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AN ABSORPTIOMETRIC DETERMINATION OF PERCHLORATE
BY MEANS OF A NOVEL COLOURED LIQUID ANION
EXCHANGER

A novel liquid anion exchanger can be prepared from tetra-*n*-hexylammonium iodide and Erdmann's salt, $(\text{NH}_4)[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$. When a solution of this quaternary erdmannate in a suitable organic solvent ($\epsilon_{\text{max}} = 15,700$ at $355 \text{ m}\mu$) is equilibrated with an aqueous solution of a salt, the coloured erdmannate ion is displaced to a greater or less extent: the effect decreases in the order $\text{ClO}_4^- \gg \text{ClO}_3^- > \text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-}$ etc. The effects of changes in the organic solvent composition, of ionic strength, and of other variables on the position of equilibrium have been studied with a view to defining the optimum conditions for the absorptiometric determination of perchlorate ion ($\geq 25 \mu\text{g}$) in the presence of chlorate and other ions. Methods are proposed for eliminating those ions that form insoluble silver salts and to allow for the presence of substantial proportions of chlorate or nitrate ions.

W. E. CLIFFORD AND H. IRVING,

Anal. Chim. Acta, 31 (1964) 1-10.

SINE-WAVE POLAROGRAPHIC DETERMINATION OF ZIRCONIUM OR NIOBIUM IN AQUEOUS MEDIA

The sine-wave polarographic determination of zirconium in aqueous media was investigated using solutions which were $0.55-5.5 \cdot 10^{-3} \text{ M}$ in zirconyl chloride and 1 M in potassium chloride and had been adjusted to pH 2.0 with hydrochloric acid. It was possible to determine zirconium in the concentration range of 0.05 to 0.4 mg per ml. The sine-wave polarographic behavior of zirconium in aqueous solutions in the pH range 2-3 is discussed. The sine-wave polarographic determination of niobium in aqueous media was investigated using concentrated sulfuric acid containing 5 to 0.1 mg of niobium per ml in a supporting electrolyte of citric acid; the determination of niobium was possible down to 0.1 mg of niobium per ml of concentrated sulfuric acid although the D.C. polarographic method was impractical for the determination of less than 0.5 mg of niobium per ml.

M. KASAGI AND C. V. BANKS,

Anal. Chim. Acta, 31 (1964) 11-16.

PRELIMINARY STUDIES OF PRECIPITATION TITRATIONS
OF ORGANIC COMPOUNDS USING POLAROVOLTRIC
END-POINT INDICATION

PART I. TITRATION OF ORGANIC BASES WITH FERROCYANIDE

Precipitation titrations of a number of organic bases have been carried out in acid solution with ferrocyanide. The influence of several factors, principally pH value, on the stoichiometry of the reactions has been examined.

M. R. F. ASHWORTH, H. GÖTTEL AND J. SCHNEIDER,
Anal. Chim. Acta, 31 (1964) 17-23.

THE FORMATION OF REDUCED PHOSPHOMOLYBDIC
COMPLEXES

(in French)

The phosphobismuthomolybdic, phosphotitanomolybdic and similar complexes are reduced at ordinary temperature, which can be understood from the constitution of these compounds. The efficacy of these elements (Bi, Ti, Zr, etc.) which are linked with the central atom of the heteropolyacid, in assisting the reaction of different reducing reagents, is emphasized.

M. JEAN,
Anal. Chim. Acta, 31 (1964) 24-32.

LIQUID-LIQUID EXTRACTION OF COBALT
THIOCYANATE WITH TRIISOCTYLAMINE

Cobalt forms a coloured complex with triisooctylamine and thiocyanate in carbon tetrachloride. The green organic phase has maximum absorbance at $627.5\text{ m}\mu$ and Beer's law is obeyed in the range 0-10 mg Co. The molar extinction coefficient is 1895. The distribution coefficient at room temperature is 5.6. A composition of the coloured species is proposed.

A. R. SELMER-OLSEN,
Anal. Chim. Acta, 31 (1964) 33-37.

AN IMPROVED DIRECT TITRATION OF α -EPOXY COM-
POUNDS USING CRYSTAL VIOLET AS THE INDICATOR

α -Epoxy compounds, such as glycidyl ethers and esters, can be rapidly determined by direct titration with perchloric acid in the presence of cetyltrimethylammonium bromide. Acetic acid is the preferred medium and crystal violet serves as the indicator.

R. DIJKSTRA AND E. A. M. F. DAHMEN,
Anal. Chim. Acta, 31 (1964) 38-44.

IODINE TRICHLORIDE IN GLACIAL ACETIC ACID AS AN OXIDIZING TITRANT

A systematic study of the redox reactions of iodine trichloride with various inorganic ions in glacial acetic acid medium is described. Sodium sulphite, arsenic trichloride, antimony trichloride, iron(II) perchlorate and mercury(I) perchlorate were examined. Potentiometric and amperometric methods were used to follow the reduction of iodine trichloride, which yields different products according to the type of reductant.

G. PICCARDI AND P. LEGITTIMO,

Anal. Chim. Acta, 31 (1964) 45-50.

DETERMINATION OF STRONTIUM COPRECIPITATED WITH BARIUM BY X-RAY EMISSION SPECTROSCOPY

X-Ray emission spectroscopy allows detection of as little as 0.02 % strontium in barium chromate. This method has been applied to evaluate the effectiveness of 4 procedures for separating barium and strontium by chromate precipitation. All of the procedures checked require at least 2 precipitations for a satisfactory separation. Of the 4 methods checked, that of BEYER AND RIEMAN is recommended on the basis of convenience and effectiveness of separation.

G. J. WONSIDLER AND R. S. SPRAGUE,

Anal. Chim. Acta, 31 (1964) 51-57.

FLAME PHOTOMETRIC DETERMINATION OF POTASSIUM IN SEA WATER AND MARINE ORGANISMS

A convenient flame photometric procedure for determining potassium in sea water and biological materials is described. Factors affecting the intensity of the spectral line emitted by potassium ions were studied. The major constituents of sea water showed no spectral interference on the potassium analysis. Chloride ions and sulphuric acid gave a negative radiation interference while sodium ions showed a positive effect. The "internal standard addition" procedure was used for eliminating the effect of these interfering constituents.

An average potassium/chlorinity ratio of 0.538 was obtained for the Pacific coastal water with potassium concentration being expressed in mg-atom. The applicability of this procedure for the determination of potassium in biological materials was also demonstrated.

T. J. CHOW,

Anal. Chim. Acta, 31 (1964) 58-63.

ASSESSING THE ACTIVITY CONCENTRATION OF β -EMITTERS BY MEANS OF THE END-WINDOW G.M. TUBE

The activity concentrations of β -emitters including ^{35}S (0.15 MeV) and presumably also ^{14}C (0.14 MeV) may be determined with satisfactory accuracy using an end-window G.M. counter. For single preparations (if weighed), the described procedure warrants that the standard error will not exceed 0.8%, if the amount of substrate is kept below 0.2 mg/cm², and if carrier-free solutions are avoided. With a minimum of 4 preparations per sample solution, the error of the mean should not exceed 0.4%.

G. H. BOLT AND B. G. M. PIETERS,

Anal. Chim. Acta, 31 (1964) 64-70.

THERMOGRAVIMETRIC INVESTIGATION OF SCANDIUM, YTTRIUM AND THE RARE EARTH METAL DILITURATES

Thermolysis curves for scandium, yttrium, lanthanum, cerium(III), neodymium, samarium, gadolinium, dysprosium and erbium diluturates are described. Scandium diluturate forms a 15-hydrate which dehydrates in 3 steps. The other diluturates all form 12-hydrates which dehydrate smoothly. All of the anhydrous diluturates are thermally stable to about 240°.

Solubilities in water for scandium, yttrium, lanthanum, cerium(III), neodymium, samarium, gadolinium, dysprosium and erbium diluturates are given. Scandium diluturate is the most soluble and neodymium diluturate the least soluble. Solubilities of rare earth diluturates not investigated can be predicted approximately.

Methods for thermogravimetric determination of yttrium, lanthanum, neodymium, samarium, gadolinium, dysprosium and erbium as the diluturates have been developed. The precipitates are quite dense, easily handled and filterable. Weighing as the diluturate salts gives these determinations a very favorable gravimetric factor.

M. W. GOHEEN AND R. J. ROBINSON,

Anal. Chim. Acta, 31 (1964) 71-80.

SELECTIVE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM(IV) WITH 2-THENOYLTRIFLUOROACETONE

A new rapid method is suggested for simultaneous extraction and spectrophotometric determination of titanium with 2-thenoyltrifluoroacetone (TTA). The greenish-yellow chelate of titanium(IV)-TTA can be extracted with isoamyl alcohol-benzene and measured at 430 m μ . The extraction can be carried out in presence of Al, Cr(III), Th, Zr, Mo, W, borate, phosphate, citrate, tartrate and EDTA.

A. K. DE AND M. S. RAHAMAN,

Anal. Chim. Acta, 31 (1964) 81-85.

SORPTION OF AMIDES BY CATIONIC EXCHANGE
RESINS FROM NONAQUEOUS SOLVENTS

Separation of weakly basic acetanilide, N-methylacetanilide, and N-n-propylacetanilide could not be accomplished using a conventional sulfonic acid resin and various mixed eluants containing methanol and acetonitrile. The chromatograms showed elution bands that were broad and that tailed badly. However, with a new macroreticular resin, some separations were obtained with the same nonaqueous eluants that had been used with the conventional resin. Although separation of acetanilide from the two N-substituted acetanilides was almost complete, the separation of the two N-substituted compounds was not.

Acetamides were separated from acetanilides because the former were not retained by the resin when a 1:9 methanol-acetonitrile eluant was used.

The two important parameters which render these separations possible are probably solvation and hydrogen bonding around the sulfonic acid group of the resin and resin matrix attraction. Methanol is a better solvating liquid than acetonitrile. In acetonitrile the amide probably associates through the carbonyl with the sulfonic acid; in methanol this association does not occur.

J. E. CASSIDY AND C. A. STREULI,

Anal. Chim. Acta, 31 (1964) 86-96.

POLAROGRAPHIC DETERMINATION OF
CYSTINE DISULPHOXIDE

(in French)

(Short Communication)

J. FONDARAI, J. L. GRAND AND P. DUBOULOZ,

Anal. Chim. Acta, 31 (1964) 97-99.

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AN ABSORPTIOMETRIC DETERMINATION OF PERCHLORATE BY MEANS OF A NOVEL COLOURED LIQUID ANION EXCHANGER

WARREN E. CLIFFORD* AND HARRY IRVING

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

(Received February 28th, 1964)

In contrast to ammonium chloride and the hydrochlorides of amines of low molecular weight, many quaternary ammonium salts and salts of amines that contain bulky or long-chain alkyl groups are soluble in solvents of low polarity such as chloroform. When such organic solutions are equilibrated with a second immiscible liquid *e.g.* an aqueous salt solution, an exchange of anions A^- and B^{n-} , may take place in accordance with the general equation:

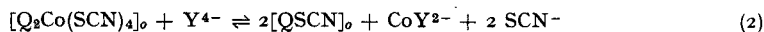


where $R = H$ or alkyl, and the subscript o is used to distinguish the species in the organic phase from those in the aqueous phase. The formal analogy to the behaviour of conventional anion-exchange resins is recognised by referring to such long-chain ammonium salts as 'liquid anion exchangers'.

Liquid anion exchangers have been used in studies of the stabilities of complex ions¹ but their main applications in analytical chemistry have been in the solvent extraction of metal complexes wherein great selectivity is possible. For example, niobium and tantalum can be separated from solutions in hydrochloric acid², zinc can be separated from manganese, cobalt, and nickel³, and zirconium from hafnium⁴. By using salts of tertiary amines, protactinium can be extracted⁵ as the complex with $Pa(NO_3)_6^-$, uranium as an anionic complex with 8-hydroxyquinoline⁶, and cobalt as thiocyanate⁷. If the organic phase is coloured an absorptiometric finish is possible and the procedure can then be adapted to the quantitative determination of the metal that has been selectively extracted.

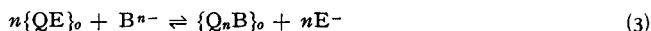
In the course of a general study of liquid anion exchangers which sought to define those factors which influence the position of equilibrium in eqn. (1) for various combinations of anions A^- and B^{n-} with a view to formulating a less empirical approach to problems of analytical separations with these materials, we were struck by the fact that ethylenediaminetetraacetic acid (EDTA; H_4Y) could be used to 'strip' many metals from the organic phase when a quaternary ammonium salt (specifically tetra-*n*-hexylammonium iodide) was employed. For example, if Q^+ is used to represent the quaternary ammonium ion the equilibrium

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lies far to the right. This implies that the complex CoY^{2-} has little tendency to displace thiocyanate ions from this liquid exchanger and experiments showed that this was equally true of halide ions. Furthermore, the ion CoY^- derived from EDTA and Co(III) was also unable to displace halide ions. This result was unexpected as our general studies had indicated that it was precisely those anions of large size and low charge that are most effective, *ceteris paribus*, in displacing chloride ions. However when a further comparison was made with another bulky uninegative complex of Co(III), *viz.* the anion of Erdmann's salt, $(\text{NH}_4)[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, this was found to be readily extracted into the organic phase to give a strongly coloured solution. A similar result was found with the anion of Morland's salt, $[\text{Co}(\text{NH}_3)_2(\text{SCN})_4]^-$.

If a solution of tetra-*n*-hexylammonium erdmannate, which we will henceforward abbreviate as Q^+E^- is prepared in, *e.g.*, chloroform it is readily possible to investigate such equilibria as



for we can determine by absorptiometry $[\text{QE}]_o$ (the equilibrium concentration of quaternary erdmannate in the organic phase) and/or $[\text{E}^-]$ (the equilibrium concentration of erdmannate ion in the aqueous phase). Both species obey Beer's law and have molecular extinction coefficients of the order of 10^4 . A further advantage of using a quaternary ammonium salt of a complex cobaltic anion is the attractive possibilities opened up of studying equilibria at high dilutions by making use of cobalt-60.

If Q^0 and B^0 are the initial concentrations of quaternary erdmannate and the anion B^{n-} respectively, we have for the mass balance of quaternary ammonium ion:

$$\text{Q}^0 = [\text{QE}]_o + n[\text{Q}_n\text{E}]_o \quad (4a)$$

for the mass balance of erdmannate ion:

$$\text{Q}^0 = [\text{QE}]_o + [\text{E}^-] \quad (4b)$$

and for the mass balance of anion, B^{n-} :

$$\text{B}^0 = [\text{B}^{n-}] + [\text{Q}_n\text{B}]_o \quad (4c)$$

It follows that the equilibrium constant of the reaction represented by eqn. (3) can be calculated from

$$K_B = [\text{E}^-]^{n+1}/(\text{Q}^0 - [\text{E}^-])^n(n\text{B}^0 - [\text{E}^-]) \quad (5)$$

if the equilibrium concentration of erdmannate ion is measured in the aqueous phase, and from

$$K_B = (\text{Q}^0 - [\text{QE}]_o)^{n+1}/(n\text{B}^0 - \text{Q}^0 + [\text{QE}]_o)([\text{QE}]_o)^n \quad (6)$$

if the equilibrium concentration of erdmannate is determined by measurements on the organic phase. Solutions of tetra-*n*-hexylammonium erdmannate are stable for at least a period of weeks if they are kept in the dark: both aqueous and organic solutions decompose fairly rapidly in bright daylight. A $10^{-4} M$ solution of quaternary erdmannate in 80% xylene-20% methylisobutyl ketone was equilibrated with 1 M sodium chloride containing $10^{-4} M$ sodium perchlorate and the phases were analysed spectrophotometrically after various times with the results shown in Table I.

Measurements of K_B for various anions, B^{n-} , showed that equilibrium constants for

the displacement of erdmannate ions decrease in the order $\text{ClO}_4^- \gg \text{ClO}_3^- > \text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{PO}_4^{3-}$. The possibility of exploiting these results for the determination of mixtures of perchlorate, chlorate, and chloride ions, such as occur in certain electrolytic oxidations, forms the main theme of this paper. To this end

TABLE I
STABILITY OF ERDMANNATE SOLUTIONS
(The figures give the percentage decomposition)

Time elapsed (min)	Organic phase		Aqueous phase	
	Dark	Light	Dark	Light
20	0	3.6	0.1	3.2
60	0	13.8	0.8	11.1
120	0	24.6	2.3	27.3
325	0	48.6	6.9	67.3

TABLE II
COMPARISON OF $(\text{C}_6\text{H}_{13})_4\text{N}^+\text{E}^-$ AND $(\text{C}_8\text{H}_{17})_3(\text{CH}_3)\text{N}^+\text{E}^-$ IN THEIR REACTIONS TOWARDS VARIOUS ANIONS

(Organic phase: $10^{-3} M \text{Q}^+\text{E}^-$ in chloroform. Aqueous phase: $0.9 M \text{Na}_2\text{SO}_4$ and $0.1 M \text{NaB}$)

Aqueous phase	$(\text{C}_6\text{H}_{13})_4\text{N}^+\text{E}^-$			$(\text{C}_8\text{H}_{17})_3(\text{CH}_3)\text{N}^+\text{E}^-$		
	$10^5[\text{QE}]_0$	10^3K_B	K_{ClO_4}/K_B	$10^5[\text{QE}]_0$	10^3K_B	K_{ClO_4}/K_B
B = ClO_4^-	1.97	492	—	1.31	752	—
B = ClO_3^-	42.6	7.73	64	79.9	16.6	45
B = NO_3^-	56.1	3.46	142	44.3	7.05	107
B = Cl^-	89.9	0.113	4340	78.8	0.572	1310

TABLE III
THE EFFECT OF VARYING Q^0 , THE INITIAL CONCENTRATION OF QUATERNARY ERDMANNATE IN CHLOROFORM ON THE CALCULATED EQUILIBRIUM CONSTANT

$[\text{NaClO}_4]$ in $0.9 M \text{Na}_2\text{SO}_4$, $\text{B}^0 =$	K_{ClO_4}		
	$0.1 M$	$0.05 M$	$0.01 M$
$\text{Q}^0 = 10^{-1} M$	0.285	0.265	0.261
$\text{Q}^0 = 10^{-2} M$	0.478	0.462	0.461
$\text{Q}^0 = 10^{-3} M$	0.503	0.486	0.492

it was necessary to determine the optimum conditions for (a) sensitivity, *i.e.* those for which K_{ClO_4} is as large as possible and (b) for selectivity, *i.e.* those for which the ratio $K_{\text{ClO}_4}/K_{\text{ClO}_3}$ is as large as possible.

It will be obvious that low solubility in water is a prime requisite for the quaternary salt and a product of high purity and well defined molecular composition is also desirable but not essential. This directs the choice among commercially available materials to tetra-*n*-hexylammonium salts; but we have also tested Aliquat 336 (a tricaprilmethyl ammonium salt) which, as shown in Table II, extracts perchlorate well but shows a poorer selectivity between perchlorate and chlorate, chloride and

nitrate. In all subsequent measurements the tetra-*n*-hexylammonium cation was used.

The equilibrium constant of eqn. (3) (where $n = 1$ and $B = \text{ClO}_4^-$) was found to vary little with the initial concentration of reactants (*cf.* Table III) provided that of the quaternary erdmannate did not rise above $10^{-2} M$: a more detailed study of this and similar equilibria will be presented elsewhere⁸.

The choice of organic solvent represents a compromise between a number of conflicting factors. A solvent lighter than water proved easier to handle than one that was denser. Xylene gave a higher value of K_{ClO_4} than chloroform and, more significantly, greater discrimination between perchlorate and chlorate, as shown in Table IV. However xylene will only dissolve tetrahexylammonium erdmannate to a limited extent to give a solution of about $6.6 \cdot 10^{-4} M$. Hexone (methylisobutyl ketone) is a much better solvent in which the solubility of the quaternary erdmannate can reach at least $0.1 M$: it also gives good discrimination between perchlorate and chlorate. However in this solvent the absolute value of K_{ClO_4} is rather low (Table IV). Mixtures of xylene and hexone were therefore examined and the composition 80% (v/v) xylene–20% hexone was selected since, in addition to its possessing the desirable properties listed above, the value of K_{ClO_4} does not appear to be sensitive to small changes in solvent composition so that errors will not be incurred by minor changes between successive batches of solvent mixtures. The molecular extinction coefficient of tetrahexylammonium erdmannate in 80% xylene–20% hexone is $1.57 \cdot 10^4$ at $355 m\mu$ where there is a well defined absorption maximum, and Beer's law is obeyed at least over the concentration range of $3 \cdot 10^{-6} M$ to $2 \cdot 10^{-4} M$ used in subsequent measurements.

TABLE IV

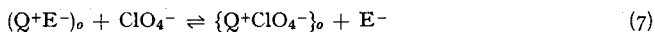
THE EFFECT OF CHANGES IN SOLVENT COMPOSITION ON VALUES OF K_B FOR PERCHLORATE, CHLORATE AND NITRATE

		Values of $10^3 K_{\text{ClO}_4}$				
Solvent: Xylene (%) 100		90	75	50	0	Chloroform
Hexone (%) 0		10	25	50	100	(100%)
<i>Aqueous phase</i>						
0.1 M NaClO ₄ ^a	1330	1260	1220	522	157	492
0.1 M NaClO ₃ ^b	2.97	2.55	2.55	0.759	0.363	7.73
0.1 M NaNO ₃ ^a	0.74	—	—	0.302	0.200	3.46

^a Together with 0.9 M sodium sulphate.

^b Together with 0.8 M sodium sulphate. The organic phase was $10^{-3} M$ quaternary erdmannate except for measurements with pure xylene when it was only $6.6 \cdot 10^{-4} M$.

The extent to which other ions might interfere in the determination of perchlorate in terms of the equilibrium



was next investigated (Table V).

Tests under slightly different conditions show that chlorate ions have a somewhat greater effect than nitrate ions (*cf.* Table IV). Cyanide and acetate interfere less than

chloride ions but some singly charged cyanide complexes (*e.g.* $\text{Ag}(\text{CN})_2^-$) may interfere strongly. Bromide and iodide have been found to displace erdmannate ions more effectively than do chloride ions and the same is true of the anions of certain substituted aliphatic carboxylic acids⁸. The small interference from hydroxide ions is

TABLE V
POSSIBLE INTERFERENCES IN THE DETERMINATION OF PERCHLORATE
(The percentage of erdmannate replaced by various anions)

<i>Aqueous phase</i>	<i>Percentage of erdmannate displaced^a</i>
0.1 <i>M</i> Sodium perchlorate	99.2
0.01 <i>M</i> Sodium perchlorate	92.9
1 <i>M</i> Potassium thiocyanate	98.1
1 <i>M</i> Sodium nitrate	58.4
1 <i>M</i> Sodium chloride	7.8
1 <i>M</i> Sulphuric acid	4.0
1 <i>M</i> Sodium hydroxide	1.3
1 <i>M</i> Sodium sulphate	1.0

^a The organic phase contained 10^{-3} *M* quaternary erdmannate.

TABLE VI
REMOVAL OF INTERFERING ANIONS BY PRECIPITATION WITH SILVER SULPHATE

<i>Interfering ions^a</i>	<i>Equilibrium concentration, $10^5[\text{QE}]_0$</i>	
	<i>Without treatment</i>	<i>After treatment</i>
None	1.62	—
10^{-2} <i>M</i> Potassium iodide	0.47	1.63
10^{-2} <i>M</i> Sodium thiocyanate	0.15	1.61
10^{-2} <i>M</i> Sodium iodate	—	1.62

^a All solutions contained in addition 0.9 *M* sodium sulphate.

especially valuable from the analytical point of view (*q.v.*) as is the even weaker interference by sulphate ions: other anions of high charge, *e.g.* PO_4^{3-} , $[\text{Fe}(\text{CN})_6]^{2-}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ show quite negligible interference.

Many of the ions that interfere seriously in the determination of perchlorate can be removed by a pretreatment with silver sulphate as shown in Table VI. Of other anions that cannot be removed with silver sulphate, interference by chlorate ions is greater than that by nitrate ions and more likely to occur. Table VII summarises the effect of chlorate ions on the determination of perchlorate and it is clear that this can be quite serious, amounting to about 5% when the ratio $[\text{ClO}_3^-]/[\text{ClO}_4^-]$ is 10, and about 35% when it is 100. This error can be reduced in several ways, *e.g.* by reducing chlorate to chloride with ferrous sulphate or sulphur dioxide, by determining the concentration of chlorate chemically and including the same amount in a calibration curve, or as we shall now show by means of a calculation based on a knowledge of the equilibrium constant, $K_{\text{ClO}_4} = 1.06$ of eqn. (7) and the value $K_{\text{ClO}_3} = 2.80 \cdot 10^{-3}$ obtained experimentally for the corresponding reaction involving chlorate ions (also in the presence of 0.9 *M* sodium sulphate).

When both perchlorate and chlorate are present simultaneously in the aqueous

phase in initial concentrations c and d respectively we have

$$[Q^+ClO_4^-]_0 = c \cdot K_{ClO_4} \cdot [QE]_0 / \{Q^0 + (K_{ClO_4} - 1)[QE]_0\} \quad (8)$$

and

$$[Q^+ClO_3^-]_0 = d \cdot K_{ClO_3} \cdot [QE]_0 / \{Q^0 + (K_{ClO_3} - 1)[QE]_0\} \quad (9)$$

On applying this latter equation to the data of Table VII for the experiment in which $Q^0 = 5 \cdot 10^{-5} M$, $c = 10^{-4} M$ sodium perchlorate, $d = 10^{-2} M$ sodium chlorate, and $[QE]_0 = 1.31 \cdot 10^{-5} M$ we have $[Q^+ClO_3^-] = 0.995 \cdot 10^{-5} M$, whence

$$[Q^+ClO_4^-] = Q^0 - [QE]_0 - [Q^+ClO_3^-] = 2.695 \cdot 10^{-5} M.$$

Finally from eqn. (7) we have

$$[ClO_4^-]_{aq.} = (Q^0 - [QE]_0) \cdot [Q^+ClO_4^-] / [QE]_0 \cdot K_{ClO_4} \\ = 7.16 \cdot 10^{-5} M,$$

whence

$c = (2.70 + 7.16) \cdot 10^{-5} = 0.988 \cdot 10^{-4} M$. Corrected values of c obtained in this way are listed in the penultimate column of Table VII from which it will be seen that the experimental error is now greatly reduced even in the presence of 100 times as much chlorate as perchlorate ion.

TABLE VII

THE EFFECT OF CHLORATE IONS ON THE DETERMINATION OF SODIUM PERCHLORATE (OF INITIAL CONCENTRATION c)

Initial aqueous phase ^a		$10^5[QE]_0$ found	K_{ClO_4} (calc.)	10^4c , calculated			
$NaClO_4, c$	$NaClO_3, d$			Using $K_{ClO_4} = 1.06$	Error (%)	Using $10^3 K_{ClO_3} = 2.80$	Error (%)
$2 \cdot 10^{-4} M$	—	0.965	1.06	—	—	—	—
$2 \cdot 10^{-4} M$	$10^{-3} M$	0.939	—	2.06	+3	2.03	+1.5
$1 \cdot 10^{-4} M$	—	1.625	1.05	—	—	—	—
$1 \cdot 10^{-4} M$	$10^{-3} M$	1.55	—	1.07	+7	1.03	+3
$1 \cdot 10^{-4} M$	$10^{-2} M$	1.31	—	1.36	+36	0.99	-1
$0.5 \cdot 10^{-4} M$	—	2.45	1.07	—	—	—	—
$0.5 \cdot 10^{-4} M$	$10^{-3} M$	2.40	—	0.526	+5	0.473	-5

^a Each aqueous phase was also 0.9 M with respect to sodium sulphate. The organic phase consisted of an equal volume of $5 \cdot 10^{-5} M$ tetra-*n*-hexylammonium erdmannate.

Errors due to nitrate ions can be corrected similarly by using the experimental value $K_{NO_3} = 7.1 \cdot 10^{-4}$. Thus measurements on a mixture of $10^{-2} M$ sodium nitrate with $10^{-4} M$ sodium perchlorate in a solution also containing 0.9 M sodium sulphate gave c (calc.) = $1.12 \cdot 10^{-4} M$ on the basis of $K_{ClO_4} = 1.06$ only, and $1.02 \cdot 10^{-4} M$ after correction for the presence of nitrate ions (error + 2%).

Since the method proposed depends on a knowledge of the actual value of K_{ClO_4} , it is important to see to what extent this is affected by changes in the ionic strength of the medium. Table VIII demonstrates the importance of this effect.

We have yet to show that K_{ClO_4} , the equilibrium constant of eqn. (7), is independent of variations in the values of $[ClO_4^-]$ and Q^0 . Although this condition is not actually essential to the development of an analytical procedure based on the displacement of erdmannate ions by perchlorate ions in that this could be made to depend on a calibration curve, the constancy of K_{ClO_4} over a wide range of variations in the para-

TABLE VIII

THE EFFECT OF CHANGES IN THE IONIC STRENGTH OF THE AQUEOUS PHASE ON THE EQUILIBRIUM BETWEEN PERCHLORATE AND A QUATERNARY ERDMANNATE

Aqueous phase	$10^6[QE]_0$	K_{ClO_4} (calc.)
— ^a	7.08 ^b	1.35
0.5 M Sodium chloride	7.48	1.26
1.0 M Sodium chloride	7.47	1.26
0.5 M Sodium sulphate	8.23	1.13
0.99 M Sodium sulphate	9.65	0.931

^a Each aqueous phase contained 10^{-2} M NaClO₄, with or without added salts.^b $Q^0 = 10^{-3}$ M quaternary erdmannate.

TABLE IX

MEASUREMENTS OF K_{ClO_4} UNDER DIFFERENT CONDITIONS TO DEMONSTRATE ITS CONSTANCY

Aqueous phase			Organic phase	
$c = \text{Initial conc. NaClO}_4$	Nature of salt added	Q^0	$10^6[QE]_0$	K_{ClO_4} (average)
10^{-1} M	—	10^{-3} M	0.751	1.32
10^{-2} M	—	10^{-3} M	7.08, 7.07, 7.10	1.55
10^{-1} M	0.9 M Na ₂ SO ₄	10^{-3} M	1.02, 1.09	0.94
10^{-2} M	0.9 M Na ₂ SO ₄	10^{-3} M	9.28, 9.19	0.98
10^{-3} M	0.9 M Na ₂ SO ₄	10^{-3} M	50.0, 50.5	0.98
—	0.9 M Na ₂ SO ₄	10^{-3} M	99.9, 99.9	—
$2 \cdot 10^{-4}$ M	0.9 M Na ₂ SO ₄	$5 \cdot 10^{-5}$ M	0.965	1.06
$1 \cdot 10^{-4}$ M	0.9 M Na ₂ SO ₄	$5 \cdot 10^{-5}$ M	1.63	1.05
$5 \cdot 10^{-5}$ M	0.9 M Na ₂ SO ₄	$5 \cdot 10^{-5}$ M	2.43	1.07
10^{-1} M	1.0 M NaCl	10^{-3} M	0.809, 0.766, 0.863	1.24
10^{-2} M	1.0 M NaCl	10^{-3} M	7.48, 7.75, 7.69	1.23
10^{-3} M	1.0 M NaCl	10^{-3} M	47.1, 47.9, 47.7	1.21
—	1.0 M NaCl	10^{-3} M	92.3, 92.2, 92.5 ^a	—
10^{-1} M	1.0 M NaNO ₃	10^{-3} M	0.772	1.38 (1.37) ^c
10^{-2} M	1.0 M NaNO ₃	10^{-3} M	6.46	1.50 (1.39) ^c
10^{-3} M	1.0 M NaNO ₃	10^{-3} M	29.9	5.5 (1.27) ^c
—	1.0 M NaNO ₃	10^{-3} M	41.2, 42.0 ^b	—

^a Whence $K_{Cl} = 6.3 \cdot 10^{-6}$.^b Whence $K_{NO_3} = 8.2 \cdot 10^{-4}$.^c Corrected values for the effect of [NO₃⁻] by calculation using $K_{NO_3} = 8.2 \cdot 10^{-4}$.

meters is established by the results shown in Table IX which further illustrate the (small) effects of different salt backgrounds.

For the particular case where $B^{n-} = ClO_4^-$, and $B^0 = c$, eqn. (6) can be rewritten in the equivalent form

$$K_{ClO_4} = (Q^0 - [QE]_0)^2 / (c - Q^0 + [QE]_0)([QE]_0) \quad (10)$$

and if this is expanded as a quadratic in $[QE]_0$, differentiation with respect to c gives

$$d(\log_e[QE]_0) = -dc + Q^0 \left(\frac{2}{K_{ClO_4}} - 1 \right) - 2[QE]_0 \left(\frac{1}{K_{ClO_4}} - 1 \right) \quad (11)$$

Since $K_{ClO_4} = 1$ for measurements in 0.9 M sodium sulphate, it happens fortuitously

that the last term in the denominator drops out and the right-hand side of eqn. (11) reduces to $-dc/(c + Q^0)$, *i.e.* to $-d \log_e(c + Q^0)$, provided that Q^0 remains constant. A plot of $\log_{10}[\text{QE}]_o$ against $\log_{10}(c + Q^0)$ should therefore be linear and of unit negative slope. This is shown to be the case in Fig. 1 which has been plotted from data in Table IX. In contrast, calibration curves with $\log[\text{QE}]_o$ plotted against $\log c$ (or $[\text{QE}]_o$ against c) are more or less strongly curved (Fig. 1, broken lines).

