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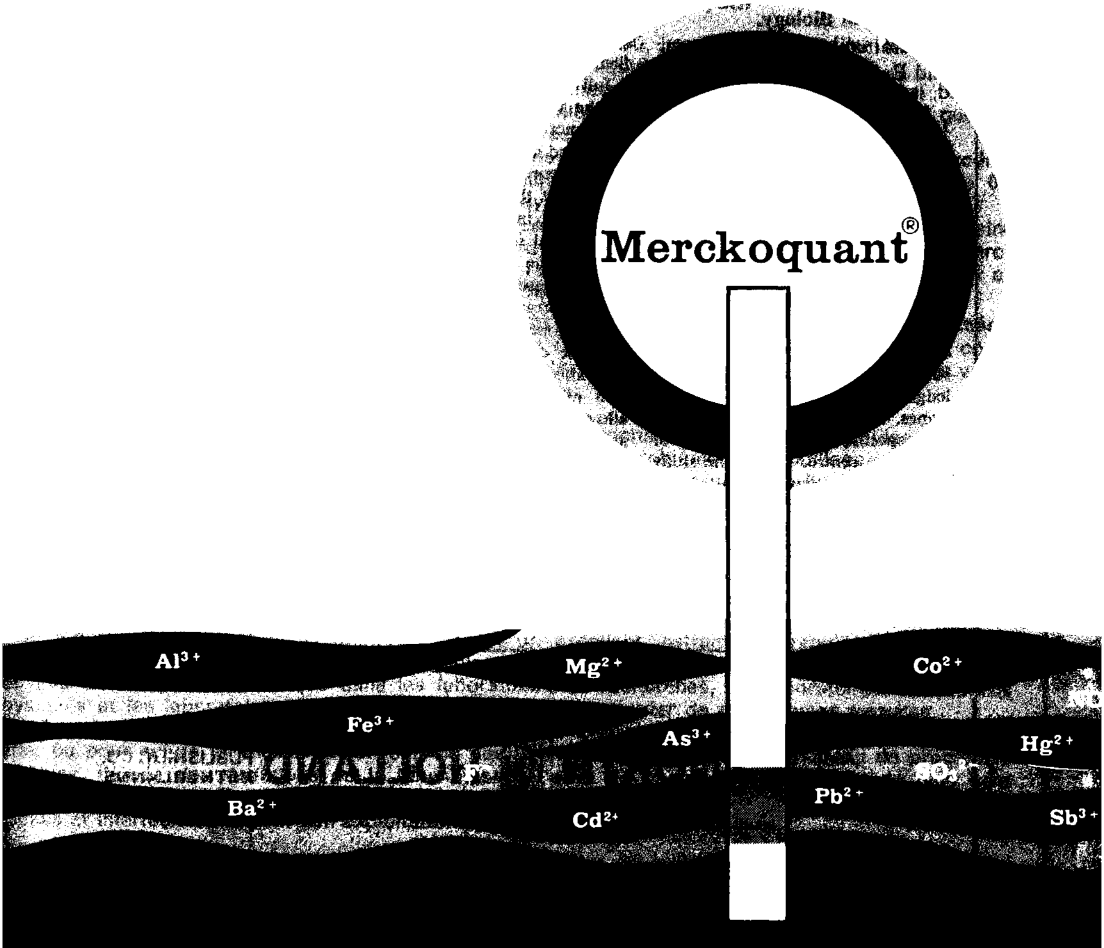
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ENZYME INHIBITORS AS SUBTRATES

Interactions of Esterases with Esters of Organophosphorus and Carbamic Acids.

Volume 26 in the series:
Frontiers of Biology.
General editors: A. Neuberger
and E. L. Tatum

1972. 344 pages.
Dfl. 65.00 (ca. $20.25)
ISBN 0 7204 7126 5

Esters of organophosphorus and carbamic acids have played a unique role in the development of our knowledge of the catalytic activity of enzymes. The initial demonstration of the specific phosphorylation of the active centre, placed the study of hydrolytic enzymes on a firm chemical basis. Recent studies have produced evidence for the presence of a reversible Michaelis complex. In addition some organophosphorus compounds appear to have affinity for the site involved in inhibition by high concentrations of substrate. Thus the analogy between substrates and such inhibitors has been finally established. This book gives a full account of the development of the hypothesis that these inhibitors act as substrates. It provides a detailed derivation and discussion of the theoretical framework for the kinetics of the process and the experimental implications.

The formal identity of the mechanism of the reaction of inhibitors with esterases, with their reaction with substrates allows inhibitors to be developed for specific purposes. The use of such inhibitors in the separation and analytical determination of different esterases (which allows the role of esterases in biological processes to be evaluated) are discussed here in book form, for the first time. It is hoped that the outcome of our understanding of the nature of these reactions will be the development of more active and safer pesticides.

Contents:

Editors' preface. Authors' preface. Abbreviations. Definitions and nomenclature. Reaction of B-esterases with acylating inhibitors. Kinetics of reaction of B-esterases with organophosphorus compounds. Deacylation of phosphorylated B-esterases. Effect of substrate on reaction of B-esterases with organophosphorus compounds. Effect of pH on reaction of B-esterases with organophosphorus compounds. Effect of temperature on reactions of B-esterases with organophosphorus compounds. Kinetics of reaction of B-esterases with carbamates. Reaction of B-esterases with organosulphur compounds. Interaction of inhibitors with enzymes analogous to inhibition by substrate. Acylated amino acids in inhibited B-esterases. A-esterases. Acylating inhibitors as tools in the study of biological processes. General conclusions. Appendices. Acknowledgments. Recommended reference works. References. Formula index. Subject index.

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On comprend donc l'intérêt du tensiomètre pour l'étude des solutions détergentes, des liquides de traitement de minerais, des bains d'électrolyse, des colles, des peintures et vernis, des catalyseurs, des suspensions, des solutions colloïdales, etc... Sant compter l'étude des liquides biologiques.

La tension superficielle des liquides est une constante physique dont la mesure systématique se révèle fructueuse. Elle est à la fois un indice de pureté et de propreté superficielle.

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THERMODYNAMIC PROPERTIES OF THE SOLVENT EXTRACTION OF ION PAIRS OF METAL CHELATE CATIONS WITH SOME ANIONS

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Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima (Japan)
(Received 21st September 1972)

The spectrophotometric determination of various anions by means of solvent extraction with tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)iron(II) chelate cations has been discussed in several papers[1]. These ion pairs can be extracted only with a limited number of solvents which have fairly high dielectric constants. Nitrobenzene with a dielectric constant of 34.8 (25°) is known to be a good solvent for ion-pair extraction. For the bipyridine series only, 1,2-dichloroethane with a dielectric constant of 10.4 (25°) can be used. Chloroform (dielectric constant 4.81, 20°) very slightly extracts the phenanthroline–iron–perchlorate ion pair.

Larger anions can be extracted more readily than smaller ones. Thus, the extractability of ion pairs seems, as Diamond and Tuck[2] pointed out, to depend on the sizes of the cation and anion as well as the dielectric nature of the solvents.

Krasnov *et al.*[3] presented a thermodynamic study of the extraction of ion pairs of some monovalent dyestuff cations with halide anions.

In the present work, thermodynamic quantities were obtained for the extraction of the ion pairs of tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)-iron(II) cations with halide ions as examples of monovalent ions and polythionates as examples of divalent anions, so that a physicochemical basis could be provided for these solvent extraction processes.

EXPERIMENTAL

Apparatus

A glass tube with stopcocks at both ends, 2.5 cm in diameter and 60 cm^3 in volume, was used as a separatory funnel. A Hitachi 139 spectrophotometer with 10-mm glass cells was used for the measurements of absorbance.

Materials

Solvents. Nitrobenzene and 1,2-dichloroethane were of analytical-reagent grade and were distilled under reduced pressures. These were saturated with distilled water before extraction.

Chelate salts. Crystals of tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)iron(II) chelate salts were prepared from Mohr's salt, the chelating reagents and the sodium salts of the corresponding anions. The crystals were prepared in aqueous solution and were recrystallized twice. Their purities were checked by analysis; the results are shown in Table I.

TABLE I

ELEMENTAL ANALYSES OF METAL CHELATE SALTS

X	*n*	*C%*		*H%*		*N%*	
		Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
$Fe(phen)_3X \cdot nH_2O$							
$(ClO_4)_2$	1	53.16	53.94	3.23	3.26	10.33	10.59
$(SCN)_2$	2	60.95	61.17	3.78	3.96	14.97	14.90
I_2	2	48.78	48.73	3.18	3.16	9.48	9.76
Br_2	6	50.02	49.55	4.21	4.16	9.73	9.70
Cl_2	7	54.49	54.53	4.82	4.92	10.59	10.50
S_2O_6	7	48.99	49.99	4.34	4.45	9.52	9.49
S_3O_6	3	51.31	51.58	3.59	3.66	9.97	9.78
S_4O_6	2	50.47	51.25	3.29	3.48	9.81	9.95
S_5O_6	1	49.66	51.72	3.01	3.30	9.65	9.88
$Fe(bip)_3X \cdot nH_2O$							
$(ClO_4)_2$	0	49.82	49.69	3.34	3.38	11.62	11.63
$(SCN)_2$	3	55.33	55.06	4.35	4.37	16.13	16.03
I_2	5	41.50	41.70	3.95	3.95	9.68	9.64
Br_2	5	46.54	46.22	4.43	4.56	10.85	10.85
S_3O_6	2	47.88	48.38	3.75	3.69	11.17	11.23
S_5O_6	1	45.11	45.63	3.28	3.38	10.52	10.77

All the extractions were carried out at pH 5.3 in 0.067 *M* phosphate buffer solution, because these species showed unvaried extractabilities over the pH range 4–7 at any temperatures tested.

Procedure

To 15 ml of the aqueous solution of the salts, 15 ml of a solvent was added. Extraction was carried out for 10 min at various temperatures ranging from 7 to 50°. The two layers were separated by a centrifuge and the absorbance of each phase was measured. The concentrations were determined by using calibration curves prepared beforehand. Measurements were made at the wavelengths of maximal absorbance, *i.e.*, for $Fe(phen)_3X$, 510 nm in the aqueous phase or 516 nm in nitrobenzene, and for $Fe(bip)_3X$, 524 nm in the aqueous phase, or 527 nm in the nitrobenzene or 1,2-dichloroethane phase. In every case, extra amounts of chelating reagents were added to the organic phase (10^{-2} *M*) to prevent possible decomposition at high temperatures. Concentrations of the chelate salts in the aqueous phases are given in Table II.

RESULTS AND DISCUSSION

The possible decomposition of the chelate cations can be disregarded since their formation constants are large and, in addition, excess amounts of chelating reagents were added to the extraction systems. This was confirmed by the fact that the absorbances of the chelate cations did not decrease at high temperatures.

Because the exact dissociation constants of these ion pairs are not known in any phases, several assumptions had to be made as follows.

TABLE II

INITIAL CONCENTRATIONS OF THE CHELATE SALTS IN THE AQUEOUS PHASE

(Data in mole l^{-1})

X	*Fe(phen)$_3$X* *Nitrobenzene*	*Fe(bip)$_3$X* *Nitrobenzene*	*Fe(bip)$_3$X* *1,2-Dichloroethane*
$(ClO_4)_2$	$1.0 \cdot 10^{-4}$	$6.0 \cdot 10^{-5}$	$5.0 \cdot 10^{-4}$
$(SCN)_2$	$1.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$5.0 \cdot 10^{-3}$
I_2	$1.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-3}$
Br_2	$1.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	—
Cl_2	$1.0 \cdot 10^{-2}$	—	—
S_5O_6	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	—
S_4O_6	$8.0 \cdot 10^{-4}$	—	—
S_3O_6	$7.7 \cdot 10^{-4}$	$9.8 \cdot 10^{-3}$	—
S_2O_6	$3.9 \cdot 10^{-3}$	—	—

1. The ion pairs are completely dissociated in the organic phase as well as in the aqueous phase. With monovalent anions,

With monovalent anions,

$$[FeL_3^{2+}]_w + 2[X^-]_w \rightleftarrows [FeL_3^{2+}]_o + 2[X^-]_o$$

and the extraction constant, K_{ex}, is,

$$K_{ex} = \frac{[FeL_3^{2+}]_o[X^-]_o^2}{[FeL_3^{2+}]_w[X^-]_w^2} \tag{1a}$$

where L is 1,10-phenanthroline or 2,2′-bipyridine, and w and o refer to the aqueous phase and the organic phase, respectively. With divalent anions,

$$[FeL_3^{2+}]_w + [X^{2-}]_w \rightleftharpoons [FeL_3^{2+}]_o + [X^{2-}]_o$$

and

$$K_{ex} = \frac{[FeL_3^{2+}]_o[X^{2-}]_o}{[FeL_3^{2+}]_w[X^{2-}]_w} \tag{1b}$$

2. Complete dissociation in the aqueous phase and partial dissociation in the organic phase:

$$[FeL_3^{2+}]_w + 2[X^-]_w \rightleftharpoons [FeL_3X^+]_o + [X^-]_o$$

$$K_{ex} = \frac{[FeL_3X^+]_o[X^-]_o}{[FeL_3^{2+}]_w[X^-]_w^2} \tag{2}$$

The case (2) may apply only to the systems with monovalent anions. These extraction constants can be easily evaluated by determining the concentration of the chelate cations.

Free energy changes were obtained directly from the K_{ex} values. Enthalpy changes were calculated from the slopes of the plots, log K_{ex} *vs.* reciprocals of temperature, which were linear over the temperature range tested. The slopes were calculated by the least squares method. The thermodynamic quantities thus obtained are listed in Tables III, IV and V.

TABLE III

THERMODYNAMIC QUANTITIES FOR THE EXTRACTION OF FeL_3X_2 INTO NITROBENZENE AT 25°[a]

X	*L*	*ΔG(kcal mol^{-1})*	*ΔH(kcal mol^{-1})* ±*0.60*	*ΔS(e.u.)* ±*1.8*
According to K_{ex} from eqn. (1a)				
ClO_4^-	bip	−7.67	−15.9	−27.6
	phen	−9.31	−14.0	−15.8
SCN^-	bip	−3.18	−5.65	−8.3
	phen	−5.85	−7.05	−4.0
I^-	bip	−2.15	−5.90	−12.5
	phen	−4.82	−7.33	−8.4
Br^-	bip	3.20	1.93	−4.3
	phen	0.91	0	−3.0
Cl^-	bip	—	—	—
	phen	5.05	5.84	2.7
According to K_{ex} from eqn. (2)[b]				
ClO_4^-	bip	−2.57	−16.3	−46.2
	phen	−4.62	−14.5	−33.3
SCN^-	bip	1.67	−7.28	−30.0
	phen	−0.91	−8.76	−26.4
I^-	bip	2.93	−8.09	−37.0
	phen	0.31	−9.95	−34.4
Br^-	bip	9.09	2.73	−21.3
	phen	6.31	0.61	−19.1
Cl^-	bip	—	—	—
	phen	10.43	7.87	−8.6

[a] The errors shown are the largest values found in all the results. [b] For these values the error in ΔG was ±0.04 and that in ΔS was ±1.9.

TABLE IV

THERMODYNAMIC QUANTITIES FOR THE EXTRACTION OF FeL_3X INTO NITROBENZENE AT 25°[a]

X	*L*	*ΔG(kcal mol^{-1})* ±*0.02*	*ΔH(kcal mol^{-1})* ±*0.16*	*ΔS(e.u.)* ±*0.6*
$S_5O_6^{2-}$	bip	4.85	−3.18	−26.9
	phen	2.17	−6.03	−27.5
$S_4O_6^{2-}$	bip	—	—	—
	phen	4.23	−3.22	−25.0
$S_3O_6^{2-}$	bip	7.02	−0.09	−23.9
	phen	4.15	−2.48	−22.2
$S_2O_6^{2-}$	bip	—	—	—
	phen	7.11	0.59	−21.9

[a] See footnote (*a*) of Table III.

TABLE V

THERMODYNAMIC QUANTITIES FOR THE EXTRACTION OF $Fe(bip)_3X_2$ INTO 1,2-DICHLOROETHANE AT 25°

X	ΔG(kcal mol^{-1})	ΔH(kcal mol^{-1})	ΔS(e.u.)
ClO_4^-	−0.69	−18.5	−59.9
SCN^-	2.90	−6.9	−32.9
I^-	3.91	−11.1	−50.4

The free energy and the enthalpy changes were plotted against the reciprocals of the ionic radii of the counter anions in Figs. 1 and 2, where linear relationships can be observed. From the plot of the bipyridine–halide–nitrobenzene system, the free energy change of the chloride salt can be roughly estimated (about 14 kcal mol^{-1}).

