumcarbonat untersucht und ein vollständiger Trennungsgang der Anionen und Kationen beschrieben.

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THE USE OF CONTINUOUS EXTRACTION FOR THE REMOVAL OF INTERFERING ELEMENTS IN THE DETERMINATION OF CALCIUM AND MAGNESIUM

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Many elements interfere in the determination of calcium and magnesium by titration with ethanediaminotetraacetic acid (VERSENE). The interference of some of these elements can be reduced by combining them with reagents such as cyanide, 2,3-dimercaptopropanol[1], and triethanolamine[2-5], which form very strongly bound complexes with them. Although methods using complexing agents are satisfactory when small amounts of interfering elements are present, the end-points of the titrations of calcium and magnesium are not so sharp if large amounts of such elements are present.

Certain of the interfering elements can be removed by precipitation with ammonium hydroxide, but others, such as copper and nickel, which form soluble ammines, remain in the solution. This method of separation is rather tedious, since, owing to the coprecipitation of calcium and magnesium, one or two reprecipitations are necessary to free the precipitate of alkali earth metals. With organic precipitants, such as 8-hydroxyquinoline (oxine), the risk of co-precipitation is reduced, but some calcium and magnesium are still carried down by the precipitate. Methods of separation employing solvent extraction are often more satisfactory than those using precipitation, since co-extraction of elements does not usually occur. ESKELUND AND BROWN[6] have extracted iron as its diethyldithiocarbamate with ether before the titration of calcium and magnesium. CLULEY[7] has described a procedure for the determination of calcium in soda–lime glasses, in which iron and aluminium are separated by extraction of their oxinates at pH 5.0 with chloroform.

The author[8,9] has used a similar method in silicate analysis for the removal of iron, aluminium and titanium before titration of calcium and magnesium. The extraction was carried out at pH 5 using a continuous extractor instead of a separating funnel. This had the following advantages:
a. less manipulation was required; b. excess oxine was rapidly removed; c. emulsions, which formed in the presence of much iron, when a separating funnel was used, were avoided.

Since many other elements which interfere in the determination of calcium and magnesium also form oxinates which are soluble in chloroform, it was expected that this method could be used in the analysis of silicate minerals and other materials, containing large amounts of such elements. This paper describes an investigation into the removal of such elements with a continuous extractor. Phosphate, arsenate

and selenate, when present in major amounts, seriously interfere in the determination of calcium and magnesium.They can be removed by precipitation as their insoluble zirconium salts; excess zirconium is removed as its oxinate during the extraction process.

Titration of calcium and magnesium

The use of Eriochrome Black T (E.B.T.) as an indicator in the titration of total calcium + magnesium in ammoniacal medium with ethanediaminotetraacetic acid, is well known and gives satisfactory end-points, either visually or with a photo-electric titrator.

The titration of calcium in the presence of an equal, or larger amount of magnesium is more difficult, and a number of indicators such as murexide, calcein[10-13], Eriochrome Blue Black R (Calcon)[14,15], and Calred[16], have been used for the purpose. Before the titration, the solution is made alkaline to precipitate magnesium as its hydroxide, which does not titrate. Some calcium is co-precipitated with the magnesium hydroxide, but this can be removed by vigorous stirring during the titration. The co-precipitation of calcium can be minimized by precipitating the magnesium hydroxide at a lower pH using a diethylamine buffer[15] or by the addition of sucrose to the solution[17].

An intercomparison of the four above mentioned indicators for the titration of calcium, in the presence of considerable amounts of magnesium, was made as described in the experimental section. It was found (Table I) that Calcon was a very satisfactory indicator for work with *ca*. 1–2 mg of calcium, particularly if the end-point was detected photoelectrically. Calcein when used as a fluorescent indicator in screened ultra-violet radiation, gave a very sharp end-point which was much sharper than the normal visual end-point obtained with this indicator.

TABLE I

DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM USING CALCEIN AND CALCON AS INDICATORS

Calcein used fluorimetrically		*Calcon used with photometric end-point*	
mg MgO present	*(wt. of CaO taken 5.00 mg) mg CaO found*	*mg MgO present*	*(wt. of CaO taken 1.00 mg) mg CaO found*
10	4.98 / 4.99 / 5.01	1	0.999
30	4.98 / 4.97 / 4.99	3	0.996
50	4.97 / 4.94	6	0.992

EXPERIMENTAL

An "Eel" photoelectric titrator was used for all titrations with Eriochrome Black T and Calcon indicators.

Reagents

For separation of interfering elements: Zirconium nitrate 2% w/v. Dissolve 2 g of "Specpure" zirconium nitrate in 100 ml of 1 N nitric acid. Filter the solution through a fine textured filter paper.

8-Hydroxyquinoline reagent. Prepare a 20% w/v solution of 8-hydroxyquinoline in acetone.
Acetylacetone.
Sodium acetate 2 M. Dissolve 272 g of sodium acetate trihydrate in water and dilute to 1 l.
Chloroform B.P.,
Sodium chlorite (85%),
Acetic acid 0.2 N.

For titration of calcium + magnesium: Ethanediaminotetraacetic acid (VERSENE). Prepare a solution containing 2.50 g of the disodium salt of ethanediaminotetraacetic acid and 0.1 g of hydrated magnesium chloride in 2 l of water. Add *ca.* 2 ml of chloroform to prevent the growth of moulds.

Ammonium hydroxide–ammonium chloride buffer. Dissolve 70 g of ammonium chloride in 600 ml of ammonium hydroxide ($d = 0.880$) and dilute to 1 l with water.

Eriochrome Black T indicator (E.B.T.). Prepare a solution containing 0.2% w/v of the solid indicator in ethyl alcohol.

For titration of calcium, using Calcein as indicator: Ethanediaminotetraacetic acid (VERSENE). Add 1 ml of calcein indicator to 2 l of VERSENE reagent prepared as described above.

Sodium hydroxide 10% w/v. Store in a polyethylene bottle.

Calcein indicator. Dissolve 1 g of Calcein[10] in 12.5 ml of N sodium hydroxide and dilute to 50 ml.

Using Calcon as indicator: Ethanediaminotetraacetic acid (VERSENE). Dilute 125 ml of VERSENE reagent to 1 l.
Diethylamine.
Calcon indicator. Dissolve 0.1 g of powdered Calcon[14] in 25 ml of methyl alcohol. Prepare as required.
Standard solutions: Magnesium solution. Dissolve 0.3015 g of "Specpure" magnesium in a slight excess of dilute hydrochloric acid, dilute to 1 l. 1 ml of this solution is equivalent to 0.5 mg of MgO.

Calcium solution: Dissolve 0.8925 g of calcium carbonate (dried at 110°) in a slight excess of hydrochloric acid. Dilute to 1 l. 1 ml of this solution is equivalent to 0.5 mg of CaO.

PROCEDURE

Removal of interfering elements in the absence of manganese, phosphate, arsenate and selenate

The continuous extractor used for the removal of interfering elements is that described in an earlier communication[8]. Place about 250 ml of chloroform in the 500-ml flask attached to the extractor and 50–75 ml of chloroform in the body of the extractor.

Pipette a suitable aliquot of the solution to be analysed (containing up to 50 mg each of CaO and MgO, and having an acidity of not more than 0.2 N) into a 500-ml conical flask, and add water to a total volume of *ca.* 200 ml. Add, with shaking, 10 ml of the solution of 8-hydroxyquinoline in acetone and 20 ml of 2 M sodium acetate. The pH of the solution should now be 4.9–5.2; if it is less than this, add more sodium acetate solution. If lead, molybdenum, uranium or zirconium are present, filter the solution through a Buchner funnel using a hardened filter paper (Whatman No. 52); wash the precipitate with water and add the washings to the filtrate. If cerium, chromium or beryllium are present add 5 ml of acetyl acetone and warm to 100° for 30 min under reflux.

Extract the cold solution with chloroform in the continuous extractor for 30 min, when it should be completely clear and colourless. Any coloured droplets adhering to the walls of the extractor are of no consequence since they are removed later. Pour the liquid in the extractor into a 500-ml separating funnel, rinse the extractor well with water and add the rinsings to the separating funnel. Run off the lower layer. Filter the aqueous layer through a Whatman No. 1 filter, and collect the filtrate in a 500-ml graduated flask. Wash the separating funnel and filter paper and make the solution up to volume.

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Removal of manganese

Manganese is not extracted by 8-hydroxyquinoline in chloroform at pH 8 and remains with calcium and magnesium in the extracted solution. It can be quantitatively precipitated from this solution by boiling with sodium chlorite. Boil the extracted solution (not diluted to volume) for 10 min to remove dissolved chloroform. Cool for a few min and then add *ca.* 0.3 g of sodium chlorite and boil until the precipitated manganese dioxide has coagulated. Allow the precipitate to settle for a short time and then decant the supernatant liquid through a Whatman No. 1 filter. Wash the precipitate once with 50 ml of water and twice with 30-ml portions of 0.2 N acetic acid to remove adsorbed calcium and magnesium. Combine the filtrate and washings and add 10% hydroxyammonium chloride dropwise until the yellow colour caused by oxides of chlorine is discharged. When cold, dilute to 500 ml.

Removal of phosphate, arsenate and selenate

Dilute the sample solution to *ca.* 150 ml and make it *ca.* 0.1 N in hydrochloric acid. Heat it almost to boiling and add a macerated 5.5-cm ashless filter paper and 25 ml of 2% zirconium nitrate solution. Boil for 5 min and filter through a hardened filter paper using suction. Wash the precipitate thoroughly with hot 0.05 N hydrochloric acid. Combine the filtrate and washings, cool, and add 10 ml of 8-hydroxyquinoline and 50 ml of 2 M sodium acetate solution. Filter off the precipitate, which consists principally of zirconium quinolinolate, using a hardened paper with suction. Wash the precipitate with 20–30 ml of water. Add a further 10 ml of 8-hydroxyquinoline reagent to the filtrate and extract it as described above.

Titration of magnesium + calcium

Place 12.5 ml of the extracted solution (≯ 7.5 mg of Ca + Mg) in the 60-ml beaker of a photoelectric titrator, add 5 ml of ammonium hydroxide buffer and 0.5 ml of the E.B.T. indicator. Titrate the solution with VERSENE solution using a microburette and a photoelectric titrator with a filter having maximum transmission at 600 mμ (Ilford No. 607). If the titration is performed visually, 50 ml of the extracted solution should be taken and the amounts of buffer and indicator doubled. The end-point of the titration occurs when the solution becomes a pure blue green colour free from all traces of pink.

Titration of calcium

Using Calcein. Pipette 100 ml of the extracted solution (≯ 5 mg CaO) into a porcelain basin. Add 10 ml of 10% sodium hydroxide, stir vigorously for 1 min and then add 0.06 ml of Calcein indicator. Titrate the solution in screened ultra-violet light with VERSENE reagent containing calcein. The approach of the end-point is indicated by a change in the fluorescence of the solution from bright yellow to dark brown. Continue the addition of VERSENE reagent, dropwise, with stirring after the addition of each drop, until no brown colour is formed where the drop enters the solution.

Using Calcon. Pipette 12.5 ml of the extracted solution into a 60-ml beaker of the photoelectric titrator. Add 1 ml of the standard magnesium solution (0.25 mg MgO/ml) and 4 ml of diethylamine to bring the solution to about pH 12.3. Stir the solution vigorously for 3 min with a magnetic stirrer to complete the precipitation of

magnesium hydroxide. Add 0.5 ml of Calcon* indicator, and titrate the solution with dilute VERSENE solution on the photoelectric titrator, using a filter having its maximum transmission at 600 mμ (Ilford No. 607). If the titration is performed visually, it is continued until all traces of pink have disappeared and the solution has become a pure blue green colour.

Standardization of VERSENE *solutions*

During the extraction, a small amount of the aqueous phase (less than 1%) becomes entrained or dissolved in the chloroform; it is therefore necessary to standardize the VERSENE solutions with extracted calcium and magnesium solutions. Carry out extractions, as described above, on distilled water, to which 50 ml of standard calcium solution have been added, and on distilled water containing 50 ml of standard magnesium solution. Titrate 12.5 ml aliquots of the extracted calcium and magnesium solutions with VERSENE reagent, using E.B.T. as indicator. If the titration of calcium is carried out using Calcein indicator, titrate 100-ml portions of the extracted standard calcium solution; if it is performed photometrically using Calcon, titrate 12.5-ml portions of the extracted standard solution. Normally, the reagent blanks for the method are negligible, but they should be determined by extracting distilled water, as described above, with each fresh batch of reagents.

RESULTS

In order to test the proposed method, mixtures of known amounts of metals (known to interfere in the VERSENE titration) with the equivalent of 25 mg each of calcium and magnesium oxides were extracted as described above. The extracted solutions were then titrated to determine calcium and magnesium remaining. The results (Table II) show that in most cases removal of the interfering element was complete and satisfactory recoveries of calcium and magnesium were obtained. Some elements, such as cerium, beryllium and chromium were not extracted as their 8-hydroxyquinoline complexes but were readily extracted after chelation with acetylacetone[18].

Manganese is not extracted at all by 8-hydroxyquinoline in chloroform at pH 5.0, and is not completely removed by extraction with acetylacetone. It is readily precipitated quantitatively at pH 5 as the hydrated dioxide by boiling the extracted solution with sodium chlorite. Provided that the precipitate is filtered as soon as it has coagulated, only small amounts of calcium and magnesium are co-precipitated, and these may be removed by washing the precipitate with dilute acetic acid. Determination of 20 mg each of CaO and MgO in the presence of 50 and 100 mg of manganese gave recoveries of CaO + MgO of 99.6% and 99.4% respectively after removal of manganese as the dioxide. Small amounts of manganese can be tolerated in the VERSENE titrations. No correction is necessary for its presence in the titration of calcium using Calcein as indicator; manganese can be titrated with VERSENE reagent in ammoniacal solution using E.B.T., provided that a reducing agent such as ascorbic acid is present.

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* In preliminary work, both murexide and Calred were tested as indicators under these conditions, but were found to be less sensitive than Calcon, if much magnesium was present.

TABLE II

REMOVAL OF INTERFERING ELEMENTS BEFORE TITRATION OF CALCIUM AND MAGNESIUM

Element	Wt. (mg)	CaO found (mg)		MgO found (mg)	
Aluminium	200	24.98	25.03	24.96	25.07
Beryllium[a]	100	24.84	25.05	24.85	25.12
Bismuth	200	24.90	—	25.10	—
Cadmium	100	25.03	25.02	25.10	25.07
Cerium[a] (Ce^{+3})	50	24.89	24.77	25.20	25.25
Chromium[a] (Cr^{+3})	100	25.00	25.03	25.00	24.90
Cobalt	100	24.93	24.86	25.12	25.16
Copper	100	24.94	24.92	25.14	25.15
Gallium	100	25.04	24.94	24.92	24.95
Indium	100	25.03	25.05	25.10	25.10
Iron (Fe^{+3})	100	25.03	24.97	24.96	25.03
Lanthanum[c]	100	25.34	25.24	27.14	26.94
Lead[b]	100	24.96	24.82	25.04	25.12
Manganese	5	24.90	24.90	—	—
Mercury (Hg^{+2})	100	24.89	24.90	25.20	25.25
Molybdenum[b] (Mo^{+6})	100	25.01	25.06	24.92	24.97
Nickel	200	24.95	—	24.97	—
Thallium (Tl^+)	100	25.00	25.00	25.00	25.06
Thorium	100	24.94	24.88	24.85	24.80
Tin (Sn^{+2})	200	25.10	24.95	25.04	25.04
Titanium (Ti^{+4})	10	25.00	24.96	24.92	24.93
Tungsten[b] (W^{+6})	100	24.91	24.94	24.91	24.95
Uranium (UO_2^{+2})	100	24.94	24.92	25.04	25.08
Vanadium[a] (V^{+5})	100	25.16	25.20	25.13	25.23
Zinc	200	24.93	—	25.15	—
Zirconium (Zr^{+4})	200	24.97	25.08	25.13	25.11

[a] Precipitate of oxinate filtered off, 5 ml of acetylacetone added.
[b] Oxinate precipitate filtered off before extraction.
[c] Not completely extracted even when 5 ml of acetylacetone was used.

Lanthanum and the rare earths are not extracted by 8-hydroxyquinoline and chloroform at pH 5.0, but it is very probable that they could be extracted at a pH of *ca*. 8.0. Their extraction by acetylacetone was not investigated.

Although small amounts of phosphate, arsenate and selenate are without effect on the titration of calcium and magnesium with VERSENE reagent, their presence in large amounts leads to low results owing to the formation of stable calcium and magnesium complexes. These interfering anions are readily removed by precipitation

TABLE III

REMOVAL OF INTERFERING ANIONS FROM CALCIUM AND MAGNESIUM

Anion	Wt. of element	CaO recovered (mg)		MgO recovered (mg)	
Arsenate	100 mg As	24.87	25.10	25.07	24.89
Phosphate	100 mg P	25.03	25.06	25.13	24.87
Selenate	100 mg Se	25.11	24.89	25.05	24.95

in acid solution as their insoluble zirconium salts; excess of zirconium is easily removed as its oxinate during the extraction process. Table III shows the excellent recoveries of calcium and magnesium obtained from solutions, originally containing the equivalent of 25 mg each of CaO and MgO, when interfering anions had been precipitated as their zirconium salts.

SUMMARY

Solvent extraction with a continuous extractor has been used to separate Al, Be, Bi, Cd, Ce, Cr, Co, Cu, Ga, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn and Zr, from calcium and magnesium, before titration of the latter with ethanediaminotetraacetic acid. Most of these elements are extracted at *ca.* pH 5.0 as their chelates with 8-hydroxyquinoline using chloroform. Be, Ce and Cr are not extracted under these conditions and are converted into their acetylacetonates, before extraction with chloroform. Manganese is not quantitatively removed by any of these processes and is precipitated as its hydrated dioxide by boiling the extracted solution with sodium chlorite. Phosphate, arsenate and selenate can be removed by precipitating them in acid solution with excess zirconium nitrate, and removing the latter with 8-hydroxyquinoline.

RÉSUMÉ

L'auteur propose une séparation du calcium et du magnésium d'avec de nombreux ions (Al, Bi, Cd, Ce, Cr, Co, Cu, Ga, Gl, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn et Zr) en effectuant une extraction par solvant au moyen d'un extracteur continu. Le calcium et le magnésium peuvent être finalement titrés par l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Calcium und Magnesium können von vielen anderen Ionen (Al, Bi, Cd, Ce, Cr, Co, Cu, Ga, Gl, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn und Zr) nach einem kontinuierlichen Extraktionsverfahren mit Hilfe eines Lösungsmittels abgetrennt und dann durch Titration mit Aethylendiaminotetraessigsäure bestimmt werden.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH QUINOLINIC ACID

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Quinolinic acid as a reagent for the gravimetric and volumetric estimation of palladium has already been described[1]. Quinolinic acid, like picolinic and quinaldinic acids[2], forms with ferrous iron a soluble yellow complex, which at pH 5.9 exhibits maximum absorption at 420 mμ. On the addition of potassium cyanide, however, the colour changes to orange yellow and the region of maximum absorption to 440 mμ. The latter colour reaction is specific for ferrous iron and a thorough study of quinolinic acid as a spectrophotometric reagent for iron has been made. The complex obeys Beer's law at 440 mμ with ferrous ion concentrations of 1 to 16 p.p.m., the optimum range being 4–16 p.p.m. with a relative error of 2.94% per 1% absolute photometric error. The molar extinction coefficient of the complex at 440 mμ is 2946.

EXPERIMENTAL

Apparatus and solutions

Spectrophotometric measurements in 1-cm quartz cells were made with a Hilger Uvispeck spectrophotometer. Corrections were made, when necessary, to compensate for slight differences in the transmittancies of the cells.

Iron solution

Standard iron solution was prepared by dissolving a known amount of ferric nitrate (A.R., B.D.H.) in 100 ml of water containing 5 ml of conc. A.R. nitric acid. The solution was boiled to oxidize any ferrous iron, cooled and made up to 1 l. The iron content was determined gravimetrically (1.727 mg of iron per ml). Weaker solutions were prepared by proper dilution.

Reagent solution

Quinolinic acid[3] was prepared by the oxidation of 8-hydroxy-quinoline with fuming nitric acid. The reagent was crystallized first from 40% acetic acid, and then several times from water. A 1% aqueous solution of the reagent, m.p. 192–194°, was prepared for spectrophotometric study.

Other solutions

A 0.15 M (approx. 1%) solution of potassium cyanide (standardized by silver

nitrate solution) and a 1% solution of hydroxylamine hydrochloride were used.

Solutions of diverse ions were prepared from their reagent grade, iron-free chemicals and the amount present per ml of each solution was determined by standard methods.

Colour reaction and maximum absorption

Aliquots of standard iron solutions were taken in 25-ml flasks. To each flask, 1 ml of the hydroxylamine hydrochloride solution, 6 ml of the reagent solution, 10 ml of the potassium cyanide solution and a few ml of water to make up the volume were
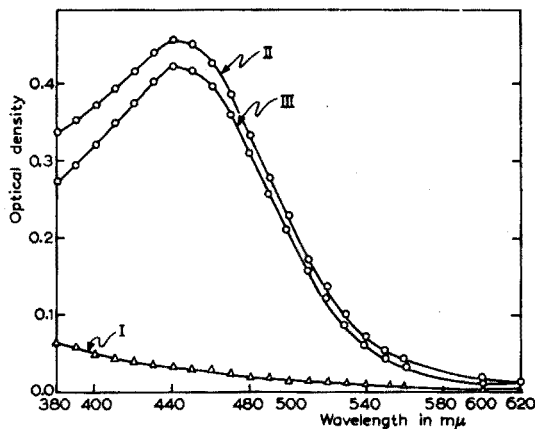

Fig. 1. Spectral transmittancy curve. Curve I: absorption of reagent against water as blank. Curve II: absorption of the complex corresponding to 8 p.p.m. of iron against water as blank. Curve III: absorption of the above complex against reagent as blank.

added. The orange–yellow complex formed instantaneously on the addition of cyanide showed maximum absorption at 440 mμ. At room temperature, it was highly stable and maintained its transmittancy for 12 h. Curve I (Fig. 1) shows the absorption of the reagent against water, while curves II and III represent that of the complex corresponding to 8 p.p.m. of iron against water and reagent respectively as blanks.

Effect of the reagent, cyanide and the reducing agent

The effects of quinolinic acid, potassium cyanide and hydroxylamine hydrochloride were studied at 440 mμ; the amount of one reagent was varied while the concentrations of the other two were kept constant. For the maximum colour development, the respective amounts of the reagent, cyanide and hydroxylamine hydrochloride were about 250, 250 and 50 times that of the ferrous iron (Table I).

Effect of pH

The pH's of 1% solutions of quinolinic acid, and its mono- and disodium salts are respectively 2.1, 3.6 and 6.5. Under the experimental conditions, the pH of the coloured

complex formed by ferrous quinolinate with potassium cyanide is 9.0, but without potassium cyanide (ferrous: reagent as 1:2) the pH must be maintained between 5.4 and 6.5 (Table II).

TABLE I

Iron 8 p.p.m., reagent 5 ml, cyanide 5 ml, hydroxylamine hydrochloride 1 ml

Reagent ml	O.D.	Cyanide ml	O.D.	Hydroxylamine hydrochloride ml	O.D.
1	0.381	1	0.103	0.25	0.381
2	0.399	2	0.152	0.5	0.418
3	0.411	3	0.211	1.0	0.422
4	0.420	4	0.415	1.25	0.422
5	0.422	5	0.422		
6	0.422	6	0.422		

TABLE II

pH	O.D.	pH	O.D.
1.5	0.031	6.0	0.164
2.2	0.062	6.5	0.164
3.0	0.074	7.0	0.150
4.0	0.089	8.0	0.143
5.0	0.160	9.0	0.132
5.4	0.164		

Beer's law and optimum range

To verify Beer's law, the optical densities of the solutions prepared from 1–40 p.p.m. of iron were measured at 440 mμ against a reagent blank. Fig. 2, representing the optical density – concentration curve, shows that Beer's law is obeyed up to 16 p.p.m. of iron.
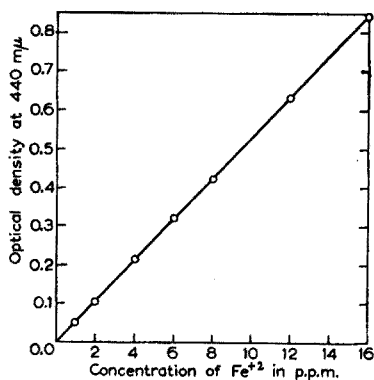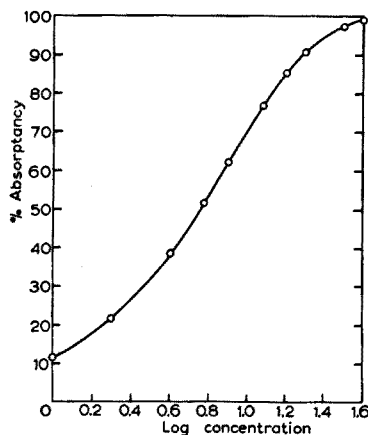

Fig. 2. Beer's law for the iron complex.

Fig. 3. Calibration curve for the iron complex.

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In order to define a suitable concentration range and to evaluate the accuracy in photometric analysis, the % absorbance as ordinate was plotted against the log of concentration as abscissa, as proposed by RINGBOM[4]. The accuracy is greatest at the steepest slope of the curve (Fig. 3), and the optimum concentration range, is 4–16 p.p.m. In this range, the relative error per 1% absolute photometric error is readily obtained by AYRES method[5] as 2.94% from the following equation:

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometer error}} = \frac{230}{\dfrac{dI}{d\log C}}$$

where I and C have their usual significance.