It also follows from eqn. (11) that the error in measuring c will decrease as c in-

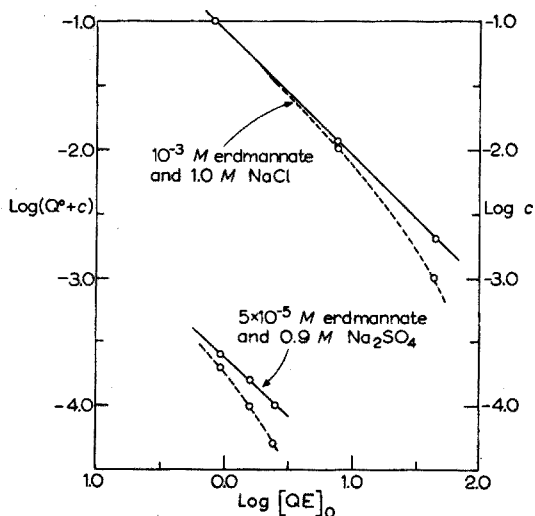


Fig. 1. Plots of $\log[\text{QE}]_o$ against $\log(Q^0 + c)$ (solid lines of unit negative slope) and against $\log c$ (broken lines) for the extraction of perchlorate ions by a solution of tetra-*n*-hexylammonium erdmannate dissolved in 80% xylene–20% hexone (v/v).

creases for any value of Q^0 . With these points in mind a detailed procedure can readily be developed for optimum working conditions such that the final equilibrium concentration of erdmannate in the organic phase, $[\text{QE}]_o$ should be at least $10^{-5} M$ thus giving an absorbancy of 0.16 in a 10-mm cell: the equilibrium concentration of perchlorate in the aqueous phase should be comparable with that of the initial erdmannate, Q^0 , so that the favourable range for B^0 can readily be deduced from eqn. (10).

Experience has shown that $Q^0 = 10^{-3} M$ is convenient in practice and that this permits a favourable range for c of $1-100 \cdot 10^{-3} M$. If the sample is very concentrated and contains unspecified amounts of interfering ions, the maximum possible dilution (to, *e.g.*, $10^{-4} M$ perchlorate) by means of 0.9 *M* sodium sulphate should be attempted and the determination carried out with $5 \cdot 10^{-5} M$ erdmannate. If on the other hand the concentration of perchlorate is inconveniently low, it can be concentrated by preliminary extraction with a tertiary amine after acidification with sulphuric acid. Thus three stages of extraction with 0.3 *M* Alamine 336 in xylene in a volume ratio of 1 organic : 100 aqueous phase followed by a strip with 2 *M* sodium hydroxide in a volume ratio of 3 organic : 1 aqueous phase will give an overall concentration factor of at least 100-fold. The presence of hydroxide ions will not influence the subsequent

determination of perchlorate by equilibration with an organic solution of tetra-*n*-hexylammonium erdmannate.

It is not our object here to give detailed procedures for specific types of analytical samples since these will vary with the nature and relative concentration of other ions present. About 25 μg of perchlorate (5 ml of a $5 \cdot 10^{-5}$ *M* solution) is about the minimum acceptable for analysis, and obvious simplifications in procedure can be made when interfering ions are absent. Direct determination of $[\text{QE}]_o$ as described below and reference to a standard curve, or calculation using $K_{\text{ClO}_3} = 1.06$ for measurements carried out in the presence of 0.9 *M* sodium sulphate will give results accurate to $\pm 5\%$ if $[\text{ClO}_3^-]$ is less than $5[\text{ClO}_4^-]$ and $[\text{NO}_3^-]$ is less than $15[\text{ClO}_4^-]$. With larger amounts of chlorate, the appropriate correction can be made mathematically as indicated in the text. Most other interfering ions can be removed with a pretreatment with silver sulphate. Although many synthetic mixtures have been analysed in this way the data recorded in the above Tables are representative and typical of what can be achieved.

EXPERIMENTAL

Erdmann's salt was prepared according to JÖRGENSEN's method⁹ and recrystallised from water. All other salts were of AnalaR quality and organic solvents were purified by standard methods before use.

Stock solutions of quaternary ammonium erdmannate were prepared by equilibrating a solution of tetra-*n*-hexylammonium iodide in hexone (about 0.1 *M*) with 4 successive portions of equal volumes of an aqueous solution containing a large excess of ammonium erdmannate (Erdmann's salt). These were then diluted with xylene to the desired concentration.

In order to determine the concentration of a displacing anion (*e.g.* perchlorate), equal volumes of aqueous and organic phase were shaken vigorously by hand in a small separating funnel for 1 min. The whole was then left to stand for at least 1 h to allow the phases to separate although it is preferable to expedite this by centrifuging for 5 min. Brown or opaque glassware should be used throughout and undue exposure to bright sunlight avoided as far as possible. The concentration, $[\text{QE}]_o$ of erdmannate remaining in the organic phase is then determined spectrophotometrically at 355 $m\mu$. A calibration curve of $\log [\text{QE}]_o$ against $\log(c + Q^0)$ should be linear (*cf.* Fig. 1). All measurements were conducted at room temperature.

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SUMMARY

A novel liquid anion exchanger can be prepared from tetra-*n*-hexylammonium iodide and Erdmann's salt, $(\text{NH}_4)[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$. When a solution of this quaternary erdmannate in a suitable organic solvent ($\epsilon_{\text{max}} = 15,700$ at 355 $m\mu$) is equilibrated with an aqueous solution of a salt, the coloured erdmannate ion is displaced to a greater or less extent: the effect decreases in the order $\text{ClO}_4^- \gg \text{ClO}_3^- > \text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-}$ etc. The effects of changes in the organic solvent composition, of ionic strength, and of other variables on the position of equilibrium have been studied with a view to defining the optimum conditions for the absorptiometric determination of perchlorate ion ($\geq 25 \mu\text{g}$) in the presence of chlorate and other ions. Methods are proposed for eliminating those ions that form insoluble silver salts and to allow for the presence of substantial proportions of chlorate or nitrate ions.

RÉSUMÉ

Un nouvel échangeur d'anions liquide peut être obtenu à partir d'iodure de tétra-*n*-hexylammonium et de sel d'Erdmann, $(\text{NH}_4)[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$. Lorsqu'un „erdmannate" quaternaire, en solution dans un solvant organique approprié ($\epsilon_{\text{max}} = 15,700$ à $355 \text{ m}\mu$) se trouve en présence d'une solution aqueuse d'un sel, l'ion „erdmannate" coloré est plus ou moins déplacé ($\text{ClO}_4^- \gg \text{ClO}_3^- > \text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-}$). Les auteurs ont examiné l'influence de divers facteurs en vue d'établir les conditions optimales d'une détermination absorptiométrique des perchlorates ($\geq 25 \mu\text{g}$), en présence de chlorates et d'autres ions.

ZUSAMMENFASSUNG

Es wurde ein neuer flüssiger Anionenaustauscher aus Tetra-*n*-hexylammoniumjodid und Erdmannschem Salz, $(\text{NH}_4)[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, hergestellt der die spektralphotometrische Bestimmung von Perchlorat ermöglicht. Wird eine Lösung dieses quaternären Erdmannats in einem geeigneten organischen Lösungsmittel ($\epsilon_{\text{max}} = 15,700$ bei $355 \text{ m}\mu$) mit einer wässrigen Lösung eines Salzes ins Gleichgewicht gesetzt, so wird das gefärbte Erdmannation mehr oder weniger stark verdrängt, und zwar in der Reihenfolge $\text{ClO}_4^- \gg \text{ClO}_3^- > \text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-}$ usw. Es wurde der Einfluss einer wechselnden Zusammensetzung des organischen Lösungsmittels, der Ionenstärke und anderer Größen auf die Lage des Gleichgewichts untersucht, um die optimalen Bedingungen für eine spektralphotometrische Bestimmung des Perchlorations ($\geq 25 \mu\text{g}$) in Gegenwart von Chlorat- und anderen Ionen zu bestimmen. Es werden Methoden zur Eliminierung der Ionen, die unlösliche Silbersalze bilden, vorgeschlagen, die die Bestimmung in Gegenwart wesentlicher Anteile von Chlorat- oder Nitrationen erlauben.

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SINE-WAVE POLAROGRAPHIC DETERMINATION OF ZIRCONIUM OR NIOBIUM IN AQUEOUS MEDIA*

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Generally, the polarographic determination of zirconium in aqueous media is accompanied by difficulties, because zirconium hydrolyzes and polymerizes easily to form complex species in aqueous media¹. Therefore, the polarographic determination of zirconium has been studied by making use of chelate compounds²⁻⁴, by indirect methods^{5,6}, by polarographic titration⁷, or in non-aqueous media^{8,9}.

The D.C. polarography of zirconium in aqueous media was first investigated by LAUBENGAYER AND EATON¹⁰. They found that zirconium(IV) gave a reduction wave which followed the hydrogen decomposition wave in solutions which were 0.001 *M* in zirconyl chloride and 0.1 *M* in potassium chloride, and had been adjusted to within the pH range of 3 to 4. The half-wave potential was shifted to more negative potentials with a decrease of the pH, and the average in the pH range of 3 to 4 was -1.69 V vs. N.C.E. LAUBENGAYER AND EATON¹⁰ did not suggest that this reduction wave could be used to determine zirconium. In fact, it seemed quite difficult to establish a D.C. polarographic method for zirconium by measuring this reduction wave, because it was obtained as a relatively small wave on the top of a large hydrogen decomposition wave, thus making its measurement impractical. This difficulty would be expected to be more pronounced below pH 3 even though the hydrolysis of zirconium would be largely suppressed.

The fact that a preceding large wave for hydrogen does not present a serious problem in sine-wave polarography suggested that it might be profitable to study the sine-wave polarography of zirconium at pH values below 3. However, at pH values below 2, many bubbles of hydrogen formed around the drop of mercury on the cathode above the decomposition potential of hydrogen and made it difficult to obtain a satisfactory result. Consequently, the possibility for the sine-wave polarographic determination of zirconium in a solution of 1 *M* potassium chloride which had been adjusted to pH 2.0 with hydrochloric acid was indicated; however, the suitable concentration range for this determination was rather small.

The D.C. polarographic behavior of the niobium-citrate complex was investigated in detail by KENNEDY¹¹, although some studies had been done by ELSON¹² and

* Contribution No. 1436. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

FERRETT AND MILNER^{13,14}. KENNEDY found that niobium(V) in concentrated citric acid solution in the pH range 2 to 4 gave a well-defined wave by a reversible reaction between -0.8 and -1.0 V *vs.* S.C.E. Then he proposed a suitable supporting electrolyte buffered at pH 3.0 for the determination of niobium. With this supporting electrolyte, niobium was determined at a half-wave potential of -0.951 V *vs.* S.C.E. without serious interferences by tantalum, molybdenum, thallium, and tungsten. It seemed apparent that quite satisfactory results could also be obtained by the sine-wave polarographic method using the same supporting electrolyte as proposed by KENNEDY. The sine-wave polarographic method was superior to the D.C. method in the sensitivity of the determination. The supporting electrolyte proposed by KENNEDY for studying sodium niobate was also found to be quite satisfactory for studying niobium in concentrated sulfuric acid.

EXPERIMENTAL

Apparatus

The polarograms for zirconium were obtained with a Yanagimoto AC and DC Polarograph Model PA-102. The measurements were made at $25^\circ \pm 0.2^\circ$ using a Yanagimoto Constant-Temperature Bath for Polarograph, Model PC-4. A conventional cell with a mercury pool electrode was used. Dissolved oxygen in solutions for polarography was not expelled and did not lead to poor results. The drop time of the capillary seemed to increase with use and was replaced with a new capillary after about thirty polarograms had been recorded.

The polarograms for niobium were obtained with a Yanagimoto AC and DC Polarograph Model PA-101. The measurements were made at 25° , using a conventional cell with a mercury pool electrode. Nitrogen was used to expel the dissolved oxygen from solutions for polarography.

Reagents

Specially purified zirconyl chloride and pure niobium metal from Ames Laboratory stock were used to prepare the standard sample solutions. 'Baker Analyzed' reagents and de-ionized distilled water were used for the preparation of all solutions.

The supporting electrolyte for niobium was identical to that proposed by KENNEDY¹¹. One ml of concentrated sulfuric acid containing the niobium to be determined was added to 80 ml of the supporting electrolyte and diluted with water to 100 ml in a volumetric flask. The final pH was 2.4 and was kept constant in all solutions used for the polarography of niobium. As good results were obtained at this pH, it was not necessary to adjust to pH 3.0 as proposed by KENNEDY¹¹.

RESULTS AND DISCUSSION

Determination of zirconium

A measurable peak for zirconium(IV) was obtained after a peak for hydrogen in each sine-wave polarogram for solutions which were $(0.55 \text{ to } 5.5) \cdot 10^{-3}$ M in zirconyl chloride (0.05 to 0.5 mg Zr/ml) and 1 M in potassium chloride and had been adjusted to pH 2.0 with hydrochloric acid (Fig. 1). The peak was not typical in that following the summit the curve fell a little and merged into the supporting electrolyte decomposition wave. The summit potential was about -1.85 V *vs.* the mercury pool electrode, although the exact value could not be measured because of the gentle summit.

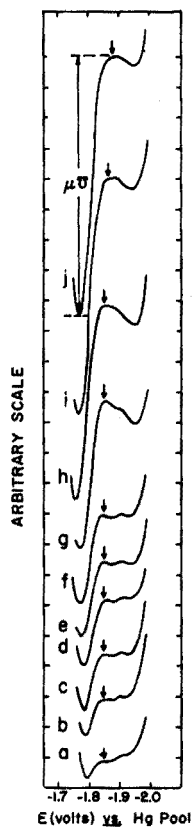


Fig. 1. Polarograms of zirconium at the various concentrations. Solutions were [0.55(a), 0.66(b), 0.77(c), 0.88(d), 0.99(e), 1.1(f), 2.2(g), 3.3(h), 4.4(i), 5.5(j)] $\cdot 10^{-3}$ M in $ZrOCl_2$ and 1 M in KCl, and had been adjusted to pH 2.0 with HCl.

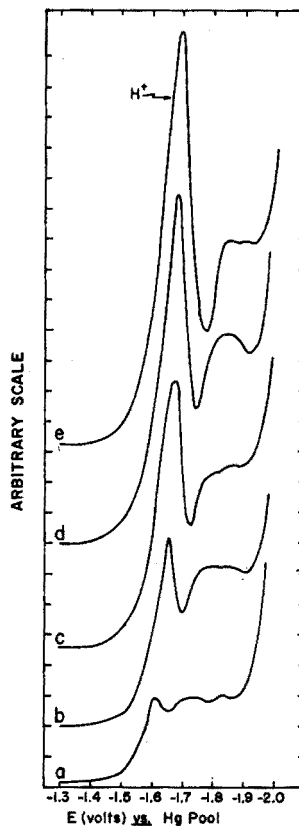


Fig. 2. Polarograms of zirconium at various pH values. Solutions were $1.1 \cdot 10^{-3}$ M in $ZrOCl_2$ and 1 M in KCl, and had been adjusted at pH 2.7(a), 2.5(b), 2.3(c), 2.2(d), 2.0(e) with HCl.

The peak height increased with the concentration of zirconium in a non-linear manner. The slope of the curve decreased as the concentration of zirconium was increased. Representative data for this relationship are summarized in Table I. The peak for 0.5 mg of zirconium per ml was not distinctly higher than that for 0.4 mg of zirconium per ml, presumably because the hydrolysis of zirconium at this concentration was not sufficiently suppressed at pH 2.0. Therefore, it seemed impractical to determine more than 0.4 mg of zirconium per ml. On the other hand, it seemed quite difficult to obtain a measurable peak for less than 0.05 mg of zirconium per ml. The reproducibility of the peak height was somewhat poorer than one usually expects in sine-wave polarography when the drop time changes or a bubble of hydrogen remains on the cathode.

Similar results were also obtained in 1 M lithium chloride which had been adjusted to pH 2.0 with hydrochloric acid. However, the peak height for zirconium(IV) was lower than that in 1 M potassium chloride. Therefore, it seemed difficult to obtain a measurable peak for less than 0.1 mg of zirconium per ml.

LAUBENGAYER AND EATON¹⁰ suggested that the variation of the reduction potential of zirconium(IV) with pH in the range of 3 to 4 seemed to indicate changes in the nature of the complex ions with changing solution conditions. Therefore, the effect of pH lower than 3 on the reduction wave for zirconium(IV) in sine-wave polarography was investigated using solutions which were $1.1 \cdot 10^{-3} M$ in zirconyl chloride (0.1

TABLE I

RELATIONSHIP BETWEEN CONCENTRATION OF ZIRCONIUM AND THE PEAK HEIGHT IN THE SINE-WAVE POLAROGRAM

(Characteristics of the capillary used: $m = 0.803$ mg (at a height of 70 cm), $t = 2.90$ sec (at -1.8 V vs. Hg pool)

Concn. of Zr (mg/ml)	Peak height ^a (μ V)		
0.05	50	50	50
0.06	120	120	120
0.07	170	170	170
0.08	210	220	210
0.09	250	250	250
0.1	290	290	300
0.2	480	490	490
0.3	650	640	630
0.4	765	765	760
0.5	810	800	790

^a Values were obtained from 3 polarograms for each solution, at sensitivity = 10.0μ V/mm.

mg Zr/ml) and 1 M in potassium chloride, and had been adjusted to various pH values (2.7, 2.5, 2.3, 2.2, 2.0) with hydrochloric acid (Fig. 2). At pH 2.7, two relatively small peaks for zirconium(IV) were observed closely following the peak for hydrogen. These summit potentials were about -1.75 and -1.85 V vs. the mercury pool electrode, although the exact values could not be measured because of the indefinite summits. As the pH was decreased from 2.5 to 2.2, an increasing peak for zirconium(IV) was observed. The summit potential was shifted negatively from -1.8 to -1.85 V vs. the mercury pool electrode with the decreasing pH. However, this peak seemed to include two peaks. At pH 2.0, in addition to the relatively large peak for zirconium(IV) at -1.85 V vs. the mercury pool electrode which was used for the determination, an indefinite peak was observed. The summit potential was estimated at -1.9 V vs. the mercury pool electrode. This peak was fairly definitely observed for less than 0.1 mg of zirconium per ml, but it was hardly observable for more than 0.1 mg of zirconium per ml because of the preceding large peak.

Consequently, the reduction wave for zirconium(IV) at each pH might include the reduction waves for two or more different species of quadrivalent zirconium which might be formed in various ratios at different pH values. Therefore, the reduction potential for zirconium(IV) might vary with pH. Also the peak for zirconium(IV) in sine-wave polarography might be an unusual peak having a gentle summit because of the closely following peaks for the different species of zirconium(IV). Two summits were actually observed in some cases.

It was concluded that it is impossible to determine zirconium by measuring polaro-

graphically all kinds of the quadrivalent species in aqueous media. However, it is possible to determine zirconium in the concentration range of 0.05 to 0.4 mg per ml in solutions which were 1 *M* in potassium chloride and had been adjusted to pH 2.0 with hydrochloric acid by measuring the peak for zirconium(IV) at -1.85 V vs. the mercury pool electrode in the sine-wave polarogram, using a calibration curve.

Determination of niobium

With citric acid as the supporting electrolyte, as recommended by KENNEDY¹¹, standard sample solutions containing 1 to 5 mg of niobium per ml of concentrated sulfuric acid, gave a well-defined peak or wave for niobium(V) which was observed between -1.1 and -1.3 V vs. the mercury pool electrode in the sine-wave polarogram or the D.C. polarogram, respectively. The summit potential or the half-wave potential was -1.20 V vs. the mercury pool electrode. The peak and wave heights were fairly stable with time. A decrease of only about 1% was observed after 2 h. The relationship between the concentration of niobium and the peak height in the sine-wave polarogram or the wave height in the D.C. polarogram was linear, respectively, as shown in Table II, Series I. Good results were also obtained by sine-wave polarography

TABLE II

RELATIONSHIP BETWEEN CONCENTRATION OF NIOBIUM AND THE PEAK HEIGHT IN THE SINE-WAVE POLAROGRAPH OR THE WAVE HEIGHT IN THE D.C. POLAROGRAPH

(Characteristics of the capillary used: $m = 0.950$ mg (at a height of 70 cm), $t = 4.11$ sec (at -1.3 V vs. Hg pool)

Series	Concn. of Nb in H ₂ SO ₄ (mg/ml)	Concn. of Nb in supporting electrolyte (mg/ml)	Peak height ^a		Wave height ^d (μ A) ^b
			(μ V) ^b	(μ V) ^c	
I	1	0.01	25.0	21.0	0.105
	2	0.02	49.0	42.0	0.200
	3	0.03	71.0	62.0	0.310
	4	0.04	94.0	86.0	0.410
	5	0.05	114.5	105.0	0.490
II	0.1	0.001	1.6	1.4	—
	0.2	0.002	3.4	2.4	—
	0.3	0.003	5.4	4.6	—
	0.4	0.004	7.0	6.0	—
	0.5	0.005	7.8	7.2	—

^a At sensitivity, 1.0 μ V/mm for Series I; 0.4 μ V/mm for Series II.

^b Oxygen expelled with nitrogen.

^c Oxygen not expelled.

^d At sensitivity, 0.010 μ A/mm and parallel capacitance, 100 μ F for Series I.

even though dissolved oxygen was not expelled. Although the peak height was a little less than that observed when the dissolved oxygen was expelled, the relationship with the concentration was still linear.

Standard solutions containing 0.1 to 0.5 mg of niobium per ml of concentrated sulfuric acid were investigated. For each case, a fairly definite peak for niobium(V) was observed in the sine-wave polarogram, but the wave in the D.C. polarogram was hardly measurable. The relationship between the concentration of niobium and the

peak height in the sine-wave polarogram was nearly linear, whether or not the dissolved oxygen was expelled, as shown in Table II, Series II. However, it seemed that a definite peak could not be obtained for the sample solutions containing less than 0.1 mg of niobium per ml of concentrated sulfuric acid. Excessive amounts of sulfuric acid in the supporting electrolyte caused the peak height for niobium(V) to be decreased and to become quite unstable with time. A 25% decrease was observed after 2 h even when the sample solution was increased from 1 ml to 2 ml.

Consequently the determination of niobium is possible down to 0.1 mg of niobium per ml of concentrated sulfuric acid by sine-wave polarography and the D.C. method is impractical for the determination of less than 0.5 mg of niobium per ml of concentrated sulfuric acid.

The authors wish to thank Yanagimoto Co., Ltd. in Japan and Jarrell-Ash Company for supplying the sine-wave polarograph.

SUMMARY

The sine-wave polarographic determination of zirconium in aqueous media was investigated using solutions which were $0.55-5.5 \cdot 10^{-3} M$ in zirconyl chloride and $1 M$ in potassium chloride and had been adjusted to pH 2.0 with hydrochloric acid. It was possible to determine zirconium in the concentration range of 0.05 to 0.4 mg per ml. The sine-wave polarographic behavior of zirconium in aqueous solutions in the pH range 2-3 is discussed. The sine-wave polarographic determination of niobium in aqueous media was investigated using concentrated sulfuric acid containing 5 to 0.1 mg of niobium per ml in a supporting electrolyte of citric acid; the determination of niobium was possible down to 0.1 mg of niobium per ml of concentrated sulfuric acid although the D.C. polarographic method was impractical for the determination of less than 0.5 mg of niobium per ml.

RÉSUMÉ

Les auteurs ont examiné le dosage du zirconium et du niobium par polarographie à ondes sinusoïdales. Ils proposent comme solution de base pour le zirconium, une solution de chlorure de potassium/acide chlorhydrique (possibilité de doser ainsi 0.05 à 0.4 mg Zr/ml) et pour le niobium, un milieu acide sulfurique/acide citrique (0.1 à 0.5 mg Nb/ml).

ZUSAMMENFASSUNG

Eine polarographische Methode (sine-wave polarography) zur Bestimmung von Zirkonium und Niob in wässrigen Lösungen wurde untersucht. Es liessen sich Zirkoniumgehalte von 0.05-0.4 mg/ml bestimmen. Die Lösungen enthielten $0.55-5.5 \cdot 10^{-3} M$ Zirkoniumoxidchlorid, $1 M$ Kaliumchlorid und waren mit Salzsäure auf den pH-Wert 2.0 eingestellt. Die Bestimmung des Niobs war bis hinab zu 0.1 mg in einer Lösung, die Schwefelsäure und Citronensäure enthielt, möglich.

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PRELIMINARY STUDIES OF PRECIPITATION TITRATIONS OF ORGANIC COMPOUNDS USING POLAROVOLTRIC END-POINT INDICATION

PART I. TITRATION OF ORGANIC BASES WITH FERROCYANIDE

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For polarovoltric end-point indication¹ an essentially constant, small current of the order of a few microamperes is maintained between two small platinum electrodes immersed in a stirred solution and the change in potential difference across these electrodes is measured during titration of the solution. The potential difference depends amongst other factors on the nature and concentration of the solutes. In the vicinity of the equivalence point of a titration reaction, the relative changes of concentration of the solutes taking part in the reaction, are a maximum. The change of potential difference across the electrodes is then also a maximum. The point of maximum rate of change of potential difference per unit added titrant is taken as the end-point and is identical to or closely related to the desired equivalence point.

Certain solutes exercise a greater influence than others on the established potential difference, *i.e.* the electrodes (usually principally one of them) respond more markedly to these solutes. Notable examples are oxidising and reducing species, so that polarovoltric end-point indications using such species as reagents are practicable and sensitive.

Polarovoltric end-point indication in precipitation titration has so far been little used. Some examples are: inorganic halide ions with silver²; large organic cations with triiodide and with lauryl sulphate³; and picric acid and naphthol yellow S with methylene blue³. It was consequently considered to be of interest to undertake a more systematic study of precipitation titrations, especially of organic compounds. It is hoped first to publish a series of shorter, preliminary studies with various reagents, indicating the possibilities but without entering into any detailed discussion.

In this publication, examples of the use of ferrocyanide reagent are given. Although ferrocyanide yields a good electrode response for polarovoltric end-point indication, it is a comparatively mild reducing agent; reducing side-reactions are therefore less likely to interfere as much as they might with, for example, dithionite.

The ferrocyanides of numerous organic compounds (quaternary ammonium; primary, secondary and tertiary amines and heterocyclic bases; hydrazines; hydrazo compounds; dyes) have been prepared by precipitation from acid, neutral or alcoholic solution⁴⁻⁹. There are, however, few examples of the use of ferrocyanide as a reagent in precipitation titrations. In 1887, BECKURTS¹⁰ published a method for the titration

of strychnine in dilute hydrochloric acid, using iron(III) as external indicator. More recently, DUŠINSKÝ¹¹ titrated some alkaloids, using an amperometric end-point indication. Some indirect precipitation titrations with ferrocyanide can also be quoted: KOLTHOFF¹² determined antipyrine in the presence of pyrimidone, concluding by titrating the precipitate, formulated as $(C_{11}H_{12}N_2O)_2H_4Fe(CN)_6$, with sodium hydroxide to phenolphthalein. In the determinations of some non-ionic detergents, based on ethylene oxide polymers, unreacted reagent was back-titrated with zinc(II)¹³⁻¹⁵.

The compounds examined in the present work were salts or bases containing or yielding (in acid solution) substituted ammonium cations $RR'R''R'''N^+$. The nitrogen atom was linked to an aliphatic chain or to an aromatic or heterocyclic nucleus, or was part of a heterocyclic ring. The primary aim of the work was first to establish under what conditions polarographic end-point indication was possible, and then to study the influence of these conditions (*e.g.* pH, concentration of the titrated compound, colloid stabiliser) on the stoichiometry of the reactions. The influence of temperature, electrode size and rate of stirring, all of which affect the position and sensitivity of indication of the end-point, have not been studied.

EXPERIMENTAL

Reagents and solutions

Standardised solutions of acetic, hydrochloric, sulphuric and nitric acids in concentrations ranging from 0.05 *N* to *N*.

Acetate buffers, pH 4.6 and 3.6, *ca. N*.

Aqueous solution (1%) of the colloid stabiliser polyvinyl pyrrolidone (BASF, Ludwigshafen).

Potassium ferrocyanide (Merck) 0.1 and 0.05 *M* aqueous solutions.

The organic bases and salts were of variable purity; this probably exceeded 98% except for the detergents and dyes. Stock solutions were made in water, dilute acid or methanol, in concentrations ranging from 0.005 *M* to 0.1 *M*.

Apparatus and procedure

The apparatus used was the commercially available "Titrait", equipped with sensitivity positions ranging from 0.1 to 1 scale division per millivolt change in potential difference.

The electrodes were of platinum wire, of diameter 0.5 mm and length 5 mm, standing about 3 mm from each other. After nearly every titration they were washed with water, dried and brought briefly to a dull red heat in a small flame. This was found to be the only satisfactory method of cleaning off adhering precipitate.

The solutions were magnetically stirred in a vessel with a small rounded depression in the centre of its base, into which the rim of the stirring magnet fitted. This gave smooth rotation, improving the reproducibility of the results.

Ca. 20 ml of buffer solution or dilute acid were placed in the titration vessel and a blank titration was first carried out, taking as the end-point, the point of maximum steepness of the curve of potential difference across the electrodes (expressed as the cumulative deflection of the instrument needle) against added volume of titrant. The requisite aliquot of solution of the material being investigated was then added, which usually led to turbidity formation or precipitation and a displacement of the

instrument needle through removal of the reagent from solution. Titration was then continued slowly, allowing time for chemical and electrical equilibrium to be established. As with the blank titration, the end-point of maximum gradient of the curve was taken. This was usually recorded directly but sometimes by plotting data graphically. Where possible, a second (and sometimes a third and fourth) aliquot was added and a further end-point or further end-points located. Some of the materials investigated were poorly soluble and larger volumes of the dilute stock solutions were needed to give reasonably sized titrations. Mixtures of buffer or acid and larger aliquots were then made up separately and titrated without the preliminary blank titration. Occasionally a few drops of the colloid stabiliser solution were added to the solution before the addition of the aliquot.

RESULTS

Sensitivity of end-point indication

The sensitivity was highest in the blank titration and fell with increasing amount of material titrated. Hence it was rarely possible to titrate a fourth aliquot. This is probably largely due to increasing contamination of the electrode surfaces and also partly to increasing volume of solution.

TABLE I
SENSITIVITY OF END-POINT INDICATION
(Ca. 20 ml solution. Speed of stirring ca. 500 rev./min)

<i>Titration of</i>	<i>No. of measurements on which the average is based</i>	<i>Change in P.D. (mV) by addition of 1 μmol ferrocyanide reagent (0.01 ml 0.1 M solution)</i>
Solvent only (blank)	34	360
+ 0.1 mmol	29	220
+ 0.2 mmol	27	190
+ 0.3 mmol	20	150
+ 0.4 mmol	6	120

Some data illustrating this are shown in Table I but it must be emphasised that they are the averages of rather widely fluctuating figures. It may be mentioned that there seemed to be no evident correlation with the reaction medium used (pH or anion).

Influence of pH

Where titration of a compound was found possible, it was usually within only a limited range of acidity, sometimes as narrow as one pH unit. Outside these limits one of three interferences occurred: the compound could not be maintained in solution (especially with bases in the more weakly acid solutions); no precipitate was formed with the reagent; or no end-point could be observed.

Three fairly well-defined examples of pH influence on the stoichiometry were found and the data are given in Table II.

Influence of the amount of compound titrated

Where it was possible to titrate a second and third aliquot of solution, a variation

TABLE II
RELATION OF STOICHIOMETRY AND pH OF THE REACTION MEDIUM

<i>Compound titrated (in ca. 20 ml solution)</i>	<i>Estimated pH</i>	<i>Ratio mols ferrocyanide/mols compound</i>
Phenanthridine (0.2 mmol)	1.1 1.5	0.52-0.56 0.63-0.66
Proflavine hemisulphate (0.05 mmol)	0.35-0.9 2.2-4.6	ca. 0.6 ca. 0.3
7,8-Benzoquinoline (0.1-0.3 mmol)	0.35 0.75 1.1 1.35	0.34 0.37 0.39 0.40

TABLE III
INFLUENCE OF AMOUNT TITRATED ON THE STOICHIOMETRY
(Ca. 20 ml solution)

<i>Compound titrated</i>	<i>Medium</i>	<i>Amount of compound (mmol)</i>	<i>Ratio mols ferrocyanide/mols compound</i>
Acridine	pH 0.35	0.1	0.33
		0.2	0.355
		0.3	0.37
	pH 1.1 and 2 drops colloid stabiliser	0.1	0.325
		0.2	0.36
		0.3	0.40
		0.1	0.30
7,8-Benzo- quinoline	pH 1.1 and 5 drops colloid stabiliser	0.2	0.375
		0.3	0.37
		0.1	0.34
	pH 0.35	0.2	0.41
		0.3	0.45
pH 1.1	0.1	0.39	
	0.2	0.465	

TABLE IV
INFLUENCE OF ACID ANION IN THE TITRATION MEDIUM ON THE STOICHIOMETRY
(Ca. 20 ml solution)

<i>Methylene blue (0.04-0.16 mmol)</i>			<i>Safranine (0.05-0.15 mmol)</i>				
<i>Acid and concentration</i>	<i>Estimated pH</i>	<i>Ratio</i>	<i>Acid and concentration</i>	<i>Estimated pH</i>	<i>Ratio</i>		
H ₂ SO ₄ {	0.043 N	1.5	0.475	H ₂ SO ₄ {	0.085 N	1.2	0.14
	0.085 N	1.2	0.50		0.25 N	0.65	0.14
	0.2 N	0.75	0.55		0.94 N	0.13	0.135
HNO ₃ {	0.1 N	1.1	0.31	HNO ₃ {	0.1 N	1.1	0.15
	0.2 N	0.75	0.31		0.2 N	0.75	0.15
	0.4 N	0.45	0.31		0.4 N	0.45	0.145
HCl {	0.05 N	1.35	0.44	HCl {	0.1 N	1.1	0.12
	0.1 N	1.1	0.37		0.24 N	0.65	0.11
	0.2 N	0.75	0.345		1.0 N	0.1	0.10

of stoichiometry was sometimes found. Table III contains some data. With most compounds, the variations were within the limits of experimental error.