The slopes of the plots of the two series, $Fe(phen)_3X_2$/nitrobenzene and $Fe(bip)_3X_2$/nitrobenzene, coincide (130 kcal per r^{-1}) for the complete dissociation in nitrobenzene. This may indicate that the behaviors of anions are independent of the chelate cations. This slope is much larger than the value expected from the Born equation: $\Delta G = \frac{1}{2}Ne^2(D_o^{-1} - D_w^{-1})r^{-1}$, which is only 5.4 kcal per r^{-1} for the two counter anions. Here, D_o is the dielectric constant of nitrobenzene and D_w is that of water. In addition, the Born equation predicts that the free energy changes for the transfer from water to nitrobenzene will always be positive, which is not the case for the present systems. The only agreement between the experimental

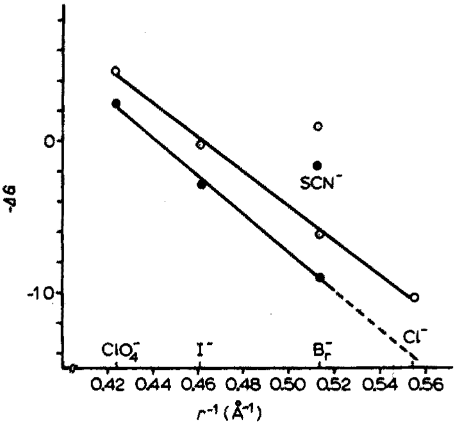

Fig. 1. Free energy changes *vs.* reciprocal radii of anions for the extraction of $Fe(phen)_3X_2$ (○) and $Fe(bip)_3X_2$ (●) into nitrobenzene (*cf.* Table III).

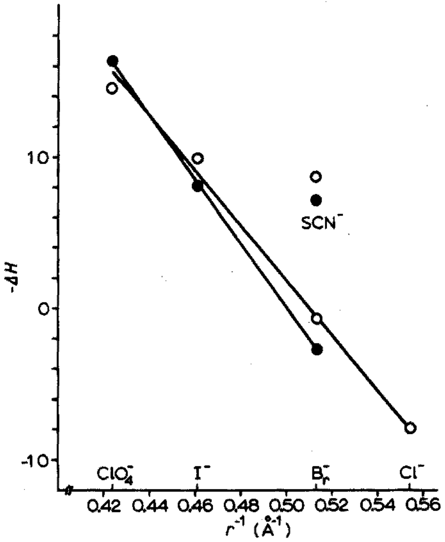

Fig. 2. Enthalpy changes *vs.* reciprocal radii of anions for the extraction of $Fe(phen)_3X_2$ (○) and $F(bip)_3X_2$ (●) into nitrobenzene (*cf.* Table III).

results and the Born equation is the dependence of the free energy changes on the reciprocals of ionic radii. Thus the Born equation fails to explain adequately the transfer of these ionic species from the aqueous phase to the nitrobenzene phase. This is because it assumes a continuous medium of uniform dielectric constant. In reality, however, discrete interactions between ions and solvent molecules occur. Such solvation phenomena have been observed for the systems studied above[4].

A detailed discussion on the results in Tables III, IV and V is given below for the three systems: phenanthroline–nitrobenzene, bipyridine–nitrobenzene, and bipyridine–dichloroethane.

Phenanthroline–nitrobenzene system

The ΔH values for perchlorate, thiocyanate and iodide (Table III) are very negative, which suggests that these species are strongly solvated by nitrobenzene. ΔG for perchlorate is negative, which is in accordance with the fact that this species is very easily extracted. For thiocyanate and iodide, the ΔG values are very close to each other, and are more positive than that for perchlorate, which is also in agreement with their extractability. For bromide, the ΔH values are almost zero, indicating that the heat of solvation of nitrobenzene is compensated by the heat absorbed during the process of releasing solvated water molecules. Chloride may have more affinity to water than to nitrobenzene as is shown by the positive value of ΔH.

With regard to the divalent polythionate series (Table IV), similar arguments may apply. The ΔH and ΔS values are in the order of the anion sizes. No difference was observed between the ΔG values for the trithionate and the tetrathionate.

Bipyridine–nitrobenzene system

Tris(2,2′-bipyridine)iron(II) chelate ion pairs are less readily extracted than the phenanthroline–iron ion pairs. This fact is clearly indicated by the more positive ΔG values found for the bipyridine systems (Tables III and IV). ΔH and ΔS values for perchlorate in this system are more negative than those in the phenanthroline system. This may mean that bipyridine–iron(II) perchlorate is more strongly solvated by nitrobenzene. For chloride and dithionate, accurate measurements were not feasible because of their extremely low extractability. The purity of the synthesized tetrathionate salt was somewhat dubious and so results are not listed here.

For the salts with monovalent anions in the two systems just discussed above, K_{ex} from eqn. (1a) or eqn. (2) may apply. The thermodynamic quantities calculated with these two extraction constants show a very similar trend and therefore it seems impossible to determine which K_{ex} is the more probable. However, nitrobenzene, which is known to be an excellent solvent for ion-pair extraction owing to its relatively high dielectric constant and large dipole moment, may favor complete dissociation. In addition, almost complete dissociation of ion pairs in nitrobenzene has been reported for some cases[5–7]. Thus, for the monovalent halide series, the K_{ex} value of eqn. (1a) may be used satisfactorily, and for the divalent polythionate series the K_{ex} value of eqn. (1b) may suffice.

Bipyridine–1,2-dichloroethane system

Results were obtained only with perchlorate, thiocyanate and iodide. Since the dielectric constant of the solvent is very low compared to that of nitrobenzene, the chelate salt may be only partly dissociated. To this system, therefore, the K_{ex} value of eqn. (2) may be reasonably applied. For this system, the enthalpy changes are more negative than those for the nitrobenzene system, though the degrees of extraction are much lower. The entropy changes also are negative, much more negative than for the nitrobenzene system. This must be due to ion pairing as well as solvation. For the extraction of the chelate salts used here, the free energy changes are determined by the entropy changes.

The less negative ΔH and ΔS values of thiocyanate suggest that its degree of solvation is smaller. The behavior of thiocyanate is somewhat unpredictable because the shape and the size of thiocyanate ion are ambiguous.

SUMMARY

Thermodynamic quantities were determined for the extraction of ion pairs of tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)iron(II) chelate cations with halide, pseudohalide and polythionate anions from aqueous phase into nitrobenzene. Ion pairs with larger anions have more negative enthalpy changes with higher extractability. No clear trend was observed for the entropy changes. Linear relationships were observed between the free energy changes and the reciprocal radii of monovalent counter anions.

RÉSUMÉ

Une étude est effectuée sur les propriétés thermodynamiques de l'extraction dans un solvant de paires ioniques de cations chélates métalliques en présence de certains anions. On examine en particulier les cations chelates tris(1,10-phénanthroline)fer(II) et tris(2,2′-bipyridine)fer(II) avec halogénures, pseudohalogénures et polythionates, de la phase aqueuse dans le nitrobenzène.

ZUSAMMENFASSUNG

Thermodynamische Grössen wurden ermittelt für die Extraktion der Ionenpaare von Tris(1,10-phenanthrolin)eisen(II)- und Tris(2,2′-bipyridin)eisen(II)-Chelatkationen mit Halogenid-, Pseudohalogenid- und Polythionatanionen aus wässriger Phase mit Nitrobenzol. Ionenpaare mit grösseren Anionen haben eine negativere Enthalpieänderung bei höherer Extrahierbarkeit. Für den Entropiewechsel wurde kein eindeutiger Zusammenhang beobachtet. Lineare Beziehungen wurden festgestellt zwischen der Änderung der freien Energie und den reziproken Radien der einwertigen Gegen-Anionen.

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THERMAL STUDIES ON ARSENIC, ANTIMONY AND BISMUTH ALKYLXANTHATE COMPLEXES

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Derivatives of xanthic acid and dithiocarbamic acid have been known for a very long time. The method of preparing xanthates by the reaction of carbon disulphide with metal alkoxides in the presence of alcohols was first described in 1815[1], and a derivative of dithiocarbamic acid, sodium diethyldithiocarbamate, was recommended[2] as an analytical reagent for copper and iron in 1908. In recent years, interest in fundamental studies on metal dithiocarbamates has increased markedly[3,4] and many different types of investigations have been reported. However, investigations on the thermal behaviour of dithiocarbamates and xanthates are few in number.

D'Ascenzo and Wendlandt[5] have determined the thermal properties of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) diethyldithiocarbamates, and D'Ascenzo *et al.*[6] have reported the thermal behaviour of tin(IV) diethyldithiocarbamate. Bernard and Borel[7] have also examined thermally the dithiocarbamates of lead, zinc and cadmium. Recently, in this laboratory, thermal studies on nickel alkylxanthates were carried out[8], but apart from this no thermal data seem to be available for metal xanthates.

This paper reports thermogravimetric analysis data for six xanthate derivatives of arsenic(III), antimony(III), and bismuth(III), $[ROCSS]_3M$, where R = methyl, ethyl, isopropyl, *n*-butyl, cyclohexyl and benzyl. A thermal decomposition mechanism for the complexes is proposed.

EXPERIMENTAL

Preparation of the metal alkylxanthates

A careful control of pH is necessary in the reaction of Group Vb elements with alkylxanthates in aqueous solution, because of the instability of the ligand ion at lower pH values and the possibility of precipitation of the metal hydroxide at higher pH values. All the water used in the following procedures was triply distilled and deoxygenated.

Arsenic. Sodium arsenite was dissolved in a small volume of water. The pH of the solution was adjusted to 5–5.5 by the dropwise addition of concentrated hydrochloric acid. A greater than 3-fold excess of the appropriate ligand in 50 ml of water was added in small portions with continuous stirring, and the pH re-adjusted to 5–5.5 with concentrated hydrochloric acid. The precipitate formed was filtered, quickly washed several times with a small volume of water and dried by leaving overnight under vacuum in a desiccator with silica gel. The complexes were recrystallized by dissolving in benzene and evaporating slowly under vacuum. The complexes were stored in dark bottles and kept under vacuum in a desiccator over silica gel in a dark, cool place.

For *n*-butyl-, cyclohexyl- and benzylxanthates, the pH of the solutions was adjusted with (1+1) or (1+4) hydrochloric acid, as very impure products were obtained with concentrated hydrochloric acid.

Antimony. For this element, the same procedure was for arsenic was used. The starting material was antimony potassium tartrate and the pH of the solution was adjusted to 5.0–5.5 by the dropwise addition of a concentrated solution of tartaric acid, except in the case of *n*-butylxanthate, where the pH was adjusted to 6.0 by 1.25 *M* tartaric acid to obtain a product with a better yield and purity. Better results were also obtained for the cyclohexylxanthate, if the pH was adjusted to 1.0–2.0 with 2.5 *M* tartaric acid.

Bismuth. Bismuth nitrate was dissolved in the minimal volume of 1.0–1.5 *M* nitric acid and diluted to 50 ml with water. A greater than 3-fold excess of the ligand, dissolved in 30 ml of water was added in small portions with constant stirring. The product was further treated in a manner similar to that for the arsenic alkylxanthates.

No crystallization of the methyl derivative could be carried out because of its poor solubility in organic solvents. The *n*-butyl derivative was crystallized from hot absolute ethanol and the cyclohexyl derivative from hot benzene.

Preparation of the ligands

The potassium salts of the appropriate ligand were used throughout and were prepared by the method of Vogel[9]. Purification was carried out by the method of Dewitt and Roper[10].

Elemental analysis of complexes

Analyses for carbon, hydrogen and sulphur were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne. Arsenic was determined iodometrically[11]; antimony[12] and bismuth[13] were determined spectrophotometrically as the yellow iodo-species produced when potassium iodide is added to an acidic solution of the metal. The analytical data are presented in Table I.

Thermal studies

Thermogravimetric analyses were carried out on a Stanton TR-01 Thermobalance at a heating rate of 4° min^{-1}.

Volatility measurements

The complexes were sublimed at *ca.* 0.1 mm Hg pressure in a sublimation apparatus immersed in an oil bath. The sublimates were collected on a cold finger.

Infrared spectra

These were measured on a Perkin-Elmer 457 Grating Spectrophotometer in the range 4000–250 cm^{-1} by the KBr disc technique.

TABLE I

ELEMENTAL ANALYSIS OF COMPLEXES OF ARSENIC, ANTIMONY AND BISMUTH

Ligand	*Formula*	*Elemental analysis*					
			%*C*	%*H*	%*S*	%*M*[a]	*M.wt.*
Arsenic complexes							
Methyl	$As(CS_2OCH_3)_3$	Calcd.	18.2	2.9	48.5	18.9	396
(M.p. 80–81°)		Found	18.5	2.4	48.7	18.8	381
Ethyl	$As(CS_2OC_2H_5)_3$	Calcd.	24.6	3.4	43.9	17.1	438
(M.p. 89.5°)		Found	24.5	3.3	44.0	16.5	425
Isopropyl	$As(CS_2OC_3H_7)_3$	Calcd.	30.0	4.4	40.0	15.6	480
(M.p. 150–151°)		Found	30.1	4.4	40.3	15.1	464
n-Butyl	$As(CS_2OC_4H_9)_3$	Calcd.	34.5	5.2	36.8	14.3	523
(M.p. 35–36°)		Found	34.5	5.3	36.3	15.8	524
Cyclohexyl	$As(CS_2OC_6H_{11})_3$	Calcd.	42.0	5.5	32.0	12.5	601
(M.p. 171–172°)		Found	41.8	5.4	32.1	12.5	622
Benzyl	$As(CS_2OC_7H_7)_3$	Calcd.	46.1	3.4	30.8	12.0	625
(M.p. 85°)		Found	46.9	3.7	31.0	12.7	631
Antimony complexes							
Methyl	$Sb(CS_2OCH_3)_3$	Calcd.	16.3	2.0	43.4	27.4	443
(M.p. 114–115°)		Found	16.3	2.3	43.2	27.2	425
Ethyl	$Sb(CS_2OC_2H_5)_3$	Calcd.	22.3	3.1	39.6	25.1	485
(M.p. 75°)		Found	22.4	3.2	40.0	25.2	477
Isopropyl	$Sb(CS_2OC_3H_7)_3$	Calcd.	27.3	4.0	36.5	23.1	527
(M.p. 141–147°)		Found	27.6	3.9	36.8	23.4	547
n-Butyl	$Sb(CS_2OC_4H_9)_3$	Calcd.	31.6	4.8	33.8	21.4	569
(oily liquid)		Found	32.1	4.7	32.2	21.7	563
Cyclohexyl	$Sb(CS_2OC_6H_{11})_3$	Calcd.	39.0	5.1	29.7	—	648
(M.p. 187°)		Found	39.1	5.2	30.0		638
Bismuth complexes							
Methyl	$Bi(CS_2OCH_3)_3$	Calcd.	13.6	1.7	36.3	39.4	—
(M.p. 130–131°)		Found	13.7	1.9	35.9	39.7	
Ethyl	$Bi(CS_2OC_2H_5)_3$	Calcd.	18.9	2.6	33.6	36.5	572
(M.p. 94–95°)		Found	19.2	2.7	33.2	36.2	588
Isopropyl	$Bi(CS_2OC_3H_7)_3$	Calcd.	23.4	3.4	31.3	34.0	615
(160–162°)[b]		Found	23.3	3.3	30.9	33.8	628
n-Butyl	$Bi(CS_2OC_4H_9)_3$	Calcd.	27.4	4.1	29.3	31.8	657
(M.p. 30.0°)		Found	27.7	4.1	29.3	31.4	654
Cyclohexyl	$Bi(CS_2OC_6H_{11})_3$	Calcd.	34.3	4.5	26.2	—	735
(M.p. 160–161°)		Found	34.0	4.5	26.2		733

[a] M = As, Sb or Bi.

[b] Decomposes without melting.

Mass spectra

Mass spectra were carried out on a 12-in radius single focusing magnetic sector spectrometer constructed in this Department.

Molecular weight measurements

Molecular weight measurements were made at 25° in benzene using a

Mechrolab Vapour Pressure Osmometer Model 302. The bismuth(III) methylxanthate was insufficiently soluble in benzene so that measurements could not be carried out. Results are given in the final column of Table I.

RESULTS AND DISCUSSION

Thermogravimetric studies

Arsenic alkylxanthates. After an initial period of heating over which all the complexes were stable, all the derivatives exhibited the following stages with further increase in temperature (Fig. 1).

Stage I. A sudden and rapid loss of weight which is attributed mainly to volatilization of the complex.

Stage II. A slower weight loss region where decomposition and volatilization of the decomposition product appear to be taking place simultaneously, the extent of each varying with the complex. A temperature is reached at which the sample container is empty.

The individual characteristics of these stages are presented in Table II.

The curves in Fig. 1 and the data in Table II clearly show that only the *n*-butyl and benzyl derivatives are essentially completely volatile. The remaining chelates tend to show decomposition in addition to volatility. However, for all the chelates examined, volatility is clearly the major factor in the observed weight loss. The product(s) of the decomposition, probably As_2S_3 and some organic material, are also volatile as all material is lost at higher temperatures. The results also indicate that the cyclohexyl derivative is the most stable and the methyl derivative the least stable.