Influence of foreign ions

The effect of ions was studied by measuring the colour intensity of the iron complex from 8 p.p.m. of iron in presence of the ion. An ion was considered to interfere if it caused a difference of 0.005 unit in optical density from that of the original complex. (cf. Table III).

TABLE III

Ion	Added as	Limiting concentration p.p.m.
Cd^{+2}	$Cd(NO_3)_2$	100
Pb^{+2}	$Pb(NO_3)_2$	150
Hg^{+2}	$HgCl_2$	60
Al^{+3}	$Al(NO_3)_3$	150
Zn^{+2}	$Zn(NO_3)_2$	70
Mn^{+2}	$MnCl_2$	80
Co^{+2}	$Co(NO_3)_2$	40
Ni^{+2}	$Ni(NO_3)_2$	50
Ca^{+2}	$CaCl_2$	100
Ba^{+2}	$BaCl_2$	80
Sr^{+2}	$Sr(NO_3)_2$	75
Mg^{+2}	$MgCl_2$	100
Th^{+4}	$Th(NO_3)_4$	150
Ti^{+4}	$Ti(SO_4)_2$	30
UO_2^{+2}	$UO_2(NO_3)_2$	200

The alkali metals, silver, chloride, iodide, nitrate, sulphate, acetate, tartrate, vanadate and molybdate have no effect on the colour system. In some cases, an excess of the cyanide solution was needed to maintain the required alkalinity or to dissolve the precipitate formed.

Composition and dissociation of the complex

The empirical formula of the complex in solution was determined by Job's method of continuous variation[6], and by the molar-ratio[7] and slope-ratio[8] methods.

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Job's method: For the evaluation of the composition of the complex formed in presence of potassium cyanide, the iron content was varied from 1 to 9 ml of the
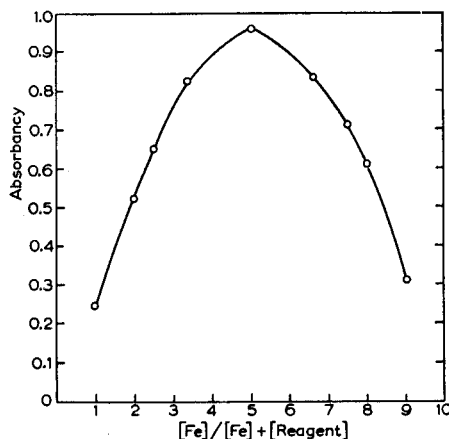

Fig. 4. Determination of the ratio of iron(II) to reagent by Job's method.

$2.66 \cdot 10^{-3}$ M solution. The photometric data are shown graphically in Fig. 4. The maximum point in the graph indicates that in solution the iron and the reagent are in a ratio of 1:1. In the absence of potassium cyanide, the complex formed at pH 5.9 (buffered with sodium acetate and acetic acid) shows a maximum absorption at 420 mμ and this complex as determined by the above procedure with $5 \cdot 10^{-3}M$ iron solution has a 1:2 ratio of iron to reagent.

Molar ratio method: With equimolar solutions $(5.32 \cdot 10^{-3}$ $M)$ of the reagent and iron, the ratio of iron to reagent was varied from 1 : 0.2 to 1 : 1.6 and the optical densi-
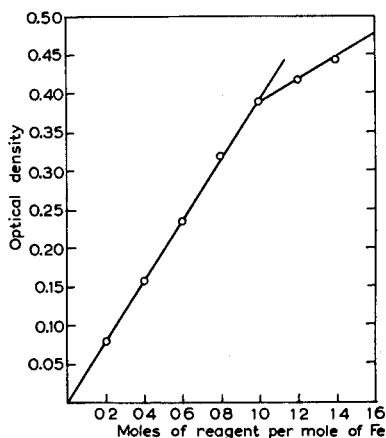

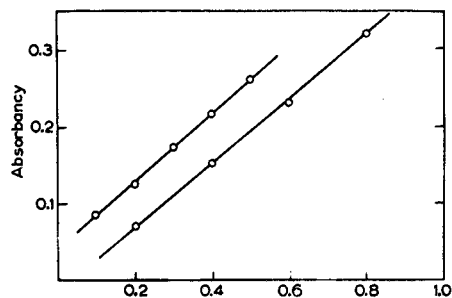Fig. 5. Determination of the ratio of iron(II) to reagent by the molar-ratio method.

Fig. 6. Determination of the ratio of iron(II) to reagent by the slope-ratio method.

References p. 330

ties of the solutions prepared with hydroxylamine hydrochloride and potassium cyanide were measured at 440 mμ. The curve (Fig. 5) obtained shows a break at a ratio of 1 mole of reagent to 1 mole of iron. But the coloured product formed at pH 5.9 in the absence of cyanide gave a break at an iron to reagent ratio of 1:2.

Slope ratio method: This method helped to confirm the composition. Two series of solutions were used. In one series varying amounts of $5.32 \cdot 10^{-4} M$ reagent solution were added to a constant amount of iron solution (1 ml of $5.32 \cdot 10^{-3} M$), while in the other series, the iron solution ($5.32 \cdot 10^{-4} M$) was varied and the reagent solution was kept constant (4 ml of $5.32 \cdot 10^{-3} M$). All transmittancy measurements were made at 440 mμ (Fig. 6). The ratio of the slopes of the two straight lines confirms that the complex formed in presence of potassium cyanide contains the metal and the reagent in a ratio of 1:1. The composition of the complex without potassium cyanide could not be ascertained by this method, because the large excess of reagent added changes the nature of the complex and shifts the region of maximum absorption to 440 mμ.

Thus the formulae of the 1:1 and 1:2 complexes may be suggested as $K_4[Fe(C_7H_3NO_4)(CN)_4]$ and $Na_2[Fe(C_7H_3NO_4)_2(H_2O)_2]$ and represented respectively as
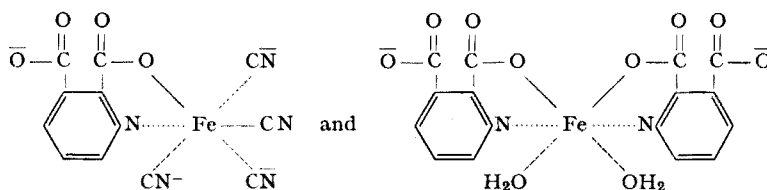
Dissociation

The degree of dissociation, a, and the instability constant, K, were calculated according to the equations of HARVEY AND MANNING[8]. The degree of dissociation, $a = (E_m - E_s)/E_m$, where E_m is the absorption at 440 mμ due to a given amount of the metal ion completely complexed with an excess of the reagent and E_s is the absorbance calculated for the same amount of the metal ion complexed with a stoichiometric amount of the reagent.

The values for E_m and E_s being 0.422 and 0.260 for the complex with cyanide, a equals 0.384; without cyanide, E_m and E_s are 0.162 and 0.085 respectively and a equals 0.478.

The instability constant, K, of the complex is obtained by substituting the value of a in the equation $K = aC(naC)^n/C(1-a)$, where C is the concentration of the metal ion in moles per l and n is the number of moles of the reagent required for complex formation with 1 mole of the metal ion. Thus for the complex with cyanide, $K = 2.73 \cdot 10^{-5}$ and for the complex without cyanide, $K = 1.72 \cdot 10^{-9}$.

SUMMARY

Quinolinic acid forms two complexes with ferrous ion. One is formed at pH 5.9 and has maximum absorption at 420 mμ; the metal to reagent ratio is 1:2 and the instability constant is about $1.7 \cdot 10^{-9}$. The other complex is formed with an excess of potassium cyanide and shows maximum absorption at 440 mμ; the metal to reagent ratio is 1:1; the instability constant is only $2.73 \cdot 10^{-5}$. The latter complex adheres to Beer's law from 1 to 16 p.p.m. of iron, and its optimum concentration range is 4–16 p.p.m. of iron, where the percent relative error per 1% absolute photometric error is only 2.94.

The reagent is highly specific and can be used spectrophotometrically for the determination of very small quantities of iron in presence of many cations.

RÉSUMÉ

L'acide quinoléique est proposé pour le dosage spectrophotométrique du fer(II). Ce réactif, en présence de cyanure de potassium, permet le dosage de très petites quantités de fer, à côté d'un grand nombre de cations étrangers.

ZUSAMMENFASSUNG

Sehr kleine Mengen Eisen(II) lassen sich neben einer ganzen Anzahl von Fremdionen spektrophotometrisch mit Hilfe von Chinolinsäure in Gegenwart von Kaliumcyanid bestimmen.

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SEPARATION OF NIOBIUM AND TANTALUM WITH PHENYLARSONIC ACID

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Phenylarsonic acid has been used as reagent for the separation and estimation of zirconium, thorium[1], tin[2] and bismuth[3] in presence of other interfering elements. FUCKE AND DAUBLANDER[4] attempted the separation of niobium and tantalum in a sulphuric acid–hydrogen peroxide solution, whereas DUPRAW[5] used *n*-propyl-arsonic acid for the separation in a sulphuric acid–oxalic acid solution.

In the present work, no precipitate of niobium or tantalum could be obtained with phenylarsonic acid from a sulphuric acid-hydrogen peroxide solution. However, tantalum was precipitated completely from oxalate solutions of acidities varying from 10% (v/v) sulphuric acid up to pH 5.8; but the precipitation of niobium was complete only when the pH exceeded 4.8. Much ammonium oxalate tended to keep both the niobium and tantalum in solution; not more than 25 times the amount of the oxides of niobium or tantalum should be present. Thus from a mixed solution tantalum was precipitated at a pH below 3.0 or preferably from a 5% (v/v) sulphuric acid solution, and niobium was recovered from the filtrate after adjusting the pH to 5.0 with ammonium acetate. When the concentration of ammonium oxalate in the filtrate exceeded

the above limit, cupferron was found suitable for the recovery. This method worked well with ratios of Ta_2O_5 to Nb_2O_5 greater than $1 : 2$. But when the $Nb_2O_5 : Ta_2O_5$ ratio was more than 2.0, dissolution and reprecipitation of the tantalum was necessary to free it from the co-precipitated niobium, and even then the results were not very accurate.

With complexone III as the masking agent, tantalum could be separated at pH 2.0–3.0 from numerous ions, except titanium, zirconium, lead, barium and strontium. In presence of an excess of stannous, thorium and uranyl ions, a double precipitation of tantalum was needed to obtain the pure oxide.

As phenylarsonic acid failed to precipitate niobium in presence of complexone III, its separation from other ions was attempted by the cupferron method as suggested by MAJUMDAR and RAY CHOWDHURY[6]. But the claim of the authors that niobium, in presence of complexone III, can be separated from iron, aluminium, chromium, zirconium, thorium, and antimony at a pH 4.5 to 5.5 could not be confirmed; for those ions remained in solution only at a high pH of about 7.0, where the precipitate due to niobium became colloidal. However, at pH 4.5 to 5.5 complexone III masks, in presence of cupferron, the influence of the ions of zinc, manganese, nickel, cobalt, arsenic, copper, cadmium, bismuth, mercury, calcium, magnesium, vanadate, molybdate, tungstate, chromate and arsenate.

<div align="center">EXPERIMENTAL</div>

Reagents, solutions and apparatus

Chemicals and their solutions used were the same as reported previously[7]. Phenylarsonic acid was prepared according to the method of PALMER AND ADAMS[8]; a 5% aqueous solution was used as the precipitant. The wash solution was made by dissolving 0.5 g of the reagent and 1 g of ammonium nitrate in 100 ml of warm water.

Standard solutions of niobium and tantalum were prepared from their pentoxides (specpure, Johnson, Matthey & Co.). A weighed quantity was fused with potassium bisulphate (G. R. E. Merck) and extracted with an ammonium oxalate solution of a particular strength and diluted with water to a definite volume. The niobium or tantalum content of the solution thus obtained was determined from an aliquot portion of the solution by the cupferron method[9].

A Cambridge pH meter was used for all pH measurements.

Effect of complexing agents

From a tartrate solution maintained at any acidity between 10% (v/v) sulphuric acid and pH 1.6, both niobium and tantalum are precipitated, but when the pH is increased to over 3.0, both dissolve. From an ammonium oxalate solution, however, they are precipitated at different acidities or pH regions; the presence of ammonium oxalate in excess of 25 times the amount of the tantalum or niobium oxide keeps the oxide concerned in solution. Although the tantalum precipitate has no definite composition, it contains on average about 2 moles of the reagent per gram atom of tantalum. About 0.5 g of the reagent per every 10 mg of the pentoxide is required for complete precipitation.

Effect of pH

An aliquot of the standard solution of niobium or tantalum was mixed with sufficient ammonium oxalate solution to keep its concentration between 20 and 25 times the amount of oxide present, the solution was diluted to 150 ml and its pH

was adjusted either with dilute sulphuric acid or with ammonium acetate solution. An excess of the reagent solution was then added to the boiling hot solution and the boiling continued for 2–5 min. The precipitate was filtered, washed with the wash solution (to prevent its becoming colloidal), dried, ignited to oxide in a muffle furnace and weighed. The region of complete precipitation for tantalum was from an acidity of 10% (v/v) sulphuric acid to a maximum pH of about 5.8. For niobium, precipitation began at pH 4.0 and was complete when the pH was raised to above 4.8.

TABLE I

Ta_2O_5 taken mg	Nb_2O_5 taken mg	Ta_2O_5 found mg	Nb_2O_5 found mg
8.4	12.2	8.6[a]	12.0[a]
16.8	18.3	16.4[a]	18.0[a]
8.4	24.4	8.6[b]	24.0[b]
8.4	183.0	8.0[c]	182.2[c]
20.2	5.5	20.6[a]	5.0[a]
93.2	14.8	93.6[a]	15.0[a]
186.4	14.8	186.8[a]	14.6[a]

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

Separation of niobium and tantalum

After the addition of ammonium oxalate, about 25 times the quantity of tantalum pentoxide present, to the solution containing both niobium and tantalum, the acidity was adjusted to 5% (v/v) with respect to sulphuric acid and the tantalum was precipitated, washed, ignited and weighed as above. The filtrate and washings of the tanta-

TABLE II

Ta_2O_5 taken mg	Ions added	mg	Ta_2O_5 found mg	Ta_2O_5 taken mg	Ions added	mg	Ta_2O_5 found mg
20.2	Fe^{+3}	240.0	20.2	20.2	Sn^{+2}	108.0	20.6
20.2	Cr^{+3}	100.0		20.2	Cu^{+2}	100.0	
	Al^{+3}	100.0			Cd^{+2}	100.0	20.2
	R.E.	100.0	20.6		Bi^{+3}	100.0	
	Ce^{+4}	100.0			Hg^{+2}	100.0	
	Be^{+2}	60.0					
				20.2	Zn^{+2}	100.0	
20.2	UO_2^{+2}	120.0	20.0				
					Mn^{+2}	100.0	20.2
20.2	Th^{+4}	120.0	20.4		Ni^{+2}	100.0	
					Co^{+2}	100.0	
20.2	Ca^{+2}	100.0		18.4	As^{+3}	100.0	18.4
	Mg^{+2}	100.0	20.2		Sb^{+3}	100.0	
9.2	PO_4^{-3}	100.0	9.6	9.2	WO_4^{-2}	125.0	9.6
9.2	CrO_4^{-2}	120.0	9.2	9.2	MoO_4^{-2}	130.0	9.4
9.2	VO_3^-	100.0	9.2				

R.E. = Rare Earths.

lum precipitate were mixed and heated to boiling, and niobium was precipitated after raising the pH to 5.0 by neutralisation. However, if the ammonium oxalate concentration of this solution was higher than the stated limit, as was usually the case when the amount of niobium pentoxide was less than in the 1 : 1 ratio of Ta_2O_5 : Nb_2O_5, niobium was recovered in the cold by cupferron. When the above ratio was lower than 1 : 2, that is when the niobium content was very high, reprecipitation of tantalum was necessary for complete separation. Results are given in Table I.

Separation of tantalum from other ions

After the addition of an excess of complexone III to mask interfering ions, tantalum was precipitated at pH 2–3 according to the above procedure. Tantalum was thus separated from all the ions except those of titanium, zirconium, lead, barium and strontium. The presence of a large excess of stannous, thorium and uranyl ions required a second precipitation. Results are given in Table II.

SUMMARY

Phenylarsonic acid permits satisfactory separation of niobium and tantalum and estimation of tantalum from an oxalate solution containing sulphuric acid up to pH 5.8. For complete precipitation of niobium the pH should exceed 4.8. In mixtures, tantalum is precipitated below pH 3.0 and niobium is then precipitated above pH 5.0. When the oxalate concentration is high, recovery of niobium with cupferron is recommended. When the ratio of Nb_2O_5 to Ta_2O_5 exceeds 2 : 1, reprecipitation of tantalum is necessary. The effect of interfering ions is studied.

RÉSUMÉ

L'acide phénylarsonique est proposé comme réactif pour la séparation du niobium et du tantale, en solution oxalique. L'auteur a étudié les conditions de précipitation et l'influence des agents complexants. En présence de fortes concentrations d'oxalate, on recommande le dosage du niobium au moyen de cupferron.

ZUSAMMENFASSUNG

Es wird die Trennung von Niob und Tantal in oxalathaltiger Lösung mit Hilfe von Phenylarsinsäure beschrieben. Die Fällungsbedingungen und der Einfluss anderer Kationen in Gegenwart von Komplexon III wurden untersucht. In Gegenwart von viel Oxalat wird die Fällung des Niobs mit Kupferron empfohlen.

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STUDIES IN THE SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN MATERIALS DECOMPOSED BY HYDROFLUORIC ACID

I. LOSS OF SILICON BY DECOMPOSITION WITH HYDROFLUORIC ACID

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INTRODUCTION

Most of the proposed methods for the photometric determination of silicon are based on the formation of yellow silicomolybdic acid or its reduction product, molybdenum blue. Yellow silicomolybdic acid is formed in acid solution by reaction between silicate ions and molybdate ions. Silicon in materials not decomposed by the acids normally applied is converted to acid soluble silicates by fusion or heating with an alkali. By acidification small amounts of hydrated silica remain in solution.

Hydrofluoric acid is not usually applied for the decomposition of samples in which silicon is determined, because of the fear of losing silicon as the volatile silicon tetrafluoride. A survey of the extensive literature on the spectrophotometric determination of silicon shows only a limited number of procedures in which hydrofluoric acid is used as decomposing agent. In these cases hydrofluoric acid is applied in combination with other acids. It has not been possible to find procedures in which hydrofluoric acid is used as the sole decomposing agent.

CASE[1] used hydrofluoric acid in addition to the usual acids to increase the rate of dissolution of certain nonferrous alloys in which silicon was finally determined photometrically as yellow silicomolybdic acid. CASE made the important observation that a given amount of silicon, whether it is present as fluosilicic acid or as hydrated silica, gives the same extinction when measured photometrically as the yellow silicomolybdic acid. CASE used boric acid to complex the excess of hydrofluoric acid.

An important discovery concerning the spectrophotometric determination of silicon was made by STRICKLAND[2], who found that yellow silicomolybdic acid exists in two modifications, one of which is an unstable β-acid which is more or less rapidly converted to the stable α-acid. The extinctions of the two modifications are different at the wavelengths usually applied for photometric measurement. This discovery explains the many contradictory data given in earlier publications on the yellow silicomolybdic acid. Recent publications[3,4] recommend that the stable α-silicomolybdic acid be used for analytical purposes.

The present series of papers describes experiments in which silicon-containing materials are decomposed by hydrofluoric acid and the content of silicon is determined spectrophotometrically.

The present paper describes series of experiments in which known amounts of silica are decomposed by excess hydrofluoric acid.

In one series of experiments the content of silica (present as fluosilicic acid) is determined spectrophotometrically as α-silicomolybdic acid immediately after dissolution. The resulting extinction data are compared with those obtained from another, corresponding series of solutions of α-silicomolybdic acid prepared from standard solutions of hydrated silica. Solutions of hydrated silica are prepared by the conventional decomposition of silica with sodium carbonate.

In another series of experiments solutions of fluosilicic acid in hydrofluoric acid are evaporated at different temperatures. The amounts of silica remaining in solution are then determined at different stages of evaporation.

<div align="center">EXPERIMENTAL</div>

Instruments

Extinction measurements were made at 20° ± 1° C with a Zeiss spectrophotometer PMQ II. Matched sets of 1,000-cm silica and glass cells were used.

For the measurement of pH a Beckman pH-Meter model H-2 (glass and calomel electrodes) was used.

Reagents

Spectrographically standardized silicon dioxide (Johnson, Matthey & Co.) was used for the experiments. This product left no residue when volatilised by evaporation with hydrofluoric acid.

Reagent grade hydrofluoric acid (35–40%) always contains some fluosilicic acid. The content of the latter was determined (by the procedure to be described in paper No 2 of this series) in the hydrofluoric acid used (E. Merck) and corrections were made for the amounts present.

Other chemicals were of reagent grade quality with the exception of aluminium chloride hexahydrate which was of pharmaceutical grade. Ordinary distilled water was used.

The pH was adjusted with solutions of hydrochloric acid and ammonia.

Apparatus

The experiments on evaporation at temperatures above room temperature were carried out in teflon beakers (50 mm outer, 47 mm inner diameter, height 50 mm, capacity about 100 ml) made from compact teflon rod. The beakers fitted closely into cylindrical aluminium blocks (75 mm outer, 50 mm inner diameter) placed on an electrically heated magnetic stirrer, the temperature being regulated with a Sunvic energy regulator. A teflon-covered magnet was used for stirring.

The temperature of the hydrofluoric acid solutions was measured with a special sensitive thermocouple, one branch consisting of 70% gold and 30% palladium, the other of 90% platinum and 10% rhodium. The thermocouple was standardized against a standard mercury thermometer. The unisolated end of the thermocouple dipped into the solution to be measured. .

For experiments at room temperature ordinary plastic beakers (capacity about 300 ml) were used.

A special pipette made from thin-walled teflon tube (inner diameter about 2 mm) was constructed for sampling solutions containing hydrofluoric acid. The teflon tube was placed inside a glass tube and extended about 2 cm at the lower end. A rubber suction bulb fitted on to the upper end. The pipette was calibrated to contain 1 ml.

Basic chemical equilibria

When silica is dissolved in excess hydrofluoric acid the ternary system $HF-H_2SiF_6-H_2O$ is formed; this system was investigated by MUNTER, AEPLI, AND KOSSATZ[5], who found a constant-boiling ternary solution of composition 10% hydrofluoric acid, 36% fluosilicic acid and 54% water (boiling point 116.1° at 759.7 mm pressure).

The azeotropic mixture of $HF-H_2O$ was found by the same authors to have a composition of 38.26% HF (boiling point 112.0° at 750.2 mm pressure).

The liquid–vapour equilibria diagram of the system $HF-H_2SiF_6-H_2O$ shows that a liquid mixture of the three components which has a composition in the vicinity of constant-boiling hydrofluoric acid, is in equilibrium with a vapour mixture in which the concentration of fluosilicic acid is considerably lower than in the liquid.

This fact makes it possible to decompose silicon-bearing samples of hydrofluoric acid without losing any, or only negligible amounts of, silicon by evaporation.

Loss of silicon by the decomposition of silica with hydrofluoric acid

A series of experiments was carried out in which weighed amounts of silica were dissolved in known amounts of 35–40% hydrofluoric acid. The amounts of silicon remaining in solution were determined spectrophotometrically as yellow α-silicomolybdic acid. Time, temperature and volumes of hydrofluoric acid were varied in these experiments.

For the photometric determination of silicon in the different solutions, a calibration curve was needed and was prepared by fusing 1.0000 g of silicon dioxide with 10.0 g of sodium carbonate. The melt was dissolved in diluted hydrochloric acid, and the solution was transferred to a 1-l volumetric flask and made up to the mark. This solution contained 1 mg of SiO_2 per ml and was stored in a plastic bottle. Varying amounts of this standard solution were pipetted into 300-ml plastic beakers containing about 50 ml of water, 10 ml of 10% ammonium molybdate solution were added, the pH was adjusted to 1.0 $\pm$ 0.5, and the silicomolybdic acid was converted to the stable α-acid by heating the solutions for 3 h on a boiling water bath (watch glass). The solutions were then cooled to room temperature, transferred to 100-ml volumetric flasks and diluted to the mark. The extinction of the series of solutions was measured at 415 mμ against a blank containing all the reagents and prepared in exactly the same way.

The extinction data at 415 mμ showed that Beer-Lambert's law is followed up to at least 10 mg of SiO_2 per 100 ml.

Another calibration curve was prepared by dissolving (in a 300-ml plastic beaker) 100.0 mg of silicon dioxide (moistened with 2–3 drops of water to avoid a violent reaction) in 5 ml of hydrofluoric acid (35–40%). The silicon dioxide, which was in a very reactive form, dissolved rapidly without heating. To the solution were added 200 ml of 25% aluminium chloride solution. After being transferred to a 500-ml volumetric flask the solution was diluted to the mark with distilled water. This standard solution contained 0.2 mg of SiO_2 per ml.

From this solution different volumes were pipetted into a series of 300-ml plastic beakers, 10 ml of 10% ammonium molybdate were added and the solutions were diluted to about 90 ml. With the pH-meter, the pH was adjusted to 1.0 $\pm$ 0.5, and the beakers were placed on the boiling water bath for 3 h. These solutions were then treated and their extinctions measured as above.

Table I gives the extinction data for the two series of solutions of α-silicomolybdic acid prepared from silicic acid and from fluosilicic acid.

When the usual errors of photometric determinations are considered, the two curves can be said to be identical. Consequently, no silicon seems to be lost by evaporation when silica is decomposed by hydrofluoric acid. The data in Table I also confirm the observation made by CASE that the extinction of α-silicomolybdic acid is the same whether silicon is present as silicate or as fluosilicate ions.