Influence of colloid stabiliser

The stabiliser was used only in a few attempts to achieve or improve end-point indication and no systematic study was undertaken. Clearly it may have a marked effect. Thus acridine could be titrated satisfactorily in 0.1 *N* and 0.2 *N* hydrochloric acid (pH *ca.* 1.1 and 0.75 respectively) in the presence of 2–5 drops of the 1% stabiliser solution, but not in the stronger 0.5 *N* hydrochloric acid (pH *ca.* 0.35) and the weaker *N* acetic acid (pH *ca.* 2.2), where an end-point was obtainable only in absence of the stabiliser. Similarly, 9(5)-methylacridine could be titrated in the presence of stabiliser in 0.1 *N*, 0.2 *N* and 0.5 *N* hydrochloric acid but not in *N* acid, where the titration was, as with acridine, practicable only in the absence of the stabiliser.

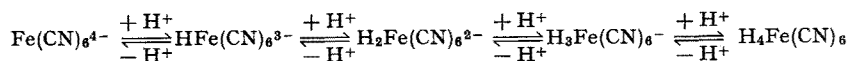
Influence of acid anion

Some results for the two dyes methylene blue and safranin (quoted purities of 91% and 87% respectively) in different acid solutions are given in Table IV.

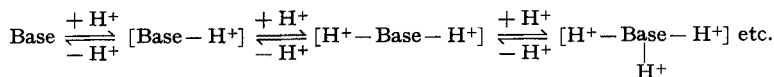
The influence of acid concentration on the stoichiometry varies from acid to acid. With methylene blue, increase in $[\text{H}_2\text{SO}_4]$ progressively raises the stoichiometric ratio, whereas increase in $[\text{HNO}_3]$ has a negligible effect, and increase in $[\text{HCl}]$ lowers it. The absolute values of the ratio, compared at a particular acid concentration such as 0.2 *N* or *ca.* 0.1 *N*, also vary markedly from acid to acid. The influence on the data for safranin is less marked but at least a contrast between hydrochloric acid and the other acids is evident. (It may be mentioned that concentration of the dyes had essentially no influence on the stoichiometry within the range used.)

DISCUSSION OF RESULTS

The following equilibria may be expected in solution:



and



(for bases with more than one basic centre).

Theoretically ferrocyanide and cations of the base could combine in any ratio between 0.25 (corresponding to $[\text{Base}-\text{H}^+]_4 [\text{Fe}(\text{CN})_6^{4-}]$) and 3 or higher, depending on the charge on the cation.

In the preparative work quoted above⁴⁻⁹, many determinations of the composition of the salts were carried out. Most salts had a ratio of 0.5, corresponding to the composition written as $(\text{Base})_2 \cdot \text{H}_4\text{Fe}(\text{CN})_6$ and which may be formulated $[\text{Base}-\text{H}^+]_2 [\text{H}_2\text{Fe}(\text{CN})_6^{2-}]$ or, for a di-acid base, $[\text{H}^+-\text{Base}-\text{H}^+]_2 [\text{Fe}(\text{CN})_6^{4-}]$. Other ratios of 1.0, 0.33, 0.25 and even an example of 0.67 (for the quaternary ammonium salt, written as $[\text{C}_6\text{H}_5(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{N}]_3 [\text{H}_5\text{Fe}_2(\text{CN})_{12}]$) were given. In the titration data summarised in Table V, the stoichiometric ratio is usually below 0.5 and never exceeds 0.66. Under titration conditions, the organic compound is always present in

excess and it is therefore not surprising that the ratios are in general low. There appears to be no clear correlation between the stoichiometry and the nature of the base titrated. Bases containing several basic centres with the chance of forming poly-positive cations, might have been expected to yield higher stoichiometric ratios. In fact, the opposite was found, as *e.g.* with melamine (0.25), safranine (0.10–0.15) and 9(5)-aminoacridine (0.22).

The variation of stoichiometry with pH and concentration of the organic compound can be explained by the participation of different ions. The jump by a factor of two for proflavine when passing from higher to lower pH (Table II) can in this way be explained by the participation of a dipositive cation. The stoichiometric ratios of 0.3 and 0.6 correspond approximately to the compositions of the reaction product of: $[\text{Base}-\text{H}^+]_3[\text{HFe}(\text{CN})_6^{3-}]$ at higher pH and $[\text{H}^+-\text{Base}-\text{H}^+]_3[\text{HFe}(\text{CN})_6^{3-}]_2$ at lower pH. It is surprising that no more examples were found of a marked pH influence, since hydrogen ions are involved in the equilibria between the various anions and cations.

An explanation of the results in Table IV is hard to find. Further data are necessary. The dyes were admittedly impure but the wide variations in stoichiometry can hardly be attributed entirely to the influence of impurities.

TABLE V
SUMMARY OF RESULTS

<i>Compound titrated</i>	<i>pH range</i>	<i>Average ratio mols ferrocyanide/ mols compound</i>
Acridine	0.35–2.2	0.30–0.40
9(5)-Aminoacridine	2.2–4.6	0.22
7,8-Benzoquinoline	0.35–1.35	0.34–0.465
Cetylpyridinium (chloride)	1.1–2.2	0.57
Cetyltrimethyl- ammonium (chloride)	0.1–2.2	0.58
Melamine	2.5–3.6	0.25
9(5)-Methylacridine	0.1–1.1	0.5
Methylene blue	0.45–1.5	0.31–0.55
Oleylamine	2.2–3.6	0.23
Phenanthridine	1.1–1.35	0.52–0.66
D-Phenylquinoline	0.1–2.2	0.41
Proflavine	0.35–0.9	0.6
(hemisulphate)	2.2–4.6	0.3
Safranine	0.1–1.2	0.10–0.15
Stearylamine	2.2–2.8	0.23

Some of the titrations were inconveniently slow but the titration method could be used for determination of most of the compounds listed in Table V, excepting those where the stoichiometry was found to be dependent on the amount titrated. Solutions of concentrations of the order of $5 \cdot 10^{-3} M$ could be titrated with an accuracy of a few per cent. It is hoped to investigate the analytical aspect more fully.

SUMMARY

Precipitation titrations of a number of organic bases have been carried out in acid solution with ferrocyanide. The influence of several factors, principally pH value, on the stoichiometry of the reactions has been examined.

RÉSUMÉ

Les auteurs ont effectué des titrages par précipitation, d'un certain nombre de bases organiques, en solution acide, au moyen de ferrocyanure. Ils ont examiné l'influence de divers facteurs (principalement le pH) sur la stœchiométrie des réactions.

ZUSAMMENFASSUNG

Fällungstitraktionen mehrerer organischer Basen wurden in saurer Lösung mit Ferrocyanid durchgeführt. Der Einfluss einiger Faktoren, hauptsächlich der des pH-Wertes, auf die Stöchiometrie wurde untersucht.

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FORMATION DU COMPLEXE PHOSPHOMOLYBDIQUE RÉDUIT

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L'acide phosphomolybdique étant, en vue du dosage du phosphore, formé à froid, par exemple dans les techniques prévoyant sa séparation par extraction au moyen d'un solvant, est ensuite réduit en bleu phosphomolybdique (voir, par exemple, ref. 1). Dans la majorité des techniques, il est cependant, dans un même milieu, formé et réduit à chaud, sous la forme du phospho-conjugué bleu réduit²; des dispersions des résultats sont souvent observées, imputables à des irrégularités de la réaction, sensible aux conditions éventuellement irrégulières du chauffage.

Certains éléments susceptibles de se combiner dans le complexe suscitent la formation de la coloration bleue dès l'ambiante; une méthode de dosage du phosphore dans les aciers a été établie sur ce principe, faisant intervenir le bismuth³⁻⁵. Une action propre au bismuth sur l'acide phosphomolybdique lui-même, provoquant un changement de sa coloration jaune, avait été antérieurement signalée⁶. La propriété de favoriser la réduction de l'acide phosphomolybdique est mentionnée pour le zirconium et le titane, comme pour le bismuth³. Sur ce principe, se fonde une méthode de dosage du bismuth⁷. De même, l'antimoine exerce semblable action sur la réduction de l'acide phosphomolybdique⁸. Il apparaît que les éléments donnant lieu à cette observation sont en particulier ceux donnant des phosphates insolubles en milieu acide.

Il est observé, dans le travail évoqué⁸, que le milieu de formation du bleu phosphomolybdique, réduit avec l'aide du bismuth et de l'acide ascorbique, présenterait un trouble par suite de l'hydrolyse du bismuth à l'état de sel basique, et que la sensibilité de la mesure ainsi opérée n'atteindrait qu'environ la moitié de celle que l'on pourrait obtenir, le bismuth étant supprimé⁸; ces critiques semblent bien ne pas viser la réaction telle qu'elle est prévue dans le milieu original de pH inférieur à zéro³, mais plutôt la réaction telle qu'elle serait opérée dans le milieu beaucoup moins acide, qu'envisagent les auteurs évoqués⁸.

Suit une étude de la formation à l'ambiante du bleu phospho-conjugué, avec addition des différents adjouvants actifs.

PARTIE EXPÉRIMENTALE

La formation de l'hétéropolyacide et sa réduction imposent des plages d'acidités optimales du milieu, pouvant d'ailleurs être différentes selon les réducteurs; dans ces zones d'acidité, il importe que l'acide molybdique (essai à blanc) ne soit pas lui-même

réduit en bleu molybdique (forme oxyde). La majorité des réducteurs impose une acidité du milieu de pH 2 à pH \leq 0; la règle de STRICKLAND:

$$\frac{[H^+]}{[MoO_4]} = 3 \text{ à } 5; \quad [MoO_4^{2-}] = 5.6 \cdot 10^{-2}$$

valable pour l'acide silicomolybdique a été prise en considération et étendue à l'acide phosphomolybdique dans le travail expérimental⁹.

Les formes de l'acide molybdique, stables dans le milieu d'acidité convenable à la formation et à la réduction de l'acide phosphomolybdique, sont réductibles en bleu de molybdène (forme oxyde). Ainsi, en milieux d'acidité 0.2 à 1.6 N (calculée), soit de pH final: 1 à $<$ 0 (mesuré), une coloration jaune (que l'on attribue à l'acide tétramolybdique) apparaît lors de l'acidification de la solution molybdique, que suivra la formation du bleu de molybdène (forme oxyde), après addition du réducteur (acide ascorbique, par exemple); l'une et l'autre de ces colorations sont plus accusées, s'agissant du paramolybdate d'ammonium que du molybdate de sodium, et également d'autant plus que l'acidité est moins élevée. Le bleu de molybdène (forme oxyde) ($\lambda_{max} = 810-820 \text{ m}\mu$) se différencie du bleu molybdique (forme phospho) par son absorption maximale ($\lambda_{max} = 725-750 \text{ m}\mu$). L'introduction d'un métal susceptible d'entrer dans le complexe (bismuth) ne modifie pas ces observations.

A 20 ml d'eau, sont ajoutés: 10 ml de solution de molybdate de sodium (20 g/l) ou de molybdate d'ammonium (14.67 g/l); 2 à 10 ml d'acide sulfurique 5 N; 1 ml de solution d'acide ascorbique (50 g/l); et de l'eau en quantité suffisante pour 50 ml. Les colorations jaune de l'acide tétramolybdique, puis bleue du milieu réduit apparaissent, et le plus fortement avec le molybdate d'ammonium.

L'addition de solution de métabisulfite de sodium (5 ml à 150 g/l) au milieu, avant acidification sulfurique et addition du molybdate de sodium, inhibe la polymérisation de l'acide molybdique, et l'apparition de la forme polymérisée jaune; le bleu molybdique (forme oxyde), que donnerait l'action ultérieure du réducteur avec ces formes polymérisées, est également par là-même, inhibé; les observations sont identiques en présence de métal combiné dans le complexe. Mais s'il est fait usage du paramolybdate d'ammonium, les colorations jaune, puis bleue, se produisent encore nettement.

Le bleu molybdique (forme oxyde) est, en la présence de métabisulfite, inhibé plus fortement aux acidités finales du milieu les plus élevées, de pH 2 à pH \leq 0, et cela quel que soit le réducteur: acide ascorbique, sel de Mohr, sulfate d'hydrazine, acide *p*-amino-1-naphtol-2-sulfonique-4; la *p*-semidine ne confère aucune réduction de pH 1.5 à pH \leq 0, ni la phénylsemicarbazide ou l'hydroquinone de pH 9.6 à pH \leq 0. Les éléments combinés (Bi, Zr, Sn, Sb) laissant apparaître des troubles hydrolytiques dans les milieux d'acidités (calculées) inférieures à 0.8 N (pH final $>$ 1.8 environ), en général, et pH $>$ 0.2 environ pour l'antimoine: en acidité (calculée) de l'ordre de 0.1 N, le trouble hydrolytique de l'antimoine cesse toutefois d'être observé.

Réactifs

Solution de bismuth sulfurique (1 ml \equiv 1.25 mg Bi; SO_4H_2 5 N). Dissoudre 1.44 g de BiO_2 dans 50 ml d'acide sulfurique (1.83) au demi, chauffer pour dissoudre, refroidir, ajouter 115 ml d'acide sulfurique (1.83), diluer au litre.

Afin d'atteindre les milieux de moindres acidités, les solutions suivantes, sensiblement neutres, ont été utilisées:

- (a) Solution de dibismuthoditartrate de sodium¹⁰ à 4.45 g/l (1 ml \equiv 3 mg Bi).
 (b) Solution de lactate de bismuth ($C_6H_9O_6$)OBi \cdot 7H₂O à 7.3746 g/l (1 ml \equiv 3 mg Bi).
 (c) Solution de citrate de bismuth et d'ammonium à 7.28 g/l (1 ml \equiv 3 mg Bi).

Essais

A 20 ml d'eau sont ajoutés: 2 ml de solution sulfurique de bismuth (ou 1 ml de solution d'un sel organique de bismuth, suivi de 1 ml d'acide sulfurique 5 N), 5 ml de solution de métabisulfite de sodium (100 g/l), 10 ml de solution de molybdate de sodium (20 g/l), 0 à 8 ml d'acide sulfurique 5 N, 1 ml de solution d'acide ascorbique (50 g/l), et de l'eau pour 50 ml.

Les mêmes essais sont faits avec: 1 ml de solution d'oxychlorure de zirconium (10.6 g/l; 1 ml \equiv 3 mg Zr); ou 1 ml de solution de chlorure stannique SnCl₄ \cdot 5H₂O (6 g/l dans l'acide sulfurique 5 N; 1 ml \equiv 2 mg Sn); ou 1 ml de solution d'émétique d'antimoine (5.484 g/l; 1 ml \equiv 2 mg Sb).

La Fig. 1 montre la décroissance de coloration du "blanc", en fonction de l'acidité croissante. Aucune influence nette de l'anion organique n'est observée dans le cas des différents sels de bismuth.

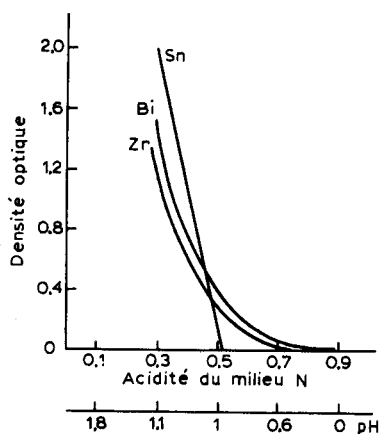


Fig. 1. Densité optique des témoins en fonction de l'acidité.

Les différents réducteurs se classent par ordre de sensibilité décroissante: acide ascorbique, acide aminonaphtolsulfonique, semidine, hydroquinone, phénylsemicarbazide, sel de Mohr.

Réactifs

Solution de phosphate disodique (0.116 g/l; 1 ml \equiv 10 μ g P).

Réactif de Fiske et Subbarow: dans une solution de 7 g de sulfite de sodium anhydre dans 100 ml d'eau, sont dissous 1.5 g d'acide amino-1-naphtol-2-sulfonique-4, et est ajoutée une solution de 90 g de métabisulfite de sodium dans 800 ml d'eau, compléter au litre.

Solution de chlorhydrate de N-phényl-*p*-phénylènediamine: 50 mg de *p*-semidine, humectés de quelques gouttes d'alcool, sont dissous dans une solution de bisulfite (ou de métabisulfite) de sodium à 1%, et compléter à 100 ml avec celle-ci (filtrer si nécessaire)¹¹.

Solution de carbonate (200 g) et de sulfite de sodium (75 g) anhydres, pour 1.5 l.

Essais

A 20 ml d'eau sont ajoutées: solution de phosphate = 0 à 3 ml; solution de métabisulfite de sodium (100 g/l) = 5 ml; solution de molybdate de sodium (20 g/l) = 10 ml; acide sulfurique (5 N) = 8 ml; solution du réducteur: acide ascorbique (50 g/l) = 1 ml; ou solution de sel de Mohr (50 g/l) = 1 ml; ou solution de sulfate d'hydrazine (25 g/l) = 2 ml; ou réactif de Fiske-Subbarow = 2.5 ml; ou semidine = 10 ml; et de l'eau pour 50 ml. Dans le cas de la solution d'hydroquinone (20 g/l) = 5 ml, ou de celle de phénylsemicarbazide (0.5 g/l) = 10 ml, il est ajouté 10 ml du réactif carbonate-sulfite.

La coloration bleue que donne l'acide ascorbique est d'une densité optique une fois et demie supérieure à celle que donne le réactif de Fiske-Subbarow, à $\text{pH} \leq 0$; l'hydroquinone¹², la phénylsemicarbazide, dans le domaine des pH finaux du milieu 9.7 à 2 confèrent, à l'optimum de pH 7 à 8, une coloration de densité optique sensiblement égale à celle que donne l'acide aminonaphtolsulfonique.

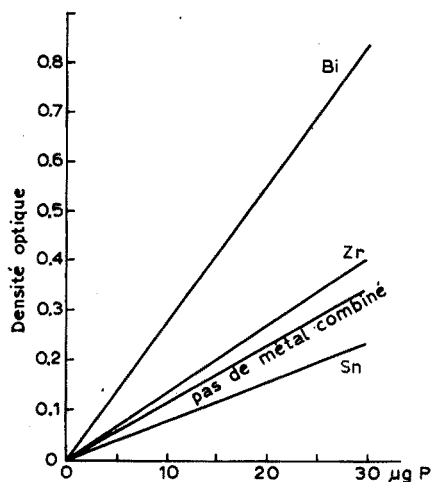


Fig. 2. Densité optique en fonction du phosphore; absence et présence de bismuth, zirconium et étain (présence d'acide ascorbique).

Dans le milieu précédemment décrit, est ajouté 1 ml des solutions des différents éléments combinables, après l'addition du phosphate. Lorsqu'il est fait emploi de l'acide ascorbique, à $\text{pH} \leq 0$, la Fig. 2 montre leur influence; celle du titane est analogue à celle du zirconium; l'antimoine laisse apparaître des troubles hydrolytiques.

La réduction par le réactif de Fiske et Subbarow, au même pH, dans le même milieu, est de même accrue par le bismuth.

Le sel de Mohr, la résorcine (5 ml de solution à 20 g/l) sont des réducteurs faibles et leur action n'est pas influencée par les différents éléments combinables (Fig. 3).

La réduction par l'hydroquinone, la phénylsemicarbazide (Figs. 4 et 5) à pH 1.5, est accrue par le bismuth, mais non par le zirconium, l'étain et l'antimoine, ce dernier donnant lieu à des troubles hydrolytiques. La semidine (Fig. 5), à pH 0.2 environ, se comporte comme les deux précédents. Le sulfate d'hydrazine confère des colora-

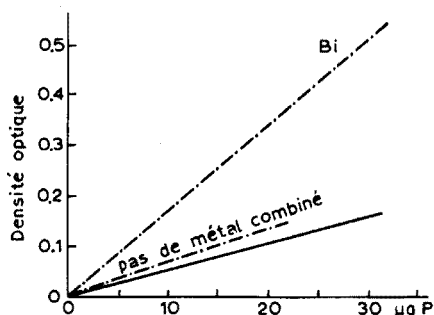


Fig. 3. Densité optique en fonction du phosphore, différents réducteurs, absence et présence de bismuth: — sel de Mohr, sans ou avec bismuth; — — — Fiske et Subbarow.

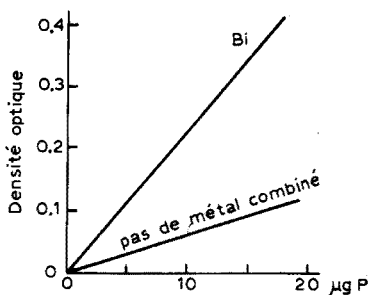


Fig. 4. Densité optique en fonction du phosphore, différents réducteurs, absence et présence de bismuth: — hydroquinone.

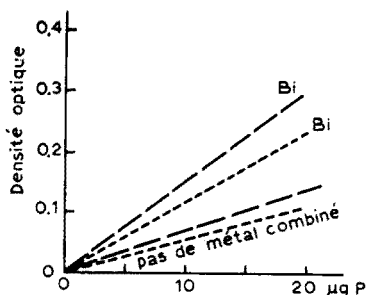


Fig. 5. Densité optique en fonction du phosphore, différents réducteurs, absence et présence de bismuth: - - - - phénylsemicarbazide; — — *p*-semidine.

tions tendant vers le jaune et qui se superposent aux bleus molybdiques. La réduction par le réactif molybdoso-molybdique¹³ n'est pas provoquée à froid par le bismuth.

Dans tous ces essais, la coloration des "blancs" (absence de phosphore) est restée nulle ou négligeable.

En définitive, les deux réactifs: bismuth et acide ascorbique sont les plus efficaces pour la réduction à l'ambiante des bleus phosphomolybdiques.

L'intensité de la coloration, pour une même quantité de phosphore mise en oeuvre, est fonction de l'acidité finale du milieu, aussi bien pour les essais "à blanc", que pour

les mesures du phosphore (Fig. 6). Dans la zone de constance de la densité optique (pH voisin de zéro), dans le cas de l'acide ascorbique, une variation même importante de l'acidité de la solution de phosphate (3 à 6 ml d'acide perchlorique au dixième) n'apporte qu'une erreur absolue de 0.01 de la densité optique.

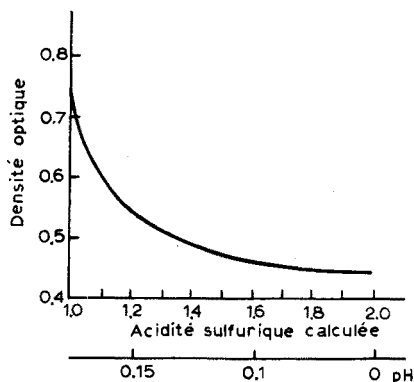


Fig. 6. Décroissance de la densité optique avec l'acidité.

En présence d'une solution de fer (50 mg) perchlorique^{3,4}, l'acidité étant contrôlé à $\text{pH} \leq 0$, une variation d'acidité de la solution ferrique atteignant le double ou la moitié de l'acidité normale résultant de l'attaque est sans incidence sur le résultat des mesures. L'addition d'un tampon (borate de sodium) aurait pour effet d'amenuiser encore l'effet des variations d'acidité. Le temps d'attente avant la mesure photométrique, dans le domaine de 15 min à une heure, est également sans influence sur le résultat de la mesure.

Une courbe d'étalonnage, obtenue en présence de 50 mg de fer, est indiquée en Fig. 7.

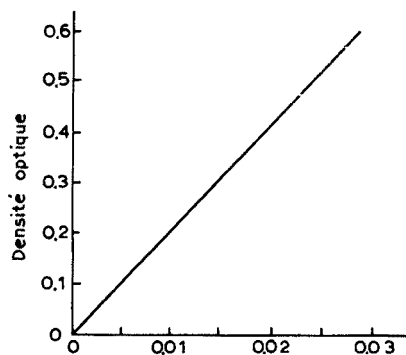


Fig. 7. Courbe d'étalonnage (présence de fer).

DISCUSSION

La combinaison de l'acide phosphomolybdique et du bismuth n'a pas pu être isolée, et l'effet du bismuth sur la réduction est considéré comme catalytique⁷.

Le titane est dosé (dans les aciers entre autres) sous la forme du complexe phosphotitanomolybdique réduit en bleu conjugué¹⁴⁻¹⁷. Selon les auteurs, le molybdène serait partiellement remplacé dans le groupement de coordination molybdique, par le titane, et le vanadium, le niobium¹⁴⁻¹⁵, de l'osmium¹⁵, le zirconium¹⁶ seraient capables d'entrer aussi en coordination dans ce complexe.

Le niobium est dosé (dans les aciers en particulier), à l'état du complexe phosphomolybdoniobique réduit^{15, 18-20}.

Le complexe phospho-antimonio-molybdique a pu être isolé, et présente le rapport Sb: P de 1 : 0.97 à 0.94 (soit sensiblement 1 : 1)⁸.

Ce même rapport est retrouvé dans le complexe titanique²¹, de constitution P : Ti : Mo = 1 : 1 : 12. Il est établi que le titane n'entre pas dans le groupement de coordination molybdique, mais en association avec l'atome central (phosphore); et qu'il confère au complexe phosphotitanomolybdique une stabilité plus grande que celle du complexe phosphomolybdique; de plus, que les indices de coordinence des groupements molybdiques sont différents dans l'un et l'autre complexes.

Leurs constitutions et leurs constantes de dissociation s'écrivent :

$$K_{APM} = \frac{[P(Mo_2O_7)_4] [Mo_2O_7]^2}{[P(Mo_2O_7)_6]} = 1.4 \cdot 10^{-6}$$

$$K_{APTm} = \frac{[P] [Ti] [Mo_2O_7]^6}{[PTi (Mo_2O_7)_6]} = 3.2 \cdot 10^{-5}$$

La représentation de l'atome de titane situé dans le groupement central se rapproche de celle des complexes titanomolybdique²²⁻²⁴, niobiomolybdique²⁵ et cerimolybdique: $CeMo_{12}O_{42}H_8$ ²⁶⁻²⁷, et dans lesquels le métal constitue seul l'atome central. Dans les complexes phosphovanadomolybdiques ou tungstiques classiques, ou dans les composés 2-molybdovanadique²⁸ et 3-tungstovanadique²⁹, le vanadium ou le tungstène entrent au contraire en position de coordination.

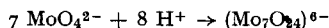
A noter que la réduction de l'acide phosphomolybdique à froid n'est pas en fait provoquée par le vanadium ou le tungstène.

L'atome de titane (éventuellement des autres éléments: Bi, Zr, etc.) est donc lié au groupement central. La stabilité plus grande, le mode de liaison des groupements molybdiques différente du complexe titanique comparé à l'acide phosphomolybdique, font apparaître la différence de comportement observée vis à vis des réducteurs. L'acide molybdique n'étant réductible qu'à l'état de forme polymérisée par l'acidification de la solution de molybdate, de même, dans les composés hétéroconjugués, est réductible le groupement molybdique coordiné, donc polymérisé. L'effet du métal supplémentaire lié au groupement central serait donc de rendre la liaison de coordinence des groupements polymolybdiques plus labile vis à vis du réducteur, au même titre que le chauffage de l'acide phosphomolybdique en présence du réducteur provoquerait la réduction des groupements polymolybdiques, à la faveur de leur libération hydrolytique par l'acidité du milieu.

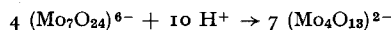
La polymérisation des solutions de molybdate de sodium ou d'ammonium en milieu acide est observée par la coloration jaune résultante, attribuée à l'ion tétramolybdique³⁰; elle s'accompagne régulièrement, par addition du réducteur, de la coloration du bleu molybdique, de $\lambda_{max} = 810 \mu\mu$ environ.

Les formes polymolybdiques résultant de l'acidification des solutions de molybdates alcalins peuvent être approximativement, et pour les besoins de l'exposé, résumées ainsi³¹⁻³⁶.

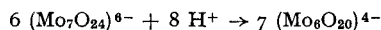
La forme paramolybdique, d'abord formée



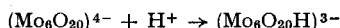
conduit, en solution suffisamment diluée, à la forme tétramolybdique



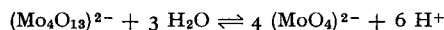
ou, en solution plus concentrée, à la forme trimolybdique



elle-même donnant le tétramolybdate:



Enfin, celui-ci est dissociable en solution étendue:



La forme tétramolybdique (jaune) est donc inhibée par dilution ou diminution de la concentration du milieu en ions molybdiques, et par l'introduction d'un tampon; le métabisulfite joue ce rôle et inhibe ainsi la formation des formes polymérisées (tétramolybdiques), et par suite celle du bleu de molybdène (forme oxyde) lors de l'addition du réducteur. A remarquer que l'addition du métabisulfite sert également à réduire l'acide arsénique éventuellement présent dans les applications technologiques.

Parmi les substances susceptibles d'inhiber la réduction des ions molybdiques, la mannite³⁷ s'oppose également à la réduction du phospho-conjugué; elle a pu être employée pour l'obtention des essais témoins destinés aux mesures photométriques du phosphore, dans le cas particulier des aciers, et ainsi à corriger la coloration propre des éléments d'alliage; la méthode a été appliquée au dosage du phosphore dans les aciers (Fig. 7).

RÉSUMÉ

Les complexes phosphobismuthomolybdique, phosphotitanomolybdique, etc. sont réduits dès l'ambiante, ce qu'explique la constitution de ces composés. L'efficacité des éléments (Bi, Ti, Zr, etc.) liés à l'atome central de l'hétéropolyacide, en présence de plusieurs réducteurs, est mise en évidence.

SUMMARY

The phosphobismuthomolybdic, phosphotitanomolybdic and similar complexes are reduced at ordinary temperature, which can be understood from the constitution of these compounds. The efficacy of these elements (Bi, Ti, Zr, etc.) which are linked with the central atom of the heteropolyacid, in assisting the reaction of different reducing reagents, is emphasized.

ZUSAMMENFASSUNG

Die phosphobismuthomolybdischen, phosphotitanomolybdischen — usw. — Komplexe sind bei Raumtemperatur reduzierbar. Das ist durch die Konstitution dieser Stoffe zu erklären. Die Wirkung der Elemente (Bi, Ti, Zr, usw.), die mit dem Zentralatom der Heteropolysäure komplexiert sind, ist in Zusammenhang mit mehreren reduzierenden Reagenzien geklärt.

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LIQUID-LIQUID EXTRACTION OF COBALT THIOCYANATE WITH TRIISOCTYLAMINE

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Long-chain aliphatic amines are used as liquid anion exchangers. Among these are *n*-trioctylamine and triisooctylamine (TIOA). The uranium industry uses TIOA dissolved in kerosene to extract uranium from sulfuric acid leaches of uranium-bearing ores. Loss of amine to the aqueous phase has been found by ASHBROOK¹. He utilized the complex formation between cobalt, thiocyanate and amine for a spectrophotometric determination of small amounts of TIOA.

In this paper TIOA in conjunction with thiocyanate, is proposed as a reagent for the spectrophotometric determination of small amounts of cobalt. The distribution coefficient of cobalt between the organic and aqueous phases and the composition of the coloured solution have been determined.

EXPERIMENTAL

Apparatus

A Zeiss spectrophotometer model PMQ II with 1.000-cm cells was used for determination of optical densities. A Beckman DB spectrophotometer was used for recording the absorption curves. The extractions were performed in ordinary separatory funnels.

Reagents

Stock solutions of cobalt were prepared by dissolving cobalt nitrate in distilled water. They were standardized by titration with a standard EDTA solution using murexide as indicator. Stock solutions of thiocyanate were prepared by dissolving the appropriate amounts of potassium thiocyanate (dried at 120°) in distilled water. The commercial product TIOA was distilled before use. The extractions were mostly performed with 20% (v/v) TIOA in carbon tetrachloride.

RESULTS AND DISCUSSION

Absorption curve

An acidic aqueous solution of cobalt thiocyanate gives a green organic phase when treated with TIOA dissolved in carbon tetrachloride. The absorption curve of this green solution measured against TIOA dissolved in carbon tetrachloride is given in Fig. 1. Maximum absorption is observed at 340 and 627.5 m μ . A characteristic shoulder on the absorption curve is seen around 590 m μ .

Effect of acid

The effect of different acids in varying amounts was studied. Solutions with constant cobalt and thiocyanate concentrations but different acids and concentrations were treated with 20% TIOA. The optical densities of the organic phases measured at 627.5 m μ are given in Table I. Nitric, perchloric and hydrochloric acids seemed to give the highest extinction values. A maximum absorption was obtained when the acid concentration is 0.2–0.5 M.