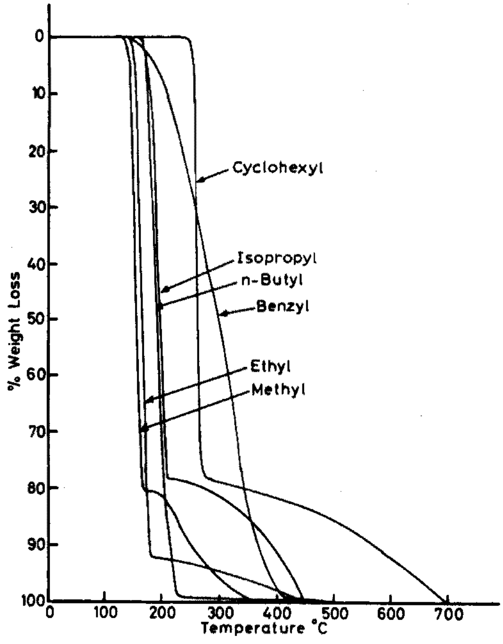


Fig. 1. Thermogravimetric curves for arsenic(III) xanthate complexes.

TABLE II

THERMOGRAVIMETRIC CHARACTERISTICS OF ARSENIC ALKYLXANTHATES

	Methyl	*Ethyl*	*Isopropyl*	*n-Butyl*	*Cyclohexyl*	*Benzyl*
Stage I	130–170°	140–180°	160–210°	160–220°	240–270°	180–400°
Percent weight loss in Stage I	80.4	91.9	78.2	99.1	72.8	~100
Stage II	170–350°	180–450°	210–450°	220–450°	270–700°	400–500°

Antimony alkylxanthates. Two stages are clearly observed in the thermogravimetric curves of all the antimony derivatives (Fig. 2).

Stage I. A rapid loss of weight in the temperature range 100–260°.

Stage II. A gradual loss of weight over a wide temperature range, which appears to be complete around 500–600°.

The data for the various antimony complexes are summarized in Table III.

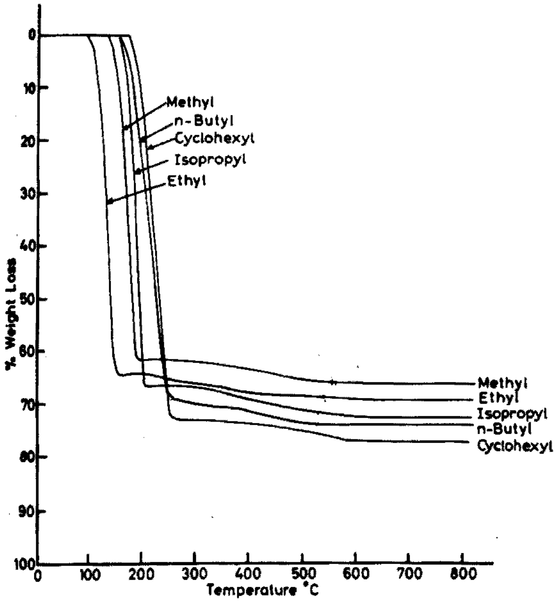


Fig. 2. Thermogravimetric curves for antimony(III) xanthate complexes.

TABLE III

THERMOGRAVIMETRIC CHARACTERISTICS OF ANTIMONY ALKYLXANTHATES

	Methyl	*Ethyl*	*Isopropyl*	*n-Butyl*	*Cyclohexyl*
Stage I	140–200°	100–160°	160–210°	160–260°	180–260°
Percent weight loss in Stage I	61.6	64.6	66.6	69.0	72.8
Stage II	200–550°	160–600°	210–600°	260–600°	260–600°

Stage I appears to result in complete decomposition of the complexes to the sulphide, Sb_2S_3. After Stage II in every case, the residue obtained on completion of the pyrolysis (above 600°) was white and water-insoluble. Infrared examination of this residue indicated the absence of sulphate and calculations on the final weight of the residue correlated well with that expected for the oxide, Sb_2O_3; *e.g.*, for the isopropyl derivative, the residue observed was 27.3% and that expected for Sb_2O_3 was 27.6%.

Bismuth alkylxanthates. In the initial stage, the derivatives of bismuth showed a thermal behaviour similar to that of the antimony complexes, but the second stage was more complex (Fig. 3).

Stage I. A rapid loss of weight over the temperature range 120–290°.

Stage II. The weight remained essentially constant up to about 450°, where the sample gradually increased in weight before further loss commenced at about 550°. Finally, the weight stabilized again around 750°.

The data for the bismuth complexes are presented in Table IV.

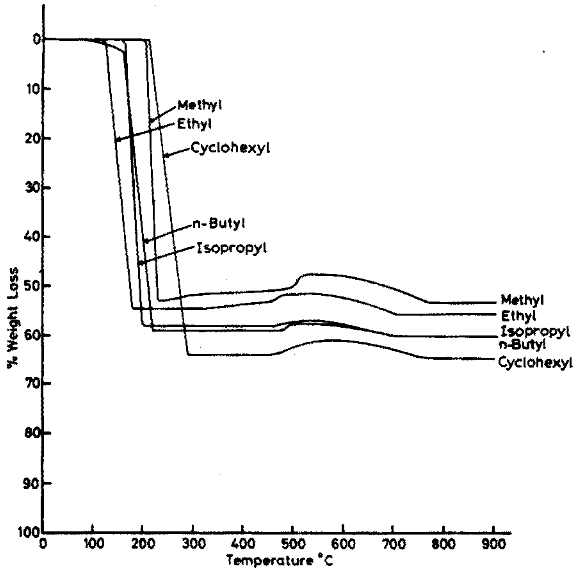


Fig. 3. Thermogravimetric curves for bismuth(III) xanthate complexes.

TABLE IV

THERMOGRAVIMETRIC CHARACTERISTICS OF BISMUTH ALKYLXANTHATES

	Methyl	*Ethyl*	*Isopropyl*	*n-Butyl*	*Cyclohexyl*
Stage I	200–230°	120–180°	160–200° [a]	160–220°	200–290°
Percent weight loss in Stage I	52.7	54.5	58.0	59.0	64.0
Stage II	230–770°	180–700°	200–700°	220–700°	290–760°

[a] The *n*-butyl complex begins to lose weight at 75°.

Calculations on the expected weight loss for Stage I indicate that the complexes are decomposed to the sulphide, Bi_2S_3. It is suggested that the increase in weight in Stage II is due to partial oxidation to the sulphate, which in turn is decomposed to a mixed oxide or a mixture of oxide and sulphides. The residue was light yellow in colour, water insoluble, and the i.r. spectrum showed no absorption by sulphate. It was not possible from calculations on the weight of the residue to assign a definite stoichiometry. Heating around 950° for several hours initiated further loss in weight, but in no case was a constant weight ever obtained.

Volatility studies

Under reduced pressure, the various complexes behaved in a manner similar to that observed in the thermogravimetric analyses. The arsenic complexes volatilized almost completely, whereas the antimony and bismuth complexes were generally involatile. Qualitative tests on the involatile residues indicated them to consist of metal sulphides.

Mass spectral analysis of the gaseous products

For this investigation, antimony(III) isopropylxanthate and bismuth(III) *n*-butylxanthate were selected. The samples were subjected to temperatures sufficient to cause decomposition and the gaseous products were analysed by the mass spectrometer.

TABLE V

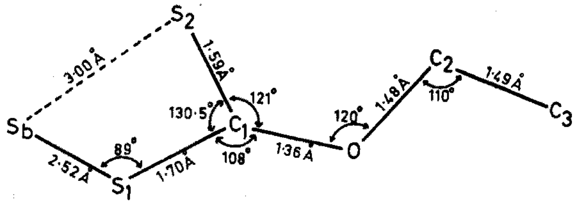
MAJOR PEAKS OF MASS SPECTRA OF TWO ALKYLXANTHATES

m/e	*Species indicated*
76	CS_2
64	S_2
60	COS
44	CS
32	S
28	CO

For both complexes, the major peaks observed in the mass spectra are shown in Table V. The most intense peaks were those appearing at $m/e = 76$ and $m/e = 60$. The identities of the ions were confirmed by isotopic ratios. Mass peaks for ions with *m/e* greater than 100 were small in intensity relative to the most intense peaks. The peak attributed to CS_2 in the antimony isopropylxanthate is approximately equal in intensity to that for COS, whereas the COS peak in the bismuth compound has the greater intensity.

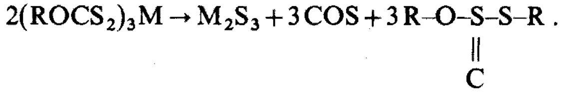
Mechanism of thermal decomposition

From the results, an attempt was made to draw up a mechanism for the thermal decomposition of the alkylxanthates of arsenic, antimony and bismuth. The crystal structures of arsenic(III) and antimony(III) ethylxanthates have been determined[14, 15] and both were found to be similar. Each metal atom is surrounded by six sulphur atoms, which together form a somewhat distorted octahedron. Three of the non-bonded sulphurs are at a greater distance (3.00 Å) from the central metal than the bonded sulphur atoms (2.52 Å). The C–S (C_1–S_1) single bond in both complexes is longer than the C=S (C_1–S_2) double bond.



As discussed above, the thermogravimetric curves for antimony and bismuth alkylxanthates suggest that the thermal decomposition of these complexes leads initially to formation of metal sulphide (M_2S_3) as one of the products. Although the curves of the arsenic complexes are complicated by the volatility of these complexes and their decomposition products (if any are formed), there is no reason to doubt that any decomposition taking place will not lead to the formation of As_2S_3, which is also volatile.

However, the mass spectral data indicate that the gaseous products from the thermal decomposition consist largely of carbonyl sulphide and carbon disulphide. To explain the formation of these gaseous products, it is proposed that the first step in the thermal decomposition involves the rupture of the C–S single bonds (1.70 Å) producing the metal sulphide (M_2S_3) and a mixture of gases:



$$2(ROCS_2)_3M \rightarrow M_2S_3 + 3COS + 3R\text{–}O\text{–}\underset{\overset{\|}{C}}{S}\text{–}S\text{–}R\,.$$

It is possible for the product ROCSSR to decompose further in a number of ways to produce COS, CS_2, olefins, etc. In the mass spectrum of the antimony complexes, the mass peaks for COS and CS_2 were approximately equal in intensity. On this evidence, it is also possible to envisage the decomposition of the metal xanthate without formation of the moiety ROCSSR.

$$2(ROCS_2)_3M \rightarrow M_2S_3 + 3COS + 3CS_2 + 3H_2O + 6\underset{\text{olefin}}{(R\text{–}H)}$$

Besides the intense peaks for COS and CS_2 which are found in the mass spectra, there is evidence of small amounts of unsaturated hydrocarbons and water but no indication of the presence of ROCSSR.

We wish to express our thanks to Mr. J. F. Smith (La Trobe University) for his assistance with the mass spectral work.

SUMMARY

Six xanthate derivatives of arsenic(III), antimony(III), and bismuth(III) $\{(ROCS_2)_3M$; R = methyl, ethyl, isopropyl, *n*-butyl, cyclohexyl and benzyl$\}$ have been prepared and the thermal behaviour investigated by thermogravimetry. A thermal decomposition mechanism for the complexes is proposed on the basis of the thermogravimetric data and mass spectral measurements.

RÉSUMÉ

Six dérivés de xanthates d'arsenic(III), d'antimoine(III) et de bismuth(III) $[ROCS_2]_3M$ (R = méthyl-, éthyl-, isopropyl-, *n*-butyl-, cyclohexyl- et benzyl-) ont été préparés. Leur comportement thermique a été examiné par thermogravimétrie. Un mécanisme de décomposition thermique est proposé pour ces complexes, basé sur les résultats thermogravimétriques et les mesures spectrales de masse.

ZUSAMMENFASSUNG

Sechs Xanthogenatderivate von Arsen(III), Antimon(III) und Wismut(III), $[ROCS_2]_3M$ (R = Methyl-, Äthyl-, Isopropyl-, *n*-Butyl, Cyclohexyl- und Benzyl-), wurden dargestellt; deren thermisches Verhalten wurde durch Thermogravimetrie untersucht. Ein Mechanismus für die thermische Zersetzung der Komplexe wird auf der Basis der thermogravimetrischen Ergebnisse und von massenspektrometrischen Messungen vorgeschlagen.

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ÉTUDE DES FACTEURS INFLUENÇANT LA FIXATION DE GALLIUM(III) SUR RÉSINE DOWEX 50-X8 EN MILIEU HCl–EAU–DIOXANNE

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Après une étude systématique du comportement des éléments de la première série de transition sur Dowex 50-X8 en milieu HCl–eau–dioxanne[1], nous avons examiné plus en détail le comportement du gallium. La variation du coefficient de distribution (K_D) en fonction de la concentration en dioxanne est en effet particulièrement importante, dans le cas du gallium, en milieu HCl 0.6 *M* (Fig. 1).

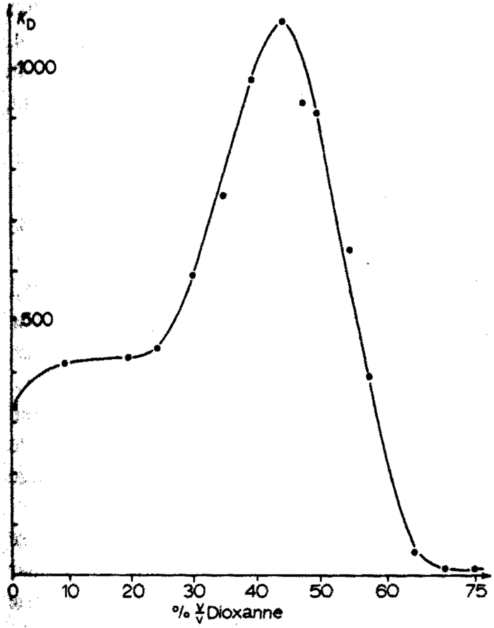

Fig. 1. Variation du coefficient de distribution K_D en fonction de la concentration en dioxanne (HCl 0.6 *M*).

Nous avons étudié également l'influence du milieu: complexant (HCl) et non complexant (H_2SO_4), et déterminé expérimentalement la composition et la quantité du solvant absorbé par la résine Dowex 50-X8 sous forme H^+ et sous forme gallium(III), la résine étant en équilibre avec des mélanges eau–dioxanne (0–70%)–HCl 0.6 *M*. Nos résultats montrent que l'influence du dioxanne s'exerce par de nombreux paramètres, le facteur le plus important étant sa faible constante diélectrique ($\varepsilon = 2$).

Des études analogues ont été menées pour de nombreux milieux hydro-organiques: eau + alcools[2–10], + acétone[3,6,7,10], + dioxanne[2,6,10–14], + pyridine[3,7], + acide acétique[3], + DMSO[15], + HMPT[16], + éthanolamine[17,18], + acétonitrile[19], + éthylènediamine[20].

TECHNIQUE EXPÉRIMENTALE

L'utilisation du radioisotope $^{72}Ga^*$, obtenu par la réaction $^{71}Ga(n, \gamma)\ ^{72}Ga^*$, permet de suivre la fixation de cet élément. La mesure des radioactivités est réalisée par spectrométrie γ à l'aide d'un scintillateur NaI(Tl).

La résine cationique Dowex 50-X8 (200–400 mesh) est sélectionnée par tamisage[21]. Elle est prétraitée par HCl 6 *M*, puis lavée à l'eau, jusqu'à neutralité des eaux de rinçage, et séchée à l'air.

Détermination des coefficients de distribution

1 g de résine est agité avec 20 ml de solution 10^{-4} *M* de l'élément étudié, préalablement marqué (en volume: 0 à 75% de dioxanne*, 10% d'acide; on complète à 100% par l'eau). Le mélange est agité pendant 6 h dans des flacons de polyéthylène fermés hermétiquement, à température ambiante (23° ± 2°). Après centrifugation, la liqueur surnageante est prélevée et la radioactivité restante A_x est comparée à la radioactivité initiale A_0 en tenant compte de la décroissance du radioisotope. La radioactivité étant proportionnelle à la masse totale de l'élément, le coefficient de distribution limite est calculé suivant la relation:

$$K_D = (A_o - A_x)_R / (A_x)_S$$

Les indices R et S désignent les radioactivités ramenées respectivement à 1 g de résine et à 1 ml de solution.

On détermine le gonflement de la résine en la traitant par le solvant, HCl 0.6 *M* + dioxanne. La quantité de solvant absorbé par la résine est déterminée par centrifugation, suivant la méthode de Pepper *et al.*[22]. Après centrifugation et pesée, le solvant est désorbé de la résine par lavage avec 25 ml d'eau tiède (60°).