It now remained to determine the loss of silicon from solutions evaporated at room or a higher temperature.

In plastic or teflon beakers weighed amounts of silica (about 50 mg) were dissolved

TABLE I

EXTINCTION AND EXTINCTION INDEX (E/C) FOR SOLUTIONS OF α-SILICOMOLYBDIC ACID PREPARED
FROM SILICIC AND FLUOSILICIC ACID. WAVE-LENGTH 415 mμ, 1.000-cm CELLS

Mg SiO₂ per 100 ml	Extinction and extinction index of solutions of α-silicomolybdic acid			
	Prep. from silicic acid		Prep. from fluosilicic acid	
	Extinction	*Extinction index*	*Extinction*	*Extinction index*
1.0	0.100	0.100	0.099	0.099
2.0	0.194	0.097	0.193	0.097
3.0	0.296	0.099	0.294	0.098
4.0	0.388	0.097	0.388	0.097
5.0	0.482	0.096	0.480	0.096
6.0	0.578	0.096	0.575	0.096
7.0	0.683	0.098	0.680	0.097
8.0	0.781	0.098	0.779	0.097
9.0	0.878	0.098	0.880	0.098
10.0	0.980	0.098	0.979	0.098
		0.977		0.973

in weighed amounts of hydrofluoric acid (35–40%). The fluosilicic acid originating from the hydrofluoric acid was included in the amounts of silicon dissolved.

The silica was weighed into the beaker and moistened with 2 drops of water. Hydrofluoric acid was weighed in a small plastic beaker with a tightly fitting plastic stopper. The acid was then added to the silica which rapidly dissolved.

The series of beakers to be kept at room temperature was placed in a hood, precautions being taken to avoid contamination by dust. Beakers to be heated were prepared and placed singly in the aluminium block and stirring and heating was started. After 5–10 min the prefixed temperature was reached and then maintained. After a suitable amount of acid had evaporated, the beaker was removed and rapidly cooled to room temperature in ice water. The beaker (teflon or plastic) was weighed (equipped with a plastic stopper) and the remaining amount of solution was calculated. When the residue weighed less than 1 g, it was transferred quantitatively to a plastic
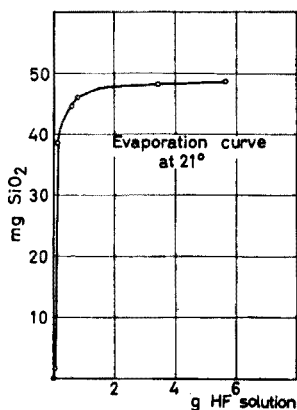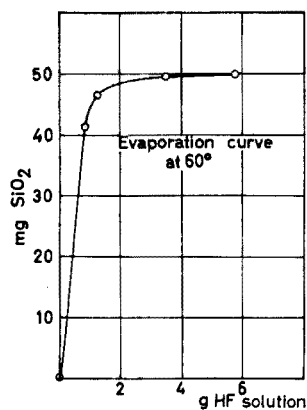

Fig. 1

Fig. 2

beaker (300 ml) containing 50 ml of 25% aluminium chloride solution and 10 ml of 10% ammonium molybdate solution. The mixture was diluted to about 90 ml with water, the pH was adjusted and the solution heated and diluted as described above. Finally, the extinction was measured at 415 mμ against a blank containing ammonium molybdate and aluminium chloride and adjusted to pH 1.0 $\pm$ 0.5. The amount of silica remaining was then calculated.
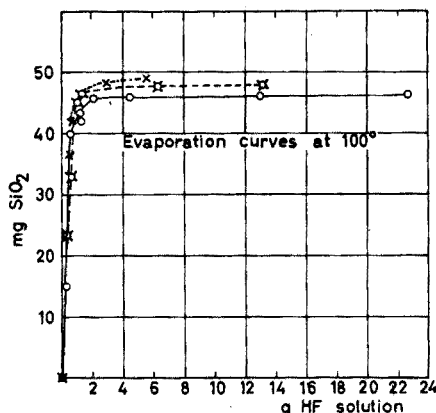

Fig. 3.

When the remaining solution weighed more than 1 g, about 1 ml was pipetted out (with the teflon tube pipette) into a plastic beaker and the solution was reweighed. The further treatment was as described above.

Experiments were carried out at room temperature (21° $\pm$ 2°) and at 60° $\pm$ 2° and at 100° $\pm$ 2°. The volumes of hydrofluoric acid used were normally about 5 ml; for the experiments at 100°, 10 and 20 ml were also used.

Solutions of about 5 ml, maintained at room temperature and at 100°, were evaporated to dryness in the course of about 110 h and 30 min, respectively. In Figs. 1, 2 and 3 the curves giving the loss of silicon by evaporation are reproduced.

CONCLUSION

It can be concluded that silica is decomposed by excess of hydrofluoric acid without any detectable loss of silicon through evaporation. It is interesting to note that this decomposition can also be carried out safely at higher temperatures, *e.g.* 100°.

When solutions of fluosilicic acid in hydrofluoric acid are evaporated by standing at room temperature or higher temperatures, only small amounts of silicon are lost initially; this is evident from the horizontal part of the evaporation curves. The break in these curves indicates that the composition of the constant-boiling ternary mixture of hydrofluoric acid, fluosilicic acid and water is reached. This ternary mixture then evaporates undecomposed, as indicated by the nearly vertical part of the curves. The concentration of fluosilicic acid in these final ternary solutions is roughly the same as given by MUNTER, AEPLI AND KOSSATZ[5] for this mixture, *i.e.* 36%.

Finally, it may be mentioned that solutions evaporated to dryness, *e.g.* at room temperature, contain only traces of silicon. In one experiment at room temperature the residue contained 0.1 mg SiO_2, corresponding to 0.2% of the original amount.

SUMMARY

Hydrofluoric acid can be used to dissolve silicon-containing materials without loss of silicon by evaporation. Silicon (present as fluosilicic acid) can then be determined spectrophotometrically as the yellow α-silicomolybdic acid. The loss of silicon from solutions evaporated at room temperature and higher temperatures is also determined.

RÉSUMÉ

Les substances renfermant du silicium peuvent être dissoutes dans l'acide fluorhydrique, sans risque de perte de cet élément par évaporation. Après dissolution, le silicium (sous forme d'acide fluosilicique) peut être dosé par spectrophotométrie, comme acide α-silicomolybdique jaune.

ZUSAMMENFASSUNG

Siliziumhaltige Substanzen können in Fluorwasserstoffsäure gelöst werden ohne Gefahr eines Verlustes an Silizium durch Verdunstung. Das in der Lösung als Silikofluorwasserstoffsäure vorliegende Silizium kann durch Überführung in die gelbe α-Silikomolybdänsäure spektrophotometrisch bestimmt werden.

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A NEW INDICATOR FOR THE COMPLEXOMETRIC DETERMINATION OF CALCIUM

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INTRODUCTION

Glyoxal bis-(2-hydroxy-anil) was first described by BAYER[1] as a complex-former for different metal ions. Later it was found that this anil in alkaline solution forms a red salt with calcium ions which permits a specific and sensitive identification of the cation[2].

The red calcium salt is destroyed by an aqueous solution of ethylenediaminetetraacetic acid (EDTA), hence the indicator properties of glyoxal bis-(2-hydroxy-anil) in the complexometric titration of calcium were examined.

EXPERIMENTAL

Reagents

1. Glyoxalbis (2-hydroxy-anil), 0.02% ethanolic solution. The compound was obtained as described by BAYER[1,2]. 2. Calcium chloride. A stock solution containing 0.5 g Ca/l was prepared by dissolving calcium carbonate in the minimum amount of hydrochloric acid. From this more diluted solutions were prepared. 3. EDTA (disodium salt). Approximately 0.01 M aqueous solution. This was standardized against the calcium chloride solution by using either Eriochrome Black T or the new indicator. In both cases the same results were obtained. 4. Potassium cyanide. 0.5% aqueous solution. 5. 1 N sodium hydroxide.

PROCEDURE

To 100 ml of the test solution add 10 ml of 1 N sodium hydroxide, 1 ml of potassium cyanide solution and 10 ml of the indicator solution. Stir until a red or pink colour appears. Titrate with EDTA to a pure yellow.

Table I shows typical results obtained.

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DISCUSSION

The end-point of the titration is indicated by a sharp change from pink to yellow.

The ethanolic solution of the indicator is colourless. If stored in a dark bottle and refrigerated it remains almost colourless for at least three months. If kept in a clear bottle, the solution turns yellow after a few days, but may still be used for at least a month. Because of the insolubility of glyoxal bis-(2-hydroxy-anil) in water, the results were better with 10 ml of an ethanolic solution than with a smaller volume of a more concentrated solution.

TABLE I

Ca taken mg	Ca found mg	Deviation
10.00	10.00	0.00
	10.01	+0.01
5.00	5.00	0.00
	5.00	0.00
	5.00	0.00
5.00 + 5 mg Mg	5.00	0.00
	5.01	+0.01
2.50	2.51	+0.01
	2.52	+0.02
	2.52	+0.02
2.50 + 5 mg Mg	2.51	+0.01
	2.52	+0.02
1.00	1.00	0.00
	1.02	+0.02
1.00 + 5 mg Mg	0.99	—0.01

Cyanide should be added before the indicator, otherwise the red colour disappears shortly after it has developed, probably owing to the destruction of the complex in alkaline solution in the absence of excess reagent. The effect of cyanide in the stabilization of the colour is not fully understood.

Under the above conditions barium and strontium interfere.

SUMMARY

Glyoxal bis-(2-hydroxy-anil) is proposed as a new indicator for the complexometric titration of calcium. The end-point is indicated by a sharp change from pink to yellow.

RÉSUMÉ

Un nouvel indicateur, le glyoxal bis-(2-hydroxyanile), est proposé pour le titrage complexométrique du calcium.

ZUSAMMENFASSUNG

Glyoxal bis-(2-hydroxy-anil) wird als neuer Indikator für die komplexometrische Titration von Calcium vorgeschlagen. Der Endpunkt wird durch einen scharfen Umschlag von Rosa nach Gelb angezeigt.

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PHOTOMETRIC DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS WITH HEXANITRODIPHENYLAMINE. II

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In an earlier paper[1] it was shown that quaternary ammonium compounds form complexes with hexanitrodiphenylamine which can be extracted with chloroform or methylene chloride from an aqueous solution of pH 10-11.

The solubility of the complexes in the organic solvents varies with the quaternary ammonium ion involved, but methylene chloride is generally a much better solvent than chloroform. In certain cases, however, the extraction cannot be carried out at the pH 10-11 even with methylene chloride. Primarily, compounds containing several quaternary ammonium groups yield precipitates which are insoluble in reasonable amounts of the organic phase. Experiments have not revealed any solvent which gives better results than methylene chloride under these conditions.

Hexanitrodiphenylamine in water is a moderately strong monobasic acid[1], but in an anhydrous solvent of basic character such as pyridine, hexanitrodiphenylamine can be titrated with tetrabutylammonium hydroxide as a dibasic acid[2]. A study of the conditions in water showed that the univalent anion of hexanitrodiphenylamine also reacts further with base in strongly alkaline aqueous solution. The product formed does not give slightly soluble compounds with quaternary ammonium ions. The reaction with base in a strongly alkaline medium is such that it is possible to determine in this medium the quaternary ammonium compounds which are precipitated at pH 11.

HEXANITRODIPHENYLAMINE IN STRONGLY ALKALINE AQUEOUS SOLUTION

Experimental

Absorption spectrum

The reaction in strongly alkaline aqueous medium involves changes in the absorption spectrum of the substance. In Fig. 1 are given the spectra of $2 \cdot 10^{-5}$ M solutions of hexanitrodiphenylamine containing varying concentrations of sodium hydroxide. The determinations were made with a Uvispec spectrophotometer (band width about 5 mμ) between 1 and 5 min after the addition of sodium hydroxide. Longer reaction times gave further changes of the absorption spectra when the sodium hydroxide concentration exceeded 0.2 N.

Irreversibility of the reaction

If the strongly alkaline solution of hexanitrodiphenylamine is partly neutralized (about pH 11) and tetraethylammonium bromide (TEABr) is added, a complex can be extracted with chloroform. The absorption spectrum of the complex in the

region 340–550 mμ was the same as that obtained with a reagent that had not been treated with strong alkali. Possible irreversible reactions do not appear to yield interfering products.

If an excess of TEABr was added, all the univalent anion of hexanitrodiphenylamine could be extracted, and thus the extent of irreversible reactions could be determined.

Method

1.0 mg ($2.3 \cdot 10^{-6}$ M) of hexanitrodiphenylamine was dissolved in sodium hydroxide of the stated strength to a total volume of 50.0 ml. After the stated time 5.00-ml samples were removed and neutralized with conc. hydrochloric acid. 0.2 ml of 1 N NaOH and 1 mg ($5 \cdot 10^{-6}$ M) of TEABr were added, and after cooling to room temperature the solution was extracted with 3 × 3 ml of chloroform. The chloroform phases were combined, diluted to 10.00 ml and 1 mg of tetrabutylammonium iodide (TBAI) was added. The extinction was determined at 420 mμ. The value obtained was compared with that given by a sample untreated with alkali. The irreversible decomposition was calculated from the decrease in extinction. The results are presented in Table I.

Extraction of the complexes from strongly alkaline aqueous solution

Two methods of extraction were compared. In method 1 hexanitrodiphenylamine was added when the extraction was begun, whereas in method 2 the reagent was added to the alkaline aqueous phase 1 min before the quaternary ammonium compound was added and the extraction started.

Method 1. $8 \cdot 10^{-7}$ equivs. of quaternary ammonium compound were dissolved in 25.0 ml NaOH of the given concentration. 10^{-6} mol of hexanitrodiphenylamine was added dissolved in 25.0 ml of methylene chloride and the mixture was shaken for the stated time. The organic phase was drawn off, centrifuged and 2 mg of TBAI added. The extinction was determined at 420 mμ.
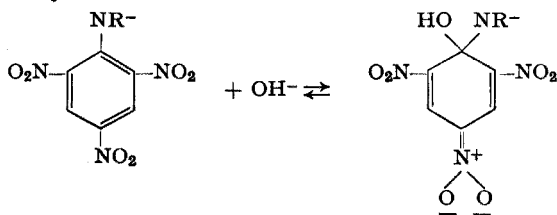
Method 2. 25.0 ml of sodium hydroxide solution of the given concentration were mixed with 10^{-6} mol of hexanitrodiphenylamine dissolved in 25.0 ml of methylene chloride. The mixture was shaken for a few seconds so that the hexanitrodiphenylamine passed into the aqueous phase. After 1 min, $8 \cdot 10^{-7}$ equivs. of quaternary ammonium compound were dissolved in the aqueous phase. The mixture was shaken for the stated time and the determination was completed as in method 1.

The results are shown in Table II.

DISCUSSION

Hexanitrodiphenylamine is an acid of p$K_a = 2.81$. At pH above 6 it is thus present almost entirely as anion, and its absorption spectrum in aqueous solution remains unchanged up to a pH of about 13. Changes in the absorption spectrum begin to occur when the concentration of alkali in the solvent exceeds 0.1 M and the changes increase markedly with the hydroxide concentration (Fig. 1). From Table I it is evident that less than 10% of the substance is irreversibly changed when the reaction time exceeds 5 min and the concentration of sodium hydroxide $\leqq 2$ N. However the changes in the absorption spectra are too great to depend solely on these irrevers-

ible reactions, and part of the reactions appear to be reversible. The following reaction is a possibility:

$$O_2N-\overset{\overset{NR^-}{|}}{\underset{NO_2}{\bigcirc}}-NO_2 \;+\; OH^- \rightleftarrows \; O_2N-\overset{\overset{HO\;\;NR^-}{|}}{\underset{\overset{||}{N^+}}{\bigcirc}}-NO_2$$

or written in a simplified way

$$He^- + OH^- = HeOH^{-2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

The assumption of an equilibrium is also supported by the results obtained by extraction of the complexes with quaternary ammonium ions from a strongly alkaline solution.

In the aqueous solution the following equilibrium may be assumed to exist (besides 1)

$$He^- + Kv^+ = KvHe(aq). \quad \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

On shaking with methylene chloride the partition equilibrium appears to be

$$KvHe(aq) = KvHe(org) \quad \ldots \ldots \ldots \ldots \ldots \ldots (3)$$
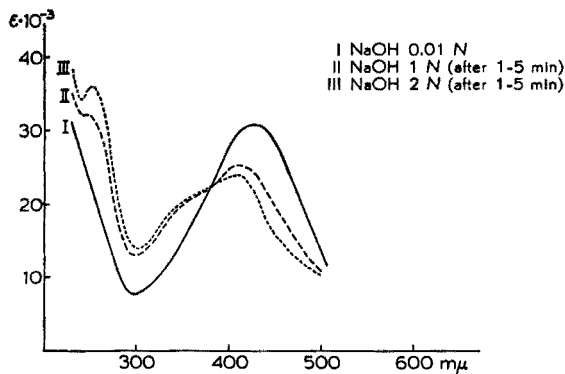
(Kv^+ = quaternary ammonium ion).

Fig. 1. Absorption spectra of hexanitrodiphenylamine in sodium hydroxide solutions of different concentration.

TABLE I

IRREVERSIBLE CONVERSION (IN%) OF HEXANITRODIPHENYLAMINE IN AQUEOUS SOLUTIONS CONTAINING VARYING CONCENTRATION OF NaOH

Time (min)	Molar concentration of NaOH				
	0.01	1	2	3	4
5	—	7	9	15	16
10	—	10	15	21	22
30	—	20	31	47	50
60	0	38	53	61	71

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TABLE II

TRACTION OF QUATERNARY AMMONIUM COMPLEXES OF HEXANITRODIPHENYLAMINE FROM
STRONGLY ALKALINE SOLUTION

| Aqueous phase | Shaking period (sec) | Quaternary ammonium ion | | | | | |
| | | Pentamethonium | | Hexamethonium | | Tetraethylammonium | |
		1	2	1	2	1	2
NaOH 2 N	5	0.54	0.26	0.74	0.42	0.74	0.26
	15	0.54	0.41	0.77	0.56	0.82	0.49
	60	0.53	0.47	0.78	0.71	0.98	0.83
	300	0.45	—	0.83	—	1.02	1.01
NaOH 3 N	5	0.32	0.03	0.52	0.04	0.63	0.07
	15	0.26	0.05	0.47	0.07	0.65	0.09
	60	0.16	0.10	0.40	0.08	0.70	0.23
	300	0.11	0.11	0.39	0.32	0.97	0.87

1. Hexanitrodiphenylamine dissolved in methylene chloride was added at the same time as the shaking was started.
2. Hexanitrodiphenylamine was added to the aqueous phase 1 min before the shaking was started.
Organic solvent: CH_2Cl_2. In the table $E^{1\,cm}$ at 420 mμ is given for the organic phase after the shaking.

From Table II it is seen that the amount of complex in the organic phase KvHe (*org*) is markedly altered on a change in the alkalinity of the aqueous phase. Higher concentrations of NaOH give lower final concentrations of KvHe(*org*), possibly because a greater part of the hexanitrodiphenylamine is changed to $HeOH^{-2}$.

It has been reported[2-5] that reactions analogous with 1 attain their equilibria slowly. This can explain why remarkably low values are obtained when hexanitro-diphenylamine is allowed to react in the strongly alkaline solution 1 min before the extraction is started (method 2, Table II). By this method the reagent at the beginning of the extraction occurs chiefly as $HeOH^{-2}$, and the slow reaction (1) gives rise to low initial concentration of He^- and KvHe(*org*). When the extraction is started with hexanitrodiphenylamine chiefly as He^- (method 1) the initially obtained concentration of KvHe(*org*) is markedly higher.

In experiments according to method 1 the concentration of KvHe(*org*) sometimes falls and sometimes rises on prolonged shaking, probably because the partition equilibrium is not reached immediately even on intensive shaking. The concentration of $HeOH^{-2}$ obtained at the beginning can be higher or lower than the final concentration depending on the partition coefficient of the complex. In any case, the slow change of the concentration of KvHe(*org*) by prolonged shaking may be assumed to depend mainly on reaction (1).

PROPERTIES OF THE COMPLEXES

Experimental

Extraction

For extraction of the complexes the following three methods have been employed:
1. Extraction with chloroform from an aqueous phase at pH 11. 2. Extraction with methylene chloride from an aqueous phase at pH 11. 3. Extraction with methylene chloride from strongly alkaline aqueous phase (3 N NaOH).

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Details of the methods are given on page 349. No TBAI was added to the solutions of the complexes in the organic solvent. The results with different types of quaternary ammonium compounds are shown in Tables III and IV.

TABLE III

EXTRACTION OF COMPOUNDS CONTAINING ONE QUATERNARY AMMONIUM GROUP AS COMPLEXES
WITH HEXANITRODIPHENYLAMINE

Substance	Formula of the cation	Method		
		1	*2*	*3*
Tetramethylammonium iodide (TMAI)	$(CH_3)_4N^+$	—	—	+
Tetraethylammonium bromide (TEABr)	$(C_2H_5)_4N^+$	+	+	+
Tetrabutylammonium iodide (TBAI)	$(C_4H_9)_4N^+$	—	—	+
Choline chloride	$HO.CH_2CH_2.N^+(CH_3)_3$	o	+	—
Carbamylcholine chloride	$NH_2.CO.O.CH_2.CH_2.N^+(CH_3)_3$	—	+	—
Bethanechol chloride	$NH_2.CO.O.CH.CH_2.N^+(CH_3)_3$ $\overset{\mid}{CH_3}$	—	+	—
Neostigmine bromide	$(CH_3)_2N.CO.O.C_6H_4.N^+(CH_3)_3$ (m)	+	+	—
Cetiprine ® bromide	$(C_6H_5)_2CH.CH_2.CH_2.N^+\overset{\diagup (CH_3)_2}{\diagdown C_2H_5}$	—	—	+
Propantheline bromide	9-xanthene-$CO.O.CH_2.CH_2.N^+\overset{\diagup CH_3}{\diagdown (isopropyl)_2}$	—	—	+
Dylamon ® bromide	$(C_6H_5)_2CH.O.CH_2.CH_2.N^+(CH_3)_3$	—	—	+
Methylatropine bromide	—	+	+	+
Methylhomatropine bromide	—	—	+	+
Methylscopolamine nitrate	—	—	+	—

+ = quantitative extraction. — = incomplete extraction. o = no extraction.
Method 1: Extraction with chloroform from an aqueous phase of pH 11. Method 2: Extraction with methylene chloride from an aqueous phase of pH 11. Method 3: Extraction with methylene chloride from a strongly alkaline phase (3 N NaOH).

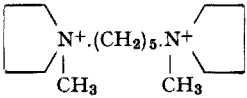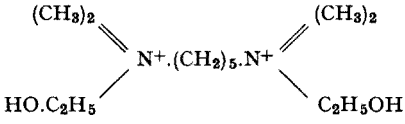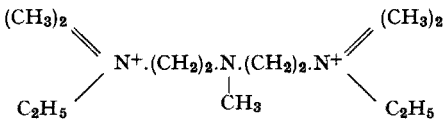*Stability*

The majority of the complexes exhibit very good stability in the organic solution, and the extinction is unchanged for several hours. However, some compounds yield less stable complexes with hexanitrodiphenylamine (Table V).

Especially noticeable is the decrease in extinction of the pentamethonium complex, which is largely due to the fact that the complex precipitates. In Fig. 2 are

TABLE IV

EXTRACTION OF COMPOUNDS CONTAINING SEVERAL QUATERNARY AMMONIUM GROUPS AS COMPLEXES WITH HEXANITRODIPHENYLAMINE

Substance	Formula of the cation	Method		
		1	*2*	*3*
Pentamethonium bromide	$(CH_3)_3N^+.(CH_2)_5.N^+(CH_3)_3$	o	—	+
Pentolinium tartrate	$N^+.(CH_2)_5.N^+$ with CH_3 groups	o	—	+
Agentit ® chloride	$(CH_3)_2$ $N^+.(CH_2)_5.N^+$ $(CH_3)_2$ $HO.C_2H_5$ C_2H_5OH	—	+	—
Hexamethonium bromide	$(CH_3)_3N^+ . (CH_2)_6.N^+(CH_3)_3$	o	—	+
Azamethonium bromide	$(CH_3)_2$ $N^+.(CH_2)_2.N.(CH_2)_2.N^+$ $(CH_3)_2$ C_2H_5 CH_3 C_2H_5	—	—	+
Gallamine triethiodide	$C_6H_3 (O.CH_2.CH_2.N^+(C_2H_5)_3)_3 (1,2,3)$	—	—	+
Tubocurarine chloride	—	+	+	o

+ = quantitative extraction. — = incomplete extraction. o = no extraction.
Method 1: Extraction with chloroform from an aqueous phase of pH 11. Method 2: Extraction with methylene chloride from an aqueous phase of pH 11. Method 3: Extraction with methylene chloride from an strongly alkaline aqueous phase (3N NaOH).

TABLE V

CHANGES IN MOLAR EXTINCTION OF COMPLEXES ON STORAGE

Quaternary ammonium ion	Method	Molar extinction · 10^{-4}	
		After 5 min	*After 18 h*
Pentamethonium	3	5.36	0.56
Azamethonium	3	5.92	5.68
Agentit ®	2	5.80	5.64
Pentolinium	3	6.10	5.78

shown extinction curves for a solution of the pentamethonium complex 5 min (II) and 18 h (III) after its preparation. Curve I was obtained after addition of a large excess of TBAI (5 mg to 50 ml of solution). Solution I is stable and exhibits no change in extinction even after several days.