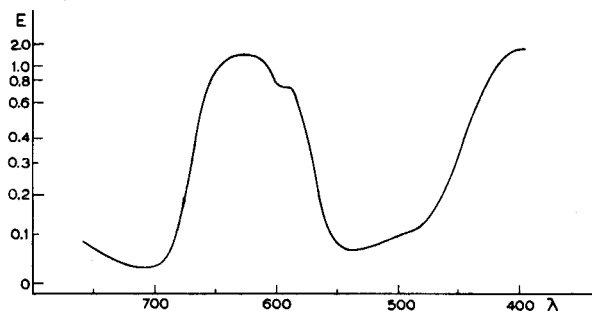


Fig. 1. Absorption curve of the cobalt-thiocyanate-TIOA complex. $1.7 \cdot 10^{-5}$ mole Co in 25 ml of carbon tetrachloride/TIOA.

TABLE I

THE EFFECT OF ACIDS AND ACID CONCENTRATION ON THE Co-SCN-TIOA COMPLEX

(The extinctions were measured at 627.5 m μ)

Added	HCl	HClO ₄	HNO ₃	CH ₃ COOH	HF	H ₂ SO ₄	H ₃ PO ₄	NaCl
0 mole	0.186	0.186	0.186	0.186	0.186	0.186	0.186	0.186
0.0086 mole	0.645		0.652			0.352		0.406
0.024 mole	0.645	0.640	0.650	0.580	0.572	0.182	0.017	0.512
0.050 mole	0.610					0.297		0.527
0.120 mole	0.205							0.563

Effect of potassium thiocyanate

The potassium thiocyanate concentration in the aqueous phase was varied while the other components were kept constant. As indicated in Fig. 2 the absorption of the organic phase measured at 627.5 m μ increased with increasing potassium thiocyanate concentration. When the thiocyanate concentration was about 250 times the cobalt concentration, a maximum was reached and a further increase in the thiocyanate concentration had no influence on the absorption.

Beer's law

Different cobalt solutions mixed with 0.4 g of potassium thiocyanate and 0.4 g of hydrochloric acid in 50 ml were treated twice with 10-ml portions of 20% TIOA. After separation these two portions were mixed and diluted with carbon tetrachloride to 25 or 250 ml depending on the cobalt concentration. In order to get rid of small

amounts of water, the organic phase was filtered through dry filter papers into the cells. The extinction plotted against the cobalt concentration showed a straight line when measured at $627.5 \text{ m}\mu$. Beer's law was obeyed in the concentration range 0 to 10 mg of cobalt. The molar extinction coefficient of the cobalt complex in the organic phase was 1895.

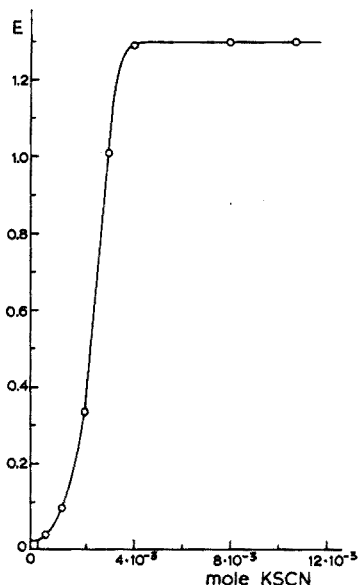


Fig. 2. The effect of potassium thiocyanate on the complex. $1.7 \cdot 10^{-5}$ mole cobalt treated with different amounts of thiocyanate, extracted into TIOA and diluted to 25 ml with carbon tetrachloride. The extinctions are measured at $627.5 \text{ m}\mu$.

The complex seemed to be stable for months in the organic phase provided that it was completely dry. In contact with the aqueous phase decomposition occurred.

Method for determination of cobalt

On the basis of the above results, the following procedure for the determination of cobalt with TIOA is suggested. Solutions containing up to 10 mg of cobalt are treated with hydrochloric, nitric or perchloric acid and 0.4–0.5 g of potassium thiocyanate is added; the aqueous phase is then diluted to about 50 ml. (The acid concentration should be 0.2–0.5 *M*.) The aqueous phase is extracted twice with 10-ml portions of 20% TIOA in carbon tetrachloride. The organic phases are collected and diluted with carbon tetrachloride to 25 ml for cobalt contents up to 1 mg, or to 250 ml if the cobalt content is between 1 and 10 mg. The organic phase is filtered through a dry filter paper into the cell if it is not quite clear. The extinction is then measured against a blank at $627.5 \text{ m}\mu$.

Interferences

Nickel, manganese(II) and zinc gave no colour with TIOA/KSCN. It is thus possible to determine cobalt in presence of these metals. The iron complex had a maximum absorption at $475 \text{ m}\mu$ but nearly no absorption at $627.5 \text{ m}\mu$ where the cobalt complex

had maximum absorption. It is therefore possible to determine small amounts of iron and cobalt in the presence of each other.

The distribution coefficient

Different concentrations of TIOA in carbon tetrachloride were treated with solutions containing excess cobalt(II), hydrochloric acid and potassium thiocyanate. The distribution coefficients were calculated from the cobalt concentrations in the organic phase (TIOA + CCl₄) and aqueous phase when equilibrium was achieved.

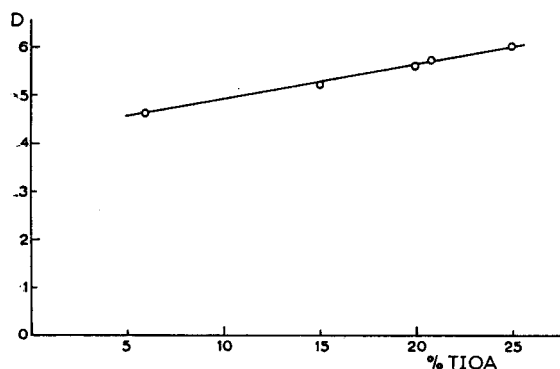


Fig. 3. The distribution ratio of Co plotted against the TIOA concentration.

Figure 3 shows the distribution coefficient at room temperature, plotted against the TIOA concentration. The coefficient was 5.6 when a 20% TIOA solution in carbon tetrachloride was used. At increasing temperature the coefficient decreased.

The composition of the complex

Some experiments were performed in order to find a relation between the available TIOA and the amounts of cobalt, acid and thiocyanate which enter the organic phase. An equilibrium was achieved after shaking for 2–3 min. The cobalt, acid and thiocyanate concentrations in the organic phase were calculated as the difference between the added and the available amounts in the aqueous phase after the equilibrium was reached. Table II shows the analytical results. At room temperature one mole of cobalt required about 4 moles of TIOA, 6 moles of thiocyanate and 6 moles of acid.

LASKORIN AND TIMOFEEVA² who mixed cobalt and thiocyanate in ratios 1 : 1 up to 1 : 9 and extracted into *n*-trioctylamine, found that the extraction maximum was obtained at a ratio 1 : 2. They concluded that one mole of cobalt needed 2 moles of thiocyanate and 2 moles of *n*-trioctylamine. Figure 2 in the present work shows that much more thiocyanate than twice the cobalt concentration is needed to get the coloured complex.

The distribution of hydrochloric acid between water and TIOA showed that one mole of TIOA reacts with one mole of acid. However, if potassium thiocyanate is present the organic phase contains 2 moles of acid per mole of TIOA (Table II). BOCH³ found that the extraction of thiocyanic acid into ethyl ether increases with increasing thiocyanate concentration. A similar effect is obtained when thiocyanic

TABLE II
RESULTS FROM TIOA EXTRACTIONS WHEN EQUILIBRIUM IS REACHED

	Total added (mole)	In aqueous phase (mole)	In organic phase (mole)
TIOA	0.0030		0.0030
H_3O^+	0.0587	0.0558	0.0029
TIOA	0.0040		0.0040
SCN^-	0.4140		
H_3O^+	0.0564	0.0488	0.0076
TIOA	0.00294		0.00294
Co^{2+}	0.00171	0.00097	0.00074
SCN^-	0.2155	0.2115	0.0040
H_3O^+	0.0605	0.0564	0.0041
TIOA	0.00998		0.00998
Co^{2+}	0.0051	0.0026	0.0025
SCN^-	0.7830	0.7680	0.0150
H_3O^+	0.0726	0.0571	0.0155
TIOA	0.00925		0.00925
Co^{2+}	0.00445	0.00212	0.00233
SCN^-	1.0030		
H_3O^+	0.0497	0.0357	0.0140

acid is extracted into TIOA and this explains why one mole of TIOA needs more than one mole of acid if thiocyanate is present.

The coloured organic phase was stripped with water. Cobalt, thiocyanate and chloride ions were afterwards detected in the water.

The results given in Table II indicate that the organic phase consists of: $[\text{Co}(\text{SCN})_4]^{2-} \cdot 2(\text{R}_3\text{NH})^+ \cdot 2\text{R}_3\text{NHCl} \cdot 2\text{HSCN}$. TIOA is written as R_3N . The colour is probably due to the components in the brackets.

The present results compared with those of LASKORIN AND TIMOFEEVA² indicate that cobalt and thiocyanate form more than one complex in TIOA depending on the thiocyanate concentration.

SUMMARY

Cobalt forms a coloured complex with triisooctylamine and thiocyanate in carbon tetrachloride. The green organic phase has maximum absorbance at 627.5 $\text{m}\mu$ and Beer's law is obeyed in the range 0–10 mg Co. The molar extinction coefficient is 1895. The distribution coefficient at room temperature is 5.6. A composition of the coloured species is proposed.

RÉSUMÉ

Le cobalt forme un complexe coloré avec le triisooctylamine et le thiocyanate, dans le tétrachlorure de carbone. La phase organique verte présente un maximum d'absorption à 627.5 $\text{m}\mu$; la loi de Beer est suivie pour des teneurs en cobalt de 0 à 10 mg. Coefficient d'extinction molaire 1895; coefficient de partage 5.6.

ZUSAMMENFASSUNG

Kobalt bildet einen gefärbten Komplex mit Triisooctylamin und Thiocyanat in Tetrachlorkohlenstoff. Die grüne organische Phase besitzt eine maximale Extinktion bei 627.5 $\text{m}\mu$ und gehorcht dem Beerschen Gesetz in dem Bereich von 0–10 mg Co. Der molare Extinktionskoeffizient beträgt 1895; der Verteilungskoeffizient bei Raumtemperatur 5.6. Die Zusammensetzung der gefärbten organischen Phase wird diskutiert.

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AN IMPROVED DIRECT TITRATION OF α -EPOXY COMPOUNDS
USING CRYSTAL VIOLET AS THE INDICATOR

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Most methods for the determination of α -epoxy compounds are indirect titrations based upon the formation of chlorohydrin by the relatively slow reaction of the epoxy group with an excess of hydrogen chloride. For hydrogen bromide the addition reaction is far more rapid; DURBETAKI's method¹ for the determination of epoxides by direct titration with 0.1 *N* hydrobromic acid in glacial acetic acid takes advantage of this.

On titrating glycidyl esters in this manner we found that the reaction may still be annoyingly slow, especially towards the end of the titration: after each addition of titrant a fairly long wait was necessary before the colour of the indicator no longer changed.

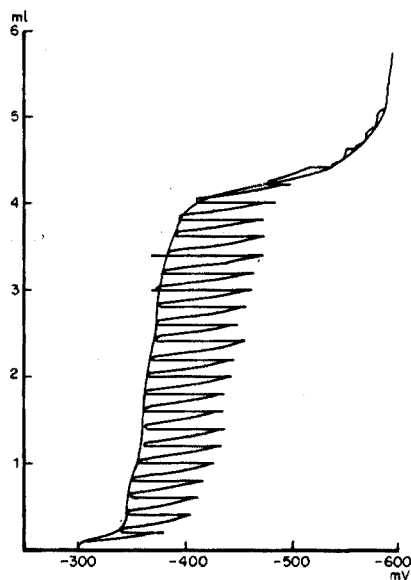


Fig. 1. Intermittent titration of epichlorohydrin with hydrogen bromide. Electrodes: glass/calomel.

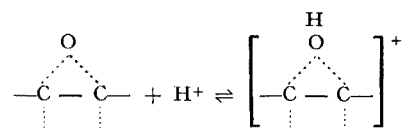
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The course of the titration could be made more clearly visible by means of potentiometric titration combined with a recorder. A Dow Precision Recordomatic Titrometer was modified in such a way that a 0.2-ml portion of titrant was added in 10 sec, after which there was a pause of 50 sec before the next portion was added. The titration of epichlorohydrin with 0.1 *N* hydrobromic acid in glacial acetic acid using glass and calomel electrodes thus yielded the curve reproduced in Fig. 1. The peaks in the Fig. correspond to the potential changes caused by each portion of titrant. The smooth curve — drawn in later — is the normal titration curve. Apparently, DURBETAKI'S method can be used successfully, but the slow reaction prevents expeditious titrations.

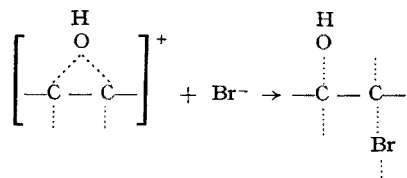
A closer look at the reaction mechanism suggested modifications in the titration procedure which should speed it up. These modifications, the principle of which was published already some years ago², and the results are discussed in the following sections.

Mechanism of the addition reaction

The mechanism of the addition of hydrogen bromide to epoxy compounds is well known. It involves two steps³: a rapid protonation



followed by a slow addition of the anion



According to this mechanism, an increase in anion concentration should accelerate the slow reaction and consequently the addition as a whole. To check this a potentiometric titration was carried out in the presence of 3 equivalents of tetrabutylammonium iodide*. Figure 2 shows the curve obtained. Not only has the addition of the iodide eliminated the peaks, but at the same time the potential jump at the equivalence point has increased, which favourably influences the accuracy of the titration.

A further conclusion to be drawn from the reaction mechanism is that any sufficiently strong acid should be able to effect the protonation. *p*-Toluenesulfonic acid and perchloric acid can indeed replace hydrogen bromide in the titration. In practice, the highly stable solution of perchloric acid in acetic acid is to be preferred, because with this titrant the jump in potential at the equivalence point is about the same as for hydrogen bromide. Figure 3 shows the curve for the titration of the glycidyl ester

* A pure bromide was not available.

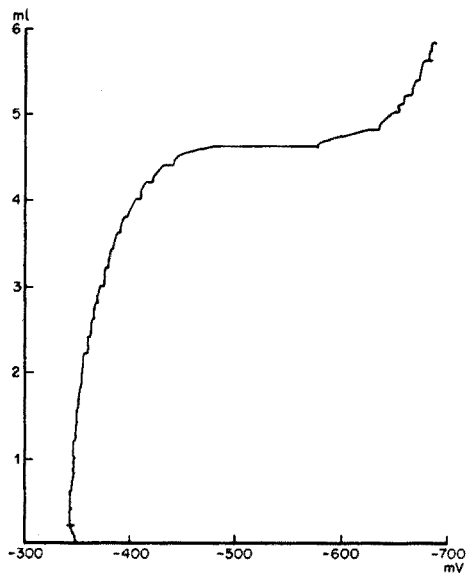


Fig. 2. Influence of tetrabutylammonium iodide on the intermittent titration of epichlorohydrin with hydrogen bromide.

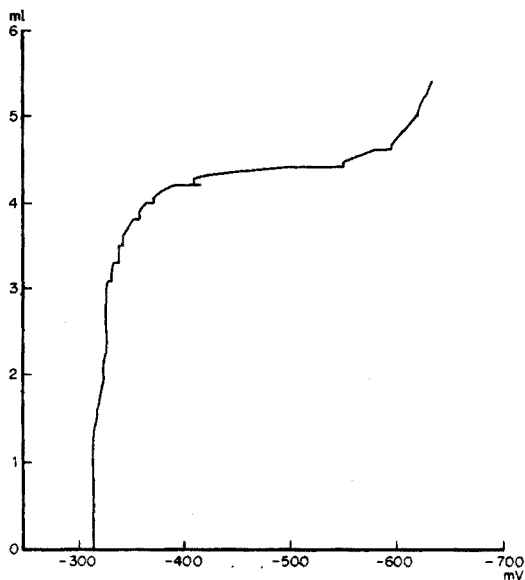


Fig. 3. Intermittent titration of glycidyl ester with perchloric acid after addition of 0.5 g of tetrabutylammonium iodide.

of cyclohexane carboxylic acid with perchloric acid in the presence of 3 equivalents of tetrabutylammonium iodide*.

* Later experiments have shown that when the added anion is iodide and the titrant HClO_4 one should protect against direct light. Otherwise, decomposition occurs yielding a yellow colour and high results. This can easily be prevented by coating the titration beaker externally with a black paint, and covering the beaker with a piece of black paper with holes for the electrodes.

Details about the experiments concerned will be published elsewhere.

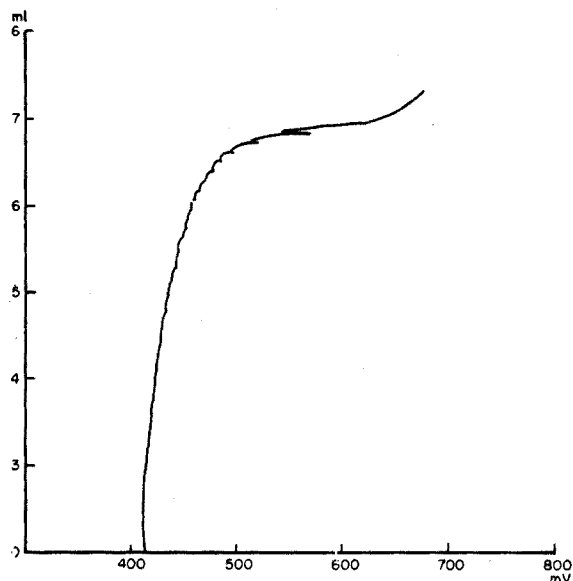


Fig. 4. Intermittent titration of a crystallized epoxy resin with perchloric acid in the presence of 6 equivalents of cetyltrimethylammonium bromide ("Cetavlon").

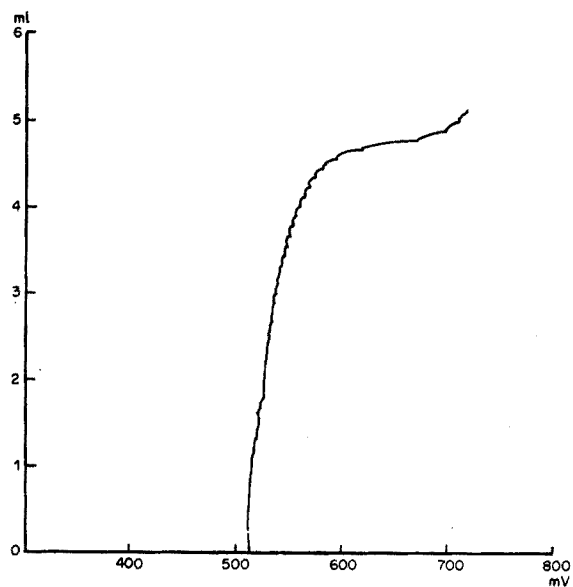


Fig. 5. Intermittent titration of a crystallized epoxy resin with perchloric acid in the presence of 2 equivalents of lithium bromide.

The solvent also influences the rate of the addition reaction. Acetic acid proved to be the most suitable medium in combination with the titration technique described here; addition of chlorobenzene or benzene slows the reaction down.

For routine application tetrabutylammonium iodide is too expensive, and accordingly a cheap substitute was sought. Cetyltrimethylammonium bromide, which is sold

under a variety of trade names, gave satisfactory results, provided that the amount of anion-supplying salt was increased from 3 to nearly 6 equivalents (Fig. 4). Lithium bromide, which is fairly readily soluble in acetic acid, is another possible substitute, although in this case the potential jump at the equivalence point is relatively small (Fig. 5).

Titrations with crystal violet as an indicator

If, for a titration with perchloric acid in acetic acid in the presence of cetyltrimethylammonium bromide, crystal violet is used as an indicator, its colour towards the end of the titration first changes slowly from violet to blue. On further addition of titrant it exhibits the familiar colour change to blue-green. At *ca.* 600 mV potential difference there is a third change, from blue-green to bright green. This last change provides a suitable visual end-point for the epoxy titration.

Here another advantage of the cheaper quaternary bromide over the tetrabutylammonium iodide comes to the fore: the iodide, which in this case cannot be protected from light, would cause yellow products to appear, interfering with the observation of the colour change.

The above-mentioned colour change to bright green does not coincide exactly with the potentiometrically determined equivalence point of the titration. The titration will only give reliable values for glycidyl ethers and esters, if a blank titration is performed. The perchloric acid can be accurately standardized against sodium biphthalate with tropaeolin oo as an indicator.

EXPERIMENTAL

Method summary

The glycidyl ester is dissolved in glacial acetic acid at room temperature. Immediately after addition of an excess of cetyltrimethylammonium bromide, this solution is titrated with 0.1 *N* perchloric acid in acetic acid, using crystal violet as an indicator.

Reagents

Solvent. Glacial acetic acid, analytical reagent quality. If the glacial acetic acid contains an appreciable amount of water, add a quantity of acetic anhydride sufficient to bind it. Heat the solvent for a short moment at nearly 70° in order to complete the reaction of the water with the acetic anhydride.

Cetyltrimethylammonium bromide, commercial grade "Cetavlon" (ICI) or similar product sold as cationic detergent and antiseptic.

0.1 N Perchloric acid in acetic acid. Mix 8.5 ml of concentrated perchloric acid (s.g. 1.70; 70%w) with 1 l of glacial acetic acid. A sufficient quantity of acetic anhydride should be added to bind the water contained in the concentrated perchloric acid. Standardize against 0.2 g of potassium biphthalate (analytical reagent grade) and titrate to the red colour of the tropaeolin oo indicator. Use 0.3 ml of a saturated solution of the indicator in glacial acetic acid for each titration.

Procedure

Weigh to the nearest 0.1 mg a quantity of sample containing not more than 0.5 mequiv of epoxide into a 50-ml beaker. Add to the sample 25 ml of glacial acetic acid,

2 g* of cetyltrimethylammonium bromide and 5 drops of a 0.1% (w/v) solution of crystal violet indicator in glacial acetic acid.

Start the magnetic stirrer and rapidly titrate, immediately after dissolution of the sample and the cetyltrimethylammonium bromide, with standardized perchloric acid solution until the bright green colour persists. The titrant should be added from a 10-ml microburet, *e.g.* a Metrohm piston buret E274. Although the correct visual end-point in this determination occurs at the first colour change of the indicator from blue to blue-green, the colour change from blue-green to bright green is much sharper and easy to observe. In this procedure distinct colour changes are caused by 0.01–0.02 ml of 0.1 *N* perchloric acid.

Make a blank test in exactly the same way as described above, but omit the sample. With "Cetavlon", blanks of not more than 0.1–0.2 ml are obtained.

Calculation

Calculate the "weight per equivalent" by means of the following equation:

$$\text{WPE(g/equiv)} = \frac{1000 W}{(V_s - V_b) \cdot N}$$

where:

W = weight of sample in g;

V_s = volume of 0.1 *N* perchloric acid solution consumed in ml;

V_b = volume of 0.1 *N* perchloric acid solution consumed in a blank, in ml;

N = normality of perchloric acid standard solution.

RESULTS OF THE FINAL METHOD

Since it is difficult to obtain a great variety of α -epoxides of high purity, only a few model compounds were at our disposal to judge the accuracy of the final procedure. Table I gives an impression of the absolute values of the results found.

The ethylene oxide, dissolved in acetone with a view to its handling, was subjected

TABLE I**

<i>Compounds</i>	<i>WPE found</i>	<i>Calculated purity (%w)</i>
Epichlorohydrin (mol.wt. 92.53) (freshly distilled)	92.8	99.6
1,2-Epoxypropane (mol.wt. 58.08) (not freshly distilled)	58.9	98.6
Ethylene oxide (mol.wt. 44.05) (freshly condensed at –80° from cylinder and a known quantity dissolved in acetone)		
(1) determined as liquid	44.0	100.1
(2) determined as vapour	44.4	99.2

* Originally 1 g of Cetavlon was used. Later experiments showed that an amount of 2 g (11 equivalents with respect to the epoxy group) is preferable to ensure a high reaction velocity for a greater variety of α -epoxides.

** The authors are most indebted to Mr. A. J. VERJAAL, who carried out the experiments mentioned in this Table.

to a determination not only in the liquid state but also in the vapour state, entrained by nitrogen. In the latter case a known amount of acetone solution was introduced into a vessel, which was externally heated at 60°, and purged with a stream of nitrogen. The resulting gas stream passed through a washing bottle with 100 ml of acetic acid containing 10 g of Cetavlon and a few drops of crystal violet indicator solution. The washing bottle was provided with a buret with 0.1 N perchloric acid solution for gradual titration of the liquid in the bottle keeping step with the absorption of the epoxide. Here we have an elegant procedure for determining α -epoxides in gas streams, which may be of interest in gas oxidation experiments.

SUMMARY

α -Epoxy compounds, such as glycidyl ethers and esters, can be rapidly determined by direct titration with perchloric acid in the presence of cetyltrimethylammonium bromide. Acetic acid is the preferred medium and crystal violet serves as the indicator.

RÉSUMÉ

Le titrage direct de composés α -époxy, tels que les éthers et les esters glycidyliques, peut s'effectuer rapidement à l'aide d'acide perchlorique, en présence de bromure de cetyltriméthylammonium. On préconise l'emploi d'acide acétique comme milieu de titrage et de violet cristallisé comme indicateur.

ZUSAMMENFASSUNG

Die direkte Titration von α -Epoxyverbindungen, z.B. Glycidyläthern und -estern, lässt sich mit Perchlorsäure in Anwesenheit von Cetyltrimethylammoniumbromid schnell durchführen. Als Titrationsmedium wird Essigsäure bevorzugt. Kristallviolett dient als Indikator.

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Anal. Chim. Acta, 31 (1964) 38-44

IODINE TRICHLORIDE IN GLACIAL ACETIC ACID AS
AN OXIDIZING TITRANT

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The behaviour of iodine trichloride in aqueous solutions as an oxidant is well known; Russian authors have described the oxidation of sulphites, stannous chloride¹, hypophosphorous acid, hypophosphites², and iodides³. Recently⁴ it has been proved that in aqueous solutions of ICl_3 , ICl_2^- and IO_3^- are only present.

Iodine trichloride is also soluble in nonaqueous media such as glacial acetic acid. Although this solution has been investigated from a physico-chemical point of view⁵, nothing appears to be known about its behaviour as an oxidant for inorganic compounds. The studies described here were done with iodine trichloride in glacial acetic acid; no work was done to elucidate the exact reactive species, present in this medium.

EXPERIMENTAL

The oxidation-reduction reactions were followed by potentiometric and amperometric methods. The apparatus was described previously⁶. The oxidizing agent was prepared by dissolving in glacial acetic acid pure ICl_3 , which had been treated previously with the same solvent to free it from any traces of iodine monochloride present.

The contents of ICl_3 were checked by iodometric titrations in aqueous solution and the compositions of the solutions were confirmed by titrating the previously reduced halides with standard silver solution.

The acetic acid used was checked for lack of reaction with chromic acid, in order to ensure the stability of the solutions, and the solutions were stored in the dark. The solutions of reducing agents were prepared as described previously⁶. Anhydrous sodium acetate was prepared by dehydrating the pure trihydrate salt, which was checked for lack of reaction with potassium permanganate.

RESULTS

Reaction of iodine trichloride with sulphite

The reaction between sodium sulphite and iodine trichloride is very slow but can give quantitative results provided that sodium acetate is present in molar concentration. Figure 1 shows the curve for the potentiometric titration; 4 potential jumps

can be seen. The first (A) corresponds to an $\text{ICl}_3/\text{SO}_3^{2-}$ ratio of 0.5; the solution remains colourless until point A is reached, *i.e.* until all iodine(III) has been converted to iodide. After this equivalence point the solution becomes yellowish-brown owing to the presence of the I_3^- complex, produced by the oxidation of iodide:

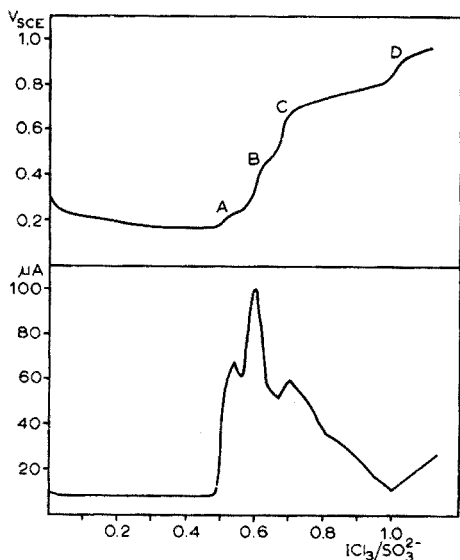


Fig. 1. Titration of sodium sulphite with iodine trichloride. Upper, potentiometric; lower, amperometric.

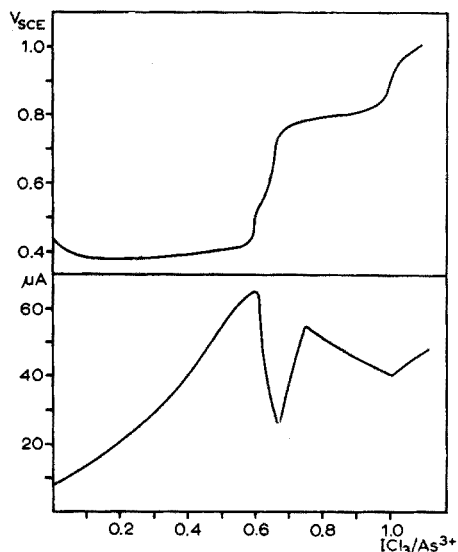
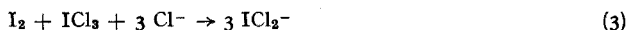


Fig. 2. Titration of arsenic trichloride with iodine trichloride. Upper, potentiometric; lower, amperometric.

Point B corresponds to an $\text{ICl}_3/\text{SO}_3^{2-}$ ratio of 0.6. After the first potential jump, the colour of iodine appears, owing to the reaction:



The third potential jump (C), corresponding to an $\text{ICl}_3/\text{SO}_3^{2-}$ ratio of 0.67, occurs when the I_2/I_3^- system is converted to $\text{ICl}_2^-/\text{I}_2$; the solution gradually becomes clear as the ICl complex is formed. Another step (D) in the potentiometric curve can be seen when the molar ratio between the oxidant and the reductant is 1, *i.e.* when the oxidation of I_2 to ICl_2^- is accomplished, according to the equation:



The solution then contains excess of ICl_3 .

These 4 experimental equivalence points were confirmed from the course of the amperometric titration at a potential difference (ΔE) of 0.8 V (Fig. 1). During the oxidation of sulphite, the current remained almost constant and low because the sulphite/sulphate system is irreversible. The $\text{ICl}_3/\text{SO}_3^{2-}$ ratio of 0.6 was characterized by a maximum current value, owing to the maximum of the I_3^- complex concentration. When all the oxidant had been converted to iodine, the current value reached

a minimum. The fourth equivalence point, corresponding to the formation of ICl, was reached at an oxidant/reductant ratio of 1 and was indicated by a second minimum current.

Reaction of iodine trichloride with arsenic(III)

The titration of AsCl₃ with ICl₃ is reasonably satisfactory only when the solution is 1.2 M in sodium acetate. When the reaction was followed potentiometrically (Fig. 2) 3 potential jumps were found corresponding to oxidant/reductant molar ratios of 0.6, 0.67 and 1; the reduction product of ICl₃ by arsenic(III) is I₃⁻; in fact, the first addition of oxidant gave the solution a brown tint. After the first equivalence point, iodine was formed and the reaction was complete at an ICl₃/As³⁺ ratio of 0.66. Further addition of ICl₃ led to ICl₂⁻ (see reaction 3). These equivalence points were checked when the reaction was followed amperometrically (Fig. 2); for the curve shows 1 maximum and 2 minima.

Reaction of iodine trichloride with antimony(III)

Antimony trichloride is oxidized in the cold by iodine trichloride solution provided that sodium acetate is present in molar concentration. The reaction proceeds very slowly but, if the titration was done very slowly, the equivalence points could be

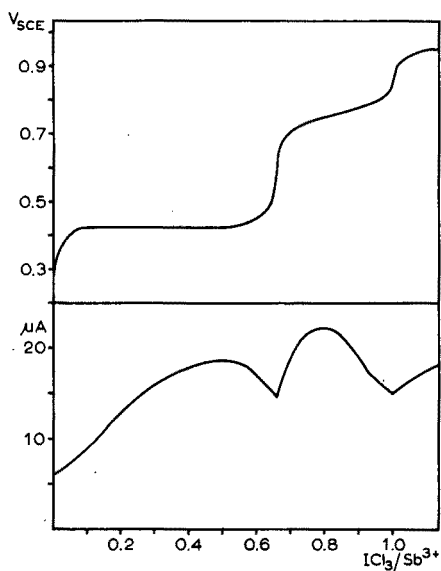


Fig. 3. Titration of antimony trichloride with iodine trichloride. Upper, potentiometric; lower, amperometric.

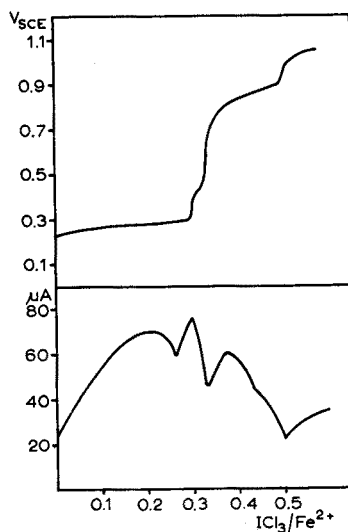


Fig. 4. Titration of iron(II) perchlorate with iodine trichloride. Upper, potentiometric; lower, amperometric.