Le dosage du dioxanne absorbé se fait dans l'éluat, par réfractométrie (appareil Hilger et Watts). La précision de ce dosage est d'environ 10%. Le dosage de l'acide chlorhydrique absorbé par effet Donnan[23], se fait également dans l'éluat (dosage acide–base).

Dans le cas de la Dowex 50-X8 sous forme Ga(III), le dosage de Cl^- se fait dans l'éluat. On utilise une quantité connue de nitrate d'argent, tracé par $^{110m}Ag^*$, pour précipiter Cl^-. L'argent en excès (Ag_x) est dosé par spectrométrie γ. La quantité de Cl^- est calculée par différence $Ag_0 - Ag_x$ (Ag_0 = quantité initiale).

RÉSULTATS ET DISCUSSION

Pour déterminer l'influence de la constante diélectrique, nous avons examiné

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* La concentration maximale de 75% en dioxanne est imposée par sa limite de solubilité dans l'acide chlorhydrique 0.6 *M*.

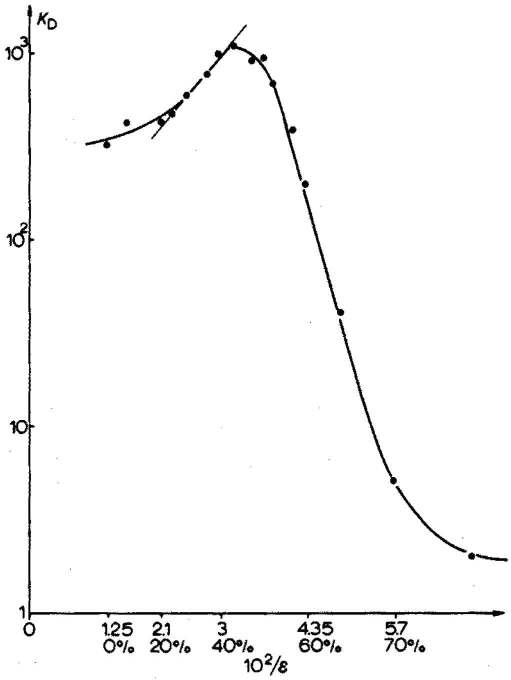


Fig. 2. Variation de log K_D en fonction de l'inverse de la constante diélectrique du milieu (HCl 0.6 *M*).

la variation du logarithme du coefficient de distribution de Ga(III) en fonction de l'inverse de la constante diélectrique du milieu[24–26] (*cf.* Fig. 2).

La partie linéaire (entre 20% et 45% de dioxanne) indique que l'attraction électrostatique entre Ga(III) et les groupements sulfoniques de la résine est le phénomène dominant. Pour les concentrations en dioxanne supérieures à 45%, la stabilisation des complexes chlorés, due également à la décroissance de la constante diélectrique, donne le sens de variation de K_D[27,28]. Pour les faibles concentrations en dioxanne (0–20%), les valeurs relativement fortes de K_D sont certainement dues à un phénomène de solvatation[16] (*cf.* Fig. 11a).

A concentration constante en dioxanne, l'examen des valeurs de K_D en milieu H_2SO_4–dioxanne, permet de mettre en évidence l'influence de la concentration en H^+; celle-ci influe alors sur deux sortes d'équilibre: on a d'une part (à faible concentration en H^+):

$$Ga^{3+} + H_2O \rightleftarrows Ga(OH)^{2+} + H^+ \qquad (1)$$

et

$$Ga(OH)^{2+} + H_2O \rightleftarrows Ga(OH)_2^+ + H^+\,, \qquad (2)$$

d'autre part:

$$Ga^{3+}_{sol} + 3\,H^+_{rés} \rightleftarrows Ga^{3+}_{rés} + 3\,H^+_{sol} \qquad (3)$$

$$Ga(OH)^{2+}_{sol} + 2\,H^+_{rés} \rightleftarrows Ga(OH)^{2+}_{rés} + 2\,H^+_{sol} \qquad (4)$$

$$Ga(OH)^+_{2\,sol} + H^+_{rés} \rightleftarrows Ga(OH)^+_{2\,rés} + H^+_{sol} \qquad (5)$$

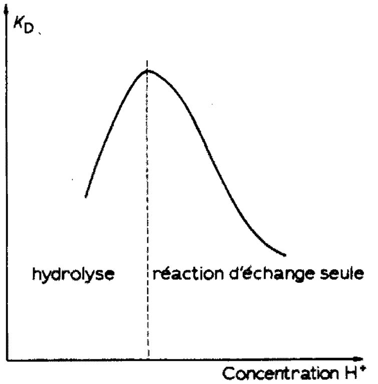
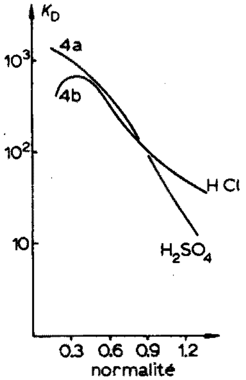
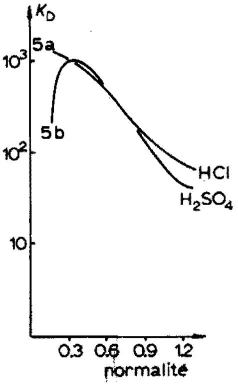


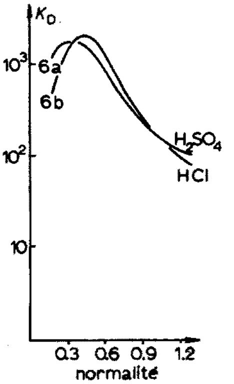
Fig. 3. Variation type du coefficient de distribution en fonction de la concentration en H^+.

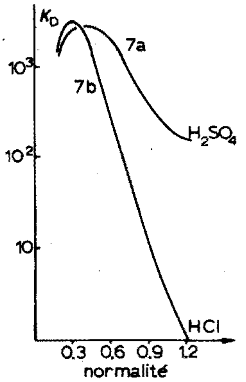
Nous pouvons donc prévoir la variation type du coefficient de distribution en fonction de la concentration en H^+ (*cf.* Fig. 3).

Quant au dioxanne[29] il favorise la stabilisation des liaisons électrostatiques









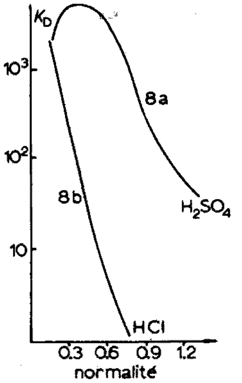
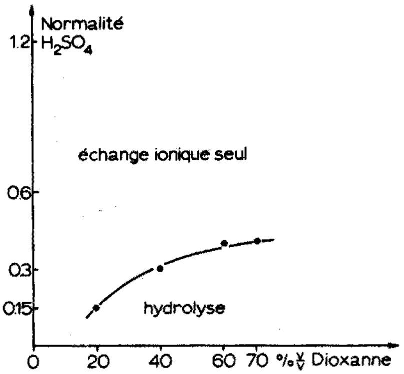


Fig. 4. Variation du coefficient de distribution en fonction de la normalité en acide. 0% dioxanne.
Fig. 5. Variation du coefficient de distribution en fonction de la normalité en acide. 20% dioxanne.
Fig. 6. Variation du coefficient de distribution en fonction de la normalité en acide. 40% dioxanne.
Fig. 7. Variation du coefficient de distribution en fonction de la normalité en acide. 60% dioxanne.
Fig. 8. Variation du coefficient de distribution en fonction de la normalité en acide. 70% dioxanne.



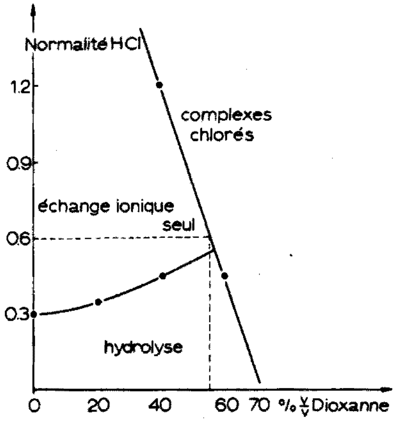
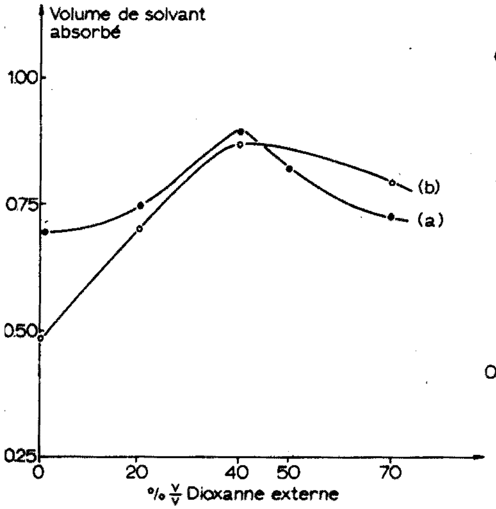


Fig. 9. Domaine où l'hydrolyse de Ga(III) influe sur l'échange ionique en milieu H_2SO_4–eau–dioxanne.

Fig. 10. Domaines où les différentes réactions de Ga(III) influent sur l'échange ionique en milieu HCl–eau–dioxanne.

Ga^{3+}–OH^-, grâce à sa faible constante diélectrique; il peut aussi favoriser les réactions (1) et (2) grâce à son caractère protophile.

Les Figures 4a, 5a, 6a, 7a, et 8a permettent de situer les domaines où les réactions d'hydrolyse influent sur la variation du coefficient de distribution, en milieu H_2SO_4–eau–dioxanne (*cf.* Fig. 9).



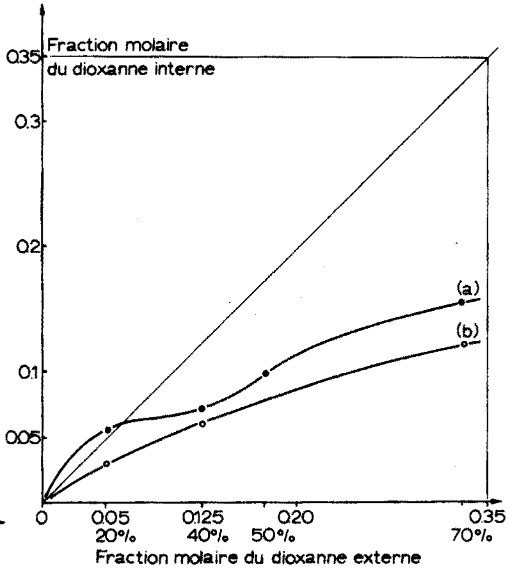


Fig. 11. Variation du volume de solvant absorbé (ml/g résine sèche) en fonction de la concentration en dioxanne externe. (a) Dowex 50-X8, forme H^+; (b) Dowex 50-X8, forme Ga(III).

Fig. 12. Partage du dioxanne entre la résine (interne) et la solution (externe) en milieu dioxanne–HCl 0,6 *M*. (a) Dowex 50-X8, forme H^+; (b) Dowex 50-X8, forme Ga(III).

Enfin, l'acide chlorhydrique étant moins dissocié que l'acide sulfurique[30] l'échange ionique en milieu HCl (pour les fortes normalités en acide) sera supérieur. C'est ce que l'on observe avec les Figures 4b et 5b. En milieu 40% de dioxanne, le coefficient de distribution pour les fortes normalités en HCl (Fig. 6b) devient inférieur à la valeur en milieu H_2SO_4 (Fig. 6a); ceci est dû à la formation de complexes chlorés (*cf.* Fig. 10). En milieu HCl 0.6 *M* la stabilisation des complexes chlorés influence la variation de K_D pour des concentrations en dioxanne supérieures ou égales à 50%.

La quantité de solvant absorbé par la résine présente un maximum en fonction de la concentration en dioxanne de la solution pour les deux formes, H^+ (Fig. 11a) et Ga(III) (Fig. 11b). Ce résultat est principalement lié à l'affinité du dioxanne pour les groupements fonctionnels et à la solvatation à l'intérieur des grains de résine.

Pour la forme Ga(III) le volume de solvant diminue moins vite que pour la forme H^+, dans les fortes concentrations en dioxanne; ceci prouve que Ga(III) est plus solvaté par le dioxanne que H^+. Ce résultat concorde avec ceux de Grunwald *et al.*[31].

Le solvant interne est beaucoup moins riche en dioxanne que le solvant externe, pour les deux formes H^+ et Ga(III) (*cf.* Fig. 12 a et b). Cependant la résine sous forme H^+ marque une préférence pour le dioxanne dans les faibles concentrations en dioxanne externe (0–20%); ceci peut être expliqué par le caractère protophile du dioxanne, vis à vis des groupements acides sulfoniques de la résine.

Nous avons pu déterminer le nombre de moles de dioxanne solvatant une mole de gallium, à l'intérieur de la résine:

% v/v dioxanne dans la solution extérieure (HCl 0.6 *M*)	0	20	40	70
Nombre moles dioxanne pour 1 mole gallium	0	0 ($\simeq$0.2)	1 ($\simeq$1.3)	2 ($\simeq$2.2)

Pour les fortes concentrations en dioxanne, le gallium est lié à deux molécules de dioxanne, ce qui confirme expérimentalement les calculs de Grunwald. Cette solvatation de Ga(III) contribue également à expliquer les faibles coefficients de distribution trouvés dans cette zone de concentration en dioxanne (*cf.* Fig. 1).

Dans le cas de la résine sous forme H^+ (*cf.* fig. 13), la concentration en HCl dans la solution interne de la résine reste constante pour des concentrations en dioxanne dans la solution extérieure comprise entre 0 et 40%. La concentration en HCl augmente rapidement pour des concentrations en dioxanne supérieures à 40%. Les complexes chlorés supérieurs du gallium pourront donc exister à l'intérieur de la résine, dans les zones de forte concentration en dioxanne dans la solution extérieure.

Dans le cas de la résine sous forme Ga(III) l'étude de la quantité de Cl^- désorbé lors du lavage de la résine a permis de déterminer les complexes chlorés existant à l'intérieur de la résine:

% v/v dioxanne dans la solution extérieure (HCl 0.6 *M*)	0	20	40	70
Forme de Ga(III) existant dans la résine	$GaCl^{2+}$	$GaCl^{2+}$	$GaCl_3$	$GaCl_3$

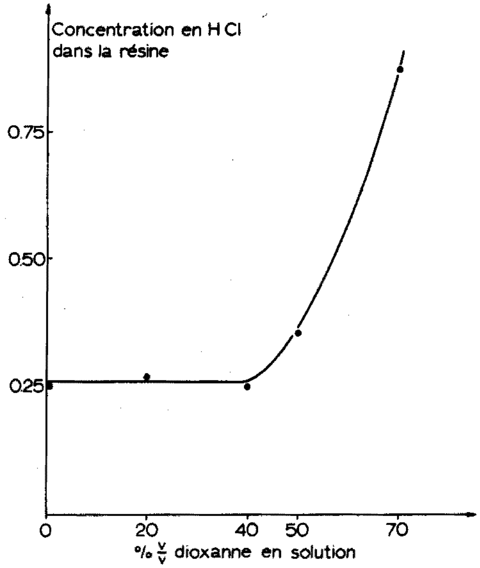


Fig. 13. Concentration en HCl dans la résine (mole/l) en milieu dioxanne (0–70%)–HCl 0.6 *M*. Dowex 50-X8, forme H^+.

La forme du gallium, $GaCl_3$, trouvée pour une solution extérieure contenant HCl 0.6 *M*–40% de dioxanne ne pourra pas exister à l'intérieur de la résine sous forme H^+, la concentration en HCl à l'intérieur de cette résine étant trop faible (*cf.* Fig 13). La forte valeur de K_D trouvée dans ce milieu (*cf.* Fig. 1) confirme cette remarque. Pour les fortes concentrations en dioxanne, il semble qu'il n'y ait plus qu'absorption du complexe neutre $GaCl_3$, due sans doute à la concentration en eau dans la résine[9]; ceci expliquerait que la valeur de K_D soit très faible (*cf.* Fig. 1).

CONCLUSIONS

Différentes influences du dioxanne sur la fixation du gallium en milieu HCl 0.6 *M* ont été mises en évidence.

(*a*) L'influence de sa constante diélectrique intervient sur la stabilisation des liaisons Ga^{3+}–groupements sulfonates de la résine ainsi que sur celle des liaisons Ga^{3+}–Cl^-; l'existence des complexes chlorés du gallium intervient sur la variation du coefficient de distribution pour des concentrations en dioxanne supérieures ou égales à 50%.

(*b*) Il solvate le gallium dans les fortes concentrations en dioxanne ($\simeq 70\%$).

(*c*) L'influence de son caractère protophile favorise la fixation de Ga(III) dans les faibles concentrations en dioxanne (0–20%).

Le facteur le plus important est la faible constante diélectrique du dioxanne; celle-ci permet de faire varier le coefficient de distribution dans des proportions très importantes (*cf.* Fig. 1), ce qui peut entraîner des séparations intéressantes d'éléments. Cependant, elle masque en partie les phénomènes de solvatation spécifique qui apparaissent dans les mélanges de solvants[15].