The varying stability of the complexes is also reflected in the behaviour on filtration. In Table VI are compared the results from determinations when each extracted portion was filtered through paper (Munktell no. 3; 5 cm in diam.) with the values obtained without filtration. The extinction after addition of TBAI (5 mg per 50 ml) is also given in this table.

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TABLE VI

EXTINCTION OF COMPLEXES PREPARED WITH AND WITHOUT FILTRATION OF THE SOLUTIONS IN
ORGANIC SOLVENTS

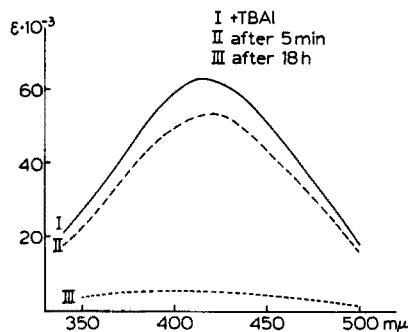| Quaternary ammonium ion	Method	Solvent	Molar extinction · 10^{-4}					
			350 mμ		420 mμ			
			filt.	unfilt.	filt.	filt. + TBAI	unfilt.	unfilt. + TBAI
Tetraethylammonium	1	CHCl$_3$	1.40	1.37	2.92	3.15	3.15	3.15
Tetraethylammonium	2	CH$_2$Cl$_2$	1.32	1.32	3.14	3.15	3.15	3.15
Carbamylcholine	2	CH$_2$Cl$_2$	1.32	1.34	2.93	3.15	3.08	3.15
Tubocurarine	1	CHCl$_3$	2.60	2.54	5.80	6.30	5.90	6.30

Fig. 2. Absorption spectra of the pentamethonium complex with hexanitrodiphenylamine in methylene chloride after storage and after addition of TBAI.

TABLE VII

EXTINCTION OF COMPLEXES BEFORE AND AFTER ADDITION OF TBAI TO SOLUTIONS OF THE
COMPLEXES IN ORGANIC SOLVENTS

Cation	Number of quatern. ammonium groups	Method	Molar extinction at 420 mμ × 10^{-4}	
			Without TBAI	With TBAI
Tetramethylammonium	1	1	3.15	3.15
Tetraethylammonium	1	1,2,3	3.15	3.15
Tetrabutylammonium	1	3	3.15	3.15
Choline	1	2	3.04	3.12
Carbamylcholine	1	2	3.08	3.15
Neostigmine	1	1	2.94	3.15
Methylatropine	1	2	3.04	3.15
Pentamethonium	2	3	5.36	6.30
Agentit ®	2	2	5.60	6.32
Hexamethonium	2	3	6.06	6.32
Decamethonium	2	3	6.08	6.30
Gallamine	3	3	9.09	9.42

Molar extinction

With the help of the methods which, according to Tables III and IV, gave complete extraction, molar extinctions were determined for the complexes of a number of quaternary ammonium compounds of different types. The determinations were carried out at the extinction maximum (420 mμ) before and after addition of TBAI (5 mg per 50 ml). The results are presented in Table VII. The extinction measurements were always made within 5 min after completed extraction. The molecular weights of the quaternary ammonium salts employed were determined by argentimetric titration.

DISCUSSION

Method 3, *i.e.*, extraction with methylene chloride from strongly alkaline medium, seems to be the most general method of extraction according to the experiments in Tables III and IV. The phenol tubocurarine and the easily hydrolysable phenol ester neostigmine cannot be determined according to this principle, since in the strongly alkaline aqueous solution they occur as water-soluble phenolates. The alcohols Agentit ® and choline as well as the choline derivatives (esters) carbamyl-choline and bethanechol also cannot be determined by this method. The quaternary tropine esters methylatropine and methylhomatropine are probably rapidly hydrolysed in the alkaline solution, and the extracted complex probably does not contain the acid component of the ester.

Compounds containing several quaternary ammonium ions and which do not have an alcoholic and phenolic character appear to be determinable only by method 3, and some of them cannot be extracted with chloroform (method 1).

Instability in organic media has been found only for the complexes of some cations containing two quaternary ammonium groups (Table V). Among these the pentamethonium complex assumes a distinct position by formation of a precipitate within a few min. If TBAI is added to a more or less changed solution of this complex, the precipitate goes into solution and the solution obtained has the same absorption spectrum as a newly extracted solution of pentamethonium complex mixed with TBAI.

The methylene chloride solution obtained on extraction seems to be supersaturated with regard to the pentamethonium complex. This can be explained by the earlier assumption that the above equilibrium (1) is attained slowly. In method 3 the concentration of He$^-$ at the beginning of the extraction is higher than the equilibrium concentration and the concentrations of KvHe(*aq*) and KvHe(*org*) become too high, (*cf.* Table II, method 1), which results in a supersaturated organic phase.

Table VI shows that filtration causes alterations in the adsorption spectra of the complex solutions; the extinction at 350 mμ remains almost unchanged, whereas that at 420 mμ is noticeably decreased. This change is obtained if part of the complex is converted to free hexanitrodiphenylamine (the extinction curves for complex and free hexanitrodiphenylamine intersect in the region 350–360 mμ[1]). After addition of TBAI the extinction values are the same in both filtered and unfiltered solutions. The filter paper does not absorb the hexanitrodiphenylamine component of the complex, but it seems to have a cation-exchanging effect; Kv$^+$ is replaced by H$^+$.

In the foregoing the compounds extracted with organic solvents have been designated complexes without any explanation. The alternative is to consider them as ion pairs, but the molar extinctions of a number of compounds presented in Table VII

References p. 352

speak in favour of the former opinion. The cations have no absorption at 420 mμ where the anion has its extinction maximum; if the compounds occurred as ion pairs, all these should have the same extinction per equivalent at this wavelength. In this case the extinction per equiv. varies with the quaternary ammonium ion included; it is probable that another type of compound is formed and this is designated as a complex.

If a large excess of TBAI is added to the organic solution, the same extinction per equiv. of quaternary ammonium compound is obtained, *i.e.* the molar extinction of the TBAI complex.

As stated above TBAI is suitable for stabilizing less stable complex solutions. All the complex solutions investigated have exhibited such good stability as to stand evaporation without alteration in molar extinction.

STANDARD METHODS AND DETERMINATION IN MIXTURES
Experimental

Standard methods

Method 1. 3–10 · 10^{-7} equivalents of quaternary ammonium compound are dissolved in water to a volume of 5.0 ml, mixed with 0.3 ml of 0.1 N NaOH, 5 ml of chloroform and 5.0 ml of hexa-chloroform-R. After shaking for at least 15 sec the organic phase is drawn off (without filtration), and the extraction is repeated with chloroform in 5-ml portions until the organic phase remains colorless. The chloroform fractions are combined and diluted with chloroform to an exact volume (usually 50.0 ml), and 5 mg of TBAI are added per 50 ml of the organic solution. The extinction of the solution is determined at 420 mμ.

Method 2. This method is analogous to method 1 but methylene chloride is used instead of chloroform and hexa-methylene chloride-R instead of hexa-chloroform-R.

Method 3. 3–10 · 10^{-7} equivs. of quaternary ammonium compound are dissolved in water to a volume of 5.0 ml, mixed with 20 ml of methylene chloride, 5.0 ml of hexa-methylene chloride-R and 2.0 ml of 10 N NaOH. The mixture is shaken for about 10 sec, and thereafter the methylene chloride phase is drawn off (without filtration). To the aqueous phase are added 5 ml of methylene chloride, and the mixture is shaken vigorously for 1 min. 1.0 ml of hexa-methylene chloride-R is added, and the mixture is shaken for 10 sec more. The organic phase is drawn off. Extraction in the manner described is repeated until the organic phase remains colorless. The methylene chloride fractions are combined and diluted with methylene chloride to an exact volume (usually 50.0 ml), and 5 mg of TBAI are added per 50 ml of the organic solution. The extinction of the solution is determined at 420 mμ.

Methylene chloride. The commercial product of boiling point stated as 41° is purified by shaking with a sodium carbonate solution and water. After being dried with calcium chloride it is distilled and the fraction of boiling point 40–41° is collected.

Chloroform. Pharmacopoeial grade.

Hexanitrodiphenylamine. Dipicrylamine p.a. is dissolved in the smallest possible volume of 1 N NaOH and the pH of the solution is adjusted to 10 with 1 M H$_3$PO$_4$. Kieselguhr is added until an almost dry mixture is obtained; this is packed into a chromatographic tube (percolator) and eluted with chloroform until all pentanitrodiphenylamine is extracted, *i.e.* the eluate gives the extinction curve of pure hexani-

trodiphenylamine[1]. The contents of the tube are removed and acidified with phosphoric acid (conc. phosphoric acid is added in small portions with intensive mixing until the color of the kieselguhr phase becomes slightly yellow). The kieselguhr phase is packed into the percolator and extracted with chloroform. The eluate is evaporated at diminished pressure to a small volume, and then the precipitated hexanitrodiphenylamine is filtered off and dried protected from basic fumes. A chromatographic control of the purity can be made[1].

Hexa-methylene chloride-R. A 10-mg sample of hexanitrodiphenylamine is dissolved in 100 ml of methylene chloride.

Hexa-chloroform-R. A 10-mg sample of hexanitrodiphenylamine is dissolved in 100 ml of chloroform.

Blank determinations

The determinations were carried out by the methods described under STANDARD METHODS. However, in all determinations 3 ml of hexa-R and 2 ml of organic solvent were added at the first extraction instead of 5 ml of hexa-R. The extraction was continued with 3 portions of the quantity and kind of extraction agent stated in the method and then the solution was diluted to 50.0 ml. After addition of TBAI the extinction was determined in a 1-cm cuvette at 420 mμ. Along with the true blank determinations, tests were also made on samples containing a high concentration of sodium and potassium ions at pH 11. Results are shown in Table VIII.

TABLE VIII

BLANK DETERMINATIONS

Method	Aqueous phase	Organic phase	E 1 cm at 420 mμ		
1	0.006 N NaOH	CHCl$_3$	0.005	0.005	0.008
2	0.006 N NaOH	CH$_2$Cl$_2$	0.008	0.011	0.009
3	3 N NaOH	CH$_2$Cl$_2$	0.008	0.005	0.007
2	0.006 N NaOH + 2 M NaCl	CH$_2$Cl$_2$	0.06	0.09	
2	0.006 N NaOH + 2 M KBr	CH$_2$Cl$_2$	0.05	0.02	

Determination of quaternary ammonium compounds in the presence of amines

The determinations were carried out by the standard methods above. The results are presented in Table IX.

TABLE IX

DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS IN THE PRESENCE OF AMINES

Sample	Method	Amount mg	
		calc.	found
1. Methylatropine bromide	2	0.300	0.303
Atropine sulfate		0.200	—
2. Methylscopolamine bromide	2	0.302	0.305
Scopolamine bromide		0.204	—
3. Cetiprine ® bromide	3	0.302	0.306
Mepyramine maleate		0.202	—

Determination of quaternary ammonium compounds in mixtures

Determinations were only carried out with mixtures where only one component was extractable with chloroform at pH 11.

Method: In a sample containing at the most 10^{-6} equivs. of quaternary ammonium compounds the component extractable with chloroform was determined using *standard method* 1, but with filtration of the chloroform phases through a paper filter which was afterwards washed with chloroform.

The component extractable with methylene chloride was then determined. The aqueous phase weakly acidified and shaken in order to dissolve any precipitated complex. The determination was continued according to *standard method* 3, but each methylene chloride phase was passed through the previously mentioned filter. When the extraction was completed, the filter was washed with 5 mg of TBAI dissolved in 5 ml of methylene chloride in order to dissolve any precipitate, and then with at least 5 ml of methylene chloride. No more TBAI was added before the final photometric measurement.

The results are presented in Table X.

TABLE X

DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS IN MIXTURE

Sample	Amount mg	
	calc.	*found*
1. Tetraethylammonium bromide	0.170	0.169
Pentolinium tartrate	0.205	0.203
2. Methylatropine bromide	0.150	0.147
Hexamethonium bromide	0.101	0.104
3. Neostigmine bromide	0.153	0.153
Pentolinium tartrate	0.122	0.123

DISCUSSION

The standard methods proved to be applicable for all quaternary ammonium compounds tested (medically used parasympatholytic, neuromuscular blocking and ganglionic blocking substances). A total volume of 50 ml was sufficient for all compounds except pentamethonium, where a total volume of 100 ml was used. The sample amounts employed, $(3–10 \cdot 10^{-7})$ equivs., give an extinction of 0.2 – 0.6 in a total volume of 50.0 ml and a 1-cm cuvette. It is possible to use smaller samples, but then after addition of TBAI the solution of the complex should be evaporated to a smaller volume before the final determination of the extinction.

From Table VIII it is seen that the blanks in all three methods are insignificant. The amount of reagent employed in the blank determinations corresponds to the excess of hexanitrodiphenylamine which is obtained when the sample contains $4 \cdot 10^{-7}$ equivs. of quaternary ammonium compound. A high content of sodium ions yields large blank values at pH 11, but in strongly alkaline solution the high sodium ion content is without greater significance. Presumably the sodium salt of hexanitrodiphenylamine is somewhat soluble in the organic phase, but in the more

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alkaline solution the reagent does not occur as univalent anion and thus is not extractable as sodium salt. The interfering effect of potassium is probably caused primarily by the precipitation of hexanitrodiphenylamine by this ion.

Amines do not seem to interfere in the determination of quaternary ammonium ions. Some amines form complexes with hexanitrodiphenylamine which are extractable with chloroform or methylene chloride, but in the standard methods such a high pH is used that most amines occur almost entirely as the free base, which does not yield extractable compounds with hexanitrodiphenylamine.

The method given for determination of quaternary ammonium ions in mixture has, previously mentioned, a limited application. Procedures based on chromatographic partition methods should, however, afford increased possibilities of separation.

SUMMARY

In strongly alkaline medium (more than 0.1 N NaOH) hexanitrodiphenylamine anion reacts with base. The reaction is rather slow and is partly reversible.

Quaternary ammonium ions can be determined by extraction of their hexanitrodiphenylamine complexes with chloroform or methylene chloride at pH 11 or with methylene chloride from 3 N NaOH. Only the latter method is applicable to compounds containing several quaternary ammonium groups. The compounds extracted have high molar extinction and good stability. Quaternary ammonium ions can be determined in the presence of amines, and in some cases determination of quaternary ammonium ions in admixture is possible.

RÉSUMÉ

Une méthode est proposée pour le dosage photométrique des ions ammonium quaternaire au moyen d'hexanitrodiphénylamine. Les complexes formés sont extraits par le chloroforme ou par le chlorure de méthylène. Ils présentent alors une extinction moléculaire élevée et une bonne stabilité.

ZUSAMMENFASSUNG

Quaternäre Ammonium-Ionen können mit Hilfe von Hexanitrodiphenylamin photometrisch bestimmt werden. Die gebildeten Komplexe lassen sich aus einer wässrigen Lösung mit Chloroform oder Methylenchlorid extrahieren. Sie sind sehr stabil und besitzen eine hohe molare Extinktion.

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DETERMINATION OF MICROGRAM QUANTITIES OF URANIUM IN THORIUM

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In the analysis of thorium of nuclear purity, a method was required for the determination of uranium in thorium at a level of about 1 p.p.m. Several methods have been reported for the separation and determination of uranium in thorium. WILLIAMS[1] used an alumina-cellulose chromatographic column and extracted uranium with ether containing 1% nitric acid. The uranium was then determined either spectrophotometrically or fluorimetrically. The method is satisfactory above 50 p.p.m. of uranium; at lower concentrations all reagents (particularly alumina) have to be first washed thoroughly with ether. EBERLE AND LERNER[2] separated uranium from thorium by extraction with tributyl phosphate (TBP); for a good separation, the organic phase containing the extracted uranium must be washed many times, first with hydrochloric acid and then with nitric acid. CLINCH AND GUY[3] extracted uranium as the thiocyanate complex into TBP, using EDTA to prevent the extraction of iron and some other elements. However, they recommend a preliminary separation of the uranium by ether extraction before applying the method to thoria samples; at low levels of uranium, the accuracy is not satisfactory. HARDWICK AND MORETON-SMITH[4] have recently reported a method for the separation of ^{233}U from irradiated thorium by extraction of the diethyl dithiocarbamate complex of uranium with hexone. The method was improved[5] by extraction of the oxine complex of uranium with chloroform in the presence of EDTA. In either method the ^{233}U is determined by α-counting.

The most sensitive method for the determination of microgram quantities of natural uranium is by measurement of its fluorescence in fused sodium fluoride melts[6]. Uranium must be in a fairly pure form because most other elements, including thorium, have a quenching effect on the fluorescence. This paper presents a method of separating uranium from thorium by means of TBP in the presence of EDTA as complexing agent. Although CLAYTON et al.[5] have reported that this extraction of uranium is not satisfactory, their conditions of pH, etc. were not described. The recovery of uranium by the proposed method was found to be quantitative within the limits of accuracy of the fluorimetric method of determination. The method was satisfactory for thoria samples having an uranium content of as low as 0.4 p.p.m. and it may be possible to extend it to other ranges by suitable adjustment of sample size.

EXPERIMENTAL

Apparatus

1. Fluorimeter, A.E.R.E., Harwell, Model 1080A; 2. pH meter; 3. separatory funnels, Squibb pear-shaped, 125-ml and 250-ml capacity.

Reagents

1. EDTA, disodium salt, A.R. Grade; 2. calcium nitrate, crystalline, A.R. Grade; 3. nitric acid, A.R. Grade; 4. ammonium hydroxide, liquor ammonia, A.R. Grade, diluted 1 : 1; 5. ammonium nitrate solution. Saturated aqueous solution of ammonium nitrate (A.R. Grade) adjusted to pH 2.5 with dilute nitric acid; 6. ammonium carbonate solution. 5% (W/V) Aqueous solution of ammonium carbonate, A.R. Grade; 7. tributyl phosphate, 5% solution. The commercial TBP was washed with a 5% solution of sodium carbonate to remove any mono- or di-butyl phosphate present, and then several times with distilled water to remove the carbonate. It was then diluted with kerosene or white spirit to give a 5% (V/V) solution. This solution was equilibrated with an equal volume of dilute nitric acid of pH 2.5, and was, after separation, ready for use.

Principle of the method

To the thorium in the form of a nitrate solution, EDTA is added in slight excess over the equimolecular ratio and the pH is adjusted. Salting agent is added and the uranium extracted with 5% TBP solution. The organic layer is scrubbed with saturated ammonium nitrate solution and the uranium back-extracted into 5% ammonium carbonate solution. Uranium is then determined fluorimetrically.

Salting agent

Various salting agents have been recommended[7] to assist the extraction of uranyl nitrate by TBP. Sodium, calcium and aluminium nitrates were studied for their salting effect in the present method. The extraction in the presence of sodium nitrate was not quite satisfactory, whereas aluminium nitrate caused the extraction of thorium into TBP, even when EDTA was present. Calcium nitrate was found to be satisfactory. It is considered that calcium nitrate not only acts as a salting agent, but also associates with the excess EDTA and thus helps in the extraction of uranium. For quantitative recovery it was necessary almost to saturate the aqueous phase with calcium nitrate and to carry out 5 successive extractions with TBP using a volume almost equal to that of the aqueous phase each time.

Effect of pH

CABELL[8] has reported that uranium forms complexes with EDTA at a pH of about 3 to 5, although these may be weak. It was, therefore, expected that the pH of the aqueous phase would have a considerable effect on the extraction of uranium. The effect of pH was studied over the range 1–4, and it was found that the recovery of uranium was quantitative between pH 2 and 3.5. Below pH 2 considerable quantities of thorium (> 0.5 mg) were extracted owing to the instability of the thorium–EDTA complex. For all further work the pH was adjusted to approximately 2.5 by means of indicator paper. At this pH the amount of thorium extracted was only about 2 μg, which did not interfere in the final fluorimetric determination.

Interferences

The interferences of several common cations and anions were investigated. The ions were added as shown in Table I; no interference was observed. Much greater amounts of these impurities could probably be tolerated.

TABLE I

INTERFERENCES STUDIED

Ion	Quantity added μg	Ion	Quantity added μg
Fe^{+3}	400	Cr^{+3}	40
Al^{+3}	200	Ni^{+2}	100
Ce^{+4}	100	Co^{+2}	40
Ti^{+4}	40	Mg^{+2}	200
Cu^{+2}	200	SO_4^{-2}	500
Zn^{+2}	100	PO_4^{-3}	500
Cd^{+2}	40	F^-	500
Pb^{+2}	200	MoO_4^{-2}	100
Sn^{+2}	100	VO_3^-	40
Bi^{+3}	40		

PROCEDURE

An aliquot of the sample was taken containing about 1 g of ThO_2 as the nitrate. If the sample contained organic matter it was evaporated in a platinum dish and ignited in a furnace at 600° to destroy all organic matter. The residue was dissolved in nitric acid with a few drops of dilute hydrofluoric acid (2%) and the solution was evaporated to dryness. The residue was then taken up with a few ml of nitric acid and again evaporated to dryness.

The dried residue was dissolved in 5 ml of water, 1.6 of EDTA was added and the pH of the solution adjusted to 2.5 with the help of indicator paper. Dry crystalline calcium nitrate (16 g) was added and the volume adjusted to 25 ml with water. The solution was then transferred to a 125-ml separatory funnel and 20 ml of equilibrated 5% TBP were added after rinsing the beaker with the same TBP. The funnel was shaken vigorously for one min, and the two layers allowed to separate. The aqueous layer was drawn off into the original beaker and the organic layer transferred to a 250-ml separatory funnel using a few ml of TBP solution to rinse the funnel stem. The extraction procedure was repeated four times and the TBP layers combined in the second separatory funnel. The combined organic phase was then scrubbed with saturated ammonium nitrate (adjusted to pH 2.5) three times to remove the small quantities of aqueous phase mechanically carried over. The uranium was stripped from the TBP extract with one 10-ml portion of distilled water, one 10-ml portion of 5% (W/V) solution of ammonium carbonate and finally with two 10-ml portions of water containing 1 ml of ammonium carbonate solution. All the uranium strippings were collected in a porcelain dish, acidified with nitric acid, and evaporated to dryness slowly over a burner. The dried residue was then ignited at 600° in a muffle furnace. The residue was taken up with dilute nitric acid, transferred to a 5-ml volumetric flask and the volume made up. Uranium was then determined fluorimetrically.

Results on synthetic samples are shown in Table II. Various quantities of uranium in the range 1 to 10 μg were added to aliquots of thorium nitrate solution containing approximately 1 g ThO_2, and the uranium content determined. A blank was run on all the reagents used, and amounted to 0.32 μg uranium. In experiment 7, 2.5 g of

ThO$_2$ were taken, thus extending the limit of determination to 0.4 p.p.m. of uranium in ThO$_2$.

TABLE II

ANALYSIS OF SYNTHETIC SAMPLES

Sr.No.	Uranium added μg	Uranium found μg	Difference μg
1	1.00	1.08	+ 0.08
2	2.00	1.88	— 0.12
3	3.00	2.98	— 0.02
4	5.00	5.05	+ 0.05
5	7.00	7.08	+ 0.08
6	10.00	10.13	+ 0.13
7	1.00	1.09	+ 0.09

SUMMARY

Uranium present in micro amounts in thorium is extracted with 5% tributyl phosphate in presence of EDTA at pH 2.5. Calcium nitrate is used as salting agent. Uranium is back-extracted with ammonium carbonate and determined fluorimetrically. Thoria samples containing as little as 0.4 p.p.m. of uranium have been analysed.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'uranium, en faibles teneurs, dans le thorium. On procède par extraction; l'uranium est finalement dosé par fluorimétrie.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von kleinen Mengen Uran in Thorium nach dem Extraktionsverfahren mit anschliessender fluorimetrischer Bestimmung des Urans.

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DETERMINATION OF THALLIUM IN BIOLOGICAL MATERIAL

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The use of thallium preparations particularly in rodenticides, as well as industrial exposures to thallium, have caused many cases of poisoning[1] so that it has been necessary to work out reliable methods for the determination of thallium in biological materials. A number of methods has been introduced; these have been reviewed in detail by ANDERSON[2]. Very small amounts of thallium can be determined specifically by spectrography, while the colorimetric methods are usually indirect and often not sufficiently specific. Recently, several new colorimetric methods based on rhodamine B and other reagents have been developed[3].

Dithizone has proved to be an exceedingly useful reagent for the determination of microgram amounts of many heavy metals[4]. The low affinity of dithizone for thallium may introduce difficulties in the development of a method for thallium based on this complexing agent. Dithizone has frequently been suggested for the isolation of thallium but as a rule other methods have been employed in the final estimation. However, BAMBACH[5], using a colorimetric dithizone method, determined lead under such conditions that thallium followed lead, and KAMERMAN[6], after removing interfering metals, determined thallium by titration with a dithizone solution.

In the present investigation conditions have been worked out which produce a stable thallium dithizonate that is well suited for spectrophotometric measurements. After the virtual completion of this work, CLARKE AND CUTTITTA[7] published a method similar to that described herein which was used for the determination of thallium in pure thallium salt solutions.

The existence of a dithizonate of tervalent thallium is uncertain, but monovalent thallium is extracted by dithizone in carbon tetrachloride at an optimal pH of 11[8]. Extraction by dithizone in chloroform is more efficient and at pH 11 or more, approximately 80% of thallium(I) is extracted[4]. At pH values around 11, dithizone reacts with many other metals, which either have to be removed or prevented from reacting with dithizone. Citrate and cyanide are commonly used as masking agents, but not all interfering metals are masked. Cyanide is used here, but fails to mask lead, bismuth and tin, and some other metals, *e.g.* mercury, are masked incompletely. A separation step must therefore precede the final extraction.