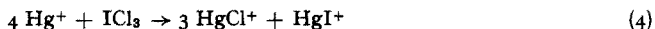
easily determined. In the potentiometric curve (Fig. 3) the 2 sharp jumps correspond to ICl₃/Sb³⁺ ratios of 0.67 and 1; the former is due to the oxidation of SbCl₃ to Sb⁵⁺ and reduction of ICl₃ to I₂, and the latter to the oxidation of iodine to ICl₂⁻. Correspondingly the amperometric curve shows 2 minima.

Reaction of iodine trichloride with iron(II)

Iron(II) can be oxidized quantitatively by iodine trichloride in the presence of 0.6 *M* sodium acetate provided that exposure to air is avoided as far as possible. In the potentiometric titration (Fig. 4), 3 jumps were observed; the first, at an $\text{ICl}_3/\text{Fe}^{2+}$ ratio of 0.3, corresponds to the formation of I_3^- ; the second, at a ratio of 0.33, corresponds to the oxidation of I_3^- to I_2 ; and the third, at a ratio of 0.5, corresponds to the oxidation of I_2 to ICl_2^- . The amperometric titration curve shows 1 maximum and 2 minima.

Reaction of iodine trichloride with mercury(I)

Mercurous perchlorate in glacial acetic acid solution is oxidized by iodine trichloride, the latter being reduced to iodide. The solution remains colourless until the following reaction is complete:



When the titration is followed potentiometrically a sudden rise in potential, corresponding to an ICl_3/Hg^+ ratio of 0.25 can be observed (Fig. 5). Even in absence of sodium acetate the equivalence point can be readily determined; but some sodium acetate (0.01 *M*) makes the reaction proceed more readily by decreasing the potential

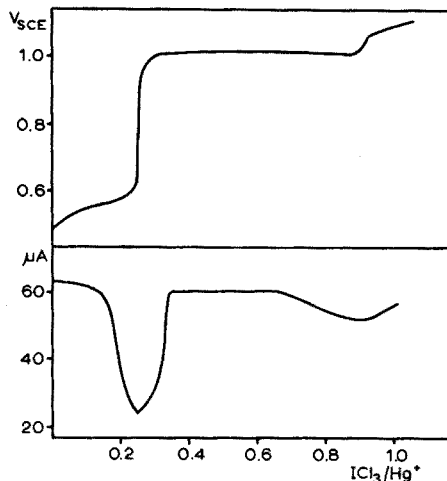
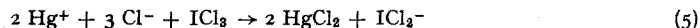


Fig. 5. Titration of mercury(I) perchlorate with iodine trichloride. Upper, potentiometric; lower, amperometric.

of the $\text{Hg}^{2+}/\text{Hg}^+$ system. After the above equivalence point, further addition of titrant causes the formation of some iodine and then iodine monochloride. At an ICl_3/Hg^+ ratio of 0.9, the solution becomes yellow and a second jump in potential can be seen.

In an attempt to explain the peculiar course of the reaction, evidenced by the second jump, the titration was repeated in the presence of chloride ions. A soluble chloride which is readily dissociated in anhydrous acetic acid, such as LiCl , was used, but the salt was added only after the first equivalence point had been reached in order to avoid the formation of calomel, which is difficult to oxidize. In the presence

of lithium chloride, the second equivalence point shifted from the ICl₃/Hg⁺ ratio of 0.9 to a ratio of 0.5, corresponding to the equation:



The reaction could be easily followed amperometrically. The first equivalence point, indicated by a minimum current value, appeared provided that the solution contained some sodium perchlorate to increase its conductivity. The second equivalence point was not obtained in the amperometric method.

DISCUSSION

The titrations of sulphite, arsenic(III), antimony(III), iron(II) and mercury(I) with iodine trichloride proved to be analogous to the reactions found when iodine monochloride was used as the oxidizing titrant⁷. However, when iodine trichloride was employed, in addition to the I⁻/I₃⁻, I₃⁻/I₂ and I₂/ICl₂⁻ steps, a further stage, corresponding to ICl₂⁻/ICl₃, was observed. The reduced form of the oxidant corresponding to the first potentiometric jump depends on the nature of the reductant. In the case of sulphite, which has the lowest redox potential of all the systems studied, the oxidant was reduced to iodide; in the case of arsenic trichloride and iron(II) perchlorate, iodine trichloride was converted to I₃⁻, whereas antimony trichloride reduced it only to I₂. All 4 reducing agents showed the distinct, successive stages in the order indicated.

Mercury(I) perchlorate has a rather high redox potential but can reduce iodine trichloride to iodide. The mercury(II) present forms stable complexes with iodide (obtained by dissociation of I₂) and thus promotes the auto-oxidation-reduction of the halogen. All the mercury(I) is oxidized at an ICl₃/Hg⁺ ratio of 0.25, so that the second

TABLE I
THE TITRIMETRIC DETERMINATION OF SOME REDUCING AGENTS WITH IODINE TRICHLORIDE

Reducing agent	CH ₃ COONa (M)	mg		Error	
		Taken	Found	mg	%
SO ₃ ²⁻	I	17.6	18.2	0.6	+3.4
	I	22.0	22.6	0.6	+2.7
	I	22.9	22.4	0.5	-2.2
	I	22.9	23.2	0.3	+1.3
	I	44.0	44.0	—	—
As ³⁺	1.6	4.53	4.48	0.05	-1.1
	1.6	7.26	7.19	0.07	-0.9
	1.6	3.63	3.59	0.04	-1.1
	1.6	2.26	2.23	0.03	-1.3
Sb ³⁺	1.8	10.4	10.1	0.3	-2.8
	1.8	12.0	11.8	0.2	-1.6
	1.8	16.0	15.3	0.7	-4.3
Fe ²⁺	0.6	13.9	14.1	0.2	+1.4
	0.8	20.9	20.7	0.2	-1.0
	0.6	17.4	17.9	0.1	-0.6
Hg ⁺	0.01	41.12	41.12	—	—
	0.01	48.34	48.14	0.2	-0.4
	0.01	61.58	61.58	—	—

equivalence point must be due to the presence of some mercury(II), which is not completely bound by iodide and chloride ions. The presence of an excess of chloride (by addition of lithium chloride) shifts the second equivalence point to a stoichiometric consumption of the oxidant (owing to the conversion of iodide to ICl or ICl_2^-); accordingly, it could be suggested that the mercury(II) forms a complex with chloride ions and so promotes the auto-decomposition of iodine trichloride to I^+ and I^{5+} .

The phenomena occurring when mercury(II) acetate is titrated by ICl_3 provide some confirmation of these suggestions. Although the reactant is coloured, its addition to the mercury(II) solution gives the yellow colour and a potential jump, only after sufficient has been added to form HgCl_2 and ICl_2^- , the latter resulting from the hypothetical auto-decomposition of I^{3+} . This phenomenon does not occur when mercury(II) chloride is used instead of mercury(II) acetate or perchlorate. Further research is in progress to elucidate the exact reactions.

SUMMARY

A systematic study of the redox reactions of iodine trichloride with various inorganic ions in glacial acetic acid medium is described. Sodium sulphite, arsenic trichloride, antimony trichloride, iron(II) perchlorate and mercury(I) perchlorate were examined. Potentiometric and amperometric methods were used to follow the reduction of iodine trichloride, which yields different products according to the type of reductant.

RÉSUMÉ

Une étude systématique a été effectuée sur les réactions redox du trichlorure d'iode, en milieu acide acétique glacial, avec divers composés minéraux (sulfite de sodium, chlorure d'arsenic(III), chlorure d'antimoine(III), perchlorate de fer(II) et perchlorate de mercure(I)). La réduction du trichlorure d'iode, donnant divers produits suivant le réducteur, a été suivie potentiométriquement et ampérométriquement.

ZUSAMMENFASSUNG

Es wird die systematische Untersuchung der Redox-Reaktionen zwischen Iodtrichlorid in Essigsäure und Natriumsulfit, Arsen(III)-chlorid, Antimon(III)-chlorid, Eisen(II)-perchlorat und Quecksilber(I)-perchlorat beschrieben. Der Verlauf der Reaktionen wurde potentiometrisch und amperometrisch verfolgt.

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DETERMINATION OF STRONTIUM COPRECIPITATED WITH BARIUM BY
X-RAY EMISSION SPECTROSCOPY

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It appears that the classical gravimetric chromate precipitation of barium is still the best available method for the separation of large amounts of barium from equivalent amounts of strontium¹. The tendency of strontium to coprecipitate with barium chromate is well recognized and most procedures call for a double precipitation to minimize this difficulty. A survey of the literature revealed the following 4 methods to be the best documented and the most effective insofar as precision and accuracy are concerned for the determination of 0.1–0.5 g quantities of barium in the presence of equivalent amounts of strontium.

SWIFT² — Precipitation of barium chromate by slow addition of a potassium chromate solution to the hot, buffered (pH 5) barium solution. Double precipitation is recommended. The procedure is very similar to that of SKRABAL AND NEUSTADTL³.

BEYER-RIEMAN⁴ — Precipitation of barium chromate by slow addition of a sodium dichromate solution to a cold, buffered (pH 4.6) barium solution, followed by boiling and cooling. Double precipitation is recommended.

NORWITZ⁵ — Homogenous precipitation of barium chromate by urea hydrolysis at a final pH of 5.5. Double precipitation is recommended. This procedure is a modification of that proposed by GORDON AND FIRSCHING⁶.

FIRSCHING⁷ — Formation of the EDTA complexes of barium and strontium in a slightly alkaline solution containing chromate, then slow addition of a magnesium ion solution to displace first the barium from its EDTA complex and so permit precipitation of barium chromate. A single precipitation is stated to be adequate.

The effectiveness of the first three of these methods was checked by essentially classical means and no direct determination of strontium in the singly or doubly precipitated barium chromates was reported. Only the fourth method, that of FIRSCHING, was justified by a determination of the strontium content of the precipitates and this was done radiochemically, using strontium-90. Since 3 of the 4 best-documented methods for separating barium and strontium by chromate precipitation have not been directly checked for coprecipitated strontium, this investigation was undertaken to apply the method of X-ray emission spectroscopy to this determination.

EXPERIMENTAL

Barium chromate precipitates were prepared according to the various authors'

directions and these were filtered and washed on medium-porosity sintered-glass filtering crucibles with suction, then were dried at 120°. Known amounts of barium and strontium were obtained from reagent-grade barium chloride dihydrate (whose water content, as determined by loss on drying at 120°, was within 0.3% relative of theory) and anhydrous strontium nitrate. When the amounts of barium and strontium taken were greater than those specified in the method as published, an appropriate scale-up of volumes, etc., was made. The dried precipitates were removed from the filtering crucibles, ground in a mortar and pestle, then were manually packed into suitable sample holders for the strontium determination by X-ray emission spectroscopy.

The instrument used was a General Electric XRD-3 unit with suitable modification for X-ray emission analysis. The exciting X-ray tube was a tungsten target Machlett AEG50-T, operated at 50 kV and 45 mA. The sample holders were of plexiglass and had rectangular cavities varying in depth from 1/100" to 3/32", but all provided the necessary "infinitely thick" sample towards X-rays. These holders required 0.2–2 g to fill them. The powdered samples were packed manually in the holders with no special precautions other than that of obtaining as smooth a surface as possible with a metal spatula or glass slide.

The flat-faced analyzing crystal was of lithium fluoride (d spacing = 2.0135 Å) and the first-order strontium $K\alpha$ line of 0.877 Å wavelength and occurring at $25.16 \pm 0.05^\circ$ was used for analysis. The detector tube was a No. 4 SPG flow-type proportional counter, operated at 2150 V and using argon–methane PR gas at 4.0 p.s.i. Pulse height discrimination was not used. The scaler was of the binary type and yielded the time (in sec) for a predetermined number of counts. Five "count numbers" were available, ranging from 1024 to 16384. When intensity measurements were made, the count number employed was such as to give counting times of *ca.* 10 or more sec, the elapsed counting time being measured to the nearest 0.1 sec.

When samples were analyzed by this method, the strontium $K\alpha$ line was located by use of a BaCrO₄–SrCrO₄ standard containing 3.91% by weight strontium and the analyzing crystal was adjusted so that this line occurred at $25.16 \pm 0.05^\circ$ on the goniometer. This standard was then counted at least 10 times, using the 16384 count number. The average counts/sec intensity was then obtained and compared with previous values to insure that no serious instrumental drift had occurred. A sample of pure barium chromate was next counted to provide background intensity, and then the desired samples were run. Each sample was run in duplicate (*i.e.*, two separate sample mountings) and each run involved at least 10 separate counting times which were finally averaged. During a set of runs, close watch was kept on the X-ray tube current and voltage and the counter-tube voltage so that any drift detected could be corrected. The pure barium chromate was then rerun after the samples, as a further precaution against change in the external background, and the two average intensity values for this barium chromate sample were finally averaged to obtain the background intensity. This background intensity was then subtracted from the average intensity values of the various samples to obtain a sample intensity corrected for background.

A calibration curve for weight % strontium in barium chromate *vs.* intensity corrected for background was prepared from 2 sets of standards. The first set of standards was prepared by simultaneous precipitation of strontium and barium

chromates from solutions containing known amounts of strontium and barium, following the directions of SWIFT² for conditions in which the more soluble strontium chromate would be completely precipitated. These precipitates were filtered by decantation through medium-porosity filtering crucibles, then washed with centrifugation, dried at 120°, and finally ground and mixed in a mortar and pestle. The second set of standards was prepared by mixing weighed quantities of pure strontium chromate and pure barium chromate (these substances being separately prepared by precipitation procedures, followed by filtration, washing, drying, and mixing) by grinding with methanol in a glass mortar and pestle. The final slurry was dried at 90°. Both sets of standards yielded essentially the same calibration curve. It may be noted that the second method of preparation is less troublesome and time-consuming than the first, since the precipitation, filtering, and washing of 5–10 g of mixed chromates is troublesome when carried out in ordinary laboratory equipment.

RESULTS AND DISCUSSION

The X-ray data obtained for the 2 sets of standards is shown in Table I. The agreement between the 2 sets of data is considered satisfactory. The calibration curve obtained was linear and had an average slope of 404 counts/sec/wt. % strontium. The

TABLE I
STRONTIUM $K\alpha$ INTENSITY DATA FOR THE 2 SETS OF STANDARDS

Standard no.	Wt. % Sr in standard	Average X-ray intensity precipitated standards (counts/sec)	Correction for background mixed standards (counts/sec)
1	0.043	21 ± 0	20 ± 1
2	0.215	84 ± 2	94 ± 1
3	0.43	182 ± 1	178 ± 0
4	0.84	344 ± 0	346 ± 6
5	1.29	517 ± 0	529 ± 4
6	2.05	809 ± 0	841 ± 6
7	3.91	1574 ± 16	1582 ± 2

background averaged 45 counts/sec which corresponds to 0.11 % strontium. Since 10 counts/sec above background is definitely detectable and measurable, the sensitivity of the method is considered to be 0.02 % strontium; and 0.1 % strontium is definitely measurable to 2 significant figures. If one starts with equal weights of strontium and barium in solution and if a barium chromate precipitate containing 0.1 % strontium is obtained, this would correspond to coprecipitation of *ca.* 0.2 % of the *original* strontium, leaving 99.8 % of the original strontium in solution. This would constitute an adequate analytical separation and it is seen that the X-ray method has adequate sensitivity for this purpose. The accuracy of the X-ray method is more difficult to state with assurance. Since the samples to be run should contain very little else besides barium chromate and strontium chromate, errors due to variable matrix absorption or multiple excitation, as discussed by CULLITY⁸, should be negligible. Assuming this to be true, the accuracy is primarily limited by the precision and this is of the order of 10% relative for 0.1 % Sr or less and *ca.* 2 % relative for 0.5–4 % Sr.

Since a linear calibration curve over the range 0–3.91 % strontium was obtained

for the 2 sets of standards, the strontium content of analytical samples was determined from the data on the 3.91 % Sr standard obtained that same day. That is, the intensity corrected for background for this standard was divided by 3.91 % to obtain the calibration factor for that day and this factor was used to convert intensity corrected for background data for the samples run that day to % strontium. Thus, compensation was made for minor day-to-day variations in the slope of the calibration curve.

TABLE II

STRONTIUM CONTENT OF PRECIPITATES OBTAINED BY THE SWIFT, BEYER-RIEMAN AND NORWITZ METHODS

<i>Swift method^a</i>		<i>Beyer-Rieman method^b</i>		<i>Norwitz method^c</i>	
<i>No. Pptns.</i>	<i>Wt. % Sr</i>	<i>No. Pptns.</i>	<i>Wt. % Sr</i>	<i>No. Pptns.</i>	<i>Wt. % Sr</i>
1	2.38	1	0.81	1	1.96
1	2.33	1	1.03	1	1.87
1	2.35	1	0.79	1	1.78
1	2.06			1	2.21
		2	0.04	1	2.50
2	0.93	2	0.03	1	1.88
2	1.16	2	0.085		
2	0.62	2	0.03	2	0.07
2	0.75	2	0.03	2	0.09
		2	0.02	2	0.07
		2	0.03	2	0.10
		2	0.04	2	0.09
		2	0.03	2	0.07

^a SWIFT method: 1.928 g BaCl₂ · 2H₂O and 1.928 g Sr(NO₃)₂ carried through the method.

^b BEYER-RIEMAN method: 0.4880 g BaCl₂ · 2H₂O and 0.4880 g Sr(NO₃)₂ carried through the method.

^c NORWITZ method: 0.2500 g BaCl₂ · 2H₂O and 0.2500 g Sr(NO₃)₂ carried through the method.

Barium chromate precipitates obtained by the SWIFT, BEYER-RIEMAN, and NORWITZ methods (both single and double precipitations) were analyzed for strontium content by the X-ray method and the results are shown in Table II. The results obtained on singly precipitated samples all show unacceptably high strontium contents, confirming the reports of the authors of these methods. The BEYER-RIEMAN and NORWITZ methods show acceptably low strontium coprecipitation in doubly precipitated barium chromate, but, surprisingly, the SWIFT method does not. Further, the precipitates obtained by the SWIFT method were very hard to handle because the particles adhered tenaciously to glass and exhibited a tendency to creep. The precipitates obtained by the BEYER-RIEMAN and NORWITZ methods, on the other hand, were coarse-grained and easy to handle.

Based on these observations, either the BEYER-RIEMAN or NORWITZ methods are to be preferred to the SWIFT method. We recommend the BEYER-RIEMAN method because it is a little quicker and easier to carry out (in our opinion) and because the degree of strontium coprecipitation is slightly less than that of NORWITZ. Since we recommend the BEYER-RIEMAN method, it was decided to check out the accuracy of this method in our hands. This was done by putting known amounts of barium and strontium through the procedure, including the double precipitation,

weighing the precipitate finally obtained, and analyzing the precipitate for strontium content. These data are shown in Table III. The results, comparing "barium taken" to "barium found" are uniformly high by 0.2 to 1.0 % relative and this error is significantly reduced in only one case when one corrects for the determined strontium

TABLE III

WEIGHT DATA FOR BARIUM CHROMATE PRECIPITATES OBTAINED BY THE BEYER-RIEMAN METHOD
(0.4880 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.4880 g $\text{Sr}(\text{NO}_3)_2$ taken for analysis in each case)

No. Ppts.	Theoretical wt. BaCrO_4 (g)	Observed wt. BaCrO_4 (g)	Observed wt. % Sr	Calculated wt. SrCrO_4 (g)	Unaccounted wt. difference
1	0.5061	0.5204	0.79	0.0096	+ 0.0047
2	0.5061	0.5079	0.085	0.0010	+ 0.0008
2	0.5061	0.5094	0.03	0.0003	+ 0.0030
2	0.5061	0.5112	0.03	0.0003	+ 0.0048
2	0.5061	0.5087	0.02	0.0003	+ 0.0023
2	0.5061	0.5094	0.03	0.0003	+ 0.0030
2	0.5061	0.5068	0.04	0.0004	+ 0.0003 ^a
2	0.5061	0.5077	0.03	0.0003	+ 0.0013 ^a

^aThese two precipitates were dried at 150° for 60 h. The others were dried at 120°.

content (assumed to be SrCrO_4). This positive error is significantly greater than that reported by BEYER AND RIEMAN⁴ who stated that 0.4–1.0 mmoles of barium could be determined with an average error of 0.003 mmole or less in the presence of up to 10 mmoles of strontium. Further, their results were low more often than they were high. The source of this error in our case was not further determined, but it is believed to be partly due to incomplete drying at 120°, since precipitates dried at 150° for 60 h showed lower unaccounted weight differences than did those dried at 120° (Table III). It is believed that the residual positive error is due to coprecipitated sodium chromate or dichromate. It should be noted that BEYER AND RIEMAN used an iodometric titration method for chromate as a final measuring step compared to our gravimetric method. Coprecipitated chromate or dichromate would certainly interfere in the iodometric method but other errors inherent in that method that are not in the gravimetric method could account for this observed discrepancy.

The FIRSCHING method was checked for strontium coprecipitated with barium chromate after a single precipitation only, since it is claimed that this method requires only one precipitation for a good separation⁷. The results that we obtained are shown in Table IV. There was some variation in the procedure from that prescribed by FIRSCHING for certain of the samples, but all gave rather consistent values for strontium content that are unacceptably high. Furthermore, the precipitates obtained were very fine-grained and tended to pass through the pores of medium-porosity filtering crucibles as well as being difficult to transfer and wash. A one-hour digestion of the precipitate did not improve this situation. Two samples were run using fine-porosity filtering crucibles so that weight data could be obtained. After correcting for strontium content (calculated as SrCrO_4), the unaccounted weight differences were positive (high results) by 0.0028 g and 0.0044 g for a theoretical weight of barium chromate of 0.2530 g. This discrepancy is quite seriously large and

is assumed to be due to a combination of incomplete drying at 120° and coprecipitated material other than strontium.

The results for coprecipitated strontium do not agree at all with those reported by FIRSCHING⁷. Using a radiochemical method, FIRSCHING found 0.09–0.25 mg of

TABLE IV
STRONTIUM CONTENT OF PRECIPITATES OBTAINED BY THE FIRSCHING METHOD
(Single precipitation used in all cases)

<i>Wt. BaCl₂ · 2H₂O taken (g)</i>	<i>Wt. Sr(NO₃)₂ taken (g)</i>	<i>Wt. % Sr found</i>	<i>Variation from Firsching</i>
0.1220	0.1060	0.61	None
0.1220	0.1060	0.50	Mg(NO ₃) ₂ instead of MgCl ₂ used to supply Mg ²⁺
0.1220	0.1060	0.60	Mg(NO ₃) ₂ used to supply Mg ²⁺ . Ppt. digested 1 h before filtration
0.2480	0.2480	0.56	Insufficient EDTA added to precipitate all the BaCrO ₄
0.2480	0.2480	0.51	

strontium in *ca.* 0.13 g of precipitate, for equivalent weights of strontium and barium originally taken. This corresponds to 0.08–0.2 % Sr in the precipitate, which is less than 1/3 the amount of coprecipitated strontium we find by the X-ray method. We cannot account for this discrepancy, but we have no reason to doubt the X-ray results. We therefore cannot recommend the FIRSCHING method because of excessive strontium coprecipitation and because of the poor filtering qualities of the precipitate.

SUMMARY

X-Ray emission spectroscopy allows detection of as little as 0.02% strontium in barium chromate. This method has been applied to evaluate the effectiveness of 4 procedures for separating barium and strontium by chromate precipitation. All of the procedures checked require at least 2 precipitations for a satisfactory separation. Of the 4 methods checked, that of BEYER AND RIEMAN is recommended on the basis of convenience and effectiveness of separation.

RÉSUMÉ

La spectroscopie d'émission à rayons-X permet de déceler jusqu'à 0.02% de strontium dans de chromate de baryum. Les auteurs ont appliqué cette méthode pour comparer 4 procédés de séparation baryum–strontium, par précipitation au chromate. Dans chaque cas, il est nécessaire d'effectuer au moins 2 précipitations pour avoir une séparation satisfaisante. C'est la méthode de BEYER ET RIEMAN qui est recommandée.

ZUSAMMENFASSUNG

Die Röntgenfluoreszenzanalyse erlaubt den Nachweis von weniger als 0.02% Strontium im Bariumchromat. Diese Methode wurde benutzt um die Wirksamkeit von 4 Verfahren zur Trennung von Barium und Strontium durch die Chromatfällung zu bestimmen. Alle geprüften Verfahren erfordern für eine befriedigende Trennung wenigstens 2 Fällungen. Von den 4 geprüften Methoden ist die von BEYER UND RIEMAN empfehlenswert.

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FLAME PHOTOMETRIC DETERMINATION OF POTASSIUM IN SEA WATER
AND MARINE ORGANISMS

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Potassium is the fourth most abundant cation in sea water. Its concentration is reported to be a function of the chlorinity of sea water, the ratio being expressed by a relatively constant number^{1,2}. JENTOFT AND ROBINSON³ have reported an average potassium/chlorinity ratio of 0.517 where potassium is expressed in mg-atom. Potassium has been determined by several gravimetric methods, *e.g.* as chloroplatinate⁴⁻⁶, cobaltinitrite⁷⁻⁹, metaperiodate³ and perchlorate¹⁰. Later results by ANDERSON¹¹ using the isotopic dilution method found 10.2 mg-atoms of potassium per litre of Atlantic surface water with a specific gravity of 1.028. The purpose of this investigation was to develop a convenient flame photometric procedure for determining potassium in sea water and marine organisms.

EXPERIMENTAL

Chemicals and equipment

All chemicals used were of analytical grade and tested for traces of potassium. A standard solution of potassium chloride, equivalent to 40 mg-atoms potassium per litre, was prepared by dissolving 2.984 g of potassium chloride in 1 l of re-distilled water. Stock solutions of the chlorides of ammonium, calcium, magnesium, sodium and strontium were prepared as well as ammonium carbonate and sulphate. Polyethylene containers were used for storing standard solutions.

The intensity of the spectral line emitted by potassium ions was measured with a Beckman DU spectrophotometer fitted with a multiplier phototube and a modified flame attachment. Tanks of hydrogen and oxygen were used as the fuel.

Procedure

The potassium spectral line of 767 $m\mu$ was chosen. The flame background at 750 $m\mu$ was equal to that at 767 $m\mu$ and was unaffected by changing potassium concentration. The difference obtained at these two wave lengths was used as the measurement of the spectral line intensity emitted by potassium ions. The sensitivity knob was set at the counterclockwise position and the selector switch on the 0.1 scale. The hydrogen and oxygen gauges were regulated to 4 and 15 p.s.i. respectively. The reproducibility of the photometer was checked with standard potassium solutions at the beginning and the end of each series of analyses.

In accord with the manufacturer's instruction, a 10,000 megohm resistor had to be installed in the phototube compartment for flame photometry. With such high input load resistance, the null device of the photometer became so erratic that precise balancing of the photometer could not be achieved. In view of this, a 22 megohm resistor was installed in the circuit for this investigation.

Since the intensity of the flame background increased with widening slit width, a compromise between the sensitivity and the accuracy of the determination must be taken into consideration. The relationship between the slit width and the flame background was determined as follows: the emission intensities of diluted sea-water samples were measured at $767\text{ m}\mu$ and $750\text{ m}\mu$ by varying the slit width with other

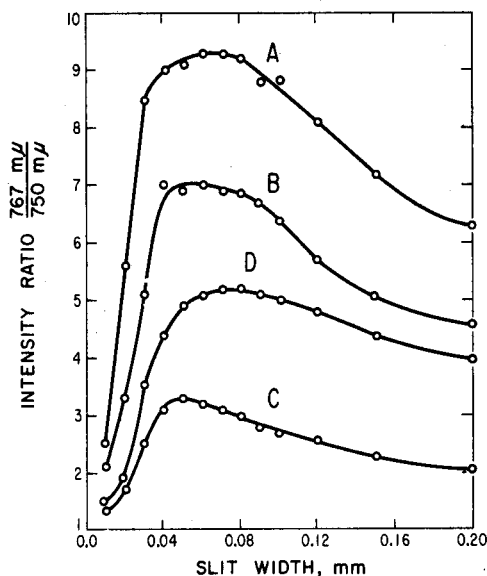


Fig. 1. Emission intensity ratio vs. slit width. (A) 10% solution of $18^0/00$ Cl sea water; (B) 5% solution of $18^0/00$ Cl sea water; (C) 2% solution of $18^0/00$ Cl sea water; (D) 0.25 mg-atom/l potassium standard solution.

controls remaining constant. The emission intensity ratio ($767\text{ m}\mu/750\text{ m}\mu$) was plotted against its corresponding slit width. A family of curves is shown in Fig. 1. The emission intensity ratio increased steadily as the slit width widened up to 0.04 mm, and then the ratio held nearly constant from 0.04 mm to 0.08 mm. Within this range, the potassium emission intensity was about 9 times that of the flame background. When the slit width was wider than 0.08 mm, the intensity ratio tapered off due to increasing flame background, and it approached unity as the limit.

Spectral interference

Studies were made to determine the extent of spectral interference on the potassium line that might be caused by the major constituents of sea water. Various standard solutions, each containing one major constituent whose concentration was several

times greater than that found in sea water, were prepared. The emission intensity of those elements or compounds is given in Table I. None of those ions emitted any appreciable amount of light at 767 $m\mu$. Several common acids also showed no interference.

Radiation interference

The radiation effect on the potassium determination due to the presence of various major ions of sea water was also examined. The net emission intensities of the solution

TABLE I
SPECTRAL INTERFERENCES

Constituents	Concentration (p.p.m.)	Net intensity at 767 $m\mu$
(Ammonium) chloride	39,000	0.0
Sodium (chloride)	22,000	0.0
(Ammonium) sulphate	7700	0.0
Magnesium (chloride)	4900	0.0
Calcium (chloride)	1600	0.0
(Ammonium) carbonate	1200	0.0
Strontium (chloride)	100	0.0
HCl	1.0 M	0.0
HNO ₃	0.4 M	0.0
H ₂ SO ₄	0.2 M	0.0
H ₃ PO ₄	0.1 M	0.0
CCl ₃ COOH	0.1 M	0.0

TABLE II
RADIATION INTERFERENCES

Interfering ions		Potassium (p.p.m.)		Interfering ions		Potassium (p.p.m.)				
Constituent	p.p.m.	Added	Found	Constituent	p.p.m.	Added	Found			
Chloride	3900	390	390	Calcium	200	390	390			
	8900	390	383		400 ^a	390	390			
	19,500 ^a	390	375		800	390	390			
	29,300	390	364		1200	390	390			
Sodium	1100	390	414	Carbonate	120 ^a	390	390			
	2200	390	422		300	390	390			
	4300	390	442		600	390	390			
	8600	390	497	Strontium	9 ^a	390	390			
	10,800 ^a	390	540		100	390	390			
Magnesium	240	390	390	HCl	1.0 M	390	387			
	730	390	390		HNO ₃	0.4 M	390	390		
	1200 ^a	390	390			H ₂ SO ₄	0.2 M	390	368	
	2400	390	390				H ₃ PO ₄	0.1 M	390	390
	3600	390	390					CCl ₃ COOH	0.1 M	390
Sulphate	500	390	390							
	1600	390	390							
	3400 ^a	390	390							
	6300	390	390							

* Denotes approximate concentration in sea water.

containing known quantities of potassium together with possible radiation interfering ions were measured. The calculated amounts of potassium recovery are given in Table II.

As shown in Table II, the presence of large quantities of chloride ions slightly suppressed the intensity of the potassium spectral line. This may be explained by the increased viscosity of the test solution which would reduce the rate of atomisation¹². Calcium, magnesium, strontium, sulphate and carbonate when present in quantities approximating that found in sea water did not interfere with the potassium determination. Sodium ions caused potassium to emit more light and, therefore, a high potassium recovery. The sodium effect is considerably lower than that reported by POLUEKTOV *et al.*¹³ and the difference may be due to the fact that the potassium concentration used in this experiment was much higher than that of POLUEKTOV *et al.* Nitric, phosphoric and trichloroacetic acids gave no radiation interference. Hydrochloric and sulphuric acids when present in large quantities gave a low potassium recovery. These interferences are much lower than those given by DEAN¹⁴. As shown by DEAN, an increase of potassium concentration from 30 p.p.m. to 80 p.p.m. reduces considerably the common acid interference. The potassium concentration used in this investigation was 390 p.p.m.

Calibration graphs of potassium

The calibration graphs were constructed by plotting the potassium concentration ranging from 0.0 to 40 mg-atom/l against its corresponding net emission intensity at 767 m μ . In order to adjust the emission intensities of varying potassium concentration to full scale on the photometer, the slit width was varied accordingly. As shown in Fig. 2, the intensity of the spectral line emitted by potassium deviated from linearity at high concentrations. However, a linear relationship was obtained between emission

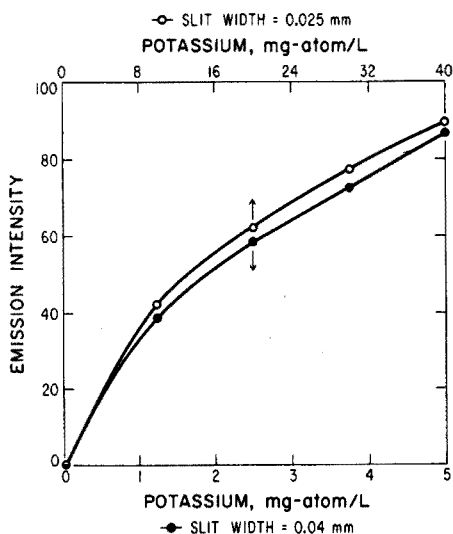


Fig. 2. Calibration graphs of potassium at high concentrations.