Nous remercions M. C. Poitrenaud d'avoir mis à notre disposition les appareils de son laboratoire et de nous avoir fourni une importante bibliographie.

RÉSUMÉ

La fixation de Ga(III) sur résine Dowex 50-X8, en milieu HCl 0.6 *M*–dioxanne a été étudiée en fonction de la concentration en dioxanne. L'étude comparée des coefficients de distribution dans le milieu complexant (HCl) et dans un milieu non complexant (H_2SO_4) a permis de situer les domaines des différentes réactions qui influent sur l'échange ionique. Nous avons déterminé expérimentalement la quantité et la composition du solvant absorbé par la résine Dowex 50-X8, sous forme H^+ et Ga(III), en équilibre avec les mélanges HCl 0.6 *M*–dioxanne (0–70%). Le facteur le plus influent est la faible constante diélectrique du dioxanne; des phénomènes de solvatations spécifiques ont cependant pu être mis en évidence.

SUMMARY

The retention of gallium(III) on Dowex 50-X8 resin in 0.6 *M* HCl–dioxan media was studied as a function of the dioxan content. The ion-exchange in complexing medium (HCl) and in non-complexing medium (H_2SO_4) was studied; the determination of the distribution coefficients indicated the reactions occurring in the different media. Solvent uptake by Dowex 50-X8 (H^+ and Ga(III) forms) from 0.6 *M* HCl–dioxan mixtures and the solvent composition in the resin were determined. The influence of the weak dielectric constant of dioxan proved to be most important; however, specific solvation phenomena were evident.

ZUSAMMENFASSUNG

Die Aufnahme von Gallium(III) durch Dowex 50-X8 in 0.6 *M* HCl–Dioxan-Medium wurde als Funktion des Dioxangehaltes untersucht. Der Ionenaustausch in komplexierendem Medium (HCl) und in nicht-komplexierendem Medium (H_2SO_4) wurde geprüft; die Bestimmung der Verteilungskoeffizienten wies auf die Reaktionen in den verschiedenen Medien hin. Die Lösungsmittelaufnahme durch Dowex 50-X8 (in der H^+- und Ga(III)-Form) aus 0.6 *M* HCl–Dioxan-Mischungen und die Lösungsmittelzusammensetzung im Harz wurden bestimmt. Von grösstem Einfluss ist die kleine Dielektrizitätskonstante von Dioxan; jedoch waren auch spezifische Lösungsmitteleffekte vorhanden.

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ION EXCHANGE IN AQUEOUS AND IN AQUEOUS–ORGANIC SOLVENTS

PART I. ANION-EXCHANGE BEHAVIOUR OF Zr, Nb, Ta AND Pa IN AQUEOUS HCl–HF AND IN HCl–HF–ORGANIC SOLVENT

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The satisfactory separation of protactinium from its homologues, *i.e.* niobium and tantalum, and also from zirconium, is often complicated by the fact that these elements easily undergo hydrolysis and polymerization, so that the handling of these elements in solution demands special conditions in which their stable complexes can be formed. The effect of the state of the element in solution on the analytical properties, and especially on the reaction with organic reagents like ion exchangers, is of considerable interest for their separation chemistry. Since the preparation and storage of solutions of these elements influence their chemical state and behaviour, special conditions are required for the preparation of stable solutions. Since fluoride ions show the greatest tendency to form complexes with Zr, Nb, Ta and Pa, and thus to break up their polymeric forms, stable conditions are found in hydrofluoric acid-containing solutions; monomolecular and stable fluoride complexes are formed and reproducible chemical reactions can then take place.

The fluoride complexes of the elements in pure hydrofluoric acid media do not show great differences in their chemical behaviour, *e.g.* the differences of their affinities for anion exchangers appear to be only slight, except in very high concentrations of hydrofluoric acid[1,2]. The application of mixed solutions with hydrochloric acid or with nitric acid improves the differentiation of the chemical behaviour of these elements in solution. Some results were reported in early work on the ion exchange of these elements in mixed solutions under a few different conditions[3–6].

The work described here includes a study of the anion-exchange equilibria of the above-mentioned elements in mixed solutions of hydrochloric acid and hydrofluoric acid of every possible combination, spanning hydrochloric acid and hydrofluoric acid concentrations from 0.01 to 12 *M* and from 0.01 to 22 *M*, respectively. On the basis of the equilibrium results, the possibilities of single or simultaneous separations of the elements have been expanded considerably. By gradually replacing the aqueous phase with various organic solvents, the equilibrium study was also directed to investigate the influence of water-miscible organic solvents on the affinities of the elements for the anion exchanger.

In the course of previous work on the ion-exchange behaviour and the separation of protactinium and its homologues in mixtures of nitric acid and acetic acid[7], it was found that, in such mixtures, originally small differences in stability and charge of the complexes are markedly enhanced, so that new separations with high separation factors become possible. The same characteristics were found in the system of HCl–HF mixed with other water-miscible organic solvents.

EXPERIMENTAL

All equilibrium experiments were done by radiochemical techniques with tracers together with the corresponding carriers. ^{233}Pa was produced by neutron irradiation of thorium nitrate. The irradiated thorium was first dissolved in 14 *M* nitric acid, and then precipitated by addition of sufficient hydrofluoric acid as $ThF_4 \cdot n\, H_2O$, which was separated by filtration. The filtrate containing ^{233}Pa was converted to a hydrochloric acid–hydrofluoric acid solution by repeated evaporation with these acids. The preliminary experiments for protactinium were carried out with an addition of ^{231}Pa at a concentration of 10^{-4} *M*, and with only ^{233}Pa tracer, in order to compare the chemical behaviours of two different concentrations. Both sets of experiments, however, gave rise to identical results, so that ^{231}Pa was not added in further experiments.

Both ^{95}Zr and ^{95}Nb, and ^{182}Ta were obtained from neutron-irradiated zirconium and tantalum metal, respectively. After a sufficient decay time, ^{95}Nb was separated from ^{95}Zr by the method described in this paper and mixed with its carrier. The concentrations of elements taken for each experiment were about 10^{-4} *M*.

For adsorption experiments, the resin used was the strongly basic anion exchanger Dowex 1-X8 (analytical-grade, 100–200 mesh, Cl^- form). The resin was air-dried in an oven at 70° and stored in a vacuum desiccator.

The distribution coefficients (K_D) were determined by the batch method. For these experiments about 300 mg of resin were exactly weighed and filled into a polyethylene vial. After addition of the acid mixture (10 ml), the tracer was added and the vial was shaken overnight at room temperature in order to reach equilibrium. The estimation of adsorption of the different elements was made by γ-ray measurement; for zirconium and niobium, γ-spectrometry with a Ge(Li) detector was used when both elements were studied simultaneously. All acids were reagent grade. The concentration of acetic acid was more than 99%.

The distribution coefficients were defined by the following equation:

K_D = mg element per g resin/mg element per ml solution.

ANION-EXCHANGE BEHAVIOUR IN HCl–HF MEDIA

For these studies, the scattered data in the literature on the K_D values of these elements in hydrochloric acid–hydrofluoric acid media[2–5,8,9] were examined and completed for all possible combinations. In the graphical representations (Figs. 1–4), where the distribution coefficients are drawn as contour lines over all the different mixtures of hydrochloric and hydrofluoric acid, it can be seen that each element changes its adsorption according to the hydrochloric or hydrofluoric acid concentration. As the ionic structures of Zr, Nb, Ta and Pa in such systems are already known to a certain extent, it is useful to consider, on the basis of these results, the ionic species of each element with respect to its adsorption.

The chemical behaviour of Zr(IV), Nb(V), Ta(V) and Pa(V) in acidic solutions is rather similar, so that it is essential for separations of these elements to establish small differences in the chemical properties, and to utilize the best experimental conditions. It is vital to handle the elements in their monomeric forms in solution, in order to secure reversible equilibrium between the resin and solution phase, for the formation of the hydrolyzed polymeric compounds leads to mutual masking effects[10] so that separation is incomplete.

The elements Zr, Nb, Ta and Pa show a tendency to hydrolyze even in aqueous solutions of high acidity. It is still questionable to what extent water molecules are coordinated to a metal ion to release the most stable coordination number. In general, the charge of such a compound changes from positive to neutral and to negative with increasing acidity and anion concentration, although this tendency is somewhat different from element to element.

The degree of hydrolysis and the stability of the hydrolyzed compounds under given conditions are different, so that different anion-exchange behaviour results. For the comparison of that behaviour in HCl–HF media, which is presented for Zr, Nb, Ta and Pa in Figs. 1–4, some information about the elemental species already known in these pure or mixed acids should be discussed.

Zirconium

In order to convert zirconium to the reactive zirconium(IV) state and to break up its polymeric forms, an acidity of 1–2 *M* is necessary[11]. As zirconium(IV) can be classified as typical complex former, complex formation with halogens is a sure way of converting zirconium to a reactive and stable state. The most typical is the halogen complex, $(ZrX_6)^{2-}$, the stability of which decreases with increase in the atomic weight of the halogen X. The following complexes are known for zirconium[12]: ZrX_5^-, $ZrX_5(H_2O)^-$, ZrX_6^{2-} and ZrX_7^{3-}. By the methods of ion exchange and electrophoresis, it has been shown that zirconium(IV) exists in pure hydrochloric acid solutions in the following forms[13]: cations in 0.1–2 *M* HCl, neutral complexes in 6 *M* HCl, and increasing amounts of anions in 3–12 *M* HCl. The average number of fluoride ions per zirconium atom in fluoride complexes is 1 in $2 \cdot 10^{-5}$ *M* hydrofluoric acid, 2 in $3 \cdot 10^{-4}$ *M*, and 3 in 10^{-2} *M*[14]. In excess of hydrofluoric acid, the predominant state is hexafluorozirconic acid, H_2ZrF_6, but with increasing hydrofluoric acid concentrations, ZrF_7^{3-} and ZrF_9^{5-} ions are also formed.

As can be seen in Fig. 1, the adsorption behaviour of zirconium on Dowex 1-X8 in $\geqslant 2$ *M* hydrofluoric acid is not influenced by hydrochloric acid additions up to 0.1 *M*. The slope of -3 for the adsorption curve in increasing hydrofluoric acid concentrations indicates the formation of ZrF_7^{3-} complex with the charge of -3 or the formation of mixed fluoro complexes with an average charge of -3[2,9]. In pure strong hydrochloric acid (>8 *M*), the adsorption increases rapidly up to 12 *M* hydrochloric acid[15], but here addition of hydrofluoric acid causes a marked decrease of the distribution coefficients. It appears reasonable to assume that the increased complexing by fluoride ions is parallelled by an increase in negative charge which causes a decrease of the adsorbability in this case[3]. The general

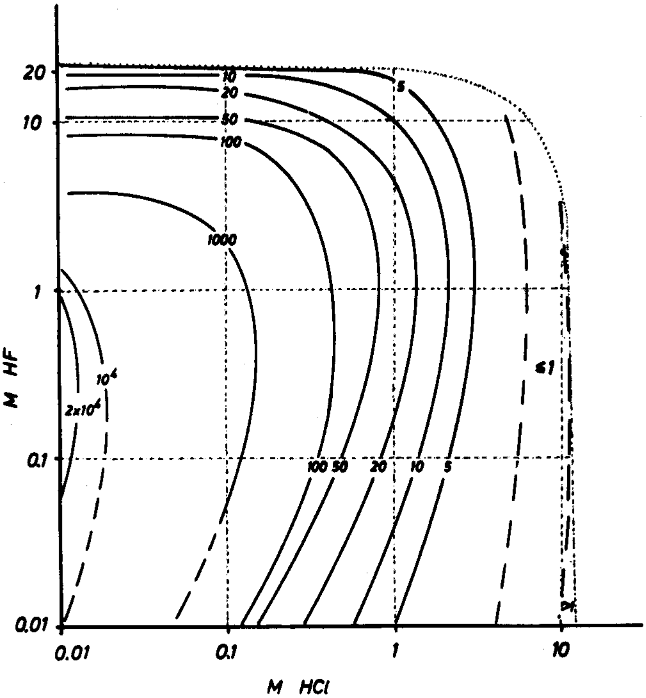


Fig. 1. Distribution coefficients of Zr(IV) as functions of the hydrochloric and hydrofluoric acid concentration.

formula for mixed chlorofluoro complexes in this mixed acid range should be $(ZrCl_xF_y)^{x+y-4}$.

Niobium

In pure hydrochloric acid media, polymeric compounds exist up to 10.7 *M* HCl in equilibrium with different monomeric species. The ionic species change from polymeric cationic complexes at low hydrochloric acid concentrations to neutral forms such as $NbOCl_3$ or $Nb(OH)_2Cl_3$ in 4–6 *M* hydrochloric acid, and to monomeric anionic species at high hydrochloric acid concentrations[16]. There exist different ionic species in solution simultaneously, such as $NbOCl_4^-$, $Nb(OH)_2Cl_4^-$ and $NbOCl_5^{2-}$. In hydrofluoric acid solutions, the anionic complex $NbOF_5^{2-}$ is stable up to high hydrofluoric acid concentrations and is the only species in 11 *M* hydrofluoric acid[17]. At higher hydrofluoric acid concentration, the NbF_6^- species begins to form[18] and to a certain extent NbF_7^{2-} also appears[16]. In view of hydrolytic difficulties, the distribution coefficients of niobium obtained for pure hydrochloric acid solutions cannot be considered sufficiently firmly established. Therefore it is indispensable to add hydrofluoric acid or another adequate complexing agent to maintain reproducible solution chemistry for niobium, and the same is true for tantalum and protactinium. In HCl–HF mixtures, polymeric ions of niobium added to the solution slowly change to monomeric forms. Six moles of hydrofluoric acid per mole of niobium suffice completely to avoid polymerization in 0.1–1

M hydrochloric acid[19]. In a mixture of 0.5 *M* hydrochloric acid and 0.25–0.5 *M* hydrofluoric acid only $NbOF_5^{2-}$ ions exist[20], which proves the preference of niobium for fluoride rather than chloride ions. At higher hydrochloric acid concentrations in such mixtures, mixed chlorofluoro complexes of the general formula $(Nb(OH)_2Cl_xF_y)^{x+y-3}$, $(NbOCl_xF_y)^{x+y-3}$ or $(NbCl_xF_y)^{x+y-5}$ appear, depending upon the hydrofluoric acid concentration. As shown by Kraus and Moore[3], in mixtures of 9 *M* hydrochloric acid with hydrofluoric acid there are probably three different species: at very low hydrofluoric acid concentrations $NbOCl_4^-$ or $Nb(OH)_2Cl_4^-$; at intermediate hydrofluoric acid concentrations $(Nb(OH)_2Cl_xF_{5-x})^{2-}$ or $(NbOCl_xF_{5-x})^{2-}$; and at high hydrofluoric acid concentrations $(NbCl_xF_{6-x})^-$ without hydroxo or oxo groups. This assumption is based on calculations from the slope of the adsorption curves in 9 *M* hydrochloric acid and increasing hydrofluoric acid concentration.

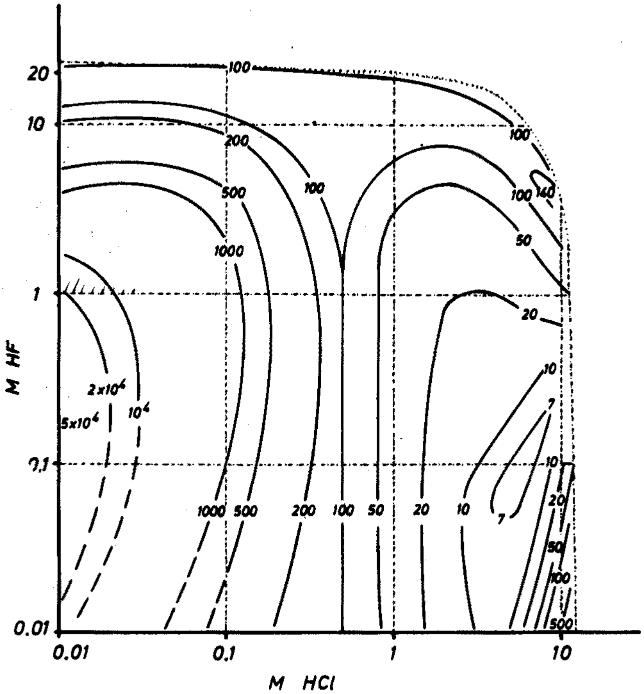


Fig. 2. Distribution coefficients of Nb(V) as functions of the hydrochloric and hydrofluoric acid concentration.