The separation is carried out by extraction of thallic chloride with ether and reextraction of thallous chloride into water; the latter procedure was introduced by REITH AND GERRITSMA[9]. Suitable conditions — extraction of thallic chloride with ether from about 1 N hydrochloric acid — were selected using the data of IRVING

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* Part of this work was carried out at the State Veterinary Medical Institute, Stockholm 50.

AND ROSSOTTI[10]. Their data also suggested, that hydrochloric acid very probably could be replaced by a sulphuric acid solution containing 1 M sodium chloride. Reextraction of thallous chloride into water is easily accomplished.

In the final extraction step dithizone is added in ammoniacal solution in order to reduce interference from chloroform-soluble impurities present in dithizone. Thallium dithizonate and some excess free dithizone are extracted into chloroform. Most of the free dithizone is removed by two washings with a dilute ammoniacal solution; the amount remaining in the chloroform phase does not affect the determination of thallium. The content of thallium is calculated from the absorbance at 510 mμ. Absorption curves for dithizone and thallium dithizonate are shown in Fig. 1.
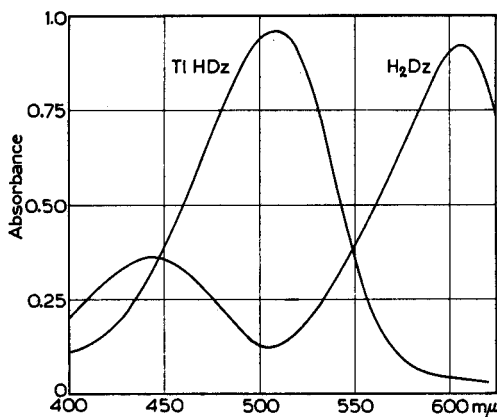

Fig. 1. Absorption curves for dithizone (H$_2$Dz) and thallium dithizonate (TlHDz) in chloroform. The heights of the maxima at 510 and 605 mμ are not comparable.

The determination of thallium, as outlined above (procedure A), is sufficiently specific for most purposes and is recommended as a standard method. However a few metals, especially when present in relatively large amounts, can interfere. A variation has therefore been worked out (procedure B) where thallium is separated from these metals by decomposing the thallium dithizonate at pH 4.6. The thus purified thallium solution is again extracted with dithizone. Procedure B is a little longer but it is highly specific and more sensitive to very small amounts of thallium in biological material.

APPARATUS AND REAGENTS

Analytical reagents and glass-distilled water are used throughout, except where otherwise stated. Daylight should be excluded during all work with solutions containing chlorine, hypochlorite, dithizone and thallium dithizonate. Consistent cleanliness is most important in this type of work.

Digestion apparatus, according to KLEIN[11], as described in a previous communication[12].

Separating funnels, Gilson model, 500, 250 and 125 ml. Only glass stoppers are used for flasks and separating funnels. *Cleaning of glassware.* After use the digestion apparatus is boiled with nitric acid, and before the next analysis boiled with water. Separating funnels, including ground surfaces, and other glassware are cleaned with raw, preferably chlorine-containing, hydrochloric acid and then rinsed very carefully with warm water and distilled water.

Thallium standard, 1 mg Tl/ml. Thallous nitrate (651.7 mg) is dissolved in water and made up to 500 ml.

Diluted thallium standard, 100 µg Tl/ml. Thallium standard is diluted with water (10:100). Stable for one week. *Hypochlorite solution*. Commercial sodium hypochlorite solution containing about 12% active chlorine and kept in the cold. *Chlorine solution*. Water (100 ml), hypochlorite solution (3 ml) and hydrochloric acid (3 N, 10 ml) are mixed immediately before use. *Sulphurous acid*. Commercial sulphur dioxide solution containing 5–6% SO_2 and kept cold. *Bromocresol green*, 0.5% in alcohol. *Ammonium hydroxide*, conc., $d = 0.91$. *Acid sulphite solution*. Water (400 ml) is carefully poured on to anhydrous sodium sulphite (25 g). After cooling in the refrigerator sulphuric acid (5 N, 50 ml) is added and gently mixed. The solution is kept cold. *Dithizone solution*, 0.5% in chloroform. Keep under a layer of acid sulphite solution in the refrigerator.

Hydroxylamine sulphate, $1M$, Hydroxylamine sulphate (16.4 g) is dissolved in water and made up to 100 ml.

Cyanide solution. Potassium cyanide (10 g) is dissolved in water (100 ml). Stable for a few weeks.

Dithizone mixture, prepared immediately before use. x is chosen to give enough mixture for an extraction blank and the samples; in procedure B enough for the second extraction with dithizone also must be taken. With $x = 1$, 37 ml of the mixture are obtained.

In a separating funnel, water ($x \cdot 10$ ml), dithizone solution ($x \cdot 2$ ml) and ammonium hydroxide ($x \cdot 5$ ml) are mixed. The funnel is shaken for 15 sec. After a few min the chloroform phase is discarded and chloroform ($x \cdot 5$ ml) added. After shaking for 5 sec, the chloroform phase is allowed to settle for 5–10 min. The chloroform layer, which should be green, is then discarded. To the separating funnel are now added hydroxylamine sulphate ($x \cdot 2$ ml), ammonium hydroxide ($x \cdot 15$ ml) and cyanide solution ($x \cdot 5$ ml). The contents are mixed.

Wash solution. Ammonium hydroxide (50 ml) and cyanide solution (10 ml) are diluted with water and made up to 1 l. Stable for one or two weeks.

Acetic acid (1:5). Glacial acetic acid (20 ml) is diluted with water to 100 ml (only for procedure B).

Acetate buffer. Sodium acetate trihydrate (27.2 g) and glacial acetic acid (12.0 g) are dissolved in water and diluted to 100 ml (pH about 4.6; only for procedure B).

PROCEDURE A

Combustion. The combustion of the organic material is carried out according to KLEIN[11] as described for the determination of mercury[12]. About 25 g of organs or 10 g of cereals are weighed. Water, nitric acid and boiling stones (quartz, acid washed) are added. To urine (100–500 ml) nitric acid is added and the solution is evaporated in the digestion apparatus to about 50 ml. The size of the sample is dependent upon its content of dry organic material. Samples with a high mineral content, such as bone, give serious bumping; in such cases the amounts weighed should be reduced. During the combustion, nitric and sulphuric acids are added and two distillations into the reflux collector are carried out as previously described[12], heating with a small flame being omitted.

After the second distillation the contents of the reflux collector are not returned to the digestion flask but discarded. The reflux condenser and collector are then removed. Ammonium sulphate (0.5 g) is added[13] through a wide glass tube into the digestion flask. The heating is resumed, gently at first, the central neck being left open. Each time the contents begin to darken, the flame is removed and 0.5–1 ml of nitric acid is added dropwise, splashing being avoided. The heating is gradually increased. When sulphuric acid begins to reflux on the sides of the flask and the contents do not darken any more, the dropping funnel is removed and a glass stopper inserted in its place. The flame is regulated so that sulphuric acid refluxes half-way up the flask walls, and heating is continued for five more min. After combustion the liquid should be nearly colourless. The flask is cooled and stoppered. Work may be interrupted at this point.

Separation. Two 500-ml separating funnels (I and II) are used for each sample. The solution in the digestion flask is diluted with water (50 ml) and filtered into I.

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Flask and filter are washed with 50 ml of water (altogether 100 ml of water are added) and sodium chloride (6.5 g) is added and dissolved. Hypochlorite solution (3 ml) is added in portions with swirling, followed after mixing, by ether (125 ml). A 10-ml cylinder is put beneath each separating funnel to catch any drops escaping. The pressure should always be released before shaking when ether is present. The funnel is then shaken vigorously for two min. A moistened potassium iodide-starch paper shows when the vapour phase contains an excess of chlorine. After a minute the water phase is run into II. Chlorine solution (20 ml) is added to the ether in I, which is shaken for 15 sec. The water phase is combined with the first water phase in II. I, containing an ether solution with most of the thallium, is stoppered. (Its stem and the cylinder beneath it are rinsed).

Hypochlorite solution (2 ml) and ether (65 ml) are added to II, which is shaken vigorously for 1 min. The water phase is discarded. Chlorine solution (20 ml) is added and II is shaken for 15 sec. The water phase is again discarded and the ether phase combined with the first ether solution in I. II is rinsed with a small amount of ether. The collected ether extracts are shaken vigorously for 1 min with sulphurous acid (15 ml). A moistened potassium iodide-starch paper, made blue above the chlorine solution, is held in the vapour phase of I. Sulphur dioxide gas should be present in excess and bleach the paper at once. The water phase, containing most of the thallium, is run into a porcelain dish (about 7 × 3 cm). Sulphurous acid (10 ml) is added to I, which is shaken vigorously for 30 sec. The water phase is combined with the solution in the porcelain dish. I is finally shaken for 15 sec with water (5 ml) and the water phase run into the dish. The water solution is evaporated on the steam bath to about one ml. (The determination may be interrupted at this point.)

Water (5 ml) and bromocresol green (1 drop) are added, followed by the dropwise addition of ammonium hydroxide with stirring until the colour changes; usually about 0.7 ml is consumed. Sulphuric acid (1 N) is added, also dropwise, until the indicator shows a neutral or acid reaction. In alkaline solution thallous ions are oxidized to thallic hydroxide. The sample is now ready for extraction.

Extraction. A special blank is prepared at the beginning of the extraction. For this extraction blank and for each sample a 250-ml separating funnel (I) and a 125-ml separating funnel (II) are required. Chloroform (50.0 ml) is added to I. For the blank, water (20 ml) is added and for the sample the contents of the porcelain dish. The dish is rinsed with three portions of water (altogether about 13 ml) and the inside walls are rubbed with a glass rod. The volume of the water solution in I is now about 20 ml. Dithizone mixture (40 ml) is added to I, which is shaken vigorously for 1 min.

The chloroform layers are run into II. The water layers are discarded (care: cyanide), and I is rinsed with distilled water. To each of the chloroform solutions is added wash solution (25 ml), and II is shaken for 15 sec. The chloroform layers are run back into I. (When using procedure B, stop at this point and continue under the heading "Procedure B".) The chloroform solutions are shaken a second time for 15 sec with wash solution (25 ml).

A couple of ml of the chloroform layers are withdrawn in order to remove water from the stopcocks. A wad of cotton is rinsed with a dilute solution of dithizone in chloroform and with chloroform and pieces are inserted into the stems of I and pushed up against the stopcocks to serve as filters. A couple of ml of the chloroform layers are drawn off through the filters and discarded. The chloroform extract from the

sample is read *versus* the extraction blank in 1-cm cells in the spectrophotometer. The absorbance at 510 mμ, A_{510}, is noted.

Calculation. Amount of thallium in the whole sample (or in an aliquot, see below), in $\mu g = k_A \cdot A_{510}$, where k_A is obtained from a standard curve.

Standard curve. The standard curve is prepared by extraction of standard thallium solutions without previous combustion and separation. Four 250-ml separating funnels (I) and four 125-ml separating funnels (II) are required. To I is added chloroform (50.0 ml), water (20, 19, 18 and 17 ml respectively), diluted thallium standard (0, 1.00, 2.00 and 3.00 ml respectively) and dithizone mixture (40 ml). All are shaken vigorously for 1 min. The procedure is continued as described under extraction. The three thallium-containing extracts are read *versus* the extraction blank at 510 mμ.

TABLE I

DETERMINATIONS WITH PROCEDURE A

25 g of human liver were used for each analysis

Liver	Added			Thallium, μg			Recovery %
	Tl μg	ion	mg	Found	Blank	Difference	
B	50	—	—	57	10	47	94
A	100	—	—	113	11	102	102
B	100	—	—	114	10	104	104
A	200	—	—	218	11	207	103.5
B	250	—	—	275	10	265	106
B	300	—	—	319	10	309	103
C	200	Fe^{II}	100	221	20	201	100.5
D	200	$\{Co^{II}$ $\{Ni^{II}$	50 50	215	10	205	102.5
E	200	$\{Mn^{VII}$ $\{Pd^{II}$	100 50	226	18	208	104
D	200	Pt^{IV}	50	223	10	213	106.5
C	200	Cu^{II}	100	227	20	207	103.5
D	200	Ag^{I} [a]	100	203	10	193	96.5
D	200	Au^{III}	48	213	10	203	101.5
C	200	Zn^{II}	100	221	20	201	100.5
C	200	Cd^{II}	100	630	20	610	305
D	200	Cd^{II}	5	213	10	203	101.5
B	200	Hg^{II}	100	815	10	805	403
C	200	Hg^{II}	10	348	20	328	164
C	200	Hg^{II}	1	237	20	217	108.5
E	200	In^{III}	100	346	18	328	164
D	200	In^{III}	10	236	10	226	113
D	200	Sn^{II}	100	215	10	205	102.5
B	200	Pb^{II}	100	239	10	229	114.5
D	200	Bi^{III}	100	417	10	407	204
D	200	$\{Bi^{III}$ $\{Cl^-$	10 1000	234	10	224	112
D	200	$\{Br^-$ $\{I^-$	500 500	210	10	200	100
D	200	$\{S_2O_3^{-2}$ $\{SCN^-$	500 500	212	10	202	101

[a] Precipitated AgCl was not filtered off.

The values of A_{510} are plotted against the amount of thallium in μg, a straight line standard curve being obtained (Fig. 2). The amount of thallium, corresponding to $A_{510} = 1.000$, is denoted by k_A. A mean value of $k_A = 328$ was obtained.

The blanks. The purpose of the extraction blank is to make the overall blank as low and uniform as possible. Blank determinations on the whole procedures have to be run frequently, and the blank values should be subtracted from the thallium values found. The blank determinations are run on tissue samples which are free of thallium. If tissue samples are not available, other organic matter such as sucrose or filter paper may be employed. The blank values may be due to interfering metals in the sample, chemicals or glass vessels; or it may be caused by an uneven distribution of free dithizone in the chloroform phases or in oxidation products from the dithizone. Blank values for human liver obtained by this procedure are given in Table I.

General remarks

The chloroform layers from blanks are faintly green and those from thallium-positive samples red. When red extracts are obtained, absorption curves should be prepared (*cf.* Fig. 1) and their maxima noted. It is sometimes possible to decide from the position of the maximum on the nature of the metal present. Mercury dithizonate, for instance, has a peak at 490 mμ, which is quite distinct from that of thallium dithizonate, where it is just below 510 mμ.

When it is believed that the sample may contain more than 300 μg of thallium, the contents of the porcelain dish are, after neutralization, quantitatively transferred to a 25-ml volumetric flask and made up to the volume with water. An adequate amount of this solution is added to the separating funnel. Water is also added to bring the volume of the aqueous phase to 20 ml.

When 10 g or less of wet tissue is weighed, the amounts of acids, water and other chemicals used during combustion and separation may be reduced by half; 250-ml separating funnels are convenient for the separation, but no changes are necessary for the extraction.

<div align="center">PROCEDURE B</div>

Procedure A is followed to the point indicated above just after the first washing of the chloroform extracts. The procedure is then as follows:

The aqueous phases are discarded and II is rinsed with distilled water. To each of the chloroform solutions are added water (20 ml), bromocresol green (1 drop) and acetic acid (1:5; about 1.6 ml). I is inverted a few times and the colours of the water phases observed. The amount of acetic acid is chosen so as to give a neutral indicator reaction, pH about 4.6. The neutral green colour should persist after shaking. I is then shaken vigorously for 30 sec. The chloroform layers are run into II. Chloroform (25 ml) is added to I, and water (15 ml) and acetate buffer (1 ml) to II, which is then shaken for 30 sec. The chloroform layers are discarded and the aqueous phases are run into I. II is rinsed with water (about 2.5 ml) which is also run into I. The volumes of the water phases in I will now be about 40 ml. II is rinsed with distilled water.

I is shaken for 15 sec, and the chloroform layers are discarded. The water solutions are washed once again by shaking for 15 sec with chloroform (25 ml), and the chloroform layers are discarded. To each of the water solutions are added chloroform (50.0 ml) and dithizone mixture (50 ml). They are then shaken vigorously for 1 min.

The determination is concluded by two washings of the chloroform extracts with wash solution as described under procedure A. The absorption of the solution is then read *versus* the extraction blank.

Calculation

Amount of thallium in the whole sample or in an aliquot, in $\mu g = k_B \cdot A_{510}$, where k_B is obtained from a standard curve. The standard curve is prepared as in procedure A, the extracts being purified as described above. The curve is drawn (Fig. 2), and k_B is read off in the same manner as k_A. A mean value of $k_B = 334$ was obtained.
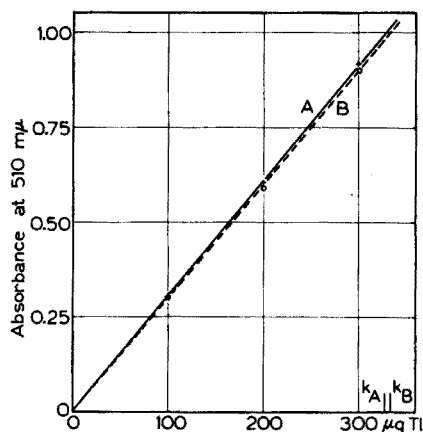
Fig. 2. Standard curves for procedures A and B.

RESULTS AND INTERFERENCES

Procedure A. Table I presents the results of determinations of thallium in liver samples to which diluted thallium standard has been added. The thallium recovered after subtraction of the blank values is given in per cent of thallium added. The method gives slightly high recoveries of about 103%. Thallium seems to be extracted more completely from sample solutions than from standard solutions.

The effects of various cations and anions on the yield of thallium are also shown in Table I. The effects of all known "dithizone metals", except polonium, in amounts up to 50 or 100 mg have been tested. In most cases the added metals interfered little or not at all, but four metals were found to interfere seriously with the thallium analysis; these are mercury in amounts exceeding about 1 mg, and cadmium, bismuth and indium when more than approximately 10 mg were present. In practice with biological samples, cadmium, bismuth or indium contents exceeding 10 mg seldom occur. Mercury contents exceeding 1 mg in 25 g of kidney occur in cases of lethal mercury poisoning. Halogen, thiosulphate and thiocyanate ions had little effect on the determination.

Procedure B. The results of determinations according to procedure B are shown in Table II. The yields were a little lower than for procedure A, being around or slightly

TABLE II

DETERMINATIONS WITH PROCEDURE B

25 g of human liver were used for each analysis

Liver	Added			Thallium, μg		Recovery %
	Tl μg	ion	mg	Found	Blank	
G	10			8	o	80
G	40			35	o	87.5
F	100			99	o	99
F	200			191	o	95.5
F	o	Hg^{II}	100	—2	o	
G	20	Hg^{II}	100	18	o	90
F	100	Hg^{II}	100	100	o	100
G	200	Hg^{II}	100	196	o	98
F	300	Hg^{II}	100	303	o	101
F	200	Cd^{II}	100	237	o	118.5
F	200	Cd^{II}	50	218	o	109
F	200	Bi^{III}	100	219	o	109.5
G	200	In^{III}	100	203	o	101.5

below 100%. At the lowest thallium content, less than 50 μg, the yields dropped to 80–90%. The low blank values, o μg for two different liver samples, made it possible to determine a smaller thallium content with procedure B than with procedure A; 10 μg in liver samples could be analysed, qualitatively and quantitatively, with reasonable accuracy.

The influence of the four metals which interfered in procedure A was studied, especially that of mercury (Table II); it was found that mercury (100 mg) and indium (100 mg) did not affect the determination whereas bismuth (100 mg) and cadmium (50 mg) interfered only slightly.

SUMMARY

Two variations of a method for the determination of microgram amounts of thallium in biological material have been worked out. After wet combustion and separation of thallium from most interfering substances by extraction of thallic chloride with ether, the metal is estimated absorptiometrically as its dithizonate, the yield being slightly greater than theoretical (procedure A). In the presence of mercury ($>$ 1 mg), cadmium, bismuth and indium ($>$ 10 mg) high results were obtained. Other metals, halogen, thiosulphate and thiocyanate ions did not interfere. With the slightly longer procedure B, serious interference was not encountered from any metal in amounts up to 50 mg. For practical purposes procedure B can be considered specific for thallium. As little as 10 μg of thallium in 25 g of liver could be determined.

RÉSUMÉ

Deux variantes sont proposées pour le dosage du thallium dans des substances biologiques. Après minéralisation et extraction, le thallium est dosé absorptiométriquement sous forme de dithizonate. L'un de ces procédés est moins rapide que l'autre; mais il peut être considéré pratiquement comme spécifique.

ZUSAMMENFASSUNG

Es werden zwei Varianten einer Methode beschrieben zur Bestimmung von Thallium in biologischem Material. Nach Zerstörung der organischen Substanz wird das Thallium als Chlorid extrahiert und als Dithizonat absorptiometrisch bestimmt. Die eine Variante benötigt etwas mehr Zeitaufwand, kann aber als spezifisch betrachtet werden.

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MULTIPURPOSE ELECTROANALYTICAL INSTRUMENT INCORPORATING AN X-Y RECORDER

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The basic quantities measured in electroanalytical chemistry are current, potential, and time. Measurement or recording of various combinations of these quantities accounts for most electroanalytical methods:

1. Current *vs.* potential, (a) voltammetry at constant potential, (*e.g.* polarography), (b) voltammetry at continuously changing potential, (c) current-electrode potential curves with macro-electrodes.

2. Potential *vs.* time, (a) chronopotentiometry, (b) potentiometric titration curves, involving coulometric generation or constant addition of titrant.

3. Current *vs.* time, (a) chronoamperometry, (b) amperometric titration curves, coulometric generation or constant addition of titrant.

Recording of current or potential *vs.* time is generally easily performed with galvanometer or "continuous-balance" strip chart recorders. The recording of current *vs.* potential, however, involves synchronizing the chart drive of the recorder with the polarizing unit drive. Since cell voltage, rather than electrode potential, is being recorded, the polarization curve inevitably includes the iR drop of the circuit. Although this iR drop generally does not cause serious error in the measured potentials when the cell resistance and current are small (*e.g.* polarography), attempts to record large currents (up to 100 mA) *vs.* potential, for example for use in predicting current efficiencies in coulometric titrations, are doomed to failure.

The direct recording of current-potential curves, as pointed out by Lingane[1], could be accomplished with an X-Y recorder (or "function plotter"), recording the e.m.f. between the working electrode and a reference electrode on one axis, and the current

flowing between the working electrode and an auxiliary electrode on the other axis. A polarograph utilizing this principle for accurate measurement of half-wave potentials and polarography in high resistance media has recently been described[2].

The present paper describes the application of an X-Y recorder, with a built-in time base, for all types of electroanalytical measurements. The instrument includes a variable polarizing source, for potential (or current) sweeps of 8 sec to 80 min, and an electromechanical amperostat–potentiostat combination for application to coulometry and controlled potential separations.

APPARATUS

The amperostat–potentiostat was essentially a combined version of the Lingane amperostat[3] and the Lamphere-Rogers potentiostat[4], utilizing the same amplifier for
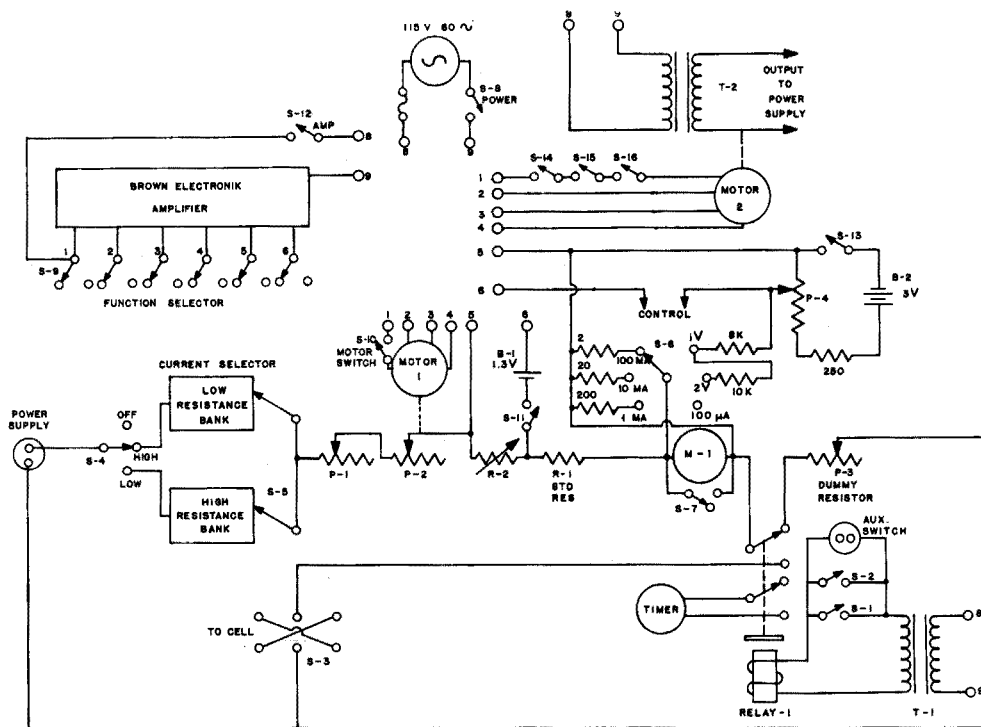
Fig. 1. Amperostat–potentiostat circuit:

M-1 = Microammeter (0–100 μA. d.c.; Simpson Panel Meter Model 29), relay-1 = Advance relay, Type AH/2C1C, T-1 = Power transformer (Merit P-2944), T-12 = General Radio Company Type V-10 Variac autotransformer (0–135 V. 10 A), P-1 = Borg micropot. Model 205, 10-turn, 0.1% linearity, P-2 = Potentiometer (General Radio Co. Type 974), P-3 = 500 Ohm potentiometer, P-4 = 500 Ohm potentiometer (General Radio Co. Type 975-J), R-1 = Precision resistor (General Radio Co. Type 500), R-2 = Decade resistor (General Radio Co. Type 1432 N), B-1 = 1.3 V mercury battery, B-2 = 3.0 V dry battery, S-1, S-7, S-10, S-11, S-12, S-13, S-14 = S.p.s.t. switches, S-2 = Microswitch, S-3 = D.p.d.t. switch, S-4 = 3-position, single pole switch (Centralab 1472), S-5 = 11-position, double pole switch (Centralab 2513), S-6 = 6-position, single pole switch (Centralab PA 2043), S-9 = 2-position, 6 pole switch (Centralab PA 2019), S-15, S-16 = Limit switches, Microswitch, leaf-action type, amplifier = Brown electronik model 356410-1, 115 V. 60 cycle. Motor 1 = Brown servo motor 364949, 115 V. 22 r.p.m., Motor 2 = Brown servo motor 364949, 115 V. 22 r.p.m., (1 : 40 reduction gear drive to T-2).