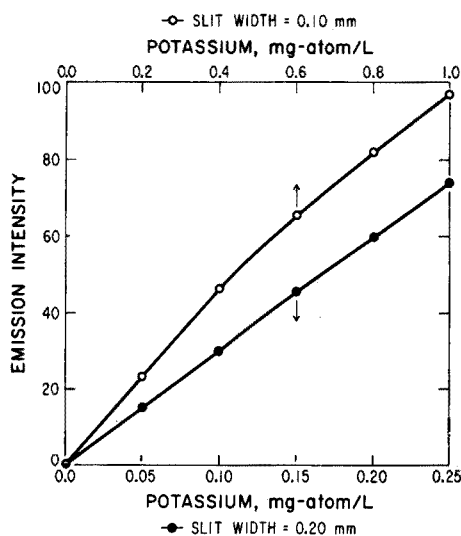


Fig. 3. Calibration graphs of potassium at low concentrations.

intensities and potassium concentrations of less than 0.50 mg-atom/l as illustrated in Fig. 3. Within this linear range, the "internal standard addition" technique of flame photometry¹⁵ was applied.

RESULTS AND DISCUSSION

The results of analysis (Tables III and IV) demonstrate the applicability of this method for determining small quantities of potassium in natural waters and biological materials. The fresh-water samples were analysed by direct interpolation with

TABLE III
OCCURRENCE OF POTASSIUM IN NATURAL WATERS

<i>Fresh water</i>		
<i>Location</i>	<i>Potassium (mg-atom/l)</i>	
Tap water, Seattle, Washington	0.038	
Lake Washington, Seattle, Washington	0.036	
Tap water, Friday Harbor, Washington	0.026	
Egg Lake, San Juan Island, Washington	0.020	
Sportsman Lake, San Juan Island, Washington	0.020	
Lawson Pond, San Juan Island, Washington	0.031	
Lime quarry, San Juan Island, Washington	0.361	
Well water, McConnell Island, Washington	0.023	
Tap water, Victoria, British Columbia	0.043	
Elk Lake, British Columbia	0.038	
<i>San Juan Channel, Friday Harbor, Washington</i>		
<i>Chlorinity (‰)</i>	<i>Potassium (mg-atom/l)</i>	<i>K/Cl</i>
16.50	9.00	0.545
16.61	9.05	0.545
18.40	9.93	0.540
18.62	10.1	0.542
18.65	9.80	0.526
18.78	9.95	0.530
18.78	10.1	0.538
18.83	10.1	0.536
		Average 0.538

TABLE IV
DETERMINATION OF POTASSIUM IN BIOLOGICAL MATERIALS

<i>Specimen</i>	<i>Chlorinity (‰)</i>	<i>Potassium (mg-atom/kg)</i>	<i>K/Cl</i>
<i>Octopus apollyon</i> - serum	16.71	10.3	0.616
- pericardial fluid	17.32	11.5	0.664
- urine	16.75	11.5	0.686
<i>Squalus</i> sp. - serum	8.93	3.36	0.376
<i>Halosaccion glandiforme</i> - fluid	17.67	9.40	0.532
<i>Fucus furcatus</i> - fluid	17.94	8.70	0.485
- ash	138	4450	32.2
<i>Laminaria</i> sp. - ash	321	8030	25.0
<i>Nereocystis luetkeana</i> - ash	419	10,330	24.7

standard potassium solution. The sea-water samples were diluted to 10% of their original strength with re-distilled water so that the light intensity would respond linearly with the potassium concentration. The average potassium/chlorinity ratio of Pacific coastal water was calculated to be 0.538 where the potassium concentration was expressed in mg-atom/l of sea water.

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SUMMARY

A convenient flame photometric procedure for determining potassium in sea water and biological materials is described. Factors affecting the intensity of the spectral line emitted by potassium ions were studied. The major constituents of sea water showed no spectral interference on the potassium analysis. Chloride ions and sulphuric acid gave a negative radiation interference while sodium ions showed a positive effect. The "internal standard addition" procedure was used for eliminating the effect of these interfering constituents.

An average potassium/chlorinity ratio of 0.538 was obtained for the Pacific coastal water with potassium concentration being expressed in mg-atom. The applicability of this procedure for the determination of potassium in biological materials was also demonstrated.

RÉSUMÉ

On décrit une méthode photométrique de flamme pour le dosage du potassium dans l'eau de mer et dans des substances biologiques. Les facteurs influençant l'intensité de la raie spectrale émise par le potassium ont été examinés. Les chlorures diminuent l'intensité de la raie du potassium, de même que l'acide sulfurique; tandis que le sodium a un effet positif. On applique alors la méthode de l'étalon interne pour supprimer l'influence de ces ions.

ZUSAMMENFASSUNG

Ein bequemes flammenphotometrisches Verfahren zur Bestimmung von Kalium im Seewasser und biologischen Materialien wird beschrieben. Faktoren, die die Intensität der durch die Kaliumionen emittierten Spektrallinie beeinflussen, werden untersucht. Die Hauptbestandteile des Seewassers ergeben allein keine Intensität bei der Kaliumlinie. Chloridionen und Schwefelsäure verringern die Intensität, während Natriumionen einen positiven Effekt zeigen. Um diese Effekte zu eliminieren, wurde das Verfahren des inneren Standards verwendet. Das mittlere Verhältnis K/Cl betrug für das Wasser des Pazifischen Ozeans 0.538. Die Anwendbarkeit des Verfahrens für die Bestimmung des Kaliums im biologischen Material wird ebenfalls gezeigt.

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ASSESSING THE ACTIVITY CONCENTRATION OF β -EMITTERS BY MEANS OF THE END-WINDOW G.M. TUBE

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Notwithstanding the rapid development of special techniques for the determination of the activity concentration of β -emitters (*e.g.* liquid scintillation counting), the end-window G.M. tube remains an important tool for this purpose. The main reason is that the relatively low cost of the G.M. counting assembly and its dependability when extensive servicing facilities are not available, place this equipment within reach of the smaller laboratories.

A limiting factor in the application of the above technique remains the reproducibility and accuracy of the results obtained. A first systematic investigation of the reproducibility of certain techniques of sample preparation was made by SCHWEITZER AND ELDRIDGE¹, who determined the percentage relative error, E , from sets of 30 preparations involving ³⁵S, ³²P and ¹³⁷Cs. For ³⁵S (the most problematic isotope of those studied because of the low-energy β -emission) the percentage standard deviation of a single observation of the activity concentration amounted to 1.5–2% at best. As this may not be satisfactory for certain purposes, the present work was designed to investigate systematically the probable causes of error in these determinations and to delineate measures for improvement. As one of the reasons for the use of radio-isotopes is the simplicity and rapidity of the analysis, the investigation was limited to the preparation of samples by direct evaporation of a known amount of solution on a planchet. Among the variables and factors studied were the shape of the planchet, method of drying, carrier concentration, use of additives and method of counting.

EXPERIMENTAL

The radio-isotopes studied are listed in Table I. They were obtained as aqueous solutions of a known specific activity. These solutions were diluted to the required activity concentrations with salt solutions of known composition and stored in polythene bottles. The G.M. counting assembly consisted of an end-window G.M. tube (Philips No. 18505 with a mica window of 1" diam., 1–2 mg/cm²) mounted in a lead castle, and a decimal scaler-timer (Philips No. 111-531). Two of these assemblies were used in the course of the experiment; except for a small difference in counting efficiency, the results obtained with these 2 sets were identical as regards reproducibility.

TABLE I
ISOTOPES USED

Isotope	Type of decay	Energy of radiation		Half-life
		γ	β	
$^{22}_{11}\text{Na}$	β^+	1.28	0.54	2.6 y
$^{32}_{15}\text{P}$	β^-	—	1.7	14.3 d
$^{35}_{16}\text{S}$	β^-	—	0.167	87.5 d
$^{36}_{17}\text{Cl}$	β^-	—	0.71	$3.1 \cdot 10^5$ y
$^{45}_{20}\text{Ca}$	β^-	—	0.25	160 d

bility and accuracy. Depending on the type of lead castle used, the background count-rate was 8 or 12 counts/min. For comparison the ^{22}Na samples were also counted with an end-window scintillation detector (EKAF No. 50301 with built-in cathode follower, thallium-activated NaI crystal of 1.5" diam.) together with a scaler-timer of the above type.

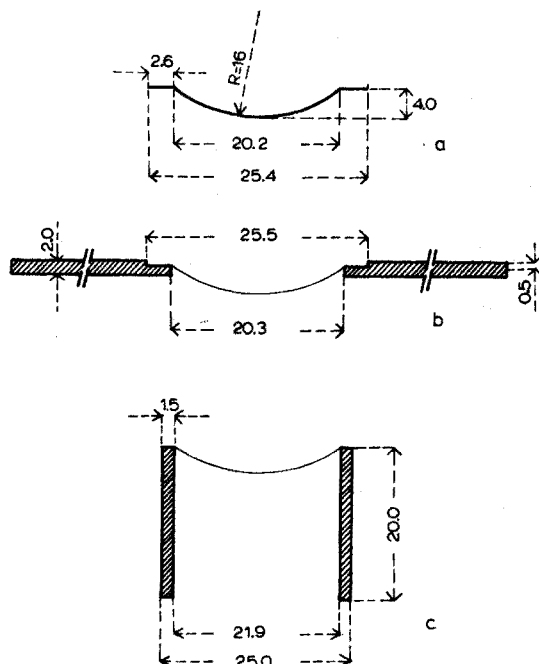


Fig. 1. (a) Counting planchet; (b) plexiglas slide used for mounting planchet in lead castle; (c) brass ring for hot-plate drying. All measurements in mm.

The planchets used were varied in shape; they were hand-pressed out of 0.3 mm aluminium foil with the help of carefully machined templates. For counting they were placed on a plexiglas slide provided with a hole (Fig. 1). The slide could be mounted at different heights in the lead castle, provisions being made for centering the hole in the slide with respect to the axis of the G.M. tube.

All samples were prepared on weight basis, *i.e.* by pipetting about 0.5-ml amounts on to the pre-tared planchet placed in a small petri dish and weighing on an automatic balance within 0.1 mg. The weight loss due to evaporation between pipetting and weighing amounted to about 0.04 mg. Both lamp drying and hot-plate drying were investigated. Preparations were usually made in series of 10 and stored in lucite boxes accommodating plexiglas slides carrying a complete series each (Fig. 2).

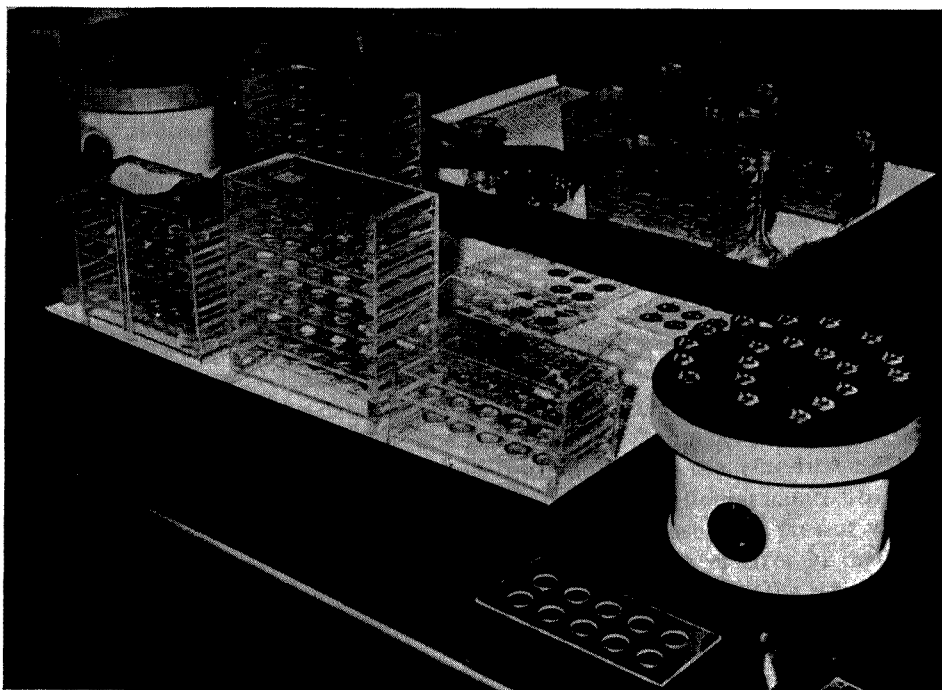


Fig. 2. Drying and storage of preparations for counting.

Unless stated otherwise, the results of the reproducibility studies are given as the percentage standard deviation of a single observation, S , as derived from the observed variation within the series of 10. In a few cases, the standard deviation of the mean count-rate of the series of 10, \bar{S} , was used.

All count-rates observed were high (2000–8000 counts/min) in comparison to the background rate. In order to calculate the net count-rate, appropriate corrections were made for background and dead time of the G.M. tube; the contribution of the variation of these corrections to the variation of the net count-rate was insignificant in all cases.

The program was based on the following approach. The percentage standard deviation of a single observation as derived from the observed spread in the count-rates of an infinite series of "identical" samples, S , is composed of 3 parts, according to:

$$S = \sqrt{\sigma_a^2 + \sigma_p^2 + \sigma_s^2}$$

In this equation σ_a indicates the error resulting from the randomness of the disintegration process and should be equal to $100/\sqrt{N}\%$, where N = total count observed; σ_p signifies the error due to the variability of placement of the sample in its holder under the G.M. tube, and σ_s is the error caused by the variability of the sample preparation procedure. The components of S may be evaluated by

(a) counting one preparation an infinite number of times, without changing its position, yielding S_a ;

(b) counting one preparation an infinite number of times while repositioning the sample between counts, yielding S_p ;

(c) counting the entire series of samples, yielding S .

Then (in the absence of apparatus failure) one finds:

$$S_a = \sigma_a$$

$$S_p = \sqrt{\sigma_a^2 + \sigma_p^2}$$

$$S = \sqrt{S_p^2 + \sigma_s^2}$$

The above procedure was applied to about 200 series of 10 preparations each, thus replacing S_a , S_p and S by the estimates of those based on the observed spread of 10 observations, S_{a10} , S_{p10} and S_{s10} . In preparing these series by different methods it was possible to indicate a preferred procedure for the preparation of samples for G.M. end-window counting.

RESULTS*

Apparatus failure

After insertion of an external voltage stabilizer between line voltage and counter, no evidence was found of apparatus failure.

Error due to placement

The evaluation of S_{p10} indicated the presence of a placement error in addition to σ_a . With a carefully machined plastic sample holder, this error could be minimized by maintaining a distance between planchet and counter window of at least 15 mm and by counting the sample 3 times to 40,000 counts in marked rotational positions differing by 120° each time.

Error due to sample preparation

(a) *Shape of counting planchet.* Several shapes of planchets were investigated. As

* Complete data are to be found in a Research Report submitted to I.A.E.A.²

in the present study 0.5-ml amounts of solution were evaporated, it was found that flat planchets with a rimmed edge gave very unreliable results ($S_{10} = 2-3\%$). In these planchets a fairly large part of the sample collects at the edge on drying, giving an irregular and eccentric distribution of the sample. Planchets in the shape of a shallow spherical segment (Fig. 1) gave a much more regular drying pattern and a better reproducibility ($S_{10} = 0.5-1.5\%$).

(b) *Method of drying.* A comparison was made between lamp drying and hot-plate drying. The hot-plate drying was effected by placing the planchet on a brass ring which was put on a hot plate at low heat. In addition to the fact that hot-plate drying proved to be much more convenient (20-50 samples may be dried simultaneously in about 15 min), the observed drying pattern was much more uniform. Presumably the heat is in this case applied from the edge of the planchet causing the liquid drop to evaporate from its circumference. With lamp drying the liquid drop dries from its center, causing irregular withdrawal of the liquid from its circumference. The reproducibility of the hot-plate samples was also better (0.3-1.5% at $3 \times 40,000$ counts in 3 positions) than with the lamp drying (0.4-3%).

(c) *Use of additives.* The use of small amounts of detergent or saccharose (the latter was meant to facilitate a more regular crystallization pattern) did not indicate a significant improvement and was therefore abandoned.

(d) *Influence of carrier salts.* The effect of carrier salts differed markedly for the different isotopes. In general, it was found the total salt concentration should be within the range of $3 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ N total salt. Below this range the drying seemed to be less regular, whereas above this level the total amount of salt (± 1 mg/cm²) gave rise to a vertical irregularity of the sample. In some cases adsorption of water by this amount of salt caused difficulties (*e.g.* CaCl₂) whereas for low energy β -emitters (notably ³⁵S) self-absorption started already at 0.1 mg/cm² (without necessarily adversely influencing the reproducibility). The reproducibility of "carrier-free" preparations, even in the presence of other salts, was usually not as good as the preparations containing a finite amount of the non-active carrier. Possibly this depends on whether or not the active ion forms a solid solution with the inert salt employed.

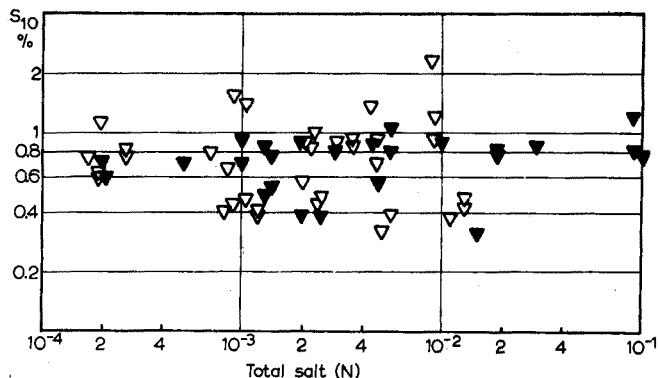


Fig. 3. Standard deviation of the individual sample, S_{10} , of about 60 series of 10 preparations, containing ³⁵SO₄ in the presence of different amounts of salts. \blacktriangledown preparations containing SO₄-carrier at about 10^{-4} N; ∇ carrier-free preparations.

(e) *Reproducibility of the suggested method.* As a final check, 60 series of ^{35}S preparations (10 preparations per series) at different electrolyte levels were analyzed for the reproducibility of the single preparation. The method used consisted of weighing a set of 10 preparations of about 0.5 ml on an automatic balance, using the shallow spherical planchet. All preparations were counted 3 times to 40,000 counts (at rotational positions differing by 120° each time). The values of S_{10} (found by determining the standard deviation of the 10 count-rates obtained by averaging over the 3 positions) are plotted in Fig. 3.

It is evident that with the above method the standard deviation of an individual sample is around 0.8%. Assuming that in practice at least 4 samples are made for each solution to be assayed for activity concentration, one may thus count on a standard deviation of 0.4% for the mean value of these 4 preparations. This seems an acceptable level of reproducibility.

Accuracy of the activity determinations

The experiments described above did not yield any information on the interaction between the radiation and the matrix of the sample, as the samples within each series were identical as regards amount of activity and amount of salt. As the accuracy of the determination depends on the reproducibility and also on the counting efficiency as influenced by the above factors, a number of series were prepared, each series containing a different amount of activity and/or accompanying salt.

(a) *Chlorine-36 series.* From a standard solution with high activity concentration in the presence of 0.2 *N* sodium chloride, 4 series of 10 preparations each were made up from dilutions of 1:10, 1:5, 1:2, and 1:1 of the above solution. With 0.5-ml amounts of these solutions the preparations contained 0.09, 0.18, 0.45 and 0.9 mg of salt per cm^2 , respectively. After back-calculation of the observed count-rates to the activity concentration of the standard solution, the variability within the set of 4 dilutions was found to correspond to a standard deviation, S_e , of 0.4%. At the same time the standard deviation of the mean value of the 3×10 counts registered for each dilution step, \bar{S}_1 , varied between 0.2 and 0.3%. Finally the dilution error was assessed separately (from repeated titrations of the 4 solutions) and found to be 0.17%. Subtracting the latter error from S_e yields 0.35%, which is very close to the values of \bar{S}_1 . Accordingly, the accuracy of the activity determination was closely equal to the reproducibility. Obviously no self-absorption was evident over the range studied.

(b) *Sulfur-35 series.* In this case a set of 10 series containing 5 preparations each was prepared at salt levels of 0.003 (2 \times), 0.03, 0.1 (2 \times), 0.4, 0.8 (2 \times), 1.5 and 4 mg/cm^2 . Self-absorption became apparent at salt levels above 0.1 mg/cm^2 . The value of S_e based on the first 5 series (no self-absorption) was 0.31% which is again very close to the reproducibility of the mean of each series, \bar{S}_1 . The value of \bar{S}_1 of the series with the highest salt concentration was considerably higher than at the low salt concentrations (up to 1%), presumably because of creeping of the substrate on drying.

(c) *Calcium-45 series.* Two sets of series containing sodium chloride and a mixture of calcium sulfate and sodium chloride as substrate (calcium chloride was impractical because of its hygroscopicity) were prepared. Self-absorption became apparent at levels above 0.5 mg/cm^2 . Although the \bar{S}_1 values were below 0.3% up to this salt level,

not enough data were available in the low salt range to calculate S_e . The superficial impression indicated that below 0.2 mg/cm^2 , the accuracy was similar to the reproducibility.

GENERAL CONCLUSIONS

From all the data collected (*cf.* ref. 2), it would seem that the accuracy and reproducibility of the activity determinations are very similar, provided that the total salt level is kept below $0.2\text{--}0.5 \text{ mg/cm}^2$. In general, it seems best to compare unknown samples with standard samples made up to contain about the same amount and type of salts.

When 0.5-ml preparations are used, weighing of the samples appears to be necessary, unless a special type of delivery pipet is used. In view of the cleaning problem the present authors prefer weighing.

A minimum of 3–4 preparations per sample is necessary if the error is to be reduced to 0.5% . If automatic counting equipment is available, it would seem that at least 5 preparations should be counted. In the absence of automatic equipment 3 preparations counted in 3 rotational positions each might suffice. The total count should be taken at least to 40,000. Especially if a number of preparations are used per sample, hot-plate drying on top of brass rings seems to insure a better uniformity than lamp drying.

The above investigation was made as part of a research contract with International Atomic Energy Agency, Vienna.

SUMMARY

The activity concentrations of β -emitters including ^{35}S (0.15 MeV) and presumably also ^{14}C (0.14 MeV) may be determined with satisfactory accuracy using an end-window G.M. counter. For single preparations (if weighed), the described procedure warrants that the standard error will not exceed 0.8% , if the amount of substrate is kept below 0.2 mg/cm^2 , and if carrier-free solutions are avoided. With a minimum of 4 preparations per sample solution, the error of the mean should not exceed 0.4% .

RÉSUMÉ

Les concentrations d'activité d'émetteurs β , comprenant ^{35}S (0.15 MeV) et vraisemblablement ^{14}C (0.14 MeV), peuvent être déterminées avec une exactitude satisfaisante, en utilisant un tube compteur à fenêtre G.M. Avec le procédé décrit, l'erreur ne dépasse pas 0.8% , à condition de maintenir la quantité de sel en dessous de 0.2 mg/cm^2 et d'éviter des solutions sans entraîneur. Avec un minimum de 4 préparations par solution échantillon l'erreur moyenne ne doit pas dépasser 0.4% .

ZUSAMMENFASSUNG

Die Aktivitätskonzentration von β -Strahlern einschliesslich ^{35}S (0.15 MeV) und wahrscheinlich ebenso vom ^{14}C (0.14 MeV) kann mit genügender Genauigkeit mit einem G.M. Fenster-Zählrohr bestimmt werden. Für ein einzelnes eingewogenes Präparat garantiert das beschriebene Verfahren eine Standardabweichung von nicht mehr als 0.8% , falls die Flächenbelegung unter 0.2 mg/cm^2 bleibt und trägerfreie Lösungen vermieden werden. Bei Herstellung von 4 Präparaten pro Probenlösung sollte der mittlere Fehler 0.4% nicht übersteigen.

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THERMOGRAVIMETRIC INVESTIGATION OF SCANDIUM, YTTRIUM AND THE RARE EARTH METAL DILITURATES

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WENDLANDT has published several excellent thermolysis studies of organic precipitants for the rare earth metals including oxalate^{1,2} and 8-hydroxyquinoline³. These reagents unfortunately do not afford many stable regions short of the rare earth oxides for thermogravimetric determinations. We have found that dilituric acid (5-nitrobarbituric acid) salts of the alkaline earth^{4,5} and alkali metals^{4,6} afford very stable regions for thermogravimetric determinations as the anhydrous salts. Because of the excellent thermal stability and favorable gravimetric factor of the diliturate salts, the thermolysis curves of scandium, yttrium, lanthanum, cerous, neodymium, samarium, gadolinium, dysprosium and erbium diliturates were investigated in the present work. Along with the thermolysis studies, the solubilities of these salts in water at 24° were determined. Methods were developed for the thermogravimetric determination of yttrium, lanthanum, neodymium, samarium, gadolinium, dysprosium and erbium as the diliturates.

EXPERIMENTAL

Equipment

An ADAMEL recording thermobalance (Chevenard System) was used to obtain the thermolysis curves.

Coors porcelain crucibles, No. 00000, and Coors porcelain filtering crucibles, No. 00000, of 15- μ porosity were used.

Reagents

The diliturate salts of yttrium, lanthanum, neodymium, samarium, gadolinium, dysprosium and erbium were prepared by treating 0.01 *M* aqueous solution of the metal chlorides or nitrates which were obtained in a minimum purity of 99.9% (Lindsay Rare Earth Chemicals Division of the American Potash and Chemical Corporation) and a 0.01 *M* aqueous solution of reagent cerous sulfate (G. Frederick Smith Chemical Company) with equivalent amounts of 0.05 *M* dilituric acid in 50% ethanol. The precipitates were allowed to form overnight and then cooled on ice until precipitation was essentially complete. The salts were then collected in glass fritted filtering crucibles, washed with distilled water, then with 95% ethanol and finally air-dried (water pump). Scandium diliturate was prepared by treating a

0.02 *M* aqueous solution of 99.9% scandium chloride (Fairmount Chemical Company) with a slight excess of 0.05 *M* dilituric acid in 50% ethanol. The precipitate was allowed to form overnight and then cooled on ice until precipitation was complete. The precipitate was collected in a glass fritted filtering crucible, washed with cold distilled water, then with 95% ethanol and finally with anhydrous ether. The salt was then air-dried in the crucible (water pump).

Nitrogen gas was dried by passing through solid calcium sulfate. The flow rate was 3 l/h.

Solutions

Saturated dilituric acid solution (0.05 *M*) in 50% ethanol was prepared from recrystallized white label dilituric acid (Eastman Kodak Company) as described by BERLIN AND ROBINSON⁷.

Yttrium, lanthanum, neodymium, samarium, dysprosium, gadolinium, and erbium solutions were prepared by making up approximately 0.01 *M* aqueous solutions and then standardizing by the oxalate-permanganate method⁸. Yttrium was found to be 0.00984 *M*, lanthanum 0.0102 *M*, neodymium 0.0102 *M*, samarium 0.0100 *M*, gadolinium 0.0102 *M*, dysprosium 0.00974 *M*, and erbium 0.00980 *M*.

The standardized yttrium solution was diluted with water to give solutions of 0.00738 *M*, 0.00591 *M* and 0.00492 *M*. By dilution of the standardized solution of lanthanum with water, solutions of 0.00510 *M*, 0.00255 *M*, 0.00204 *M* and 0.00143 *M* were prepared. The neodymium solution was diluted with water to give solutions of 0.00510 *M*, 0.00255 *M*, 0.00204 *M*, 0.00143 *M*, 0.00128 *M* and 0.00102 *M*. Similarly the samarium solution was diluted to give solutions of 0.00500 *M*, 0.00250 *M*, 0.00200 *M*, 0.00140 *M* and 0.00125 *M*. Gadolinium solutions of 0.00510 *M*, 0.00255 *M*, 0.00204 *M* and 0.00178 *M* were prepared as well as dysprosium solutions of 0.00681 *M* and 0.00487 *M* and erbium solutions of 0.00686 *M* and 0.00490 *M* by dilution with water.

RESULTS AND DISCUSSION

Solubilities of scandium, yttrium and the rare earth diliturates

The solubilities of the diliturates of scandium, yttrium, lanthanum, cerium(III), neodymium, samarium, gadolinium, dysprosium and erbium in water at 24° are reported in Table I. The solubilities were determined by saturating at room tempera-

TABLE I
SOLUBILITIES OF SCANDIUM, YTTRIUM AND THE RARE EARTH DILITURATES

	Solubility	
	Moles/l	K_{sp}
ScD ₃ · 15H ₂ O	3.3 · 10 ⁻³	3.0 · 10 ⁻⁹
YD ₃ · 12H ₂ O	2.0 · 10 ⁻³	4.3 · 10 ⁻¹⁰
LaD ₃ · 12H ₂ O	7.3 · 10 ⁻⁴	7.7 · 10 ⁻¹²
CeD ₃ · 12H ₂ O	6.4 · 10 ⁻⁴	4.5 · 10 ⁻¹²
NdD ₃ · 12H ₂ O	5.9 · 10 ⁻⁴	3.3 · 10 ⁻¹²
SmD ₃ · 12H ₂ O	6.5 · 10 ⁻⁴	4.8 · 10 ⁻¹²
GdD ₃ · 12H ₂ O	8.9 · 10 ⁻⁴	1.7 · 10 ⁻¹¹
DyD ₃ · 12H ₂ O	1.5 · 10 ⁻³	1.4 · 10 ⁻¹⁰
ErD ₃ · 12H ₂ O	2.5 · 10 ⁻³	1.1 · 10 ⁻⁹

ture ($24 \pm 1^\circ$) by stirring with an excess of the salt, letting stand for several days, filtering through Whatman No. 42 filter paper and then evaporating 25-ml portions of the filtrate by water-pump desiccation. Scandium diliturate was further heated at 160° to the anhydrous salt.

The results show a decrease in solubility from scandium to lanthanum which is similar to that found by us⁶ and by REDEMANN AND NIEMANN⁹ for the alkali and alkaline earth diliturates. From lanthanum to erbium there was first a decrease in solubility with neodymium diliturate being the least soluble, and then a smooth increase in the solubilities with erbium diliturate being the most soluble of the rare earth salts investigated. Figure 1 is a plot of solubilities of the rare earth diliturates

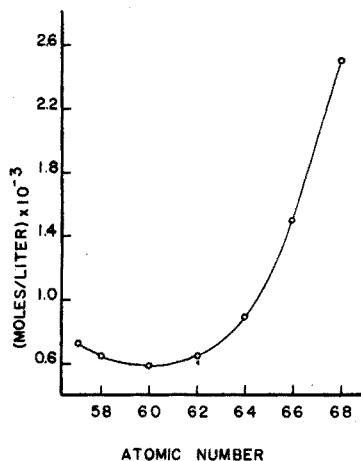


Fig. 1. Solubilities of the rare earth diliturates in water at 24° .

as a function of the atomic numbers. From this curve it is possible to predict the solubilities of the rare earth diliturates which were not investigated. It is apparent from the solubilities that dilituric acid is a better precipitant for the lighter rare earths than for the heavier members of this group.

Thermolysis curves

The thermolysis curves in Figs. 2, 3 and 4 were obtained by heating the diliturates in No. 00000 porcelain crucibles, in an atmosphere of nitrogen flowing at a rate of 3 l/h. The weights of the samples and the corresponding rates of heating for each curve are recorded on the Figs.

Scandium diliturate (Fig. 2A) formed a 15-hydrate from aqueous solution. The dehydration occurred in three steps: 5.5 moles of water were lost between 28° and 55° , 4.5 moles were lost between 55° and 89° and the last 5 moles came off between 89° and 130° . The anhydrous scandium diliturate was stable to 230° . At 230° the diliturate decomposed at first slowly then rapidly to 325° and from 325° the decomposition was slow with the production of scandium oxide (Sc_2O_3) at 572° . The scandium oxide was stable to 1000° .

Yttrium diliturate (Fig. 2B) formed a 12-hydrate which smoothly dehydrated from 67° to 165° with the production of the anhydrous salt. Anhydrous yttrium diliturate was stable to 250°. At 250° the salt decomposed rapidly to 345°. From 345° the decomposition was slow with the production of yttrium oxide (Y_2O_3) at 820°. The oxide was stable to 1000°.

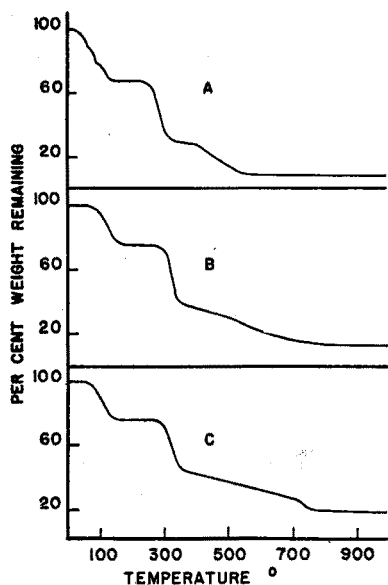


Fig. 2. Thermolysis curves of scandium, yttrium and lanthanum diliturates. (A) Scandium diliturate, 36.6 mg heated at 80°/h; (B) Yttrium diliturate, 24.0 mg heated at 300°/h; (C) Lanthanum diliturate, 25.6 mg heated at 300°/h.