Figure 2 shows that the adsorbability of niobium in very low hydrochloric acid concentrations decreases regularly with increasing hydrofluoric acid molarity up to approximately 11 *M* with a slope of -2 and then remains nearly constant. This proves that only $NbOF_5^{2-}$ ions exist up to 11 *M* hydrofluoric acid, as already mentioned[17]. Above this concentration, niobium seems to form the pure fluoro complexes NbF_6^- and NbF_7^{2-} without oxygen; the adsorbability $K_D \simeq 100$. Low hydrochloric acid concentrations in the hydrofluoric acid solution do not cause a replacement of fluoride by chloride ions[20]. Above 0.5 *M* hydrochloric acid, mixed chlorofluoro complexes appear, *e.g.*[21], $NbOCl_3F_2^{2-}$. The existence of this complex needs to be assumed in the low adsorption area in Fig. 2. The slope of the adsorption curve in 9 *M* hydrochloric acid between 0.01 and 0.1 *M* hydrofluoric acid is exactly -1.5, indicating the partial formation of a species with charge -2. In agreement with the results mentioned above[3], the slope $+1.5$ for increasing hydrofluoric acid concentrations between 0.3 and 2 *M* HF would explain the formation of probably $NbCl_3F_3^-$ without oxygen. As the adsorption curve decreases again above 3.5 *M* hydrofluoric acid, the existence of a fourth species may be assumed, probably $NbCl_3F_4^{2-}$.

A comparison of Figs. 1 and 2 makes it clear that separation of zirconium from niobium is possible under a variety of conditions in HCl–HF media. The best way to separate these two elements is to adsorb niobium from 9 *M* HCl+0.01 *M* HF on a short Dowex 1-X8 column ($K_{D(Nb)} \simeq 400$; $K_{D(Zr)} \simeq 1$) and to elute the zirconium with the same acid mixture. This method was used for the separation of tracer ^{95}Zr and ^{95}Nb. The elution of niobium was carried out with 4 *M* HCl+0.1 *M* HF ($K_{D(Nb)} \simeq 7$).

Tantalum

In pure hydrochloric acid only polymeric compounds of tantalum(V) exist up to 11.4 *M* hydrochloric acid (for $2.5 \cdot 10^{-3}$ *M* Ta)[22]. Above this concentration, $TaCl_6^-$ ions appear[23]. With increasing concentrations of hydrochloric acid, polymeric cations change to neutral particles and to polymeric anions[24] of the general form[21] $(TaO_{>1}Cl_{<3} \cdot nCl^-)_x$ or of the hydroxochloroaquo form[10]. These polymeric ions cause irreversible adsorption equilibria[25].

The polymeric forms of tantalum are broken up even at low hydrofluoric acid concentrations. Depending on the hydrofluoric acid and tantalum concentrations in solution, the species $TaOF_5^{2-}$, TaF_7^{2-} and TaF_6^- exist, partly simultaneously. Moreover, the complexes $TaOF_6^{3-}$ and $TaOF_5^{2-}$ are found in low hydrofluoric acid concentrations, just as TaF_8^{3-} appears in high hydrofluoric acid concentrations[25]. The most obvious difference between niobium and tantalum in these acid media is the fact that tantalum shows a strong tendency to form pure halogen complexes, so that the oxygen-containing species of tantalum are relatively unstable[21]. Since niobium shows the reverse behaviour, the best conditions for separating niobium from tantalum can be found in HCl–HF solutions, where niobium forms oxo or hydroxo complexes such as $(NbOCl_xF_y)^{x+y-3}$ or $(Nb(OH)_2Cl_xF_y)^{x+y-3}$, and tantalum forms pure halogen complexes such as $(TaCl_xF_y)^{x+y-5}$, so that different adsorption behaviour results.

As can be seen in Figs. 2 and 3, niobium and tantalum show totally different adsorption behaviours in HCl–HF mixtures. Niobium has a very low adsorbability in the region 3–9 *M* hydrochloric acid and 0.05–0.2 *M* hydrofluoric acid, whereas the tantalum adsorbability is very high in this area and increases with decreasing hydrochloric acid molarity in the total solution. Both Figures make it clear that the separation of niobium and tantalum is possible under a variety of conditions, reaching the maximum separation factor of *ca.* 100 in 4 *M* HCl containing 0.1–0.2 *M* HF. The elution of niobium is very easy but quantitative desorption of tantalum with the HCl–HF solution appears to be difficult. It is possible to diminish the adsorbability of tantalum by addition of ammonium chloride[2,5] or of isopropanol,

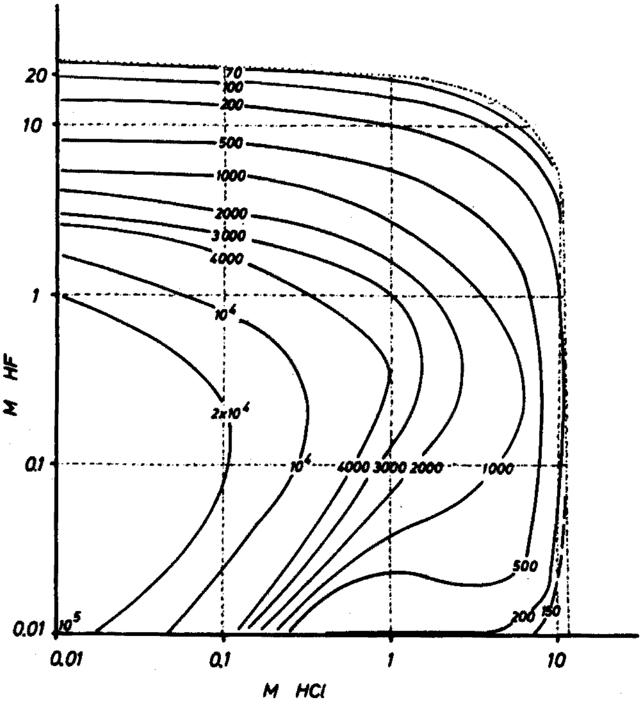


Fig. 3. Distribution coefficients of Ta(V) as functions of the hydrochloric and hydrofluoric acid concentration.

as described later, and to elute it from the Dowex 1-X8 column with a reasonable amount of eluent.

Protactinium

Protactinium(V) exists in pure hydrochloric acid solutions in the following forms: cations in 1–3 *M* HCl and cations and neutral compounds in 4 *M* HCl; above 5 *M* HCl, anions begin to form in the solution whose oxygen content diminishes with increasing acidity and whose chloride content increases leading[26–29] to $PaCl_6^-$, $PaCl_7^{2-}$ and $PaCl_8^{3-}$.

In hydrofluoric acid solutions of low acidity, protactinium forms oxo and hydroxo fluoride complexes of positive and neutral charge. Above 10^{-3} *M* hydrogen and fluoride ion concentration, mainly PaF_7^{2-} ions exist, whereas at high fluoride concentrations PaF_8^{3-} ions are present and at high acidity the $HPaF_7^-$ species is possible[29]. The existence of PaF_6^- has also been discussed[30,31].

However, even in strong hydrochloric acid solutions, protactinium changes after long aging to more colloidal dispersions, whose particles show a disagreeable tendency to adhere to the walls of the vial, be it glass or polyethylene. This can be avoided by addition of hydrofluoric acid or fluoride ions to the hydrochloric acid solution, the amount being dependent on the protactinium concentration in solution.

Figure 4 shows the adsorbability of protactinium in HCl–HF mixtures. In comparison with niobium and tantalum (Figs. 2 and 3), it is evident that protactinium

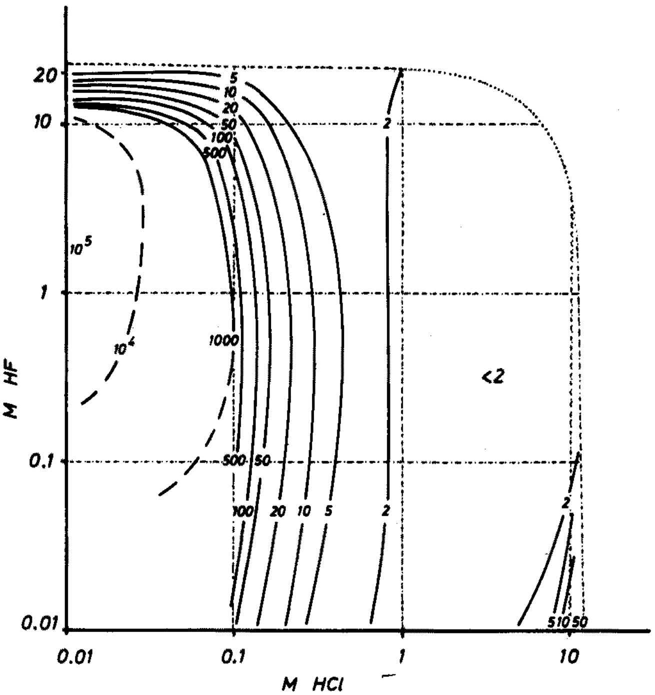


Fig. 4. Distribution coefficients of Pa(V) as functions of the hydrochloric and hydrofluoric acid concentration.

behaves differently from these two elements. Especially pronounced is the sharp decrease of its absorbability first at very low hydrochloric acid concentrations (0.01–0.05 *M*) from 10 *M* to concentrated hydrofluoric acid, and secondly over all hydrofluoric acid concentrations in the region above 0.5 *M* hydrochloric acid, where protactinium is practically no longer adsorbed. The characteristics of protactinium adsorption in these mixed media are somewhat similar to those of zirconium, although tantalum and niobium are chemically adjacent homologues of protactinium.

For the separation and purification of protactinium from Zr, Nb and Ta, Kraus and Moore[3–5] used the following eluents: 9 *M* HCl–0.004 *M* HF removed first zirconium and then protactinium from the Dowex-1 column; 9 *M* HCl–0.18 *M* HF removed niobium and 4 *M* NH_4Cl–1 *M* HF removed tantalum. Figures 1–4 show that there are several possibilities for adsorbing niobium and tantalum strongly on the resin and eluting zirconium and protactinium one after the other from the column. Provided that too low hydrofluoric acid concentrations are avoided, in order to maintain the stability of the elements in solution, another advantageous separation possibility is to elute zirconium with 9 *M* HCl–0.01 *M* HF($K_{D(Zr)} \simeq 0.5$) and then protactinium ($K_{D(Pa)} \simeq 15$), whereas both niobium and tantalum are strongly adsorbed with $K_D \simeq 300$–400. By increasing the hydrofluoric acid concentration in the mixture with 9 *M* hydrochloric acid to 0.2–0.3 *M*, the distribution coefficient of niobium decreases rapidly to $K_{D(Nb)} \simeq 7$, whereas $K_{D(Ta)}$ remains high (250), so that separation is easy. For stabilization of higher concentrations of the elements in solution, higher hydrofluoric acid concentrations are required.

As Figs. 1–4 show a variety of separation possibilities, it is possible to choose a hydrofluoric acid concentration adjusted to the concentration of the elements in solution, so that stability is maintained.

ANION-EXCHANGE BEHAVIOUR IN MIXTURES OF HYDROCHLORIC ACID AND ORGANIC SOLVENTS CONTAINING 0.1 *M* HF

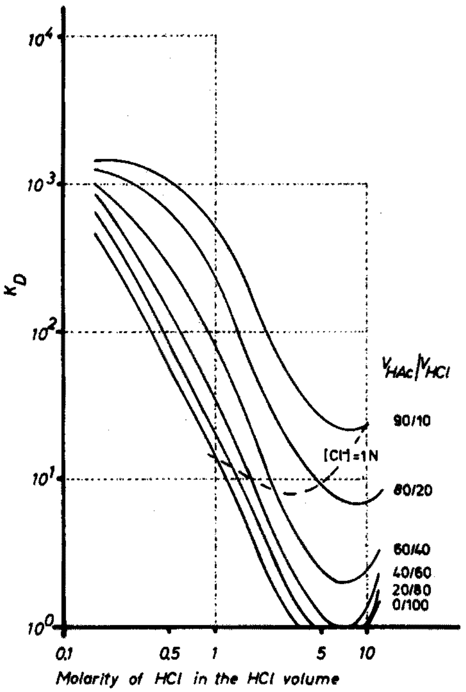
In ion-exchange equilibrium experiments, it has often been observed that replacement of aqueous solution with water-miscible organic solvents may increase the adsorption of an element; the selective adsorption and elution of metal complexes on anion exchangers from mixed aqueous–organic solvents has been shown to be a more useful tool for element separations than from pure aqueous solutions. By selecting the appropriate organic solvent and varying its amount in total solution, it is possible to increase or sometimes to decrease the adsorption of element.

According to Marcus *et al.*[32], swelling of resin, solvation and ionic interaction between molecules are mainly responsible for the increase of adsorption from aqueous–organic solvent media, resulting in ion-pair formation in anhydrous organic solvents of low dielectric constant. There are, however, no consistent theoretical explanations available upto now for the actual mechanism involved in the exchange of complex metal anions from mixed aqueous–organic solvents for the counter anions in the resin. In our experience, when the concentration of organic solvent is high, the time required to reach equilibrium of complex metal ions becomes rather long; such changes of reaction kinetics become apparent whenever the organic solvent exceeds 80% volume of total solution. This suggests that the actual mechanism of the exchange in the discussed system is not similar to that in pure aqueous solution and is far more complicated than a simple ion exchange between two phases.

In the present work, the influence of the organic solvents, acetic acid, isopropanol and methanol on the adsorption of the elements in HCl–HF system was examined. The three organic solvents were chosen because their dielectric constants differ greatly. The hydrofluoric acid concentration was maintained at 0.1 *M* for each total batch solution, while the concentrations of hydrochloric acid and of organic solvent were varied. Mixing of organic solvent with aqueous solution was done as a volume to volume relation, the hydrochloric acid concentration in the latter solution being maintained from 0.1 *M* to 12 *M*. The indication of the hydrochloric acid concentration in the Figures is not related to total solution but to the aqueous volume.

Zirconium

The results of equilibrium experiments of zirconium(IV) in hydrochloric acid–acetic acid solutions containing 0.1 *M* hydrofluoric acid are illustrated in Fig. 5, in which the results from pure aqueous solutions are given for comparison. Although the adsorption curves as a function of hydrochloric acid concentration are shown to be gradually and parallelly enhanced as the volume ratio of the acetic acid/aqueous solution is increased, the K_D values with respect to actual hydrochloric acid concentrations (molarity of hydrochloric acid in total solution) are little altered by the addition of acetic acid; acetic acid present in low or high concentrations plays



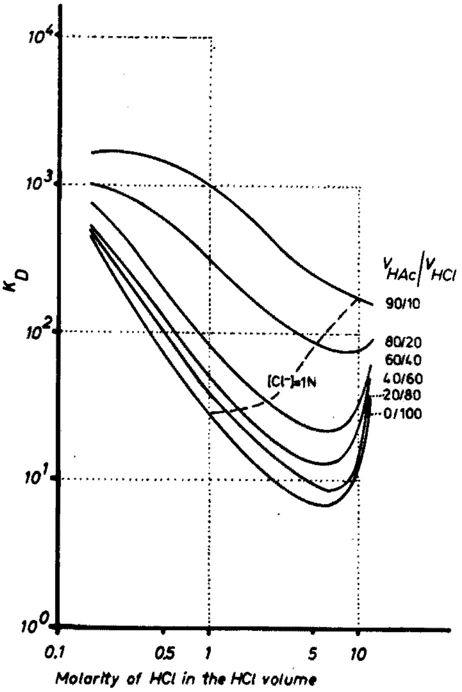


Fig. 5. Distribution coefficients of Zr(IV) as a function of acetic acid–hydrochloric acid ratio (v/v) at a constant hydrofluoric acid concentration.

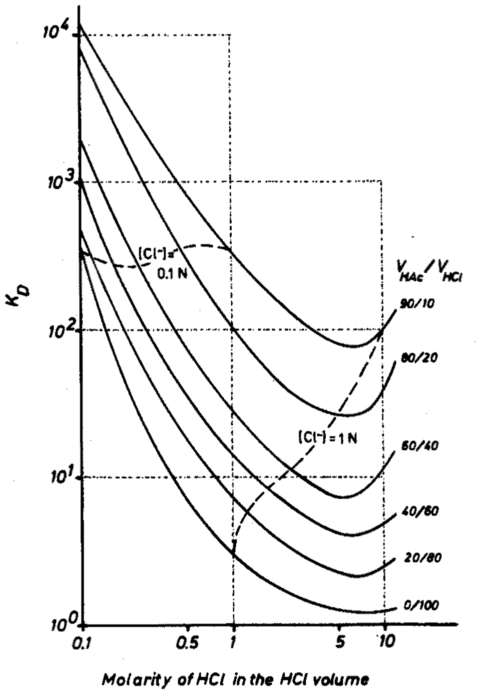
Fig. 6. Distribution coefficients of Nb(V) as a function of acetic acid–hydrochloric acid ratio (v/v) at a constant hydrofluoric acid concentration.

virtually no part in the adsorption of zirconium(IV). The K_D values lying on the crossing points between the adsorption curves and the hydrochloric acid molarity lines of 1 *M* and 10 *M* turn out to be same as the values found in pure aqueous HCl–0.1 *M* HF media with equivalent concentrations of hydrochloric acid (see Fig. 1.). At constant actual hydrochloric acid concentrations of 0.1 *M* and 1 *M*, the K_D values are little changed with increasing acetic acid concentration (dashed lines). Consideration of all the results (Figs. 1 and 5) leads to the conclusion that the net reaction of zirconium in the (HCl–HAc)–0.1 *M* HF system is the distribution of ionic complex species between the two phases, irrespective of the acetic acid concentration; this is contrary to the assumption that the distribution of uncharged complex species takes place in mixed aqueous–organic solvents at high concentrations of organic solvent. However, the conclusion made for adsorption of zirconium(IV) is not necessarily valid for the distribution of other elements, even though the same solution conditions apply.