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both instruments. A schematic diagram of the circuit is shown in Fig. 1. The device is easily assembled from commercially available components, and requires little skill in electronic circuitry. The use of an electromechanical device allows currents of from 1 μA to 100 mA, by changing only the series resistances P-1 and P-2 and adjustment of R-2. The principle of operation of this instrument is discussed in detail in the literature[1,3,4]. The unit described has the advantage of versatility and reduction in cost by use of a common chopper-amplifier system for both functions.

A Moseley Model 3S X-Y recorder (F. L. Moseley Co., Pasadena, Calif.), with a built-in time base was employed throughout. This is a flat-bed recorder, utilizing standard 8 1/2 by 11 inch graph paper as a recording medium. Employed as an X-Y recorder, voltage input to either axis is continuously variable from 5 mV to 500 V. The time base (incorporated on the X-axis) allows full-scale sweep times of from 5 to 500 sec. Each scale may be calibrated, with an accuracy of 0.1%; changes in accuracy accruing to no more than 0.25% over a 6 month period. Both axis have identical response, and require 1/2 sec for full-scale pen travel.

Potential input

Direct input to the recorder for measurement of electrode potential is usually undesirable, as sizeable current drain through the recorder input attenuator, and consequently iR drop, occurs. Potential input with negligible current drain may be obtained by several devices. The X-axis of the recorder may be modified to make it a 1 V, zero current potentiometric system[2], but this has the distinct disadvantage of allowing only one potentiometric voltage range to be used. An alternate method is to employ a preamplifier in the potential input. The versatile pH meter Model 7664 (Leeds and Northrup Co., Philadelphia, Pa.) was quite suitable for this purpose. The recorder output of the meter was connected to the X-Y recorder, with the axis set for 20 mV full scale. The input to the pH meter consisted of voltage ranges of 0 to 700 mV and 0 to 1400 mV with the zero positioned anywhere on the scale. Other voltage ranges may be obtained by putting a variable resistance across the temperature compensation input of the pH meter (80–100 Ohms per 100 mV full scale deflection). Advantages of the pH meter input are the ability for use with very high input impedances (up to 2000 megOhms) for use with glass electrode measurements or high resistance voltammetry, and the ease with which orientation of the recorder scale can be accomplished. Accuracy is limited to that of the pH meter, but careful calibration provides sufficient accuracy for most electroanalytical measurements.

Current input

Current measurements are conveniently made by measuring the iR drop over precision resistors. Employing the 5 mV input to the recorder, current measurements of 0.1 μA to 1 mA is performed using 50,000 to 5 Ohm resistors. Higher currents may be measured using higher voltage inputs. The measuring resistors employed were either a decade box (*e.g.* Type 1432, General Radio Co., Cambridge, Mass.) or plug-in precision resistors (General Radio Co. Type 500).

Time input

The Moseley Model 3S is equipped with a built-in (charging capacitor-type) time

base, providing 5 to 500 sec full scale sweeps. The linearity and reproducibility of this time base was good. For longer time sweeps, or for X-Y recorders not including time bases, a ten-turn precision helipot driven by a synchronous motor can be used.

Polarizing unit

The polarizing unit was a motor-driven infinitely variable, reversible speed reducer, Zeromax Model M14R (Revco, Inc., Minneapolis, Minn.) driving (through a 1 : 100 gear reduction) either an autotransformer (Variac Type W2, General Radio Co.,) or a helipot. This unit has the capability of voltage or current sweeps of 8 sec to 80 min, with any desired current (up to 2 A) or voltage range. Generally, the autotransformer was connected to 120 V.A.C. and was used as a source for a selenium rectifier power supply (*e.g.* General Radio Co. Type 1204 B). Alternately the usual bridge voltage sources were employed[2,5]. The reversibility of the motor allows scans to be made in either direction. Limit switches were included at both ends of the scanning range to protect the autotransformer and automatically turn off the apparatus. Since the recorder plots potential directly, usual considerations of slide wire linearity and motor speed constancy were unnecessary. However, the scan voltage circuit employed was sufficiently linear and constant for use in voltammetry with continuously rapid changing potential.

<div align="center">APPLICATIONS</div>

Amperostat

The use as a constant current source has been described[3]. One need only select the current desired and adjust for balance and current constant to at least $\pm$ 0.1% can be obtained for use in coulometric titrations or chronopotentiometry.
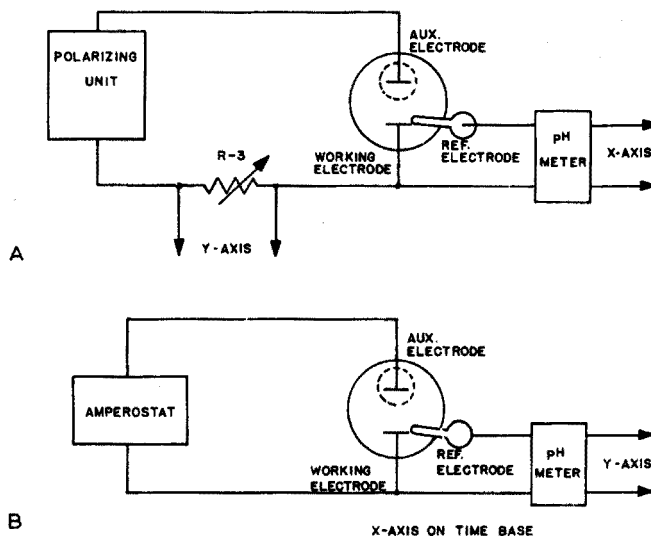

Fig. 2. A. Circuit for current-potential curves, B. Circuit for chronopotentiometry.

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Potentiostat

For use as a potentiostat, the function switch S-9 is turned to potentiostat, and the potential desired is adjusted with P-4 observing the meter (at 1 or 2 V range). Input to the autotransformer T-2 is 120 V.A.C. and the output voltage is fed to any selenium rectifier power supply. A potential of 1 V was maintained constant to within 10 mV as cell resistance varied from 500 to 1,000 Ohms in 5 min.

Current-potential curves

The set-up for any type of current-electrode potential measurement is shown in Fig. 2A. Adjustment of the variable precision resistor R-3 fixes the current range, and the total polarizing voltage and selected input to the pH meter selects the voltage range. This basic apparatus was employed for polarography (either voltage–scan or current–scan) or current–potential curves with macro-electrodes.

Chronopotentiometry

The apparatus for chronopotentiometry is shown in Fig. 2B. Current–time (chrono-amperometric) curves are recorded in a similar manner, using a current input to the Y-axis. In a similar manner both potentiometric and amperometric titration curves of various types can be recorded, using separate indicator electrodes.

The unit described has proved both versatile and convenient. The total cost of the complete instrument, including the amperostat–potentiostat, pH meter and recorder was approximately $ 2,500.

SUMMARY

A multipurpose electroanalytical instrument, incorporating an X-Y recorder with a built-in time base, is described. The instrument also includes an electro-mechanical combination amperostat–potentiostat and a variable speed polarizing unit. The instrument accurately measures electrode potential (rather than cell voltage) and hence does not involve correction of recorded potentials for iR drop. This is especially convenient for the recording of current *vs.* potential curves with macroelectrodes. It has also been successfully used for voltammetry, chronopotentiometry, coulometry and recording of titration curves.

RÉSUMÉ

Un appareil électroanalytique à usages multiples est décrit. Il convient tout particulièrement pour l'enregistrement de courbes potentiel/courant, avec macro-électrodes. Il a également été utilisé avec succès pour la voltammétrie, la chronopotentiométrie, la coulométrie et l'enregistrement de courbes de titrage.

ZUSAMMENFASSUNG

Es wird ein elektranalytisches Mehrzweck-Gerät beschrieben, das sich besonders zur Aufnahme von Potential-Stromstärke Kurven mit Makroelektroden eignet. Ferner lässt es sich für die Voltametrie, Chronopotentiometrie, Coulometrie sowie zur Aufnahme von Titrationskurven verwenden.

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SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM WITH 1,1'-DIANTHRIMIDE

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INTRODUCTION

During an investigation of the elements interfering in the spectrophotometric determination of boron with 1,1'-dianthrimide, it was observed that germanium also produced a colour with this organic reagent. The reactions of boron and germanium with 1,1'-dianthrimide take place in concentrated sulfuric acid, and the colours are developed by heating. In the literature no reference is made to the use of 1,1'-dianthrimide for the detection or determination of germanium.

The present paper describes the application of 1,1'-dianthrimide for spectrophotometric determination of germanium.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II. A matched set of 1,000-cm glass cells was used.

Reagents

The spectrographically standardized germanium dioxide (Johnson, Matthey & Co.) contained the following amounts of impurities: silicon — 3 p.p.m., silver — 1 p.p.m., copper, calcium, and magnesium $<$ 1 p.p.m., arsenic $<$ 0.05 p.p.m.

The 1,1'-dianthrimide (E. Merck) was recrystallised twice from nitrobenzene before use.

Concentrated sulfuric acid (95–97%) and other chemicals were of reagent grade quality. The strength of the sulfuric acid used was found to be 96.8%. Precautions were taken to prevent the acid absorbing water vapour.

Ordinary distilled water from an all-metal still was used.

Glassware

The germanium 1,1'-dianthrimide solutions were prepared and heated in 50-ml bottles (Jena geräteglass) with ground-in glass stoppers.

Heat treatment

The solutions were heated in a thermostatically controlled drying oven of standard construction.

EXPERIMENTAL DATA

Standard solutions

Germanium dioxide (0.1440 g) was dissolved in 50 ml of 1% sodium hydroxide solution. After dilution to 100 ml the germanium solution was stored in a plastic bottle. The standard solution contained 1 mg germanium per ml. A blank solution containing the same amount of sodium hydroxide was prepared, diluted to 100 ml and stored in a plastic bottle.

1,1'-Dianthrimide (0.500 g) was dissolved in conc. sulfuric acid, and the solution was transferred to a 1000-ml volumetric flask and diluted to the mark with the same acid.

Absorption curves

In Fig. 1, Curve 1, an absorption curve of the germanium 1,1'-dianthrimide complex is plotted. Curve 2 (Fig. 1) shows the absorption curve of a solution of 1,1'-dianthrimide.

The solutions measured photometrically were prepared in the following way. For curve 1, 1 ml of germanium standard solution, 12 ml of conc. sulfuric acid, and 5 ml of 1,1'-dianthrimide standard solution were pipetted into a 50-ml bottle. The bottle was stoppered, and the solution mixed and then kept in the oven for 16 h at 70° ± 2°. The solution was then cooled to room temperature and the extinction at different wavelengths measured against a blank solution consisting of 1 ml of the sodium hydroxide solution, 12 ml of conc. sulfuric acid, and 5 ml of 1,1'-dianthrimide standard solution. Curve 2 is the absorption curve of this latter solution measured against conc. sulfuric acid.
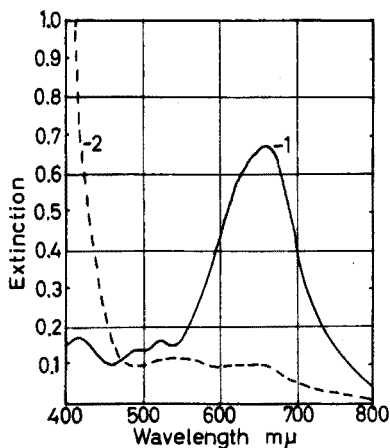

Fig. 1. Curve 1: Absorption curve of the germanium 1,1'-dianthrimide complex.
Curve 2: Absorption curve of 1,1'-dianthrimide.

The absorption curve of the germanium 1,1'-dianthrimide complex shows a distinct maximum at 660 mμ. This wavelength was chosen for the determination of germanium.

It is interesting to note that the form of the absorption curve of the boron 1,1'-dianthrimide complex in sulfuric acid of the same strength is nearly identical to curve 1 in the figure given above.

Calibration curve

The validity of the Beer-Lambert law was tested by measuring the extinction of a series of solutions containing varying known amounts of germanium. Into a series of 50-ml bottles were pipetted 0.2, 0.4, 0.5, 0.6, 0.7, 0.8 and 1.0 ml of germanium

standard solution. Volumes of less than 1 ml were diluted to that volume with the blank solution containing sodium hydroxide. Then 12 ml of conc. sulfuric acid and 5 ml of 1,1'-dianthrimide standard solution were added to each bottle, and the solutions were heated for 16 h at 70° $\pm$ 2°. The extinctions were measured against a blank prepared and treated in the same way.

Owing to contraction the volume of these solutions was not 18.0, but 17.6 ml.

TABLE I

EXTINCTION DATA FOR THE DETERMINATION OF GERMANIUM WITH 1,1'-DIANTHRIMIDE
WAVELENGTH 660 $m\mu$

Mg Ge per 17.6 ml (C)	Extinction (E)	Extinction index (E/C)
0.2	0.146	0.730
0.4	0.289	0.723
0.5	0.362	0.724
0.6	0.427	0.712
0.7	0.488	0.697
0.8	0.550	0.688
1.0	0.679	0.679

From Table I it is seen that a negative deviation from the Beer-Lambert law was obtained within the concentration range examined.

Effect of temperature

The colour of the germanium 1,1'-dianthrimide complex was developed by heating, and a temperature of 70° was chosen.

The effect of higher temperatures on the colour development was investigated. When heating was carried out at 80° or higher, the extinction of the solutions was less than that of solutions heated at 70°. At higher temperatures a red colour appeared in addition to the bluish-green colour of the germanium 1,1'-dianthrimide complex; the red colour probably originated from a decomposition product of 1,1'-dianthrimide. Consequently, a temperature above 70° cannot be recommended.

Effect of heating time

A relatively long heating time was needed to obtain equilibrium conditions. In this investigation a time of 16 h at 70° was used. Prolonged heating resulted in a decrease of extinction, probably again owing to destruction of the reagent.

Effect of concentration of sulfuric acid

The effect of the concentration of acid on the development of the colour was investigated for solutions heated for 16 h at 70°.

A series of solutions was prepared in which the concentrations of germanium and 1,1'-dianthrimide were kept constant, while the concentration of sulfuric acid was varied. The extinction of the solutions was measured against a series of blank solutions containing the same amounts of 1,1'-dianthrimide and sulfuric acid as the corresponding sample solution. The extinction of the blank solutions was measured against conc. sulfuric acid. The extinction data obtained are given in Table II.

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TABLE II

EFFECT OF CONCENTRATION OF SULFURIC ACID. CONCENTRATION OF UNDILUTED H_2SO_4 96.8%.
ALL SOLUTIONS CONTAINED 1 mg Ge AND 2.5 mg 1,1'-DIANTHRIMIDE.
WAVELENGTH 660 $m\mu$

| | | | Extinction | |
| | | | --- | --- |
ml H_2O taken	*ml H_2SO_4 (96.8%) taken*	*Conc. of H_2SO_4 after dilution %*	*Sample sol. against blank*	*Blank sol. against H_2SO_4 96.8%*
1.0	19.0	94.1	0.639	0.099
1.5	18.5	92.7	0.474	0.091
2.0	18.0	91.3	0.350	0.083
2.5	17.5	89.8	0.251	0.076
3.0	17.0	88.3	0.181	0.070
3.5	16.5	86.8	0.123	0.063
4.0	16.0	85.2	0.080	0.056

It is seen from Table II that the concentration of sulfuric acid is very critical. The extinction decreased rapidly when the acid was diluted. Further dilution resulted in the precipitation of 1,1'-dianthrimide.

Influence of foreign ions

The effect of foreign ions on the extinction of solutions of the germanium 1,1 - dianthrimide complex was not investigated, but on the basis of unpublished work on the influence of foreign ions in the determination of boron with 1,1'-dianthrimide, it is possible to obtain information about the ions interfering in the determination of germanium.

When the extinction of solutions of the germanium 1,1'-dianthrimide complex is about 0.5, the following ions affect this value by less than $\pm$ 3% (the concentrations of the different ions are given in brackets in mg per 17.6 ml):

Ag^+(2); Al^{+3}(5); Ba^{+2}(50); Bi^{+3}(1); Ca^{+2}(100); Cd^{+2}(50); Co^{+2}(20); Cr^{+3}(10); Cu^{+2}(20); Fe^{+2}(20); K^+(20); Li^+(10); Mg^{+2}(20); Mn^{+2}(10); Na^+(130); Ni^{+2}(20); Pb^{+2}(1); Si^{+4}(1); Sn^{+2}(20); Ti^{+4}(1); Tl^+(10); Zn^{+2}(50); Cl^-(200); $Cr_2O_7^{-2}$(0.01); F^-(0.01); PO_4^{-3}(100) and SO_4^{-2}(138).

The following ions interfere: B^{+3} in all concentrations, Br^- (oxidized in conc. sulfuric acid) and F^- in concentrations above 0.01 mg per 17.6 ml. Interference from fluoride ions is probably due to attack on glass and release of boron.

DISCUSSION

The authors have determined the formula of the complex between germanium and 1,1'-dianthrimide and have found it to be a 1 : 1 complex. From the data given in the present paper, it is clear that the ligand (1,1'-dianthrimide) was not added in excess compared with the amounts of germanium present. An excess was not used because of the high absorption of the 1,1'-dianthrimide blank solutions.

Even in the presence of insufficient 1,1'-dianthrimide Beer-Lambert's law was followed with only a slight negative deviation. It therefore seems clear that only a

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fraction of the amount of germanium present reacts with 1,1'-dianthrimide. Within the concentration range examined this fraction seems to be independent of the concentration of germanium. The amount of germanium reacting with 1,1'-dianthrimide was calculated to be of the order of 10% of the total amount present.

SUMMARY

In conc. sulfuric acid a coloured complex is formed between germanium and 1,1'-dianthrimide, which has an absorption maximum at 660 mμ, and can be used for the spectrophotometric determination of germanium. The method is applicable at concentrations up to at least 6 mg Ge per 100 ml. Among the more common ions serious interference is caused by boron and fluoride. The interference from fluoride is probably due to attack on the glass and release of boron.

RÉSUMÉ

En milieu acide sulfurique concentré la 1,1'-dianthrimide donne avec le germanium un complexe coloré, ayant un maximum d'absorption à 660 mμ. Une méthode est proposée pour le dosage spectrophotométrique du germanium au moyen de ce réactif.

ZUSAMMENFASSUNG

Germanium bildet mit 1,1'-Dianthrimid in conc. Schwefelsäure einen gefärbten Komplex, der sich zur spektrophotometrischen Bestimmung des Germaniums eignet; Absorptionsmaximum bei 660 mμ.

AN EVALUATION OF SOME SIMPLE SULFONIC ACIDS AS NONAQUEOUS TITRANTS*

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Although the sulfonic acids have been proved to be strong acids in a glacial acetic acid medium, they have not been widely investigated as titrants for use in nonaqueous titrimetry. HAMMETT AND DIETZ[1] dissolved benzenesulfonic acid in formic acid and used this titrant for the determination of bases in a potentiometric study of various acid–base titration systems. SMITH AND ELLIOTT[2], in an investigation of acid strengths and dissociation constants, found that methanetrisulfonic, chloromethionic, and methionic acids were stronger acids than perchloric acid. Since no information is available concerning the simpler sulfonic acids, methane- and ethane- in the aliphatic group and no further information on the aromatic benzene- and naphthalene-, this study sought to ascertain their analytical possibilities.

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* Based on experimental part of thesis submitted by Sr. Marguerite Miriam Caso, S.C., to the Graduate School, Fordham University, June 1958, in partial fulfillment of the requirements for the degree of doctor of philosophy.

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From the viewpoint of nonaqueous theory the sulfonic acids are interesting since the presence of the sulfonic acid group implies strong acid properties. By electron shifts the sulfur atom acquires a doubly positive charge and the resulting anion is stabilized by resonance. Since the proton is less firmly held, the O–H bond is weakened and greater acidity can be anticipated.

The choice of solvent system for the sulfonic acids provided the first problem. HAMMETT AND DIETZ[1] used formic acid as a solvent for their study reporting that they found this medium freer from salt effects. However, formic acid is less stable and more difficult to obtain in an anhydrous form than acetic acid, so it was decided to use the latter and more common system basing this selection on the following points:

(1) The reagent grade chemical, as obtained from the manufacturer, was pure and could be easily freed from water by treatment with acetic anhydride.

(2) The simple sulfonic acids to be used in the study were soluble in this medium.

(3) For potentiometric titrations the glass-calomel electrode system gave steady and reproducible readings in this solvent. Equilibrium was achieved quickly after the addition of each increment of titrant.

(4) During the titration with this solvent, the system remained free from the formation of precipitates or gels, so likely to occur in any anhydrous titration.

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Shell-Precision Titrometer equipped with a sleeve-type calomel electrode and a glass electrode. The titration assembly consisted of a 150-ml tall-form beaker, covered with a plastic lid. Three openings in the lid admitted the electrodes and buret tip into the titration beaker. The titrant was delivered from a 10-ml buret calibrated at 25° in the normal way. A magnetic stirrer and a glass-covered stirring bar were used to stir the solution during the titration.

Reagents and chemicals

Potassium acid phthalate (primary standard grade, Merck), was dried at 145° for 3h.
Glacial acetic acid, C. P. (Baker).
Methanesulfonic acid (reagent grade, Eastman).
Ethanemonosulfonic acid (reagent grade, Brothers Chemical).
Benzenesulfonic and naphthalene-2-sulfonic acids (reagent grades, Eastman).

Preparation of titrants

Methanesulfonic acid was found by aqueous assay to have a purity of 95.5%, the remaining 4.5% probably water. No opalescence was produced with barium chloride. Since the aliphatic sulfonic acids exhibited supercooling, the acid had to be cooled below 20°, its freezing point. It was found to solidify at 16°. Upon cooling, the acid became quite viscous, another characteristic of the entire series. It was purified by repeated fractional crystallizations, according to the method of BERTHOUD[3].

A 0.1 N solution of methanesulfonic acid was made up by dissolving 6.80 ml of the purified acid in a liter of glacial acetic acid, adding acetic anhydride to react with the trace of water present[4]. Methanesulfonic acid was found to dissolve readily and remain in solution for the entire period during which it was used.

Ethanemonosulfonic acid gave an aqueous assay of 98.5% purity. The product was purified by fractional crystallization according to the method of BERTHOUD[3]. It exhibited characteristics similar to the methane member of the series and had a freezing

point of —17°. A 0.1 N solution of this acid was prepared by dissolving 8.80 ml of the purified product in one liter of glacial acetic acid and adding acetic anhydride to react with any trace of water still remaining.

Benzenesulfonic acid was recrystallized several times from acetic acid and dried in a vacuum desiccator for over a week before use. In order to facilitate drying, the crystals were finely crushed and spread over a large surface. Due to its hygroscopic character, the material could not be weighed accurately. About 1.6 g were added to 100 ml of glacial acetic acid, acetic anhydride added to remove traces of water, and the resulting solution was permitted to stand at least overnight to insure the completion of the reaction of the anhydride with the water present. It was then titrated to determine its concentration and, subsequently, diluted to the desired normality.

Naphthalene-2-sulfonic acid gave no opalescence with barium chloride and showed the presence of a trace of water. It was recrystallized from acetic acid and dried by the same method as was used for benzenesulfonic acid above. About 2.3 g were dissolved in 100 ml acetic acid, and acetic anhydride added, to make a 0.1 N solution. The crystals did not appear to pick up water to any considerable extent during the weighings.

Procedure

Exactly 0.1635 g of potassium acid phthalate was weighed into tall form beakers and 10.0 ml of glacial acetic acid added to dissolve the sample. In order to completely dissolve the solid, it was necessary to heat the solution gently for 3 min. The solution was then cooled and titrated potentiometrically with a 0.1 N solution of each of the aliphatic and aromatic sulfonic acids.

Standard solutions of potassium acid phthalate were also prepared and aliquot portions titrated with the same apparatus as mentioned above. A few drops of crystal violet indicator solution in acetic acid were added to check the sharpness of the color change at the potentiometric end-point. For all titrations, the glass–calomel electrode system was used.