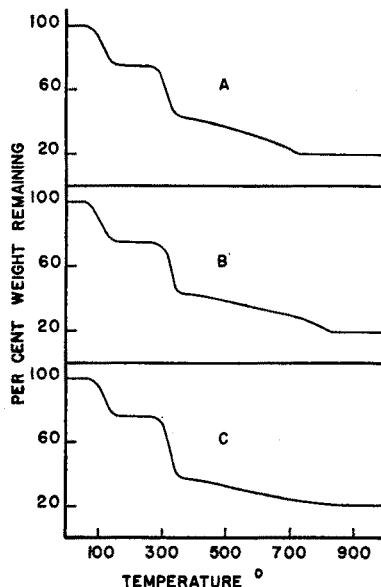


Fig. 3. Thermolysis curves of cerium(III), neodymium and samarium diliturates. (A) Cerium(III) diliturate, 23.7 mg heated at 300°/h; (B) Neodymium diliturate, 38.6 mg heated at 300°/h; (C) Samarium diliturate, 44.2 mg heated at 300°/h.

Lanthanum diliturate (Fig. 2C) formed a 12-hydrate which dehydrated smoothly from 50° to 147° with the production of anhydrous lanthanum diliturate. The anhydrous salt decomposed rapidly from 270° to 352°. From 352° to 700° the decomposition was slow; at 700° there was a fairly rapid weight loss with the final production at 770° of lanthanum oxide (La_2O_3).

Cerium(III) diliturate (Fig. 3A) formed a 12-hydrate which dehydrated between 55° and 154°. The anhydrous compound was stable to 267°. From 267° the salt decomposed rapidly to 346°. The decomposition proceeded slowly from 346° to 736° with the final production of cerium(IV) oxide.

Neodymium diliturate (Fig. 3B) was found to be a 12-hydrate which dehydrated between 63° and 165°. The anhydrate was stable to 270°. From 270° there was a rapid decomposition to 356°. This was followed by a long slow decomposition to 748° and then a faster decomposition to 835° with the production of neodymium oxide (Nd_2O_3).

Samarium diliturate (Fig. 3C) was also found to be a 12-hydrate. The dehydration

occurred between 67° and 153° with the production of the anhydrous salt which was stable to 250° . The salt decomposed rapidly between 250° and 366° and then more slowly between 366° and 900° with the production of samarium oxide (Sm_2O_3).

Gadolinium diliturate (Fig. 4A) formed a 12-hydrate which dehydrated smoothly between 54° and 163° . The anhydrate was stable to 260° . Decomposition of the salt occurred rapidly from 260° to 355° and more slowly from 355° to 910° with the production of gadolinium oxide (Gd_2O_3).

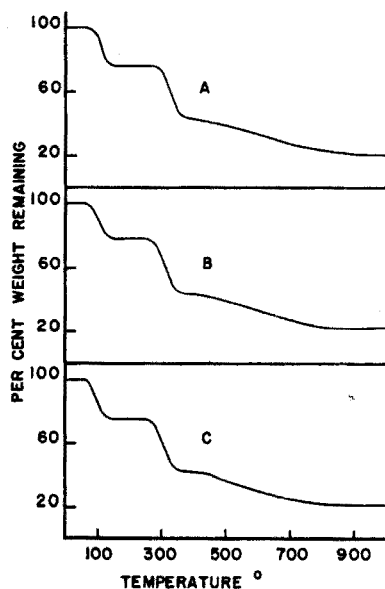


Fig. 4. Thermolysis curves of gadolinium, dysprosium and erbium diliturates. (A) Gadolinium diliturate, 34.5 mg heated at $300^{\circ}/\text{h}$; (B) Dysprosium diliturate, 24.8 mg heated at $300^{\circ}/\text{h}$; (C) Erbium diliturate, 29.9 mg heated at $300^{\circ}/\text{h}$.

Dysprosium diliturate (Fig. 4B) dehydrated from 65° to 154° losing 12 moles of water to produce the anhydrous salt which was stable to 250° . The decomposition was rapid from 250° to 360° and then a slow decomposition to 800° with the production of dysprosium oxide (Dy_2O_3).

Erbium diliturate (Fig. 4C) was also a 12-hydrate which dehydrated between 52° and 159° . The anhydrous salt was stable to 245° . The salt decomposed rapidly from 245° to 360° and then slowly until erbium oxide (Er_2O_3) was produced at 847° .

Thermogravimetric analysis of yttrium and the rare earth metals

Aliquots (10 ml) of yttrium, lanthanum, neodymium, samarium, gadolinium, dysprosium and erbium were treated with enough 0.05 M dilituric acid (50% ethanol) solution to give a 1:5 mole ratio of metal ion to dilituric acid for lanthanum, neodymium, samarium and gadolinium and a 1:6 mole ratio of metal ion to dilituric acid for yttrium, dysprosium and erbium. The precipitates were allowed to form overnight and then cooled on ice for about 1 h. The precipitates were then collected in

No. 00000 filtering crucibles, washed with 0.01 *M* diluturic acid (50% ethanol) solution, then with 95% ethanol and weighed after bringing to constant weight at 190° to 210°.

Results for yttrium

Table II lists the results obtained by this method for yttrium. From 8.75 to 6.56 mg of yttrium per 10 ml of solution the results were within 1% of the oxalate standardization with an average deviation of 0.52%. At 5.25 mg of yttrium per 10 ml the average deviation was 1.4% and at 4.38 mg per 10 ml the results were low by

TABLE II
DETERMINATION OF YTTRIUM AS YTTRIUM DILITURATE

<i>YD</i> ₃ precipitate (mg)	<i>Y</i> taken (mg)	<i>Y</i> found (mg)	Deviation (mg)
60.0	8.75	8.82	+0.07
59.8	8.75	8.79	+0.04
60.0	8.75	8.82	+0.07
44.9	6.56	6.60	+0.04
44.5	6.56	6.54	-0.02
44.7	6.56	6.57	+0.01
35.4	5.25	5.20	-0.05
35.4	5.25	5.20	-0.05
35.0	5.25	5.15	-0.10
28.1	4.38	4.13	-0.25
27.7	4.38	4.07	-0.31

TABLE III
DETERMINATION OF LANTHANUM AS LANTHANUM DILITURATE

<i>LaD</i> ₃ precipitate (mg)	<i>La</i> taken (mg)	<i>La</i> found (mg)	Deviation (mg)
66.6	14.2	14.1	-0.1
66.5	14.2	14.1	-0.1
66.3	14.2	14.1	-0.1
33.3	7.10	7.06	-0.04
33.4	7.10	7.08	-0.02
33.1	7.10	7.02	-0.08
16.6	3.55	3.52	-0.03
16.6	3.55	3.52	-0.03
16.5	3.55	3.50	-0.05
13.4	2.84	2.84	0.00
13.3	2.84	2.82	-0.02
13.1	2.84	2.78	-0.06
7.7	1.98	1.64	-0.34
7.6	1.98	1.61	-0.37
8.1	1.98	1.72	-0.25

6.4%. Higher amounts than 60 mg of precipitate were precluded by the size of the 1.3-ml filter. The optimum range for yttrium appears to lie in the range of 9 to 6 mg of yttrium per 10 ml of solution.

Results for lanthanum

Table III lists the results obtained by this method for lanthanum. From 14.2 to 2.84 mg of lanthanum per 10 ml of solution the results showed an average deviation of 0.78% from the oxalate value. At 1.98 mg of lanthanum per 10 ml of solution, the results had an average deviation of 1.6%. Higher amounts than 66 mg of precipitate were precluded by the size of the 1.3-ml filter. The optimum range for the determination of lanthanum appears to lie between 14 and 3 mg of lanthanum per 10 ml of solution.

Results for neodymium

The results obtained for neodymium are listed in Table IV. From 14.7 to 2.94 mg of neodymium per 10 ml of solution the results had an average deviation of 0.81% from the oxalate standardization. Higher amounts than 68 mg of precipitate were precluded by the size of the 1.3-ml filter. At 2.06 mg per 10 ml the average deviation was 2% and at 1.84 mg per 10 ml the results were quite low. The optimum range for this determination appears to lie in the range of 15 to 2.5 mg of neodymium per 10 ml of solution.

TABLE IV
DETERMINATION OF NEODYMIUM AS NEODYMIUM DILUTURATE

<i>NdD₃</i> precipitate (mg)	<i>Nd</i> taken (mg)	<i>Nd</i> found (mg)	Deviation (mg)
67.8	14.7	14.8	+0.1
67.8	14.7	14.8	+0.1
66.8	14.7	14.8	-0.1
33.4	7.35	7.30	-0.05
34.0	7.35	7.43	+0.08
33.8	7.35	7.38	+0.03
17.1	3.69	3.73	-0.04
16.8	3.69	3.67	-0.02
16.8	3.69	3.67	-0.02
13.3	2.94	2.91	-0.03
13.2	2.94	2.89	-0.05
13.4	2.94	2.93	-0.01
9.1	2.06	1.99	-0.07
9.3	2.06	2.04	-0.02
9.4	2.06	2.06	0.00
7.9	1.84	1.73	-0.11
8.1	1.84	1.77	-0.07
8.0	1.84	1.75	-0.09
5.6	1.47	1.22	-0.25
5.5	1.47	1.20	-0.27
5.3	1.47	1.16	-0.31

Results for samarium

The results obtained for samarium are listed in Table V. From 15.1 to 3.01 mg of samarium per 10 ml of solution the results deviated by 0.80%. At 2.11 and 1.88 mg per 10 ml of solution, the results were quite low and higher amounts than 68 mg of

TABLE V
DETERMINATION OF SAMARIUM AS SAMARIUM DILUTURATE

<i>SmD₃</i> precipitate (mg)	<i>Sm</i> taken (mg)	<i>Sm</i> found (mg)	Deviation (mg)
67.6	15.1	15.2	+0.1
67.4	15.1	15.2	+0.1
67.5	15.1	15.2	+0.1
33.8	7.53	7.61	+0.08
33.8	7.53	7.61	+0.08
33.7	7.53	7.61	+0.06
16.7	3.76	3.77	+0.01
16.8	3.76	3.79	+0.03
16.8	3.76	3.79	+0.03
13.2	3.01	2.98	-0.03
13.3	3.01	3.00	-0.01
13.3	3.01	3.00	-0.01
8.6	2.11	1.94	-0.17
8.3	2.11	1.87	-0.24
8.5	2.11	1.92	-0.19
7.3	1.88	1.65	-0.23
7.6	1.88	1.71	-0.17
7.5	1.88	1.69	-0.19

TABLE VI
DETERMINATION OF GADOLINIUM AS GADOLINIUM DILUTURATE

<i>GdD₃</i> precipitate (mg)	<i>Gd</i> taken (mg)	<i>Gd</i> found (mg)	Deviation (mg)
69.4	16.1	16.2	+0.1
69.1	16.1	16.1	0.0
69.4	16.1	16.2	+0.1
34.5	8.05	8.06	+0.01
34.4	8.05	8.05	0.00
34.8	8.05	8.13	+0.07
17.2	4.03	4.02	-0.01
17.0	4.03	3.97	-0.06
17.3	4.03	4.04	+0.01
13.0	3.22	3.04	-0.18
13.1	3.22	3.06	-0.16
13.1	3.22	3.06	-0.16
11.2	2.82	2.62	-0.20
11.6	2.82	2.71	-0.11
10.9	2.82	2.55	-0.27

precipitate were precluded by the size of the 1.3-ml filter. The optimum region for this determination appears to be 15 to 3 mg of samarium per 10 ml of solution.

Results for gadolinium

Table VI lists the results obtained for gadolinium. From 16.1 to 4.03 mg of gadolinium per 10 ml of solution the results showed an average deviation of 0.52% from the oxalate standardization. And for 3.22 and 2.82 mg per 10 ml the results were more than 5% low. The method obtains optimum results for 16 to 4 mg of gadolinium per 10 ml of solution.

Results of dysprosium

Results obtained for dysprosium are listed in Table VII. At 15.8 mg of dysprosium per 10 ml of solution the average deviation from the oxalate standardization was 0.42%, at 10.6 mg per 10 ml the average deviation was 4% low and at 7.90 mg per

TABLE VII
DETERMINATION OF DYSPROSIUM AS DYSPROSIUM DILITURATE

<i>DyD₃ precipitate</i> (mg)	<i>Dy taken</i> (mg)	<i>Dy found</i> (mg)	<i>Deviation</i> (mg)
65.4	15.8	15.7	-0.1
65.7	15.8	15.7	-0.1
66.1	15.8	15.8	0.0
44.3	11.1	10.6	-0.5
45.1	11.1	10.8	-0.3
44.8	11.1	10.7	-0.4
30.6	7.90	7.34	-0.56
31.3	7.90	7.50	-0.40
31.1	7.90	7.45	-0.45

TABLE VIII
DETERMINATION OF ERBIUM AS ERBIUM DILITURATE

<i>ErD₃ precipitate</i> (mg)	<i>Er taken</i> (mg)	<i>Er found</i> (mg)	<i>Deviation</i> (mg)
67.0	16.6	16.4	-0.2
67.4	16.6	16.5	-0.1
67.3	16.6	16.5	-0.1
45.5	11.6	11.2	-0.4
45.3	11.6	11.1	-0.5
46.1	11.6	11.3	-0.3
30.7	8.29	7.53	-0.76
31.0	8.29	7.60	-0.69

10 ml the results were quite low. Amounts of precipitate greater than 66 mg are precluded by the size of the 1.3-ml filter. The method gives optimum results at about 15 mg per 10 ml of solution.

Results for erbium

Table VIII lists the results obtained for erbium. At 8.29 mg of erbium per 10 ml of solution the average results were low by 9% and at 11.6 mg per 10 ml the results average 3% low. For 16.6 mg of erbium per 10 ml of solution the average deviation from the oxalate value was 0.8% low. Higher amounts than 68 mg of precipitate were precluded by the size of the 1.3-ml filter. The optimum results for this method are obtained at about 17 mg of erbium per 10 ml of solution.

SUMMARY

Thermolysis curves for scandium, yttrium, lanthanum, cerium(III), neodymium, samarium, gadolinium, dysprosium and erbium diliturates are described. Scandium diliturate forms a 15-hydrate which dehydrates in 3 steps. The other diliturates all form 12-hydrates which dehydrate smoothly. All of the anhydrous diliturates are thermally stable to about 240°.

Solubilities in water for scandium, yttrium, lanthanum, cerium(III), neodymium, samarium, gadolinium, dysprosium and erbium diliturates are given. Scandium diliturate is the most soluble and neodymium diliturate the least soluble. Solubilities of rare earth diliturates not investigated can be predicted approximately.

Methods for thermogravimetric determination of yttrium, lanthanum, neodymium, samarium, gadolinium, dysprosium and erbium as the diliturates have been developed. The precipitates are quite dense, easily handled and filterable. Weighing as the diliturate salts gives these determinations a very favorable gravimetric factor.

RÉSUMÉ

Les auteurs décrivent les courbes de thermolyse obtenues pour les diliturates de scandium, d'yttrium, de lanthane, de cérium(III), de néodyme, de samarium, de gadolinium, de dysprosium et d'erbium. Ils donnent les solubilités de ces sels dans l'eau. Le diliturate de scandium est le plus soluble, celui de néodyme le moins soluble. Ils ont mis au point des méthodes de dosage thermogravimétrique de ces éléments; les précipités sont denses et se filtrent facilement.

ZUSAMMENFASSUNG

Thermogravimetrisch wurden die Diliturate folgender Elemente untersucht: Sc, Y, La, Ce(III), Nd, Sm, Gd, Dy und Er. Scandiumdiliturat bildet ein 15-Hydrat, welches in 3 Stufen sein Wasser abgibt. Alle anderen Diliturate bilden 12-Hydrate, welche gleichmässig ihr Wasser abgeben. Alle entwässerten Diliturate sind bis etwa 240° thermisch stabil. Es werden die Löslichkeiten der genannten Diliturate in Wasser angegeben. Das Diliturat des Scandiums ist am stärksten, das des Neodyms am wenigsten löslich. Die Löslichkeiten der Diliturate von Seltenen Erden, die nicht untersucht wurden, können näherungsweise vorausgesagt werden. Es wurden Methoden zur thermogravimetrischen Bestimmung der Diliturate folgender Elemente entwickelt: Y, La, Nd, Sm, Gd, Dy und Er. Die Niederschläge sind leicht zu handhaben und filtrierbar. Für die Gewichtsanalyse ergibt sich ein günstiger Faktor.

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SELECTIVE EXTRACTION AND SPECTROPHOTOMETRIC
DETERMINATION OF TITANIUM(IV) WITH
2-THENOYLTRIFLUOROACETONE

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Titanium(IV) forms a greenish-yellow chelate with 2-thenoyltrifluoroacetone (TTA), which can be extracted from strong hydrochloric acid medium in isoamyl alcohol-benzene mixture. The greenish-yellow extract can be directly measured at 430 m μ . This forms the basis of a new method for extraction and determination of titanium at the milligram level.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 1-cm glass cells was used for the absorbance measurement.

TTA (Columbia Organic Chemicals, Columbia, S.C.) solutions in isoamyl alcohol were used.

A 500-ml stock solution of titanium sulphate was prepared by fusing granular titanium (Johnson Matthey and Co., London) with potassium bisulphate and leaching the fused mass with 2 *N* sulphuric acid. The solution, standardised by the oxinate method, contained 1.387 mg of titanium per ml. Test solutions (277 μ g of titanium per ml) were prepared by proper dilution of the stock solution in 2 *N* sulphuric acid.

General procedure

Ten ml of 0.15 *M* TTA solution in isoamyl alcohol and 5 ml of benzene were equilibrated with 10 ml of 11.0 *N* hydrochloric acid for 5 min in a 250-ml separatory funnel. The aqueous phase was rejected. A suitable aliquot (0.5 to 3 ml) of the titanium sulphate solution containing 277 μ g of titanium per ml was mixed with 10 ml of 11.0 *N* hydrochloric acid and then extracted for 10 min with the equilibrated TTA solution.

For studying the effect of acid concentration, hydrochloric acid of different strengths was used. For the study of diverse ions the solution containing the foreign ions under investigation was introduced before the addition of acid.

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The layers were allowed to separate. The aqueous phase was saved for determination of acidity while the organic phase was collected in a 25-ml volumetric flask and diluted to 25 ml with isoamyl alcohol. For the separation of some metal ions at lower acid concentration ($< 2 N$) the hydrolysis of titanium was prevented by adding tartaric acid (0.1 g). The absorbance was measured at $430 m\mu$ against a reagent blank. The corresponding titanium concentration was read directly from the calibration curve described below.

RESULTS AND DISCUSSION

Absorption curve

The absorption spectra of the solution of titanium(IV)-TTA chelate ($2.3 \cdot 10^{-4} M$ titanium), extracted as above from $11 N$ hydrochloric acid, and measured against a reagent blank is shown in Fig. 1. The curve shows a peak at $420 m\mu$ and, after that, the

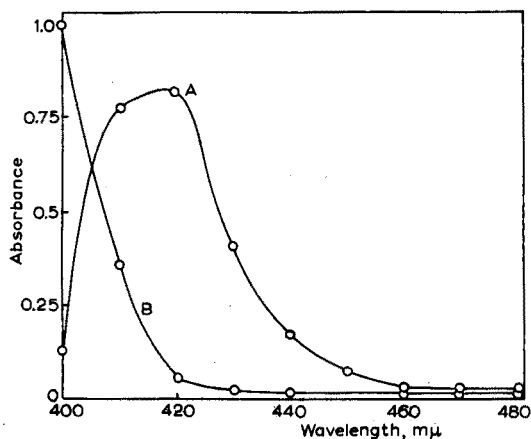


Fig. 1. (A) Absorption spectrum of titanium(IV)-TTA chelate in isoamyl alcohol-benzene ($Ti = 2.3 \cdot 10^{-4} M$; $HCl = 10.4 M$); (B) reagent blank vs. isoamyl alcohol-benzene ($TTA = 0.15 M$; $HCl = 10.4 M$).

absorption gradually decreases and becomes insignificant beyond $480 m\mu$. The reagent blank shows strong absorption below $410 m\mu$ but absorption is small above $420 m\mu$. For absorbance measurement the region of $430 m\mu$ was used throughout. The absorptivity at $430 m\mu$ is 1739.1 ± 21 .

The optimum reagent concentration is $0.15 M$ TTA and the period of extraction 5 min. The colour is stable for at least 96 h.

Effect of acid concentration

Before extraction the organic TTA-phase was saturated with the desired acid concentration. Table I shows that extraction virtually starts from $5.75 N$ (initial $6.05 N$) hydrochloric acid and becomes 100% from $10.43 N$ (initial $11.0 N$) hydrochloric acid onward. The optimum acid concentration is $\geq 10.4 N$ for quantitative extraction. The titanium in the aqueous phase after extraction was determined by the hydrogen peroxide method¹ and the distribution ratio calculated.

TABLE I
EXTRACTION OF TITANIUM(IV) AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION
(Titanium, 277 μg ; TTA, 0.15 M)

HCl at equilibrium (N)	% Extraction	Distribution ratio
5.75	3.6	0.027
6.8	23.4	0.22
7.83	54.1	0.86
8.8	75.8	2.3
10.03	97.4	28.3
10.4	100	—
11.3	100	—

Calibration curve

The absorbance of different amounts of titanium(IV), extracted from 10.4 N hydrochloric acid as above, was measured at 420, 430, 440 and 450 $m\mu$ against a reagent blank. In each case the solution of titanium was extracted exhaustively so that the aqueous phase was free from titanium. The results proved that the titanium-TTA system follows Beer's law at 430 $m\mu$ over the concentration range of 70 to 560 μg of titanium per ml.

Diverse ions

Twenty representative ions were carried through the procedure and examined for interference. The tolerance limit for each case, recorded in Table II, represents that concentration in presence of which titanium can be completely extracted and the correct absorbance can be obtained within $\pm 2\%$. It is interesting to note (Table II) that aluminium, zirconium, thorium, chromium, molybdenum, tungsten, tin, uranium, phosphate, borate, citrate, EDTA (10 mg) and tartrate (0.1 g) do not interfere. Cobalt, nickel, manganese, vanadium, iron, copper, if present, have to be removed first. Fluoride interferes but a small amount can be tolerated.

Determination of titanium in (a) iron(III)-titanium(IV), (b) vanadium(V)-titanium(IV) mixtures

Iron is first removed by extracting in 5 N hydrochloric acid with 100% TBP² and vanadium from vanadium-titanium mixture by extracting vanadium with 100% TBP in 6 N hydrochloric acid². The aqueous phase in each case is evaporated to a small volume in a water bath and titanium extracted with TTA as usual in 10.4 N hydrochloric acid.

Determination of titanium in mixtures of titanium with cobalt, nickel, manganese or copper

From the mixtures cobalt, nickel, manganese and copper are first extracted with 0.15 M TTA from pH 6 buffer³. The hydrolysis of titanium in each case is prevented by adding 0.1 g of tartaric acid before extraction. The aqueous phase is evaporated to a small volume in a water bath and titanium is extracted with TTA as usual. Complete separation was obtained in every case.

TABLE II
EFFECT OF DIVERSE IONS
(Titanium, 277 μg)

Foreign ion	Source	Tolerance limit (ion) (μg)
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	10,000
Zr ⁴⁺	ZrOCl ₂ ·8H ₂ O	10,000
Th ⁴⁺	Th(NO ₃) ₄ ·4H ₂ O	10,000
Cr ³⁺	Cr ₂ (SO ₄) ₃ ·18H ₂ O	10,000
Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	10,000
W ⁶⁺	Na ₂ WO ₄	10,000
Sn ²⁺	SnCl ₂ ·2H ₂ O	10,000
U ⁶⁺	UO ₂ (NO ₃) ₂ ·6H ₂ O	10,000
Cu ²⁺	CuSO ₄ ·5H ₂ O	10 (2,000 ^a)
Co ²⁺	CoSO ₄ ·7H ₂ O	10 (600 ^a)
Ni ²⁺	NiSO ₄ ·7H ₂ O	10 (1,000 ^a)
Mn ²⁺	MnSO ₄ ·4H ₂ O	10 (1,000 ^a)
V ⁵⁺	VOCl ₃	5 (5,000 ^b)
Fe ³⁺	FeCl ₃ ·6H ₂ O	5 (6,000 ^c)
F ⁻	NaF	Nil
BO ₃ ³⁻	H ₃ BO ₃	10,000
PO ₄ ³⁻	(NH ₄) ₂ HPO ₄	10,000
Citrate ³⁻	Citric acid	10,000
Tartrate ⁴⁻	Tartaric acid	100,000
EDTA	EDTA (disodium salt)	10,000

^{a, b, c} Interference. Figures within parentheses refer to extractions after removal of the foreign ions.

^a Foreign ion first removed by extracting with 0.15 *M* TTA from pH 6 buffer.

^b Foreign ion first extracted with 100% TBP from 5 *N* hydrochloric acid.

^c Interfering ion removed by extracting with 100% TBP from 6 *N* hydrochloric acid.

Recommended procedure

To a solution containing 70 to 560 μg of titanium, add 10 ml of 11 *N* hydrochloric acid and extract for 5 min with 10 ml of 0.15 *M* TTA in isoamyl alcohol and 5 ml of benzene, which have been previously equilibrated with the acid. Proceed as described on p. 81.

From 10 such runs with 277 μg of titanium the absorbance measurement was 0.400 ± 0.005 so that the standard deviation is $\pm 1.25\%$. The entire operation requires barely 20 min. The sensitivity of the method is 0.028 according to Sandell's definition (the hydrogen peroxide method has a sensitivity of 0.064 at 410 $m\mu$ and 0.1 at 450 $m\mu$). Thus the method is rapid, sensitive compared to the standard method and provides extraction and determination of titanium in presence of the commonly associated elements.

SUMMARY

A new rapid method is suggested for simultaneous extraction and spectrophotometric determination of titanium with 2-thenoyltrifluoroacetone (TTA). The greenish-yellow chelate of titanium(IV)-TTA can be extracted with isoamyl alcohol-benzene and measured at 430 $m\mu$. The extraction can be carried out in presence of Al, Cr(III), Th, Zr, Mo, W, borate, phosphate, citrate, tartrate and EDTA.

RÉSUMÉ

Une méthode rapide et nouvelle est proposée pour le dosage spectrophotométrique du titane, au moyen de 2-thényltrifluoroacétone. Le chélate jaune verdâtre obtenu peut être extrait à l'aide du mélange alcool isoamylique-benzène; son absorption est mesurée à 430 m μ . L'extraction peut s'effectuer en présence des éléments et composés suivants: Al, Cr(III), Th, Zr, Mo, W, borate, phosphate, citrate, tartrate et EDTA.

ZUSAMMENFASSUNG

Eine neue, schnelle Methode wird zur Extraktion und spektralphotometrischen Bestimmung von Titan mit 2-Thenyltrifluoroacetone (TTA) vorgeschlagen. Das grünlich-gelbliche Chelat des Titan(IV) mit TTA wird mit Isoamylalkohol-Benzin extrahiert und bei 430 m μ gemessen. Die Extraktion kann in Gegenwart von Al, Cr(III), Th, Zr, Mo, W, Borat, Phosphat, Citrat, Tartrat und EDTA durchgeführt werden.

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SORPTION OF AMIDES BY CATIONIC EXCHANGE RESINS FROM NONAQUEOUS SOLVENTS

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The relationship between the sorption of metallic ions from aqueous solutions by polystyrene-sulfonic acid resins and the structure of these resins has been investigated extensively during the past two decades. As a result, various quantitative treatments¹⁻³ have been presented to explain the phenomena. The sorption of non-electrolytes by these resins has not received as much attention; thus explanations for the observed behavior of these compounds are much more qualitative. Theories for the latter selectivities have included: solvation⁴, salting-out effects⁵, solubilization⁶, interaction of counter ions⁷, matrix attraction^{8,9}, and molecular size¹⁰. Aqueous and partially aqueous solutions have been used for this work, whereas little has been done in the area of sorption of organic compounds from completely nonaqueous solvents. This neglect appears to be due to the slow diffusion rates of organic molecules within the resin particle. Because of this limiting factor separations of organic compounds by column chromatography have not been feasible with nonaqueous eluants.

WATKINS AND WALTON¹¹ have recently studied the sorption characteristics of amines from water and nonaqueous solvents. In this paper they presented data that clearly demonstrate the above difficulty. Even so, they were able to separate aniline from pyridine using ethanolic hydrochloric acid (1 *M*) as eluant. But even in this instance a truly nonaqueous system was not employed since the sulfonic acid resin had only been air-dried and thus contained about 20% water. If a truly anhydrous resin had been used, even greater broadening and tailing of the elution band of aniline would probably have been observed.

If a sulfonic acid resin were available that would partially eliminate these diffusion difficulties, separation of organic compounds would probably be more feasible using nonaqueous eluants. To meet this need the Rohm and Haas Company marketed in the spring of 1961 a macroporous sulfonic acid resin¹² which is referred to as macroreticular. It has a structure entirely different from that of conventional resins and was developed primarily for use as a heterogeneous acid catalyst for organic reactions in nonaqueous solvents. Recently, interdiffusion coefficients for tetra-ethyl, *n*-propyl and *n*-butyl ammonium ions in a macroporous resin have been investigated and compared with those in a conventional ion-exchange resin¹³. The coefficient for

the tetra-*n*-butyl ammonium ion in the macroporous resin was found to be about 20 times greater than the value of the same ion in the conventional resin. This increased porosity of this new resin is probably due to a decrease in chain entanglement of the polymer network.

With this new macroreticular resin nonaqueous eluants should result in the recovery of organic compounds in narrower elution bands. In this laboratory problems associated with diffusion were apparent from elution chromatograms obtained in the sorption of the very weakly basic hydroxypyrazine by a column of conventional sulfonic acid resin (H^+) from an acetonitrile solution and in the subsequent release of this compound by methanol when used as eluant. With the macroreticular resin, elution chromatograms showed far less tailing with the same solvent system.

The solvent system, acetonitrile and methanol, is most interesting in many respects. Acetonitrile has a dielectric constant (38 at 25°) higher than that of methanol (36.6 at 25°) and a dipole (3.37) even higher than that of water (1.84). When compared to water, it is a very weak base and a much weaker acid; because of these characteristics it is a strongly differentiating solvent for acids and bases¹⁴. Methanol is a solvent with a hydroxyl group and is thus somewhat similar to water. It readily forms hydrogen bonds and is not as good a differentiating solvent as acetonitrile. In the case of very weak bases such as hydroxypyrazine sorption by a sulfonic acid resin might be expected from a solvent such as acetonitrile but not from one such as methanol.

The purpose of the present study was to investigate the important parameters in the sorption of very weakly basic amides by conventional and macroporous sulfonic acid resins in the presence of acetonitrile and methanol and to separate if possible mixtures of amides. The following series of amides were selected for investigation: acetanilide, *N*-methylacetanilide, *N-n*-propylacetanilide, acetamide, and *N*-methylacetamide having respectively pK_a values of -1.57, -0.34, -0.17, -0.70 and -0.50¹⁵.

EXPERIMENTAL

Materials

All amides except one were of the best grade commercially available and were not further purified; the one exception, *N-n*-butylacetanilide, was synthesized and then vacuum-distilled¹⁶.

The resins used were sulfonated styrene-divinyl-benzene copolymers, all of which are commercially available: Dowex 50WX2 (50-100 mesh), Dowex 50WX8 (100-200 mesh), and Amberlyst 15 (30-50 mesh). The conventional resins were pretreated as follows: they were washed with water, 5% aqueous hydrochloric acid, water, and spectral-grade methanol; then air-dried, placed in a vacuum oven at 60°, removed from the oven after the pressure remained less than 0.5 mm for 2 h with the pump off, and finally stored over P_2O_5 . The macroreticular resin was filtered to remove the toluene, washed with technical-grade methanol and then water, and subsequently treated the same as the conventional resins.

The solvents were Fisher spectral-grade methanol, Eastman spectral-grade acetonitrile, Fisher spectral-grade isopropanol, Merck reagent-grade benzene; and distilled Eastman methyl isobutyl ketone.

Mixed solvents of various ratios were prepared on a volume basis.

Sorption studies by the batch technique

To evaluate resin sorption of the acetanilides from the solvents and solvent mixtures, distribution coefficients were determined using the following relationship:

$$K_d = \frac{(\text{amount of amide on resin}) \cdot (\text{ml of solution})}{(\text{g of resin}) \cdot (\text{amount of amide in solution})}$$

About 0.17–0.19 mmole of the amide dissolved in 50 ml of solvent was mixed with 1 g of resin in an iodine flask, and then the flask was shaken for 3 h. A longer period was not used since hydrolysis of amides can occur in the presence of water and sulfonic acid resins^{17,18}. The mother liquor was removed and analyzed for the amide content. In determining the K_d values no allowance was made for the uptake of solvent by the resin.

Analytical methods

For equilibrium batch tests the acetanilide contents of the solutions were determined by ultraviolet absorption spectroscopy using a Beckman DU or a Cary Model 11 spectrophotometer. The wavelength used for acetanilide was 242 $m\mu$ and that for N-methyl-, N-n-propyl-, and N-n-butylacetanilides was 232 $m\mu$.

For batch tests using benzene as a solvent, a coulometric method at constant current was employed to determine acetanilide. A procedure reported by BUCK AND SWIFT¹⁹ had to be modified slightly in that a 5-ml aliquot of the benzene mother liquor was added to the aqueous generating solution. The end-point was not as sharp as that for an all-aqueous solution, but the recovery values for acetanilide in benzene indicated an error of only 5%.