Niobium

In contrast to the case of zirconium, the adsorption of niobium(V) is rather influenced, as shown in Fig. 6, by addition of acetic acid, especially at low and high hydrochloric acid concentrations, although the K_D values lying on the crossing points between the distribution curves and the 1 *M* hydrochloric acid line are actually the same as those found for pure aqueous HCl–0.1 M HF systems (Fig. 2) with equivalent hydrochloric acid concentrations. At high hydrochloric acid concentrations the increase of niobium adsorption becomes more apparent as the ratio of acetic acid to aqueous solution is increased. The replacement of water by acetic acid enhances the stability of the niobium chloride complexes, presumably because of further complexation of niobium chlorides with acetate groups, so that niobium chloride remains stable for a long time in presence of acetic acid (also in ethanol), even in the absence of hydrofluoric acid.

Comparisons of niobium adsorption for addition of different organic solvents are illustrated in Fig. 9. The volume ratio of organic solvent to aqueous 1 M hydrochloric acid was changed from 0% to 90%, so that the actual concentration of hydrochloric acid varied from 0.1 M to 1 M, containing a constant concentration of 0.1 M hydrofluoric acid. At these hydrochloric acid concentrations the K_D values remain identical for the solutions with and without addition of acetic acid but increase somewhat on addition of alcohols, the tendency being for the K_D values to increase with increasing chain length. However, the change of the adsorption is not only related to the dielectric constants of the organic solvents, but also to other factors such as ion solvation effects, solvent–solvent interactions, solvent–resin interactions and solvent structure changes.



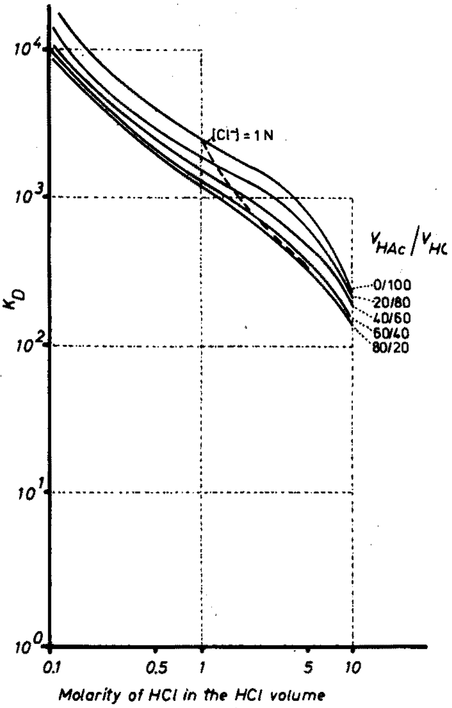


Fig. 7. Distribution coefficients of Pa(V) as a function of acetic acid–hydrochloric acid ratio (v/v) at a constant hydrofluoric acid concentration.

Fig. 8. Distribution coefficients of Ta(V) as a function of acetic acid–hydrochloric acid ratio (v/v) at a constant hydrofluoric acid concentration.

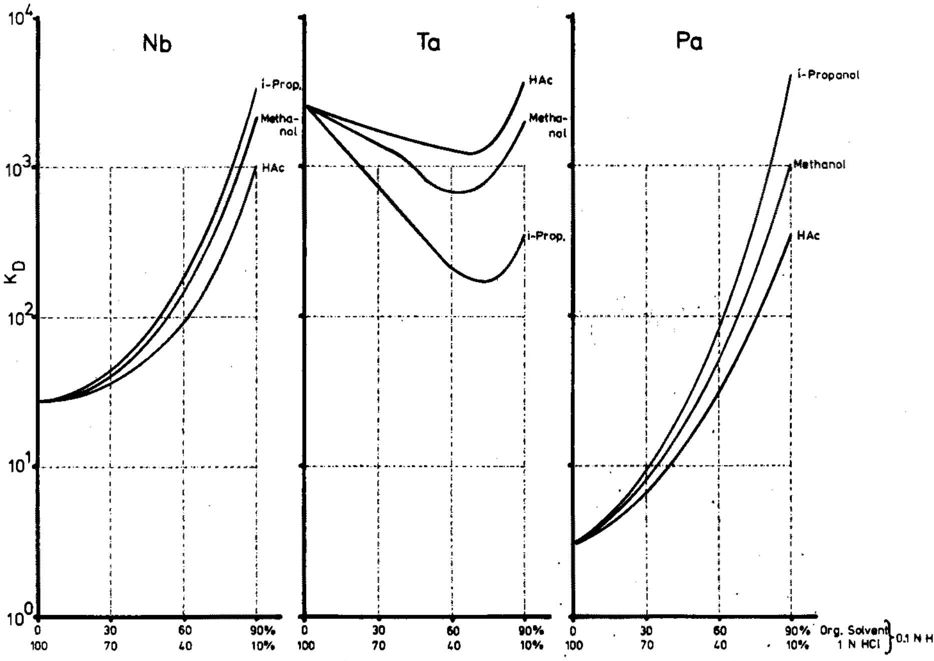


Fig. 9. Comparison of distribution coefficients of Nb(V), Ta(V) and Pa(V) in mixtures of hydrochloric acid with various organic solvents (v/v) at a constant hydrofluoric acid concentration.

Protactinium

The largest change in adsorption on addition of acetic acid was obtained for protactinium(V), especially at the higher hydrochloric acid concentrations; the net K_D value increased by 30 times for 1 *M* hydrochloric acid in a total solution containing 90% acetic acid (Fig. 7). However, as in the cases of zirconium and niobium, when the K_D values lying on the cross points between the distribution curves and the 1 *M* hydrochloric acid line are compared with the values obtained from pure aqueous HCl–0.1 *M* HF media, the results are identical. The influence of other organic solvents on the adsorption of protactinium is more pronounced than on the adsorption of niobium, although the order of influence by various organic solvents is identical for both elements (see Fig. 9).

The sharply increased adsorption of protactinium in HCl–0.1 *M* HF with addition of acetic acid—and the negligible adsorption without acetic acid present, is very useful for the separation of this element from thorium, uranium and other elements. First, a stable protactinium complex species is maintained in solution, and secondly no masking agent for fluoride ions is required before adsorption of protactinium on the exchanger.

Tantalum

As shown in Figs. 8 and 9, the anion-exchange equilibrium of tantalum(V) in HCl–0.1 *M* HF mixed with an organic solvent is different from those of niobium and protactinium. The influence of the organic solvent on the adsorption of tantalum appears reverse: the higher the concentration of organic solvent, the lower the adsorption. The addition of acetic acid, methanol or isopropanol shows a reverse effect on tantalum(V) adsorption compared with the adsorption of niobium(V) and protactinium(V). The effect of the actual concentration of hydrochloric acid in aqueous–organic solvent media on the tantalum(V) adsorption also shows a difference between tantalum and the other elements. Isopropanol decreases the affinity of tantalum for the anion exchanger more than any other organic solvent; the affinity decreases further with increasing hydrochloric acid concentration, and these effects are advantageous in the quantitative desorption of tantalum from the exchanger. The best condition for desorption of tantalum was found to be a solution containing 75% isopropanol and 25% 10 *M* hydrochloric acid with 0.1 *M* hydrofluoric acid.

Although interesting observations can be made from the anion-exchange adsorption of Ta, Nb, Pa, Zr from aqueous–organic solvent media, owing to a lack of sufficient information concerning the complex formation of these elements and the factors governing the exchange system in the mixed solutions, no explanation for the inconsistent adsorption behaviour of these elements can be proposed for the moment.

In the application of these anion-exchange methods in mixed organic media, the main advantage lies in the possibility of increasing or decreasing the affinity of the respective elements for the anion exchanger. As many fission and daughter products of Th, Pa and U show only a slight affinity for anion exchangers in hydrochloric acid–hydrofluoric acid media and do not (or only slightly) increase their adsorbability on addition of organic solvents, separation and purification problems are greatly simplified. For example, protactinium can be easily adsorbed from hydrochloric acid–hydrofluoric acid solutions with high alcohol or acetic acid content, and so purified from alkali, alkaline earth and rare earth elements through intensive washing of the column[33].

An appropriate condition can be selected, in which one element shows an increased and the other a decreased adsorbability, as the case of niobium and tantalum, or protactinium and tantalum, so that new separation possibilities can be designed. Furthermore, an addition of organic solvents usually increases the stability of Zr, Nb, Ta and Pa solutions by complexing, so that hydrolysis and polymerization in solution are avoided.

For separations of Zr, Nb, Ta and Pa from one another, an addition of organic solvents to the hydrochloric acid–hydrofluoric acid solutions does not appear much more advantageous than the use of the pure aqueous solution but organic solvents are definitely beneficial for the separation of these elements from other elements.

SUMMARY

Ion-exchange behaviours of Zr(IV), Nb(V), Ta(V) and Pa(V) on the anion exchanger Dowex 1-X8 are investigated first in a wide variety of aqueous mixed hydrochloric acid–hydrofluoric acid and secondly in the same aqueous system mixed with various organic solvents. Equilibrium adsorptions of these four elements as a function of hydrochloric acid concentration as well as hydrofluoric acid concentration, or both acid concentrations, were found to be strongly differentiated.

This fact can be utilized for convenient separations of these elements from each other. Based on the equilibrium adsorption results, the possible complex formation of the metal ions and the separation possibilities for the elements are discussed.

RÉSUMÉ

Une étude du comportement de Zr(IV), Nb(V), Ta(V) et Pa(V) sur échangeur d'ions Dowex 1-X8 est effectuée, premièrement dans de nombreux systèmes aqueux acide chlorhydrique–acide fluorhydrique, deuxièmement dans un même système aqueux mélangé à divers solvants organiques. Les résultats obtenus permettent d'examiner les possibilités de formation de complexe de ces ions, ainsi que leur séparation.

ZUSAMMENFASSUNG

Das Ionenaustauschverhalten von Zr(IV), Nb(V), Ta(V) und Pa(V) an dem Anionenaustauscher Dowex 1-X8 wurde zunächst für eine Vielzahl wässriger gemischter Salzsäure–Flussäure-Systeme und dann für dasselbe wässrige System im Gemisch mit verschiedenen organischen Lösungsmitteln untersucht. Die Gleichgewichtsadsorption dieser vier Elemente als Funktion der Salzsäurekonzentration, der Flussäurekonzentration oder beider Säurekonzentrationen erwies sich als sehr unterschiedlich. Diese Tatsache kann für bequeme Trennungen dieser Elemente voneinander ausgenutzt werden. Die erhaltenen Gleichgewichtsadsorptionswerte werden im Hinblick auf die mögliche Komplexbildung der Metallionen sowie die Trennmöglichkeiten für die Elemente diskutiert.

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ION-EXCHANGE FOAM CHROMATOGRAPHY

PART I. PREPARATION OF RIGID AND FLEXIBLE ION-EXCHANGE FOAMS

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In a recent preliminary note a new column chromatographic method was outlined for which the name "foam chromatography" was proposed[1]. It was explained that chromatographic adsorption, exchange and partition processes could be favourably influenced by giving the adsorbent a hollow spherical (cellular) form, and effecting these processes on the internal surface of the cells. This can be done by using solid, rigid or flexible foamed synthetic polymers as column fillings. Open-cell plastic foams may be regarded as a relatively regular stack of hollow spheres. In a more detailed study, "reversed-phase foam chromatography" was used for the separation of palladium, bismuth and nickel in a thiourea–perchloric acid system on open-cell polyurethane foam columns loaded with tri-*n*-butyl phosphate.

The excellent hydrodynamic properties of chromatographic columns filled with open-cell foams, and the favourable kinetics[2] of the partition processes taking place on the thin membranes separating the foam cells, suggested that the analytical application of ion-exchange foams might also be worth studying.

However, whereas for the development of reversed-phase foam chromatography the open-cell type of polyurethane foam used was commercially available, open-cell foams of reasonable ion-exchange properties, so far as is known, are not being produced on an industrial scale. The present paper is, therefore, concerned with the preparation of such foams, and with the investigation of some of their properties.

The three-dimensional lattice structure of the polymerized ion-exchange resins which are most commonly used at present could be transformed into a foam structure only with great difficulties. It appeared to be more reasonable to follow the principles applied in the preparation of ion-exchange membranes[3]. The preparation of open-cell ion-exchange foams was therefore attempted in two ways: both homogeneous and heterogeneous ion-exchange foams were prepared.

Homogeneous foams were prepared by introducing ion-exchange groups on a previously prepared plastic foam (phenol–formaldehyde, polyurethane or polyethylene) by means of surface, or more penetrating, treatment. Some of the foams, *e.g.*, phenol-formaldehyde foam, may be given cation-exchange properties by direct

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sulfonation. In other cases, ion-exchange foams can be produced by indirect methods, *e.g.* by carrying out a polymer analogue reaction after joining the foam to an easily transformable polymer, or by grafting monomers with ionogenic groups. By this method, styrene–polyurethane or styrene–polyethylene "interpolymer" foams may be produced, and sulfo- or amino-groups can be formed on them by subsequent sulfonation, or chloromethylation and amination, respectively.

In a third method, monomers with ionogenic groups are grafted on to a carrier of suitable foam structure. Grafting is carried out by radiation initiation. So far as is known, no experiments have been reported on the radiation grafting of polyurethane and polyethylene foams. Studies on the radiation grafting polymerization of monomers on solid polyethylene films were recently published by Hamil *et al.*[4]. Radiation grafting can be done[4] either by a "pre-irradiation" method, in which a polymer is "activated" by radiation in the presence or absence of oxygen, and then reacted with the monomer, or by a direct method, in which the monomer and the polymer are irradiated together in a liquid or gaseous phase. In the present work, the former method was applied, in the presence of oxygen, for the preparation of both anion- and cation-exchange foams.

Heterogeneous foams were produced by preparing a fine powder of a commercially available cation exchanger (Varion KS), and foaming this powder with the precursors of an open-cell polyurethane foam of the polyether type. In this process a heterogeneous cation-exchange foam, similar to heterogeneous ion-exchange membranes, was formed, which contained the fine cation-exchanger grains dispersed in the polyurethane matrix.

EXPERIMENTAL

Sulfonation of phenol–formaldehyde rigid foam

About 1 g of foam was accurately weighed, cut to cubes of about 5 mm edge, and reacted with excess of concentrated sulfuric acid at a given temperature for a given time. Before the reaction, bubbles of air were removed from the samples by evacuation. The reaction was carried out in a three-necked 250-ml flask, equipped with a condenser, stirrer and thermometer. The temperature of the reaction vessel was maintained within ± 1°. After the required reaction time, the flask was cooled, and its content was washed with an abundant amount of water through a sintered-glass filter.

Preparation of polyurethane–Varion KS foam

Foaming was carried out by the process of the North Hungarian Chemical Works, Sajóbábony[5].

Capacity measurement and titration curve

The capacity measurement and the determination of titration curves was carried out as described by Inczédy[6].

Styrene–polyurethane interpolymer foams

First a solution containing suitable amounts of divinylbenzene, styrene and initiator in acetone was prepared. The foam sample was weighed, cut to cubes of about 5 mm edge, and placed in a round flask, and the solution prepared previously was added to the foam. The air was removed from the flask by evacuation. The excess of styrene was removed from the foam by centrifugation, at 3000 rev $\min^{-1}$, lasting for different intervals. The polymerization was carried out in a drying oven at 70° (lauroyl peroxide), or at 80° (benzoyl peroxide).

Chloromethylation

Chloromethylation was carried out at 40° in a 1:100 excess of chloromethyl ether solution containing 25% of aluminium trichloride. Before starting the reaction, the chloromethyl ether solution was cooled below 0° with an ice–salt mixture, the foam was abundantly impregnated with the solution, and then the system was heated to 40°. After completion of the reaction (1–1.5 h) the solution was cooled to room temperature, and washed until chloride-free with methanol.

Amination

The foam was reacted at 60°, for 4 h, with an excess of an aqueous 20% solution of dimethylaminoethanol. After completion of the reaction, the foam was washed with 1 *M* hydrochloric acid solution and with water.