RESULTS

A series of 9 to 10 titrations for each acid were evaluated statistically from potentiometric data, as seen in Table I, on the basis of the height of the potential break and the maximum value of dE/dV, the rate of change of potential with volume of titrant. For a fair test of the analytical possibilities of the acids as new acidic titrants, it was thought advisable to make a comparison with perchloric acid in the same solvent. The results of this test, also listed in Table I, show the greater acid strength of perchloric acid. It is interesting to note, however, that in the course of this work with the sulfonic

TABLE I

COMPARISON OF ACID STRENGTHS OF 0.1 N SOLUTIONS OF SULFONIC ACIDS AND PERCHLORIC ACID FROM POTENTIOMETRIC DATA

Acid	Determinations	Maximum dE/dV	Potential break, mV
CH_3SO_3H	9	497	220
$C_2H_5SO_3H$	10	436	200
$C_6H_5SO_3H$	9	542	240
$C_{10}H_7SO_3H$	10	540	234
$HClO_4$	10	1300	315

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acids, it became increasingly evident that precipitates or gels are not formed during the titrations. These precipitates, reported extensively in the literature and confirmed in this work, are repeatedly obtained when perchloric acid is used as the titrant.[5]

The titration curves for the sulfonic acids, as illustrated in Figs. 1 and 2, are characteristic of strong acids from a consideration of both their shape and their large potential break at the end-points. Sharp color responses could be expected from indicators and
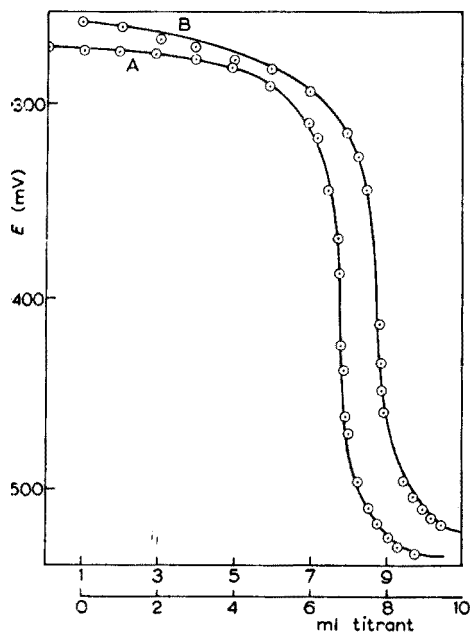
Fig. 1. Standardization of aliphatic sulfonic acids with potassium acid phthalate. Solvent: glacial acetic acid; electrode system: glass–calomel; standard: 0.80 mequivs. potassium acid phthalate; titrants: 0.1 N solutions of: A, methanesulfonic acid; B, ethanemonosulfonic acid.
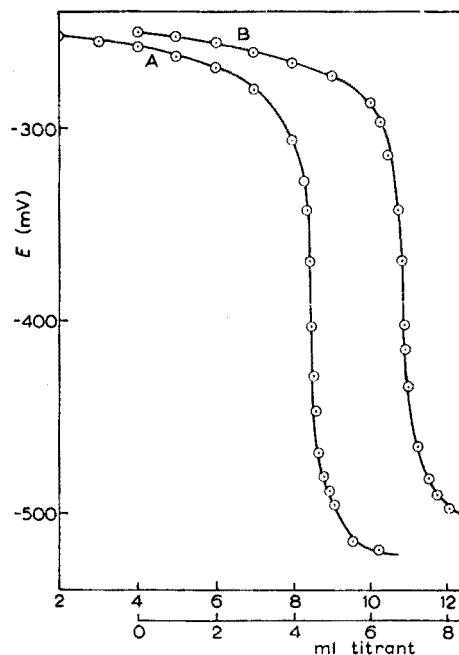
Fig. 2. Standardization of aromatic sulfonic acids with potassium acid phthalate. Solvent: glacial acetic acid; electrode system: glass–calomel; standard: 0.80 mequivs. potassium acid phthalate; titrants: 0.1 N solutions of: A, benzenesulfonic acid; B, naphthalenesulfonic acid.

TABLE II

PRECISION OF THE ALIPHATIC AND AROMATIC SULFONIC ACIDS STANDARDIZED *VS.* POTASSIUM ACID PHTHALATE

Acid titrant	Determinations	Normality	Standard deviation parts/1000
CH_3SO_3H	10	0.1014	0.00017
$C_2H_5SO_3H$	10	0.1017	0.00028
$C_6H_5SO_3H$	10	0.1059	0.00049
$C_{10}H_7SO_3H$	10	0.1010	0.00040

crystal violet was added to the titration solution to check its response. The color change at the end-point was sufficiently sharp as to suggest the possibility of visual titrations for the standardization. However, in the use of any indicator in nonaqueous work, it is advisable to check the color change at the potentiometric end-point first since a great variation has been found for different substances[6].

From the sharp potential break at the end-point in the standardization of these acids, good precision can be anticipated. Table II lists the precision found in the standardization against potassium acid phthalate. The precision is of the order of 0.2 to 0.5 % which is excellent for nonaqueous titrations.

DISCUSSION

The method described here illustrates the simplicity of preparing some sulfonic acids as nonaqueous titrants in a glacial acetic acid medium. These acids can be standardized against potassium acid phthalate by potentiometric measurements. Reproducibility of results was found to be excellent when the glass-calomel electrode system was used. The precision of the method was of the order of 0.2 to 0.5%.

For the standardization process it is also possible to use aliquot portions of a standard solution of potassium acid phthalate dissolved in acetic acid. This solution was found to be stable over the entire period during which it was used in this work.

Although none of the sulfonic acids tested were as strong as perchloric acid, they had an advantage over the latter in so far as they did not produce gels or precipitates in the titration with potassium acid phthalate. A complete study of precipitation formation in the titration of other basic substances is now in preparation.

Although the aromatic sulfonic acids tested showed less precision than the aliphatic, they likewise titrated as strong acids. The handling of naphthalene-2-sulfonic acid proved much simpler than that of benzenesulfonic acid, since the difficulty of removing water and working with a hygroscopic compound was not present.

SUMMARY

The simple aliphatic and aromatic sulfonic acids show evidence of possibilities as new titrants in a glacial acetic acid medium. Excellent precision is obtained in potentiometric titrations with both ethane- and methane sulfonic acids with a standard deviation of 0.2%. Benzenemonosulfonic and naphthalenesulfonic acids both give an average precision of 0.4%. In visual titrations with with crystal violet indicator, the color changes at the end-point are very sharp. The chief advantage of these acids as titrants lies in the fact that they dissolve readily in glacial acetic acid and can be titrated to give reproducible results with the glass–calomel electrode system. None of the sulfonic acids tested was as strong a titrant as perchloric acid, but, unlike perchloric acid, they did not form precipitates or gels in the titration with potassium acid phthalate.

RÉSUMÉ

Les auteurs proposent l'emploi d'acides aliphatiques et aromatiques sulfoniques pour des titrages en milieu non aqueux. Les acides méthanesulfonique et éthanesulfonique, en particulier, permettent d'obtenir une très bonne précision. Ces acides présentent l'avantage de se dissoudre très facilement dans l'acide acétique glacial.

ZUSAMMENFASSUNG

Für Titrationen in nicht-wässrigem Medium eignen sich aliphatische und aromatische Sulfosäuren unter denen besonders Methan- und Aethansulfosäure sehr gute Resultate ergeben. Von grossem Vorteil ist ihre gute Löslichkeit in Eisessig.

References p. 379

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OMEGA CHROME BLUE GREEN BL AS ANALYTICAL REAGENT FOR CALCIUM AND MAGNESIUM

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The present work describes the reaction of Omega Chrome Blue Green BL with various ions and its use as a metal indicator for the detection of equivalence points in EDTA titrations.

Properties of Omega Chrome Blue Green BL

It is a grey crystalline monoazo dye which is difficulty soluble in water to give a blue–green solution. In ethanol and acetone bright blue solutions are obtained; it is insoluble in chloroform and ether. Its Colour Index number is C.I. 17650[1], and it has the following structural formula
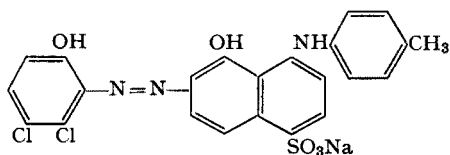
The effect of variation of pH on the colour of aqueous and ethanolic solutions of the dye was tested. Below pH 10.5 the colour is blue, and above 10.5 red. The maximum absorbance at pH 10 is at a wave length of 640 mμ, that of the dye–magnesium complex is at 580–600 mμ and that of the dye–calcium complex at 580–590 mμ with a flat peak.

Omega Chrome Blue Green BL metal complexes

The metal complexes of the dye were prepared by adding a few drops of an ethanolic solution of the dye to solutions of heavy metals. The pH of the solution was kept

constant by addition of buffer pH 10. In testing metals which precipitate at this pH, a secondary complexing agent was added; tartrate ion was found suitable. In testing for manganese, ascorbic acid was added to prevent the formation of hydrated manganic oxide.

The results obtained showed that calcium and magnesium cause a colour change to red. Strontium and manganese show a faint colour change to violet.

The following ions failed to give a colour change: aluminium, antimony, barium, beryllium, bismuth, cobalt, cerous, copper, lead, lithium, mercury, nickel, sodium, stannous, potassium, thallium, thorium, uranium, yttrium, zirconium, zinc, acetate, borate, bromate, bromide, chloride, chlorate, citrate, cyanide, iodide, nitrate, nitrite, oxalate, phthalate, persulphate, phosphate, sulphate, sulphite, tartrate and thiocyanate.

Sensitivity of determination of calcium and magnesium

The sensitivity of the end-points of EDTA titrations of calcium and magnesium with Omega Chrome Blue Green BL as indicator was determined by placing on a spot plate one drop of buffer, one drop of 1% ethanolic dye solution and one drop (0.05 ml) of calcium or magnesium solution. Progressive dilutions of the metal standard solution were prepared and tested in the same way as long as the test gave positive results. The concentration of the diluted solution taken for the test was then calculated. By this means the identification limits were found and the corresponding dilution limits were calculated. The results (Table I) show that the indicator is suitable for the detection of end-points in the EDTA titrations of calcium and magnesium, because of reversibility and reasonably good contrast. It cannot be applied to the determination of either manganese or strontium because of the poor contrast obtained.

TABLE I

COLOUR REACTIONS OF OMEGA CHROME BLUE GREEN BL WITH METALLIC IONS

Ion	Colour	Identification Limit mcg	Dilution limit
Calcium	red	0.2	$1 : 2.5 \cdot 10^5$
Magnesium	red	0.12	$1 : 4.1 \cdot 10^5$
Manganese	faint red blue		
Strontium	faint red		

EXPERIMENTAL

Reagents

Indicator solution: 0.1 g of Omega Chrome Blue Green BL (Sandoz, Basle) was dissolved in 100 ml ethanol.

EDTA solution 0.01 *M:* 3.722 g of reagent grade disodium ethylenediaminetetraacetate dihydrate were dissolved in twice-distilled water and diluted to one l. This solution was standardized against standard 0.01 *M* calcium solution.

Metal salt solutions: 0.01 *M* solutions of the various metals tested were prepared from analytical grade reagents and standardized against 0.01 *M* EDTA solution using Eriochrome Black T as indicator.

Buffer solution pH 10: 13.5 g of ammonium chloride A.R. were dissolved in water, 88 ml of conc. ammonia were added and the mixture diluted to 250 ml with twice-distilled water.

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PROCEDURES

Determination of calcium or magnesium

To an aliquot of the calcium or magnesium solution were added a few ml of buffer solution, 2 ml of ethanol or acetone and sufficient indicator solution to obtain a red colour. The solution was titrated with 0.01 M EDTA to the colour change from red to blue. The last trace of red vanishes at the end-point.

TABLE II

DETERMINATION OF CALCIUM AND MAGNESIUM WITH OMEGA CHROME BLUE GREEN BL AS INDICATOR

mg of metal		
present	*found*	*difference*
A. calcium		
0.401	0.397	0.004
0.401	0.405	0.004
0.826	0.818	0.008
1.202	1.186	0.016
1.407	1.407	0.00
1.603	1.611	0.008
1.984	1.968	0.016
2.036	2.024	0.012
B. magnesium		
0.243	0.253	0.010
0.486	0.491	0.005
0.730	0.39	0.009
0.973	0.985	0.012
1.216	1.224	0.008
1.459	1.464	0.005
1.702	1.700	0.002
1.945	1.955	0.010

Determination of magnesium in presence of aluminium

To the slightly acid solution of aluminium–magnesium mixture were added 1 ml of 30% triethanolamine, buffer and indicator and the magnesium was titrated as above.

TABLE III

DETERMINATION OF MAGNESIUM IN PRESENCE OF ALUMINIUM

Al added mg	Mg added mg	Mg found mg	Error
2.697	0.248	0.247	0.001
2.697	0.248	0.242	0.006
1.079	0.481	0.479	0.002
2.697	0.516	0.521	0.005
2.697	0.496	0.504	0.008
1.079	0.691	0.695	0.004
1.079	0.750	0.743	0.007

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RESULTS AND REMARKS

Satisfactory results were obtained by the given procedures for the determination of calcium and magnesium. The titration can be done in the cold, but better end-points are obtained at about 60°. The end-point is also improved by the addition of a few ml of acetone or ethanol.

With this indicator it is possible to titrate magnesium in presence of aluminium if aluminium is screened with triethanolamine. In this method the blue colour of the indicator remains after the end-point is reached in contrast to what usually occurs when using Erio T as indicator. It was not necessary to cool as suggested by PRIBIL[2,3], when Erio T is used as indicator. Attempts to determine aluminium by back-titration with magnesium after addition of a known excess of EDTA were unsuccessful; aluminium seems to block the indicator under these conditions.

The errors of the determinations were calculated statistically from the deviations of the results from the actual values of metal ions present and amounted to 7.2 μg for magnesium and 8.4 μg for calcium.

In contrast to Erio T, this indicator does not form red complexes with aluminium, cadmium, copper, lead, thorium, zirconium and zinc. The indicator is suitable for the direct determination of calcium, magnesium and magnesium in presence of aluminium although it does not give such sharp end-points as Erio T.

SUMMARY

The behaviour of Omega Chrome Blue Green BL towards various ions was studied. It was used as indicator in the direct EDTA titration of both calcium and magnesium and for the titration of magnesium in presence of aluminium.

RÉSUMÉ

Un indicateur est proposé pour le dosage du calcium et du magnésium par titrage au moyen de l'acide éthylènediaminotétracétique et pour le titrage du magnésium en présence d'aluminium.

ZUSAMMENFASSUNG

Als neuer Indikator für die komplexometrische Titration von Calzium und Magnesium sowie von Magnesium in Gegenwart von Aluminium wird Omega Chrom Blaugrün BL vorgeschlagen.

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THE INTERSTITIAL VOLUME OF ION-EXCHANGE COLUMNS

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The volume outside of the resin particles in an ion-exchange column is called the interstitial, void, or free volume and is often denoted by V. In the plate theory of ion-exchange elution chromatography[1] and of the closely related salting-out[2] and solubilization[3] types of chromatography, the interstitial volume is an important parameter. The distribution ratio, C, (the quantity of any particular solute in the resin phase of any plate divided by the quantity in the interstitial solution of the same plate) is readily calculated from an experimental elution graph by the equation

$$C = (U^*/V) - 1 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (1)$$

where U^* is the volume of eluate collected from the addition of the sample to the peak of the elution graph. Thus any error in the determination of V introduces an error in the value of C.

The values of V/V_b (the ratio of the interstitial volume to the bed volume) reported in the literature range from 0.25 to 0.819. The former figure was calculated[4] on the erroneous assumption that the resin consisted of spherical beads of uniform size packed as closely as possible. To find the latter value, the volume of resin in the bed was assumed[5] to be equal to the weight of dried resin divided by its density. Thus this value includes the interstitial and imbibed water. KRAUS AND MOORE[6] found a value of 0.40 for Dowex-1 (crosslinkage not stated, probably about 8%) by measuring U^* for an unabsorbed species $(C = 0)$ and using equation (1).

HARRINGTON[7] found values of V/V_b ranging from 0.385 to 0.396 for glass beads. He determined the interstitial water both by addition of water to the dry beads and by measurement of the water removed by centrifugation. Values within this narrow range were obtained both with uniform beads of 200-mesh and of 250-mesh and with a mixture of beads of 100-, 150-, and 200-mesh. If it can be assumed that that spherical beads of resin of approximately the same size as the glass beads are packed in a column similarly to the glass beads, HARRINGTON's values are applicable to resin columns. He also equilibrated beads of 20–50 mesh, sodium-form Dowex 50-X8 with saturated water vapor then treated them analogously to the glass beads, finding a mean of 0.390 for V/V_b. He treated dried beads of 20–50 mesh, hydrogen-form Dowex 50-X8 analogously, using octane instead of water, and found 0.387.

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Changes to 50–100 mesh or to the sodium form caused only minor changes (maximum of 0.015) from this value.

The method previously used in this laboratory[8] consists in equilibrating a column of resin with standard hydrochloric acid, draining the column to the upper level of the resin, rinsing the interstitial acid from the column with water and determining the amount of this acid by titration with sodium hydroxide. This quantity of acid, expressed in mequivs, divided by the normality of the standard acid, was taken as the interstitial volume. Corrections were applied for the quantity of acid in the filter disk and on the inside walls of the chromatographic tube below the filter disk. This method, or minor modifications of it, has yielded values of V/V_b ranging from 0.34[9] to 0.59. The latter value was found for a resin that consisted of irregularly shaped particles[10].

An error is inherent in the foregoing method. According to the DONNAN principle, some hydrochloric acid will penetrate the resin beads and be removed by the rinse water. This leads to high results.

The work reported in this paper was undertaken (1) to ascertain the magnitude of the error due to the DONNAN penetration, (2) to develop a reliable method for the determination of interstitial volume and (3) to investigate the effects of size, degree of crosslinkage, and chemical nature of the resin on the interstitial volume. Since very large ions are unable to diffuse into the resin, polyelectrolytes were substituted for hydrochloric acid in some of the experiments in order to eliminate the DONNAN penetration. In other experiments, hydrochloric acid was used as the interstitial solution; and a correction for the penetration was applied mathematically.

CORRECTION FOR THE PENETRATION OF HYDROCHLORIC ACID INTO THE RESINS

The uncorrected interstitial volume is

$$V_u = L/N \qquad (2)$$

where N is the normality of the interstitial hydrochloric acid and L is the number of mequivs. of acid rinsed from the column. If λ denotes the quantity (in mequivs.) of hydrochloric acid that penetrates the resin per gram of dry resin and if W denotes the dry weight of resin in the column, the corrected interstitial volume is

$$V = V_u - \frac{\lambda W}{N} \qquad (3)$$

Cation-exchange resins

For sulfonated crosslinked polystyrenes in the hydrogen form it has been shown[1] that

$$V_r = (1.003\theta + 0.628)W \qquad (4)$$

where V_r is the volume of swollen resin in the column and θ is the weight (in grams) of water imbibed per gram of dry resin. An approximate form of this equation

$$V_r = (\theta + 0.63)W \qquad (5)$$

is satisfactory for our purpose. The value 0.63 may be regarded as the specific matrix volume of the swollen resin.

Also

$$V_r = V_b - V \quad \dots \dots \dots \dots \dots \dots \dots (6)$$

From equations (3), (5), and (6)

$$\frac{V}{V_b} = \frac{\dfrac{V_u}{V_b} - B}{1 - B} \quad \dots \dots \dots \dots \dots \dots (7)$$

where

$$B = \frac{\lambda}{(\theta + 0.63)N} \quad \dots \dots \dots \dots \dots \dots (8)$$

If the values of λ and θ are known for any given resin and concentration of hydrochloric acid, the corresponding value of B can be calculated by equation (8). Then the corrected value of V/V_b can be calculated for that resin by equation (7). PEPPER, REICHENBERG AND HALE[11] have determined λ and θ for several sulfonated polystyrene resins of various crosslinkages in several different concentrations of hydrochloric acid. Their data are summarized in Table I. Since the concentrations of hydrochloric acid and the degrees of crosslinking of the resins in our work differed from those of PEPPER et al., it was neccessary to perform a double interpolation on the data of Table I in order to find the appropriate B values. These interpolated values are given in Table II.

TABLE I

VALUES OF B FOR SULFONATED POLYSTYRENE

Normality of HCl	Degree of crosslinking			
	2	5	10	15
0.00	0.000	0.000	0.000	0.000
0.11	0.096	0.085	0.000	0.000
0.52	0.218	0.055	0.013	0.016
1.05	0.322	0.090	0.026	0.016
2.30	0.411	0.163	0.055	0.014

TABLE II

INTERPOLATED VALUES OF B FOR SULFONATED POLYSTYRENE

Normality of HCl	Degree of crosslinking			
	2	4	8	16
0.01	0.020	0.005	0.001	0.000
0.1	0.090	0.035	0.005	0.000

Anion-exchange resins

Adequate data for the values of λ and θ for strong-base anion-exchange resins of the type of Dowex 1 have not been recorded in the literature. For this reason, the penetration of water and of hydrochloric acid into several samples of Dowex 1 of various crosslinkages from water and from $0.01 N$ and $0.1 N$ aqueous hydrochloric acid was determined in the course of this investigation.

<div align="center">EXPERIMENTAL</div>

Materials

Several samples of Dowex 50 and of Dowex 1 of various degrees of crosslinking and various mesh sizes were used.

A sample of Graham salt (sodium polyphosphate) was prepared by fusion of primary sodium phosphate at about 940° for 12 h and rapid cooling of the melt between steel plates. A solution of this polymer was prepared to be $0.01 M$ with respect to the monomeric unit; it was standardized by a spectrophotometric method[12].

Professor U. P. STRAUSS[13] kindly donated samples of poly-4-vinyl-N-ethylpyridinium bromide, $(CH_2\text{-}CHC_5H_4NEtBr)_n$, and a similar compound in which 15% of the alkyl groups were dodecyl, the remaining 85% being ethyl. The latter compound is hereinafter designated as "polysoap." The number-average degree of polymerization of the polyvinylethylpyridinium bromide was 265. That of the polysoap was of the order of 2000. Solutions of these compounds, $0.01 M$ with respect to the monomeric unit, were prepared; they were standardized by the Volhard method.

Measurement of the absorption of water and of hydrochloric acid by Dowex 1

Samples of Dowex 1 of various crosslinkages were equilibrated with water or standard hydrochloric acid and transferred to weighed centrifuge tubes provided with a filter disk[11]. After centrifugation to remove the interstitial liquid, the tubes and moist resin were weighed. The resins were then washed with water to remove the hydrochloric acid that had penetrated into the resin, and the washings were titrated with sodium hydroxide. The tubes and resins were then dried at 110° in a vacuum and reweighed. Corrections of 0.033 ml per ml of resin bed[14] were applied for the interstitial liquid that was not removed by the centrifugation. A correction was also applied for the amount of water and hydrochloric acid remaining in the filter disk. These measurements furnished the data needed to calculate θ and λ. Pycnometric measurements were made in water to determine the specific matrix volumes of these resins.

Determination of interstitial volume

The interstitial volumes of hydrogen-form Dowex 50 and of chloride-form Dowex 1 were determined with hydrochloric acid as previously described[8].

Sodium polyphosphate was used with sodium-form Dowex 50 as follows. The resin was slurried with water and poured into a chromatographic tube of known internal diameter. After the resin settled (about 5 min), one l of water was passed

through the column. The water in the tube was drained to the level of the resin. Then about three bed volumes of the polyphosphate solution were passed through the column to displace the interstitial water. The liquid in the tube was again drained to the level of the resin, and the height of the resin column was measured. The procedure was continued as with hydrochloric acid except that a spectrophotometric method[12] was used to determine the amount of polyphosphate in the eluate.

Solutions of the polysoap and of the poly-4-vinyl-N-alkylpyridinium bromide were applied similarly to determine the interstitial volumes of Dowex 1 in the bromide form and Dowex 50 in the hydrogen, lithium, and barium forms. The bromide washed from the interstices was determined by the Volhard method.

<center>RESULTS AND DISCUSSION</center>

Absorption of water and hydrochloric acid by Dowex 1

The specific matrix volumes of the anion-exchange resins were calculated from the pycnometric measurements as $1 - (W_3 - W_2)/W_1$ where W_3 is the weight of the pycnometer containing W_1 grams of dry resin and enough water to fill it, and W_2 is the weight of the pycnometer full of water. The values for Dowex 1-X2, X4, X8, and X10 were 0.856, 0.847, 0.845, and 0.856, respectively. The average was rounded to 0.85. Thus for these resins, instead of equation (8), the appropriate equation is

$$B = \frac{\lambda}{(\theta + 0.85)N} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

Since Dowex 1 is less dense than Dowex 50, the larger value of the specific matrix volume is to be expected.

The absorption of hydrochloric acid, λ, and of water, θ, also the calculated values of B, are listed in Table III.

As is to be expected, the absorption of water shows a regular decrease with increasing crosslinkage. This is not the case with the absorption of hydrochloric acid, λ, which seems to vary erratically. This suggests strongly that some phenomenon in addition to the DONNAN effect is causing hydrochloric acid to enter the resin beads during the equilibration and to leave them during the washing process. The presence in the resin of a relatively small number (varying erratically form batch to batch) of tertiary and secondary nitrogen atoms would account for the results in Table III. Evidence for the existence of such weakly basic groups in Dowex 1 has been observed by other investigators[14, 15]. When the resin is equilibrated with hydrochloric acid, these weakly basic groups are neutralized; but they release the acid by hydrolysis when the resin is washed with water. Thus only a part of the absorption of hydrochloric acid is due to the DONNAN effect.

Because of the variability of Dowex 1 from batch to batch, the λ-values of Table III are not applicable to other samples of Dowex 1. Nevertheless, the data of Table III are valid for calculating the corrected interstitial volumes by equations (9) and (8) provided the same batches of resins are used for the determination of interstitial volume as were used to obtain the data of Table III. This precaution was observed.