The elution characteristics of columns were followed by passing the effluents through either a variable path U.V. cell (RIIC BTF-5) in the Beckman DU or through a differential refractometer (Water Associates). The refractometer is provided with a 0.07-ml flowing reference cell, a 0.07-ml flowing sample cell, and a recorder which gives a full-scale deflection with a 0.0003 change of refractive index. This instrument was used to determine the column characteristics of the acetamides and also of the acetanilides when methyl isobutyl ketone was used as an eluant.

The effluents were collected in 10-ml fractions using a Technicon fraction collector. In some instances these fractions were used to determine recoveries of the amides and to determine elution curves following dilution of appropriate fractions.

Swelling measurements

The swelling characteristics of dried conventional resin beads were determined by measuring the change in bead diameter under a microscope. The diameter of the bead was initially measured, the bead was soaked in the desired solvent or mixed solvent, and the diameter subsequently measured again.

Column procedure

All columns were prepared from glass tubing having an inner diameter of 1.2 cm. Glass wool plugs were used to retain the resin in the columns. For columns of conventional resin having a crosslinkage of 8%, 20 g was used; for those of the macroreticular resin 10 g was used. A column was packed with resin slurried in the desired solvent or mixed solvent, allowed to stand overnight, and washed the next day with

the same solvent or mixed solvent until the ultraviolet sorption or refractive index of the effluent remained constant. A sample was dissolved in 3 ml of the same solvent or mixed solvent, and then added to the column. Five ml of the solvent was used to complete the transfer before adding a reservoir of eluant. The flow rate of all columns was 1 ml per min. To the columns of conventional resin 0.3–0.5 mmole of an amide was added and to the columns of macroreticular resin about 0.05 mmole.

RESULTS AND DISCUSSIONS

Distribution coefficients using a conventional resin

The distribution coefficients for 3 acetanilides were obtained using a conventional resin having a crosslinkage of 2 and a mesh of 50–100. This resin was selected because of its higher porosity compared with the more highly crosslinked conventional resins and because of its greater swelling characteristics which makes observation under the microscope much easier than with a highly crosslinked resin.

The distribution coefficients for the acetanilides in methanol (Table I) are quite

TABLE I
DISTRIBUTION COEFFICIENT FOR THREE ACETANILIDES
(solvent system acetonitrile and methanol; conventional sulfonic acid resin,
2% crosslinkage, 50–100 mesh)

Compound	pK_a	K_d values			
		Methanol	Acetonitrile	10 Methanol– 90 acetonitrile	5 Methanol– 95 acetonitrile
Acetanilide	–1.57	All about 5	1000	About 5	15
N-Methylacetanilide	–0.34		2300	31	233
N-Propylacetanilide	–0.17		2100	21	187

different from those for acetonitrile, the sorption being greater by a factor of 200–400 in the acetonitrile. The coefficients for the mixed solvents show that small variations in the methanol content of the acetonitrile result in definite sorption changes. As anticipated, the acetanilide, the weakest base, was sorbed the least. The N-methyl and N-n-propylacetanilides were expected to have similar sorption based on their pK_a values, yet the K_d values for these compounds are decidedly different.

When mixed solvents are used, the solvent which more readily solvates the sulfonic acid group will be preferentially taken up by the resin. This preference can readily be ascertained by measuring the degree of swelling of dried beads (Table II).

Of all the solvents used, methanol causes the greatest degree of bead swelling and thus it is preferentially sorbed when present in any of the other solvents. Though acetonitrile has a dielectric constant and dipole larger than methanol, the latter solvent, probably because of the hydroxyl group, forms a solvation shell more readily around the sulfonic acid in the resin.

The K_d values (Table I) for methanol are inaccurate because so little of the amides was taken up by the resin. The true distribution coefficients, if they could be accurately determined, would probably have the same sequence as those for acetonitrile and mixtures of methanol and acetonitrile. To verify this statement column characteristics were determined using a conventional resin (8% crosslinkage and 100–200

mesh) with methanol as eluant. Since this resin has a higher crosslinkage and a smaller mesh size than that used in the batch tests, it should enhance selectivity and decrease tailing. In reporting column characteristics, use is made of the equation $U = CV + V$ where U is the volume of effluent collected from the addition of the sample to the peak of the elution curve, C is the distribution ratio of the compound between the resin and solvent, and V is the interstitial volume of the column. The C and U values of these compounds (Table III) exhibited the expected sorption sequence.

TABLE II
INCREASE IN BEAD DIAMETER UPON SOAKING IN VARIOUS SOLVENTS
(Conventional sulfonic acid resin, 2% crosslinkage, 50-100 mesh)

Solvent	%
Hexane	0
Hexane sat. with methanol	45
Methanol	50
Chloroform	25
Acetonitrile	30

That *N*-methylacetanilide is more strongly sorbed than *N-n*-propylacetanilide may be a result of steric hindrance. To evaluate this possibility the column characteristics of *N-n*-butylacetanilide were determined. If steric hindrance is important, this compound with its large alkyl group should have the lowest column retention in the above series of compounds (Table III); and indeed it showed the expected low retention.

TABLE III
COLUMN CHARACTERISTICS WITH METHANOL AS ELUANT
(Conventional sulfonic acid resin, 8% crosslinkage, 100-200 mesh; total effluent collected, 350 ml; interstitial volume, 17.5 ml)

Compound	$U(\text{ml})$	C	pK_a^{15}
Acetanilide	87	4.0	-1.56
<i>N</i> -methylacetanilide	140	7.0	-0.34
<i>N-n</i> -propylacetanilide	103	4.9	-0.17
<i>N-n</i> -butylacetanilide	73	3.2	Approx. equal to <i>N</i> -methylacetanilide ^a

^a *N*-methyl and *N-n*-butylacetanilides titrated with 0.05 *N* HClO₄ in acetic anhydride.

Distribution coefficients using the macroreticular resin

Initial batch tests with the macroreticular resin showed it to be so porous that it sorbed most of the *N*-methylacetanilide and *N-n*-propylacetanilide from hexane or cyclohexane. When these solvents are saturated with methanol the amides remain in the liquid phase and the methanol is preferentially sorbed with characteristic changes in the color and swelling of the resin. With a conventional resin (2% crosslinkage and 50-100 mesh) no *N-n*-propylacetanilide is taken up from a hexane solution. Thus with a solvent such as hexane, only the macroreticular resin is porous enough to sorb the amide.

A series of K_d values (Table IV) was obtained for acetanilide and *N-n*-propylacetanilide using mixtures of acetonitrile and methanol in varying ratios. These values show that small changes in the amount of methanol in the acetonitrile make definite differences in the distribution coefficients and that only a small amount of methanol in the acetonitrile results in decided differences in sorption.

TABLE IV
DISTRIBUTION COEFFICIENTS FOR TWO ACETANILIDES USING MACRORETICULAR RESIN

Compound	pK_a	Ratio of methanol to acetonitrile									Acetonitrile
		8:2	6:4	4:6	2:8	1:9	0.5:9.5	0.3:9.7	0.2:9.8	0.1:9.9	
Acetanilide	-1.56	4	6	8	14	21.5	32	36	66	99	6000
<i>N-n</i> -Propylacetanilide	-0.17	—	—	—	—	61	156	—	—	—	No trace of cpd. in solvent

A drastic difference in the distribution coefficients, 6000 to 99, is observed on changing the solvent from pure acetonitrile to one containing only 1% (v/v) methanol. In the 1% solvent mixture there are about 32 mmoles of methanol present compared to 4.9 mequiv. of sulfonic and 0.17–0.19 mmole of amide. It has been estimated that there are 4 or 5 water molecules in the primary hydration shell around each sulfonic acid group in the conventional wet polystyrene resin⁴. A similar orientation may occur using methanol; thus this observed phenomenon may be explained by the displacement of the acetanilide from the sulfonic acid group by methanol.

Column characteristics

Column work was done both with the conventional resin (8% crosslinkage and 100–200 mesh) and the macroreticular resin (30–50 mesh). With the former, a separation of an equimolar mixture of acetanilide and *N-n*-propylacetanilide was attempted using a mixed eluant of methanol and acetonitrile (1:9). Based solely on distribution coefficients (Table I) and assuming no difficulties with particle diffusion, separation of these two compounds should be possible with this eluant. As expected the elution curve for the acetanilide was very broad and tailed badly. When most of the acetanilide had been eluted, the eluant was changed to methanol which resulted in the remaining acetanilide being eluted in the first methanolic fraction and the substituted acetanilide in the immediately following fractions.

An attempt was then made to separate a similar mixture by increasing the amount of methanol in the acetonitrile to 2:8. The elution band for acetanilide (Fig. 1) was still very broad. The eluant was subsequently changed to a 6:4 methanol–acetonitrile mixture. The first 3 fractions (28–30) contained mainly the acetanilide, indicating that the separation was not complete. These data (Fig. 1) indicate that equilibrium of the amide was far from being maintained between resin and solution. The diffusion of the amides in to, and especially out of, the conventional resin is probably so slow that separation of acetanilides with nonaqueous solvents is basically not feasible.

In order to determine whether slow diffusion and tailing would prevent separation with the macroreticular resin, acetanilide and *N-n*-propylacetanilide were individually characterized using a column of this resin and an eluant of 2:8 methanol–acetonitrile. To facilitate successful separation further, a smaller amount (0.05 mmole) of each

compound was used for column work with the macroreticular resin than with conventional resin. The elution chromatograms showed the acetanilide peak to be at 78 ml and the *N-n*-propylacetanilide peak at 117 ml. The elution bands were found to be narrow and showed no tailing of the acetanilide and only a slight degree of tailing of the *N-n*-propylacetanilide.

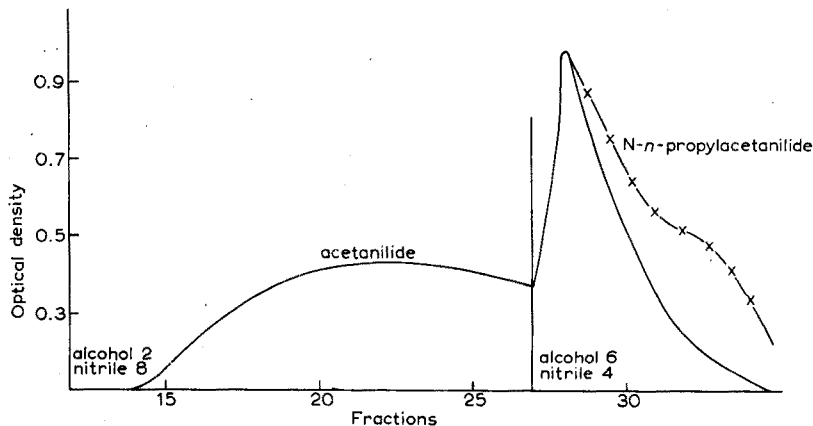


Fig. 1. Elution curve for mixture of 44.2 mg acetanilide and 55.0 mg *N-n*-propylacetanilide. Eluants, methanol and acetonitrile. Each fraction diluted 1/100; 10 ml in each fraction; flow rate 1 ml/min; 20 g of conventional resin, 8% crosslinkage, 100–200 mesh.
—, 242 $m\mu$; \times — \times , 232 $m\mu$.

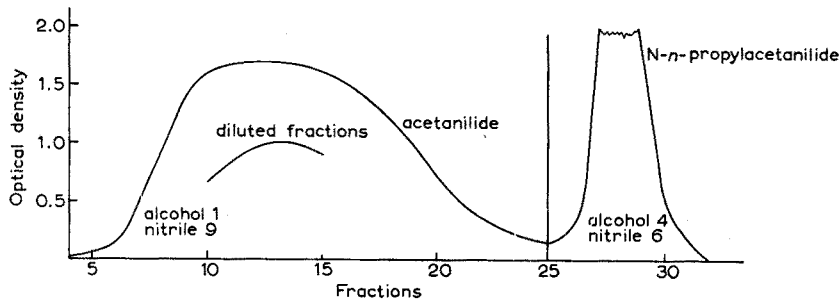


Fig. 2. Elution curve for mixture of 5.3 mg acetanilide and 7.6 mg *N-n*-propylacetanilide. Eluants, methanol and acetonitrile. 10 ml in each fraction; flow rate 1 ml/min; 10 g of macroreticular resin, 30–50 mesh.

Separation of acetanilide and *N-n*-propylacetanilide was subsequently attempted once again with a 1:9 methanol–acetonitrile eluant. Acetanilide was eluted with some evidence of tailing (Fig. 2), but the *N*-substituted acetanilide was recovered in a sharp band using a 4:6 methanol–acetonitrile eluant. Fractions 26–32 were mixed, and subsequent analysis indicated a 95% recovery of the *N-n*-propylacetanilide. The U.V. spectrum of fraction 25 indicated the presence of some *N-n*-propylacetanilide because of the slight shift in the sorption peak to a lower wavelength (242 to 239 $m\mu$). Although this separation could not be achieved with the conventional sulfonic acid resin, it was almost attained with this new macroporous one under these stated conditions (Fig. 2).

Of the 3 acetanilides, the unsubstituted, the N-methyl, and N-*n*-propyl, the latter two compounds are obviously the most difficult to separate. An attempt to achieve this separation (Fig. 3) was not completely successful with a 2:8 methanol-acetonitrile eluant. If a separation had been successful, the elution curve for N-*n*-propylacetanilide would probably have taken the form of the dashed line.

Subsequent analysis of fractions 25–33 showed that this mixture contained 4.8 mg of N-methylacetanilide or 75% of the amount added to the column.

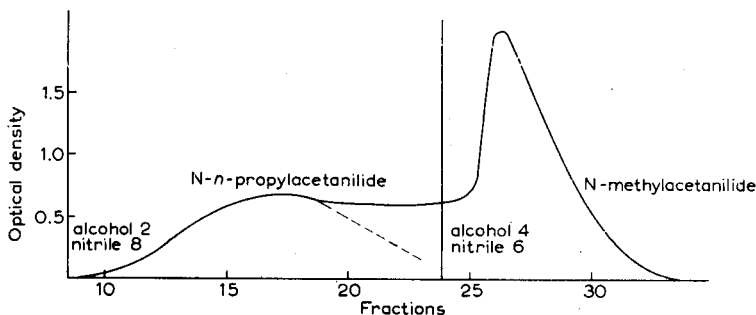


Fig. 3. Elution curve for mixture of 4.4 mg N-*n*-propylacetanilide and 6.5 mg N-methylacetanilide. Eluants, methanol and acetonitrile. 10 ml in each fraction; flow rate 1 ml/min; 10 g of macroreticular resin, 30–50 mesh.

Since acetanilide and N-*n*-propylacetanilide could be separated, it was decided to compare the characteristics of these compounds with the closely related acetamide and N-methylacetamide. The former has a pK_a of -0.70 and the latter of -0.50 . These two amides were found to have quite different column characteristics compared to the acetanilides, in that the amides were not retained by the resin with a 1:9 methanol-acetonitrile eluant. The elution curve for acetamide (6.6 mg) peaked at 32 ml, and that for the N-methylacetamide (27.4 mg) peaked at 34 ml. When just acetonitrile is used as eluant, acetamide is retained by the resin, *i.e.* 20 mg of the amide was added to a column and none of it was found in 180 ml of effluent. If acetonitrile containing 1% methanol is used as eluant the acetamide is not retained by the resin, *i.e.* 20 mg of amide was added to a column and an elution peak was found at 32 ml. Probably the differences between the retentions of the acetanilides and the acetamides can be attributed to the matrix of the resin, the acetanilides being more strongly sorbed because of their phenyl group.

Matrix attraction

To evaluate the importance of the resin matrix, batch tests and column chromatography were carried out with benzene. No acetanilide was found in the mother liquor by batch equilibration, nor was any found in 200 ml of effluent collected from a column. These results indicate that the attraction of acetanilide for the sulfonic acid group is greater than the solvating ability of the benzene for this compound. The inference of this finding is that the matrix attraction for the acetanilides is weaker than the attraction of the sulfonic acid group for these compounds. In the presence of 1:9 methanol-acetonitrile the sulfonic acid bonding plus the matrix influence are strong enough to result in the resin retaining the acetanilides even

though by comparison an excessive amount of methanol is present. The influence of the matrix appears to account for the sorption difference between the acetanilide and the acetamides when this 1:9 solvent mixture is used.

Other oxygen-containing solvents

An increase in methanol, as has been shown, is an excellent means of removing acetanilides from a column of macroreticular resin when eluant mixtures of this alcohol and acetonitrile are used. Isopropanol which is a poorer solvating medium than methanol should not be as good an eluant as methanol. Thus if isopropanol were used instead of methanol in alcohol-acetonitrile eluant, sorption of acetanilides by macroreticular resin should be greater. This statement is substantiated by the higher K_d values obtained for 1:9 isopropanol-acetonitrile mixtures: acetanilide, 34.5; *N*-methylacetanilide, 142.9; and *N*-*n*-propylacetanilide, 87.0 (see Table IV).

Consequently, separation of acetanilide and *N*-*n*-propylacetanilide with eluants of isopropanol and acetonitrile should be more difficult because of the slower particle diffusion and greater sorption compared with corresponding eluants of methanol and acetonitrile. When a 1:9 mixture was used the elution band for acetanilide was very broad (Fig. 4). After the elution peak for the acetanilide had been reached, the eluant

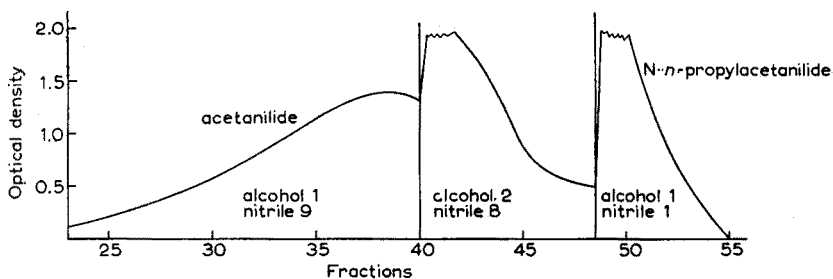


Fig. 4. Elution curve for mixture of 5.3 mg acetanilide and 8.0 mg *N*-*n*-propylacetanilide. Eluants isopropanol and acetonitrile, 10 ml in each fraction; flow rate 1 ml/min; 10 g of macroreticular resin, 30–50 mesh.

was changed to a ratio of 2:8 to decrease tailing but the tailing still persisted. In the tail fractions 47 and 48 some *N*-*n*-propylacetanilide was found. Consequently, the eluant was changed to a ratio of 1:1. The analysis of the effluent subsequently collected (fractions 49–55) showed that it contained 75% of the *N*-*n*-propylacetanilide initially added to the column.

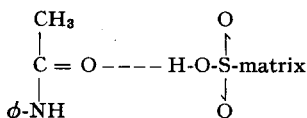
A ketonic solvent is an even poorer solvating agent than isopropanol; it probably forms a weaker bond than isopropanol with sulfonic acid, very likely one similar in strength to that for the amides. If the ketonic solvent is in great excess, it should completely replace any acetanilide. The chromatographic elution bands for acetanilide and *N*-*n*-propylacetanilide using the macroreticular resin with methyl isobutyl ketone as eluant have peaks at 35.5 ml and 37.0 ml respectively. As expected the acetanilides showed no significant retention.

CONCLUSIONS

Of all the parameters involved in the sorption of these amides, solvation of the sulfonic acid group appears to be the most important. This solvation appears to be dependent

on hydrogen bonding between the solvent molecule and the sulfonic acid and between the solvent molecules themselves. For a strong bond to be formed electronegative atoms must be bridged by hydrogen. This bridging occurs with the most electronegative elements, fluorine, oxygen, and to a lesser degree nitrogen. Although hydrogen bonding is sometimes described as a dipole interaction, it is never strong unless this hydrogen bridge is present. Though acetonitrile has a high dipole, it does not meet this other requirement for strong bonding. Methanol on the other hand does have the ability to form hydrogen bridges and consequently, is a much better solvating agent than acetonitrile.

In this work the acetonitrile appears to be only a diluent of the sulfonic acid within the resin matrix. The carbonyl of the amide when in the presence of both solvent and resin forms a hydrogen bond with the sulfonic acid:



Some weaker bonding perhaps also occurs between the acid group and nitrogen of the amide. Since methanol is a good solvating agent, it readily displaces an amide. Since isopropanol is not as good a solvating agent as methanol, it does not as readily displace an amide.

Some weaker attraction also occurs between the resin matrix and the acetanilides, and this accounts for the sorption differences between these compounds and the acetamides. Based on the work with dry benzene, bonding to the acid group appears to be more important than matrix attraction, but both are important parameters. Even the sorption characteristics of hydroxypyrazine, mentioned earlier, correlate well with the above conclusions. This compound has an OH-group capable of hydrogen bonding; it is a very weak base like acetanilide, and the pyrazine ring is very similar in structure to benzene.

The determining parameters in the separation of amides using the macroreticular resin with eluant mixtures of methanol and acetonitrile appear to be solvation and hydrogen bonding, matrix attraction, and steric hindrance. The order of importance of these parameters is probably as listed above.

The authors thank Miss IRENE PISCOPO who gathered some of the data and prepared many of the elution curves and also Dr. W. D. COOKE for his helpful discussions regarding this work.

The authors also wish to thank the Rohm and Haas Company, Resinous Products Division, for supplying the macroreticular resin.

SUMMARY

Separation of weakly basic acetanilide, N-methylacetanilide, and N-n-propylacetanilide could not be accomplished using a conventional sulfonic acid resin and various mixed eluants containing methanol and acetonitrile. The chromatograms showed elution bands that were broad and tailed badly. However, with a new macroreticular resin, some separations were obtained with the same nonaqueous eluants that had been used with the conventional resin. Although separation of acetanilide from the two N-substituted acetanilides was almost complete, the separation of the two N-substituted compounds was not.

Acetamides were separated from acetanilides because the former were not retained by the resin when a 1:9 methanol-acetonitrile eluant was used.

The two important parameters which render these separations possible are probably solvation and hydrogen bonding around the sulfonic acid group of the resin and resin matrix attraction. Methanol is a better solvating liquid than acetonitrile. In acetonitrile the amide probably associates through the carbonyl with the sulfonic acid; in methanol this association does not occur.

RÉSUMÉ

La séparation des composés faiblement basiques: acétanilide, N-méthylacétanilide et N-n-propylacétanilide n'est pas possible avec une résine sulfonique conventionnelle et des mélanges d'éluants méthanol-acétonitrile. Cependant, on a pu obtenir des séparations avec une nouvelle résine macroréticulaire. Acétamides et acétanilides ont pu être séparées, les premières n'étant pas retenues par la résine lorsqu'on utilise comme éluant le mélange méthanol-acétonitrile (1:9). Une explication du mécanisme de cette réaction est donnée.

ZUSAMMENFASSUNG

Eine Trennung des schwach basischen Acetanilids, N-Methylacetanilids und N-n-Propylacetanilids konnte unter Verwendung eines gebräuchlichen Dowex-Sulfonsäureharzes und verschiedener Elutionsmischungen von Methylalkohol und Acetonitril nicht erreicht werden. Das Chromatogramm wies breite Elutionsbanden mit starken Abflachungen auf. Mit einem neuen Harz jedoch, das eine Makronetzstruktur aufwies, waren Trennungen mit den gleichen organischen Elutionsmitteln, die für ein gebräuchliches Harz verwendet worden waren, erfolgreich. Die Trennung des Acetanilids von den beiden N-substituierten Acetaniliden war fast vollständig, die Trennung der beiden N-substituierten Verbindungen blieb unvollständig. Es wird eine Deutung der Ergebnisse vorgenommen.

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Short Communication

Dosage polarographique du disulfoxyde de cystine

Le dosage du disulfoxyde de cystine se pratique habituellement par la méthode de LAVINE¹ basée sur la libération d'iode par oxydation d'une solution concentrée et acide de IK. Excellente lorsque les quantités de substance à doser sont de l'ordre du milligramme, cette technique ne peut s'adapter au microdosage: la libération d'iode par oxydation spontanée du réactif introduit une erreur que l'on peut en principe éliminer par l'emploi d'un témoin; mais cette correction devient de l'ordre de grandeur de la mesure si l'on veut doser des quantités de disulfoxyde de l'ordre de quelques dizaines de microgrammes.

La polarographie permet un microdosage rapide et précis de cette substance. Toutes les mesures qui suivent ont été exécutées avec le polarographe MECI LX 1.

Dosage du disulfoxyde de cystine en solution pure

Placé en solution dans l'acide perchlorique *N*, le disulfoxyde de cystine donne une vague dont le potentiel de demi-palier est sensiblement égal à -0.20 V. La courbe ci-jointe (Fig. 1) montre qu'il existe une bonne proportionnalité entre la hauteur de vague et la concentration qui se maintient jusqu'à 620 mg/l au moins. On voit que 10 mg par litre donnent encore une vague mesurable.

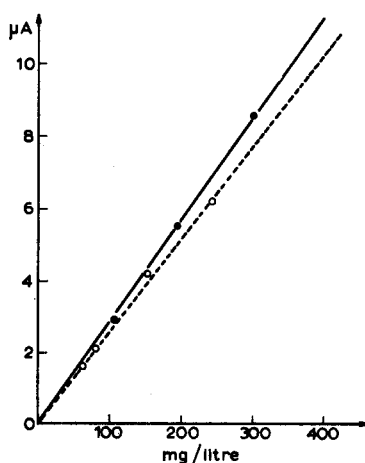


Fig. 1. Courbe donnant la hauteur de vague de la cystine (— ● —) et du disulfoxyde de cystine (--- ○ ---) en solution perchlorique.

Dosage du disulfoxyde de cystine en présence de cystine

La cystine, en solution dans l'acide perchlorique *N* donne une vague dont le potentiel de demi-palier est voisin de -0.45 V. Il existe également une relation linéaire entre la hauteur de vague et la concentration (Fig. 1).

Malheureusement, la vague du disulfoxyde se trouve sur la pente ascendante de la vague de cystine. Comme ces deux corps se trouvent fréquemment associés, le dosage devient de ce fait malaisé. La vague observée dans un mélange est bien la somme celle appartenant à chacun des corps. Mais il est difficile de faire la part de l'un et de l'autre sur un tel tracé.

On y parvient plus aisément en pratiquant le dosage en différentiel. En solutions pures, les deux corps donnent une courbe en cloche, dont la hauteur est proportionnelle à la concentration mais le sommet est à -0.20 V pour le disulfoxyde, voisin de -0.50 V pour la cystine. Dans un mélange, les ordonnées des deux courbes s'additionnent. On se trouve alors devant un problème simple, qui se présente fréquemment en spectrophotométrie, et qui se résoud de la même manière.

On procède d'abord à un étalonnage de l'appareil avec des solutions à concentrations connues de cystine et de disulfoxyde. Pour chacun des corps, on détermine le coefficient liant la hauteur de vague à la concentration, à la fois pour -0.20 V et pour -0.50 V. La figure ci-jointe (Fig. 2) montre la marche des opérations.

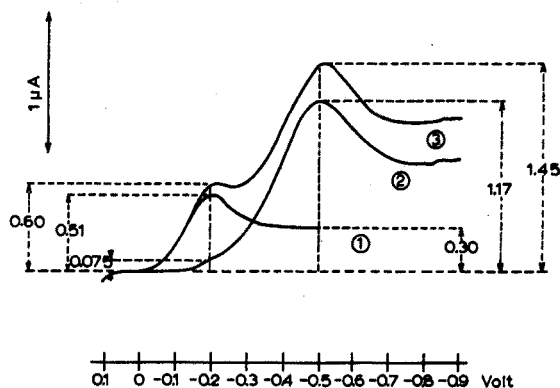


Fig. 2. Enregistrement en polarographie différentielle. Les courbes donnent l'enveloppe supérieure du tracé expérimental. Courbe 1: solution de disulfoxyde de cystine à 68 mg/l; courbe 2: solution de cystine à 155 mg/l; courbe 3: solution contenant les deux corps.

La courbe 1 a été obtenue avec une solution contenant 68 mg/l de disulfoxyde. Les hauteurs de vagues (exprimées en 10^{-6} Å) sont 51 à -0.20 V et 30 à -0.50 V.

Les coefficients seront:

$$s_1 = \frac{51}{68} = 0.75 \quad s_2 = \frac{30}{68} = 0.44$$

Sur la courbe 2, obtenue avec une solution contenant 155 mg/l de cystine, on mesure les coefficients relatifs à ce corps:

$$c_1 = \frac{7.5}{155} = 0.048 \quad c_2 = \frac{117}{155} = 0.755$$

La courbe 3 montre les vagues obtenues avec un mélange des deux corps. Les hau-

teurs sont 60 à -0.2 V et 145 à -0.5 V. Si x et y sont les quantités inconnues de disulfoxyde et de cystine, on a:

$$60 = 0.75 x + 0.048 y$$

$$145 = 0.44 x + 0.755 y$$

La résolution de ces équations donne $x = 70$, $y = 153.5$. En réalité, les concentrations sont les mêmes que dans les solutions étalons, c'est à dire 68 et 155 mg. Le dosage faisant intervenir 4 grandeurs expérimentales ne peut être très précis, et il le sera d'autant moins que les concentrations des deux corps seront plus éloignées. L'erreur vient surtout de la détermination de la ligne de base, qui reste un peu arbitraire. La technique garde cependant le mérite d'être sensible et rapide.

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¹ T. F. LAVINE, *J. Biol. Chem.*, 113 (1936) 583.

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Announcement

EIGHTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

The Determination of Interstitials and Trace Constituents in Reactor Materials and Products

The Eighth Conference on Analytical Chemistry in Nuclear Technology, on the *Determination of Interstitials and Trace Constituents in Reactor Materials and Products*, will be held in Gatlinburg, Tennessee, on October 6, 7 and 8, 1964, under the sponsorship of the Analytical Chemistry Division of the Oak Ridge National Laboratory. In addition to the technical sessions, an exhibition of modern analytical instruments and laboratory equipment will be held for the first time.

The Conference will be composed of six sessions embracing the following subjects on methods of analysis for the determination of interstitials and trace constituents in nuclear reactor materials and in the products of nuclear radiation and reactors.

1. Spectrochemical and X-Ray Methods of Analysis.
2. Mass Spectrometric Methods of Analysis.
3. Nuclear Methods of Analysis.
4. Gas Chromatographic Methods of Analysis.
5. Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals.
6. Determination of Trace Constituents by Diverse Methods.

Participation in the Conference will be on the basis of invited contributions; however, a limited number of papers, up to 25 minutes in length, are solicited and will be accepted provided that the subject matter fits in with the over-all objectives of the Conference and meets with the approval of the program committee.

Those who wish to make contributions are requested to submit an abstract of 200 to 500 words not later than July 10, giving the name of the intended speaker and the amount of time that will be required for the presentation.

The contents of the papers, to be presented at this Conference, should be directed particularly to descriptions and discussions of novel methods of analysis and of instrumental devices that have been utilized in determining the concentration of trace constituents in those materials involved

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in the construction and operation of nuclear reactors, and in the analysis of products of nuclear radiation and reactions.

The registration fee, except for full-time students, is \$5.00 per person.

Proceedings of the Conference will *not* be published; however, abstracts of all papers will be published and made available to all persons attending the Conference.

Abstracts of papers and any inquiries concerning the Conference, including requests for the program and copies of the printed abstracts, should be directed to the Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37831, Attention: C. D. SUSANO, Chairman.

Reservations for lodging should be made by direct communication with: The Mountain View Hotel, Gatlinburg, Tennessee 37738.

Anal. Chim. Acta, 31 (1964) 99-100

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Solubilities of Inorganic and Organic Compounds, Vol. I, Binary Systems, Part 2, Editors H. STEPHEN AND T. STEPHEN. Pergamon Press, Oxford, 1963. Pp. 963-1933. Price £12.10.0.

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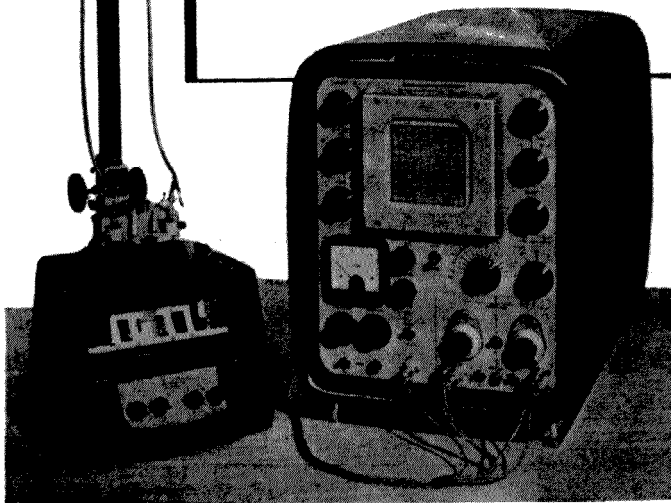
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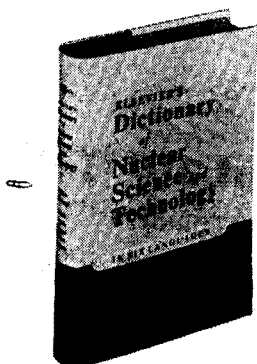
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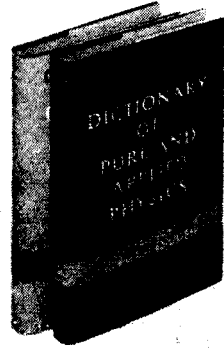
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