TABLE III

ABSORPTION OF WATER AND HYDROCHLORIC ACID BY ANION-EXCHANGE RESINS

Resin	0.01 N hydrochloric acid			0.1 N hydrochloric acid		
	λ	θ	B	λ	θ	B
Dowex 1-X2	0.0135	3.45	0.313	0.083	3.41	0.194
Dowex 1-X4	0.0018	1.55	0.075	0.016	1.47	0.069
Dowex 1-X8	0.0025	0.54	0.167	0.0158	0.64	0.105
Dowex 1-X10	0.0069	0.59	0.476	0.0176	0.59	0.121

TABLE IV

RELATIVE INTERSTITIAL VOLUMES OF RESINS, 200–400 MESH

Resin	Hydrochloric acid				Polyphosphate 0.01 M	Polysoap 0.01 M	Polyvinylethylpyridinium bromide 0.01 M	Mean	Standard deviation
	0.01 M		0.1 M						
	Uncorrd.*	Corrd.	Uncorrd.*	Corrd.					
Dowex 50-X2	0.317	0.303	0.376	0.314	0.289	0.308	0.330*	0.304	0.010
Dowex 50-X4	0.350	0.346	0.358	0.335	0.307	0.321	0.362*	0.327	0.017
Dowex 50-X8	0.385	0.384	0.391	0.388	0.365	0.378	0.439*	0.379	0.010
Dowex 50-X16	0.383	0.383	0.385	0.385	0.404	0.408	0.404*	0.395	0.016
Dowex 1-X2	0.571	0.375	0.487	0.363		0.330	0.335	0.351	0.022
Dowex 1-X4	0.406	0.358	0.412	0.368		0.338	0.338	0.350	0.012
Dowex 1-X8	0.479	0.374	0.442	0.376		0.409	0.400	0.390	0.015
Dowex 1-X10	0.672	0.375	0.452	0.377		0.421	0.412	0.396	0.024

* Excluded from mean.

Comparison of the various methods

Table IV shows the relative interstitial volumes of spherical beads, 200–400 mesh, of Dowex 50 and Dowex 1 of various degrees of crosslinking as determined by the several methods. Most of the entries are the means of three determinations, whose standard deviations never exceeded 0.016.

Sodium polyphosphate (Graham salt) contains about 4% of sodium trimetaphosphate and a smaller percentage of sodium tetrametaphosphate[16]. These compounds, because of their small concentration, would not enter Dowex 50 by the DONNAN effect appreciably; therefore sodium polyphosphate gave satisfactory results for V/V_b of this resin. On the other hand, the metaphosphate anions would enter the beads of Dowex 1 and exchange with the chloride; therefore the interstitial volume of this resin could not be determined with sodium polyphosphate.

The table indicates that satisfactory agreement for the relative interstitial volume of Dowex 50 is obtained with polyphosphate, polysoap, or hydrochloric acid of either concentration (provided that the correction for the DONNAN effect is applied).

The results for V/V_b of Dowex 50 obtained with the polyvinylethylpyridinium bromide are abnormally high. The following hypothesis is offered to explain this discrepancy. Because of the repulsion of the positive charges on quaternary nitrogen atoms, the molecules of this polymer are almost linear in shape. The exchange of any one quaternary ammonium ion with a hydrogen ion of a sulfonic acid on (or slightly below) the surface of a resin bead will serve to hold the entire polymeric molecule in the vicinity of the resin bead. Thus, after equilibration with the solution of this polycation, each resin bead is probably covered by a swarm of polymer molecules, each of which is held to the resin by one (or very few) electrovalent bond. When the interstitial solution is removed by washing, most of these surface-held polymers are washed away, and the remaining polymers are held by several electrovalents bonds. Thus the quantity of this polymer washed from the resin is greater than the quantity that was in the interstitial solution.

The presence of dodecyl groups in the polysoap, by virtue of van der Waals forces, causes the molecules of this polymer to become approximately spherical in shape[13]. Therefore the polysoap does not behave toward the resin like the polyvinylethylpyridinium bromide.

The error caused by the penetration of 0.01 N hydrochloric acid in this resin is less than the experimental error ($\pm$0.02) for all the degrees of crosslinking studied. However, with 0.1 N hydrochloric acid, this error is significant with 4% or less of divinylbenzene.

The agreement among the various methods is somewhat less satisfactory for Dowex 1 than for Dowex 50. The correction for the hydrochloric acid taken up by the anion-exchange resin and released during washing is significant for both concentrations of acid and for all the degrees of crosslinking studied. As mentioned above, this sorption and release of hydrochloric acid by Dowex 1 are due not only to the DONNAN effect but also to the presence of a small number of weakly basic groups in the resin.

Both cation- and anion-exchange resins have smaller interstitial volumes when the crosslinkage is small. This is probably due to the greater deformability of the resins of low crosslinkage.

Dowex 50 seems to have a slightly smaller interstitial volume than Dowex 1 of the same crosslinkage, especially if the degree of crosslinking is small. This may be due to the greater density of Dowex 50, which would result in better settling and closer packing of the column.

The relative interstitial volumes (V/V_b) of Dowex 50–X8, 200–400 mesh, in the lithium and barium forms were determined with the polysoap and found to be 0.400 and 0.402, respectively. Since these results do not differ greatly from the value for the hydrogen form (Table IV), it is concluded that the form of the resin influences the relative interstitial volume to a small extent only.

Several samples of Dowex 50-X8 of various mesh sizes, all in the hydrogen form, were subjected to determinations of V/V_b with 0.01 N hydrochloric acid. These results indicate that the particle size has only an insignificant effect on the interstitial volume, provided, of course, that the range of sizes is not so great that the smallest particles pack in the interstices of the large particles.

When any ion-exchange resin, especially one of low crosslinkage, is exposed to a concentrated aqueous solution, the particles become smaller and more rigid than when they are in contact with water or a dilute solution. For this reason, it is doubtful if the results of Table IV, obtained with dilute solutions, are valid for concentrated solutions. To investigate this point, Dowex 50-X2, 200–400 mesh, was converted to the sodium form, equilibrated with 1 M or 5 M sodium nitrate and subjected to determinations of V/V_b by the use of polyphosphate. Since sodium polyphosphate has very limited solubility in these concentrations of sodium nitrate, solutions of the polyphosphate as low as 0.0001 M (with respect to the monomeric unit) were prepared in the water or aqueous sodium nitrate as solvent. The results are given in Table V.

Two conclusions may be drawn from these results. (1) Within the range of con-

TABLE V

RELATIVE INTERSTITIAL VOLUMES OF DOWEX 50-X2 IN SOLUTIONS OF SODIUM NITRATE

Interstitial liquid	*Concentration of polyphosphate*			
	0.01 M	*0.001 M*	*0.0002 M*	*0.0001 M*
Water	0.289	0.294		0.284
1 M NaNO$_3$		0.327		
5 M NaNO$_3$			0.385	0.381

centrations of polyphosphate used for the determination of the interstitial volume, the concentration of this compound has no effect on the result. (2) The interstitial volume increases markedly as the concentration of ambient sodium nitrate is increased from 0 to 5 M. It is noteworthy that the relative interstitial volume of Dowex 50-X2 in 5 M sodium nitrate agrees within the experimental error of 0.02 with the values of Dowex 50-X8 or -X16 in water. This probably means that the X2 resin in 5M sodium nitrate has approximately the same degree of rigidity as the X8 or X16 resins in water.

Finally, it should be noted that irregularly shaped resins have much greater relative interstitial volumes than do spherical resins[10].

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SUMMARY

The relative interstitial volumes of ion-exchange columns were measured by equilibrating the columns with a standard solution, rinsing out the interstitial solution and determining the amount of solute in the rinsings. Solutions of three polyelectrolytes and of hydrochloric acid were used for this purpose. When hydrochloric acid was used, corrections were generally necessary because of the penetration of the acid into the resin. Satisfactory agreement was obtained among the various methods. Within the experimental error, the relative interstitial volume is independent of the exchangeable ion of the resin and of the mesh size. The interstitial volume decreases with decreasing crosslinkage.

RÉSUMÉ

Les volumes intersticiels relatifs de colonnes d'échangeurs d'ions ont pu être mesurés. Pour cela, on a équilibré les colonnes avec une solution étalon, rincé la solution intersticielle et déterminé la teneur en solute des eaux de rinçage. Le volume intersticiel relatif est indépendant de l'ion échangeable de la résine et de la grosseur de ses grains.

ZUSAMMENFASSUNG

Zur Messung des relativen interstitiellen Volumens von Ionenaustauscher-Kolonnen wurden Standardlösungen mit den Kolonnen ins Gleichgewicht gebracht und nach Auswaschen der Kolonnen der Gehalt an gelöster Substanz in dem Waschwasser bestimmt. Das relative interstitielle Volumen erwies sich als unabhängig vom austauschbaren Ion und der Korngrösse des Harzes.

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# SPECTRAL DETECTION OF TERMINAL RING QUINONES

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INTRODUCTION

Specific colorimetric methods for the analysis of all types of quinones are in critical need. Terminal ring quinones, such as benzoquinone and α-naphthoquinone, have been detected with ethyl malonate in alkaline solution[1]. KESTING has reported that color tests are given by benzoquinone, α-napthoquinone and β-naphthoquinone in alkaline alcoholic solution on reaction with malononitrile, ethyl benzoylacetate, acetylacetone, or benzoylacetone[2-4]. CRAVEN[5] has obtained brilliant, although unstable, color reactions for benzoquinone, *o*-toluquinone, chloranil, thymoquinone, and α-naphthoquinone with ethyl cyanoacetate in alcoholic ammonia. β-Naphthoquinone did not react. In dilute alkali, nitromethane is stated to give a blue color with α-naphthoquinone and a violet color with β-naphthoquinone[6]. In our laboratory, many of these reagents were tried in alkaline 2-methoxyethanol solution. In many cases unstable colors and insensitive reactions were obtained. For this reason a group of new reagents for the colorimetric analysis of quinones is introduced in this paper.

Quinones giving a positive test contain the grouping $O=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-X$, where X is hydrogen or halogen. The reagents are azonium heterocyclic derivatives containing an activated methyl group *ortho* or *para* to the azonium nitrogen. The mechanism involves addition of the methyl group to the activated double bond of the quinone followed by air oxidation to a blue or green dye, *e.g.* with *N*-methylquinaldinium iodide and α-naphthoquinone the following reaction takes place:

I: λ_{max} 660 mμ
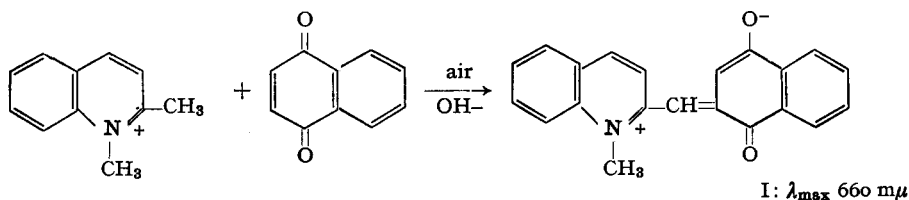
The dye, I, has been prepared by KIPRIANOV[7] and absorbs at 670 mμ in alcohol.

EXPERIMENTAL

Reagents

Lepidine, quinaldine, 2-methylbenzoxazole, 2-methylbenzothiazole, 1-ethyl-quinaldinium iodide, and 1-ethyl-2,6-dimethylquinolinium iodide were obtained from Distillation Products; 6-ethoxyquinaldine was obtained from the Aldrich Chemical Co.

The azonium methosulfates were prepared by slightly modified procedures of the following preparation of 1-methyl-quinaldinium methosulfate: 28 g of quinaldine and 25 g of methyl sulfate were mixed thoroughly in an ice bath. The mixture was allowed to stand at room temperature until an exothermic reaction had taken place and the mixture had solidified. The product was crystallized from *n*-propyl alcohol. The 6-ethoxy derivative was prepared in a small volume of boiling acetone; the lepidine derivative was prepared at room temperature. Details of these preparations can be found in the literature[8].

Benz [e] acephenanthrylene-9,12-dione, m.p. 248–249°, was prepared by literature procedure[9].

Equipment

A Cary Model 11 Recording spectrophotometer was used for wave-length measurements. For time studies an American Optical Company Rapid Scan Spectrophotometer was used.

Test procedure

To an accurately measured 5–50 ml of the 2-methoxyethanol test solution was added 1 ml of a 2% 2-methoxyethanol solution of the quinolinium reagent. The mixture was shaken, and after 8–9 min it was diluted to approximately 50 ml with 2-methoxyethanol. Ten min after the addition of reagent, 2 ml of 10% aqueous tetraethylammonium hydroxide was added, followed by dilution of the mixture to 100 ml with 2-methoxyethanol. Within ten min the absorption spectrum was determined from 500–800 mμ. The data on the more intense and much more stable long wave-length band are reported in Table I. One-tenth the volumes can also be used in the procedure.

TABLE I

SPECTRAL DETECTION OF TERMINAL RING QUINONES

Compound	λ_{max} (sens.) [a]				
	1,2-Dime [b]	*1-Et-2-me* [c]	*1-Et-2,6-dime* [c]	*1,2-Dime-6-etO* [b]	*1,4-Dime* [b]
Benzoquinone	650 (0.007)	655 (0.010)	670 (0.006)	685 (0.006)	700 (0.008)
2,5-Dichlorobenzoquinone	655 (0.012)	685 (0.025)	660 (0.025)	670 (0.014)	715 (0.014)
Chloranil	655 (0.013)	660 (0.020)	660 (0.090)	670 (0.008)	715 (0.023)
1,2-Naphthoquinone	670 (0.060)	670 (0.060)	660 (0.060)	635 (0.060)	720 (0.057)
Sodium 1,2-naphthoquinone -4-sulfonate	660 (0.045)	670 (0.30)	655 (0.045)	640 (0.040)	685 (0.044)
1,4-Naphthoquinone	660 (0.023)	660 (0.023)	675 (0.019)	685 (0.013)	700 (0.020)
2-Methyl-1,4-naphtho-quinone	635 (0.043)	675 (0.070)	650 (0.041)	665 (0.027)	670 (0.027)
2,3-Dichloronaphtho-quinone	675 (0.15)	5 (0.027)	690 (0.014)	700 (0.012)	720 (0.019)
Benz[e] acephenanthrylene -9,12-dione	715 (0.025)	670 (0.022)	735 (0.020)	750 (0.025)	775 (0.10)

[a] In μmoles per 3 ml giving an optical density of 0.1 in a cell of 1-cm path length.
[b] Quinolinium methosulfate.
[c] Quinolinium iodide.

DISCUSSION

In a previous paper a novel thermochromic test for polynuclear inner-ring *p*-quinones was described[10]. With this test the presence of large polynuclear *p*-quinonic type compounds was demonstrated in air particulates. In the present tests inner-ring *o*- and *p*-quinones, such as phenanthraquinone, 5,6-chrysenequinone anthraquinone, and naphthacenequinone gave negative results. Other types of aromatic carbonyl compounds, such as anthanthrone, benzanthrone, fluorenone, benzophenone, aceto-

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phenone, benzalacetone, salicaldehyde, 2-hydroxy-1-naphthaldehyde, and *p*-dimethylaminobenzaldehyde also gave negative results. As far as could be determined the tests described in this paper are specific for terminal-ring quinones.

Many activated methylene compounds were found to give color reactions with terminal ring quinones in alkaline dimethylformamide or 2-methoxyethanol solution, *e.g.* nitromethane, malonitrile, diketene, 3-thenoyl-1,1,1-trifluoroacetone, benzoylacetonitrile, 3-ethylrhodanine, 3-methyl-1-phenyl-5-pyrazolone, ethoxymethylenemalononitrile, and diethyl ethoxymethylenemalonate.

The nonketonic methylene reagents (*e.g.* malononitrile, nitromethane, etc.) gave unstable colors under the conditions of the procedure, while the ketonic methylene reagents apparently reacted with themselves slowly in alkaline solution to give colored dyes. This self-condensation is indicated by a study of the stability of the color obtained in the reaction of 3-ethylrhodanine with chloranil. Visually the color of the solution changed drastically with time while spectrally the 650 mμ band changed but slightly over a period of one-half hour, Fig. 1. The color change from green to dirty brown is due to the reaction of 3-ethylrhodanine, probably with itself, to give a dye absorbing at 530 mμ. This byproduct interferes with the color test but not with the spectral test.
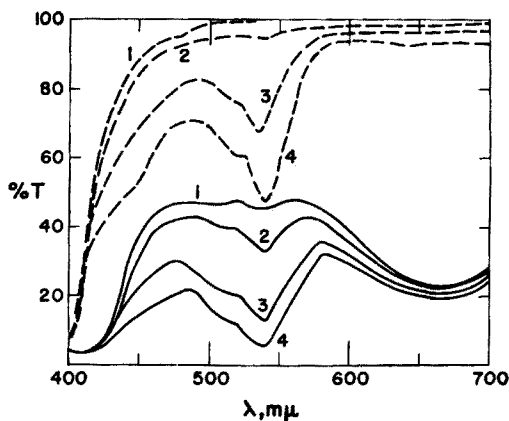
Fig. 1. Effect of time on visible absorption spectra. 10^{-4} *M* chloranil reacted with a 2% solution of 3-ethylrhodanine in 2-methoxyethanol by standard procedure. Blank solutions (minus chloranil) (– – –); Test solutions (————): 1. three min; 2. six min; 3. sixteen min; 4. thirty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

3-Ethylrhodanine appeared to be the best of the activated methylene compounds, *e.g.*, in dimethylformamide solution by the standard procedure – with *p*-benzoquinone, λ_{max} 635 mμ, sens. 0.007; chloranil, λ_{max} 650 mμ, sens. 0.04; 2,3-dichlorobenzoquinone, λ_{max} 660 mμ, sens. 0.01; 1,4-naphthoquinone, λ_{max} 715 mμ, sens. 0.025; 2-methyl-1,4-naphthoquinone, λ_{max} 720 mμ, sens. 0.05; 2,3-dichloro-1,4-naphthoquinone, λ_{max} 705 mμ, sens. 0.05, and benz[e]acephenanthrylene-9,12-dione, λ_{max} > 800 mμ. 1,2-Naphthoquinone and its 4-sodium sulfonate derivative gave green colors which faded rapidly. 2-Hydroxy-1,4-naphthoquinone gave negative results with all the reagents.

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Of all the compounds tried as reagents, the quinaldinium derivatives gave the most sensitive and stable colors (green in all instances) (Table I). The wave-length maxima for the dyes formed in the test ranged from 635–775 mμ. In most cases the benzoquinone derivatives gave the most sensitive reaction while the two 1,2-naphthoquinone derivatives gave the least sensitive reaction. If the quinones are analyzed within 10 min after they are reacted with a quinolinium derivative, there is very little change in the color or intensity of the long wave-length band. Over a period of 1–1/2 h, new bands arise near 560 mμ and gradually increase in intensity, eventually interfering with the analysis in the long wave-length region (Fig. 2).
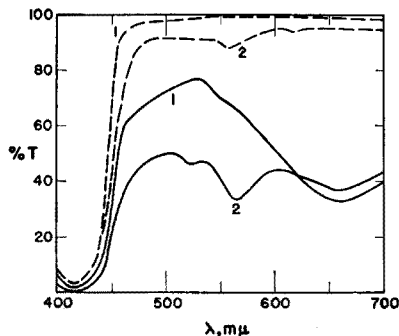
Fig. 2. Effect of time on visible absorption spectra. 2 · 10^{-5} M chloranil reacted with a 2% solution of 1-ethyl-2,6-dimethylquinolinium iodide in 2-methoxyethanol by standard procedure. Blank solution (minus chloranil) (– – –); Test solutions (———); 1. three min; 2. eighty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

SUMMARY

Terminal ring quinones can be detected specifically by a simple spectroscopic method involving reaction of the quinone with quinaldinium or lepidinium salts in alkaline solution. Other types of quinones and carbonyl derivatives have given negative results. 3-Ethylrhodanine can also be used as a reagent, especially for terminal ring p-quinones. All of these colorimetric procedures are amenable to quantitation.

RÉSUMÉ

Un groupe de nouveaux réactifs est proposé pour l'analyse colorimétrique de quinones.

ZUSAMMENFASSUNG

Chinone lassen sich colorimetrisch mit Hilfe von Chinaldin-oder Lepidin-salzen in alkalischem Medium nachweisen.

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BOOK REVIEWS

GMELINS *Handbuch der anorganischen Chemie*. 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim, 1958/9.
Fluor (Ergänzungsband), System-Nummer 5, 258 Seiten, kartoniert DM 145,—, Ganzleinen DM 150.—.

Dieser Ergänzungsband, der Prof. Dr. OTTO HAHN gewidmet ist, umfasst die Forschungsergebnisse der Jahre 1926 bis 1949. In diese Periode fällt die zunehmende Bedeutung der Fluorchemie, die zum Teil auf der Erkenntnis der Bedeutung des Fluors in der Zahnheilkunde beruht, zum grossen Teil aber auf die Entwicklung fluorierter Polymere mit technisch sehr interessanten Eigenschaften zurückzuführen ist.

Die Einteilung folgt dem üblichen Schema: Vorkommen, Darstellung, physikalisches und chemisches Verhalten, analytische Methoden. Dann folgen die Verbindungen mit Wasserstoff, Sauerstoff und Stickstoff mit Angabe der Darstellungsmethoden. Im Kapitel über die Herstellungsmethoden wird besonders auf die Gefahren im Umgang mit Fluor hingewiesen.

Als begrüssenwerte Neuerung enthält dieser Band ein zusätzliches Inhaltsverzeichnis in englischer Sprache sowie marginale Inhaltsangabe der einzelnen Kapitel ebenfalls in englischer Sprache.

Silicium, Teil C: *Organische Siliciumverbindungen*. System-Nummer 15, 501 Seiten, kartoniert DM 276.—, ganzleinen DM 281.—.

Mit dem jetzt erschienenen Band „Silicium Teil C" beginnt die neue System Nr. 15. Der vorliegende Teil C behandelt ausschliesslich die Organo-Siliciumverbindungen, die durch die Entwicklung der Silikone eine überragende Bedeutung erlangt haben. Der grösste Teil dieses Bandes behandelt die Methoden der Darstellung dieser Verbindungen und beschreibt deren Eigenschaften, wobei eine Einteilung in Tetraalkyl-, Alkylhydrogen-, Halogen-, Thio-, Amino- und Alkoxysilane, Silanole, Siloxane und Kieselsäureester erfolgte. Insgesamt werden mehr als 3000 Verbindungen, teils einzeln, teils gruppenweise zusammengefasst, aufgeführt. Etwa 100 Seiten sind einer Behandlung der Chemie der Silikone gewidmet, wobei auch spezielle Herstellungsfragen berücksichtigt wurden. Anschliessend werden die Anwendungsmöglichkeiten der Silikone. (als Oele, Pasten, Fette und Harze) einschliesslich des Silikonkautschuks und anderer Spezialprodukte besprochen.

Der Band enthält ein Inhaltsverzeichnis in deutscher und englischer Sprache und ausserdem auf den Inhalt der einzelnen Kapitel durch Randbeschriftung (englisch).

K. EDER (Genf)

English for the Scientist par Cl. DUVAL - Edition CNRS, 5ème Ed., Paris 1958, 99 pages, fr. 500.—.

La 5ème édition, revue et corrigée, de ce manuel est sortie de presse; c'est dire combien ce livre de vocabulaire scientifique et technique, et de syntaxe est apprécié de tous ceux qui désirent pouvoir se servir d'une langue dans laquelle une grande partie de la science d'aujourd'hui est écrite.

L'oeuvre est conçue de telle façon que chimiste, physicien et mathématicien, aussi bien que biologiste et médecin y trouveront à leur convenance les termes et constructions de phrase qu'ils peuvent rencontrer en feuilletant articles ou livres anglais. En outre, il permet à tous ceux qui le désirent, de s'approprier une connaissance suffisante d'anglais technique, qui leur permettra d'écrire, de suivre une discussion, de s'exprimer dans cette langue. Le livre est agrémenté de textes anglais, traitant de quelques découvertes ou expériences intéressantes. Des thèmes sont prévus qui doivent permettre à l'étudiant "de faire le point dans ses études littéraires". Celles-ci peuvent – selon l'auteur – facilement être menées à bien, moyennant un petit travail personnel de 3 heures par semaine. A recommander.
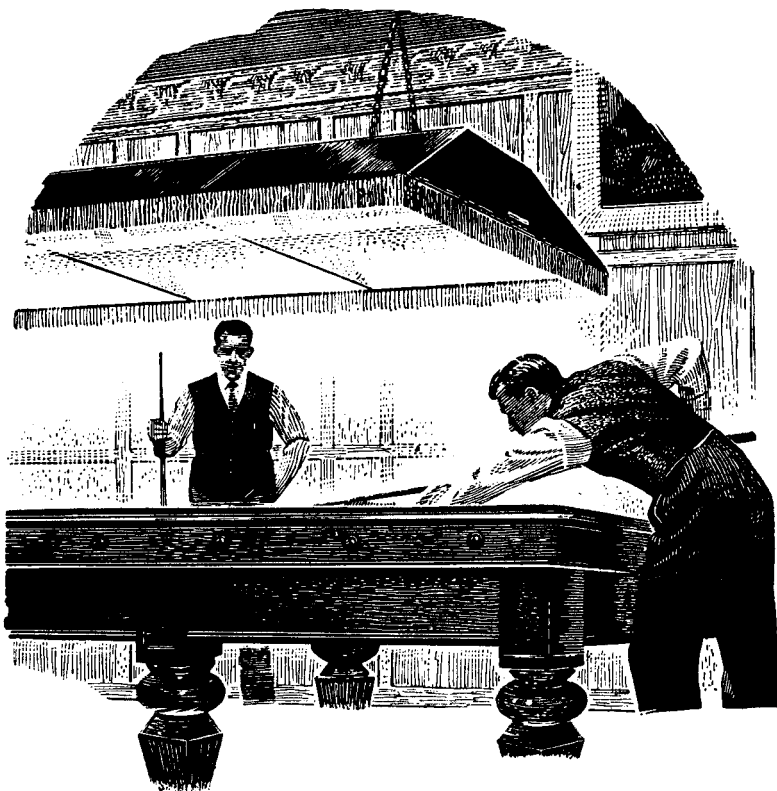
P. DE BIEVRE (Gand)

CONTENTS

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