Radiation grafting of polyurethane and polyethylene foams

The foam samples were irradiated for different periods at different dose rates. Then the samples were reacted at 90°, in an apparatus consisting of a cylindrical glass tube and a condenser fitted with ground-glass joints, for 1 h with an aqueous 20% solution of methacrylic acid, at a methacrylic acid module of 30 (*i.e.* at 1:30 polymer/MAA ratio). Before the reaction about 1 g of iron(II) sulfate heptahydrate was added for each gram of polymer (in order to avoid homopolymerization). After the reaction, the foam was washed with 1 *M* hydrochloric acid solution and with water.

Determination of capacity with ^{85}Sr

Ion-exchange foam pieces of about 0.2 g in weight (cubes of about 5 mm edge) were weighed with analytical accuracy, and were placed into 7 bottles with ground joints; 20-ml portions of water were added to each sample and air bubbles were removed by evacuation. To the contents of the bottles, strontium nitrate solution, labelled with ^{85}Sr, was added in gradually increasing concentrations. Immediately after the addition, a 0.5-ml sample was withdrawn for activity determination, and the remaining solutions in the bottles were shaken several times and allowed to stand overnight. On the next day, further samples were taken again, and their activities were determined. The activity measurements on the third day indicated that equilibrium had been established. The concentration change in the solution was determined from the activity change. The amount of strontium(II) bound by the ion-exchange foam was calculated from the difference between the original and equilibrium concentrations.

Determination of the half-period of ion exchange with ^{85}Sr

In a flask with a ground-glass joint, 20 ml of water were added to 0.20 g of foam, and air bubbles were removed by evacuation. An ^{85}Sr-labelled strontium nitrate solution corresponding to the capacity of the foam sample was prepared. The solution was added to the foam sample with a swift movement, and the contents of the flask were stirred with a magnetic stirrer. Immediately after mixing, and then at regular intervals for 90 min, samples were taken.

RESULTS AND DISCUSSION

Ion-exchange foam prepared by the sulfonation of rigid phenol–formaldehyde resin foam

The rigid, industrially produced (as insulator) foam of medium cell size and of relatively homogeneous structure appeared to be a suitable model. It can be transformed to a strong acidic cation exchanger by sulfonation, and to a weak or strong alkaline anion exchanger by chloromethylation and subsequent amination. In connection with the polymer analogue reaction, the question arose whether the structure of the foam suffers substantial mechanical damages. In order to answer this question, the preparation of cation-exchange foam by sulfonation was studied. The sulfonation reaction was followed by measuring the ion-exchange capacity as a function of the temperature and time. The results obtained are given in Table I. As can be seen, the maximum capacity that can be reached under the conditions applied is 1.85 meq g^{-1}. During the reaction, the samples were homogeneously discoloured, but the mechanical properties of the original foam did not change to a remarkable extent.

TABLE I

ION-EXCHANGE CAPACITY OF THE SULFONATED PHENOL–FORMALDEHYDE FOAM

Resin (g)	*Temperature (°)*	*H_2SO_4 (ml)*	*Reaction time (h)*	*Weight change (g)*	*Capacity (meq g^{-1})*
1.0866	70	217	1.0	−0.0206	0.47
1.0840	70	217	2.0	−0.0098	0.68
0.9835	70	198	4.0	+0.0157	0.78
0.9609	80	145	0.5	+0.0016	0.79
1.2087	80	180	1.0	+0.0547	0.92
0.9830	80	148	2.0	+0.0790	1.36
1.0079	90	175	0.5	+0.0767	0.98
0.8777	90	201	1.0	+0.0982	1.56
0.9039	90	181	2.0	+0.1654	1.85

Despite the fact that the foam obtained by this process had relatively acceptable ion-exchange properties, there is little hope, at present, for its analytical application, because rigid foams cannot be used for the homogeneous filling of chromatographic columns. However, encouraging preliminary results were obtained in experiments when the original phenol–formaldehyde resin was foamed "in vitro" in a chromatographic column of appropriate size, and the foam was subjected to sulfonation in this state. This possibility is being investigated.

Styrene–polyurethane interpolymer foams

The effects of the three-dimensional lattice structure and the amount of styrene attached to the foam on the original mechanical properties of elastic polyurethane foams were studied. The amount of styrene was varied by applying different centrifugation times, whereas the degree of cross-linking was influenced by the amount of divinylbenzene. The effect of two different initiators on the polymerization process was also compared.

Table II shows the results of polymerization experiments carried out with styrene solutions containing 8% divinylbenzene and 2% benzoyl peroxide. The physical parameters of the foam produced started to change noticeably at about 20% polystyrene content (elasticity decreased, permanent deformation occurred on pressure). Further increase in the polystyrene content led to a rapid breakdown of mechanical properties, and at 40% polystyrene the foam behaved as a rigid material of brittle structure. The sample with the highest polystyrene content (No. 1, Table II) was a sticky jelly or a completely rigid block, depending on the conditions of the polymerization.

TABLE II

STYRENE POLYMERIZATION ON POLYURETHANE FOAM WITH BENZOYL PEROXIDE

No.	*Weight of foam (g)*	*Centrifugation time (min)*	*Wet weight (g)*	*Weight after polymerization (g)*		*Styrene content after 24 h (%)*
				8 h	*24 h*	
1	1.0056	1.0	4.56	3.0785	2.3876	58
2	0.9876	2.0	2.97	1.9076	1.6687	40.7
3	1.1075	5.0	2.28	1.4752	1.3456	18
4	1.1105	10.0	2.19	1.4658	1.3510	17.5

TABLE III

STYRENE POLYMERIZATION ON POLYURETHANE FOAM WITH LAUROYL PEROXIDE

No.	*Weight of foam (g)*	*Centrifugation time (min)*	*Wet weight (g)*	*Weight after polymerization (g)*		*Styrene content after 16 h (%)*
				8 h	*16 h*	
1a	1.0678	0.25	5.14	3.9436	3.5891	71.4
2a	1.1906	0.5	3.66	2.7245	2.4019	51.0
3a	1.0040	1.0	2.99	2.1487	1.8162	43.4
4a	0.9756	2.0	2.27	1.5814	1.2876	32.1
5a	1.1073	5.0	2.86	1.8481	1.4655	24.5

Table III shows the results of experiments carried out with a styrene solution containing 8% divinylbenzene and 2% lauroyl peroxide. In this case, the elastic properties of the foam were better than in the benzoyl peroxide experiments for the same styrene content. Again, however, as the styrene content was increased, a rapid increase of rigidity was observed, and the samples hardened to a glass-like material even more quickly.

Preparation of anion-exchange foam

The formation of anion-exchange groups on polystyrene–polyurethane interpolymer foams was carried out by chloromethylation with chloromethyl ether, and by amination of the intermediate product. After these polymer analogue reactions, the capacity of the anion-exchange foam samples was determined. The results are given in Table IV.

TABLE IV

ION-EXCHANGE CAPACITY OF THE CHLOROMETHYLATED AND AMINATED FOAMS

Sample no.[a]	1	2	3	4	1a	2a	3a	4a	5a
Weight increase during chloromethylation (%)	6.1	5.5	2.8	2.6	6.3	5.8	5.6	4.3	3.8
Capacity (meq g^{-1})	2.4	2.0	1.1	1.0	2.6	2.3	2.2	1.7	1.5

[a] Sample numbers are those used in Tables II and III.

The method applied yielded a strongly basic anion-exchange foam of good quality. The most favourable results were obtained with samples containing 20–40% of built-in styrene. The mechanical properties of the foam prepared by this process depended on the quality of the initiator used. The capacity of the foam was 2.0–2.2 meq g^{-1}.

Radiation grafting of polyurethane and polyethylene foams

Irradiations of high dose rate were done with a Van de Graaff generator, and those of lower dose rate with a γ-ray (^{60}Co) source. The irradiated samples were grafted with methacrylic acid. The radiation grafting reaction was followed as a function of the dose rate. The following dose rate and dose values were applied: at 0.03 krad s^{-1} (^{60}Co), 6.0, 16.1 and 21.3 Mrad; at 20.0 krad s^{-1} (Van de Graaff), 5.0, 10.0, 15.0 and 20.0 Mrad. In this series of experiments, in addition to the radiation grafting of open-cell polyurethane foams, the grafting of closed-cell polyethylene foam was attempted. Closed-cell foams are unsuitable for chromatographic purposes, but no open-cell polyethylene foam was available, and the main goal of the experiment was to see whether an ion-exchange foam of acceptable capacity could be produced at all from foamed polyethylene by radiation grafting. The radiation grafting with methacrylic acid fixed a group of ionogenic behaviour on the foamed backbone structure, and, as such, led to the final product in a single step. The results are summarized in Table V. The foam prepared by this method is a weak carboxylic ion-exchange foam of excellent properties.

The preparation of polyurethane–Varion KS heterogeneous ion-exchange foam

As was mentioned earlier, the preparation of ion-exchange foams was attempted by a process wherein finely ground commercial ion-exchange resin was built into polyurethane foam of an open-cell polyether-type. At first, foaming was

TABLE V

ION-EXCHANGE CAPACITY OF RADIATION-GRAFTED FOAMS

Foam type	*Polyurethane*							*Polyethylene*						
Dose rate (krad s^{-1})	20.0				0.03			20.0				0.03		
Total dose (Mrad)	5	10	15	20	6.0	16.1	21.3	5	10	15	20	6.0	16.1	21.3
Weight increase (%)	2.1	4.0	5.7	8.7	10.8	20.8	37.4	3.1	7.0	7.8	11.2	15.0	26.1	31.0
Capacity (meq g^{-1})	0.19	0.35	0.48	0.72	0.93	2.10	2.62	0.27	0.65	0.77	1.03	1.62	2.22	4.02

carried out with the resin in the H^+ form. However, it was found that this acidic ion-exchange group had a great influence on the formation and foaming reactions of polyurethane. The mechanical properties of the foam produced rapidly broke down, and at a 30% ion-exchanger content the foam became completely crumbly. A foam of acceptable quality could be prepared only with a maximum of 7.0% of ion-exchange resin in the H^+ form.

Accordingly, the experiments were continued with the ion-exchange powder in the Na^+ form, and it was shown that the neutral sodium ion form has no effect whatsoever on the foaming reaction. At an 18–26% cation-exchanger content, the foam still exhibited excellent mechanical properties, and even higher amounts could be mixed in, up to about 40%. Even at this resin content, the mechanical properties of the foam were the same as those of the foam containing no ion-exchange resin; and the distribution of the grains was uniform, as proved by microscopic investigations.

In order to study the parameters of the ion-exchange foams prepared by this process, the capacity of the foams was measured, the titration curve was determined, and preliminary measurements were made in order to elucidate the kinetics of the processes taking place on the foams. The results of capacity measurements are given in Table VI. As can be seen, the capacity of the foam

TABLE VI

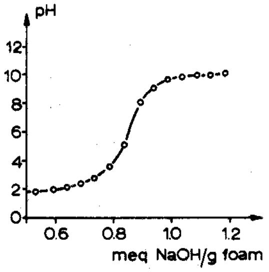
ION-EXCHANGE CAPACITY OF POLYURETHANE–VARION KS FOAM

Resin form	*Varion KS content (%)*	*Dry weight (g)*	*Capacity (meq g^{-1})*
H^+	7.0	1.8923	0.18
Na^+	18.0	0.6762	0.31
Na^+	26.0	0.7184	1.05

containing 26% cation-exchange resin was 1.05 meq g^{-1}. The original capacity (before grinding) of Varion KS cation-exchange pearl polymer was 5.0 meq g^{-1}, which shows that in the foamed form the capacity of the resin was slightly reduced.

Figure 1 shows the titration curve of the foam. The curve corresponds to the titration curves of strong acidic cation exchangers.

Preliminary investigations were' carried out on the kinetics of processes taking place on the foams prepared by these methods. Investigations of Pinfold and Karger[7] have shown that the exchange processes on finely pulverized ion exchangers proceed substantially faster than processes on pearl polymers of similar composition but considerably bigger size. Fine grains, however, cannot be used as column fillings, and their application causes difficulties even in the case of the "batch technique".



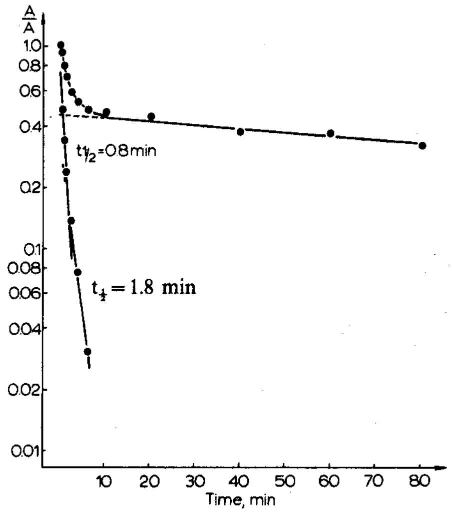


Fig. 1. pH-titration curve of polyurethane-Varion KS cation-exchange foam.

Fig. 2. Kinetics of Na^{+}-$^{85}Sr^{2+}$ ion exchange on 26% Varion KS-polyurethane cation-exchange foam.

The kinetic method with ^{85}Sr, described by Skafi and Lieser[8], was applied for the investigations, where the half-period of Sr^{2+}-Na^{+} ion exchange was determined. The results are shown in Fig. 2. The half-periods calculated from the curves, and the corresponding parameters of Dowex 50-X12 pearl polymer and of the surface-sulfonated pearl polymer prepared by Skafi and Lieser[8], as well as their capacity values, are compared in Table VII.

In the case of the foam containing 26% of ion-exchange powder, the measured capacity was also checked by the capacity measurement method of Skafi and Lieser[8]. The results of this investigation are given in Fig. 3. It is apparent that the results of the capacity determination with ^{85}Sr were in good agreement with the previous chemical measurement.

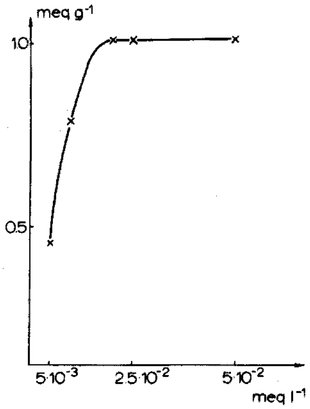


Fig. 3. Capacity determination with ^{85}Sr of 26% Varion KS–polyurethane cation-exchange foam.

TABLE VII

HALF-PERIOD OF THE ION EXCHANGE OF STRONTIUM(II) ON DIFFERENT EXCHANGERS AND THEIR CAPACITIES

Exchanger	*Half-period of the ion-exchange reaction*		*Capacity ($meq\ g^{-1}$)*	*Ref.*
	1st step $t_{\frac{1}{2}}^{I}$ *(min)* *(film diffusion)*	*2nd step* $t_{\frac{1}{2}}^{II}$ *(min)* *(gel diffusion)*		
Dowex 50-X12 resin (50–100 mesh)	0.6	3.6	5	Skafi and Lieser[8]
Superficially sulfonated styrene–DVB resin	0.6	—	$6.3 \cdot 10^{-4}$	Skafi and Lieser[8]
Polyurethane–Varion KS foam	0.8	1.8	1.0	Present work

CONCLUSIONS

The investigations have shown that it is possible to prepare homogeneous and heterogeneous ion-exchange foams. In order to decide which of the above foams are most suitable for analytical purposes, further investigations are in progress.

SUMMARY

In order to be able to apply the principles of foam chromatography to ion-exchange processes, preparative methods for open-cell ion-exchange foams were investigated. Homogeneous ion-exchange foams were prepared by introducing ion-exchange groups on previously prepared phenol–formaldehyde, polyurethane and polyethylene foams. The maximum capacity of the produced sulfonated phenol–formaldehyde cation-exchange foams was 1.85 meq g^{-1}; that of the styrene–polyurethane interpolymer anion-exchange foams was 2.2 meq g^{-1}. Weak carboxylic ion-exchange foams were prepared by radiation grafting of polyurethane and polyethylene foams; the maximum capacity of these foams was 4.02 meq g^{-1}. Heterogeneous ion-exchange foams were prepared by foaming a fine powder of a commercially available cation exchanger with the precursors of open-cell polyether-type polyurethane foam. The capacity of such a foam containing 26% ion-exchange powder was 1.0 meq g^{-1}. The kinetics of the cation-exchange process on the heterogeneous foams was measured with ^{85}Sr.

RÉSUMÉ

Une étude est effectuée sur la chromatographie sur mousse. Diverses méthodes de préparation de mousses échangeuses d'ions sont examinées. Elles consistent à introduire des groupes échangeurs d'ions sur des mousses phénol–formaldéhyde, polyuréthane et polyéthylène. Les cinétiques du processus d'échange de cations, sur mousse hétérogène sont déterminées à l'aide de ^{85}Sr.

ZUSAMMENFASSUNG

Im Hinblick auf die Anwendung der Prinzipien der Schaumchromatographie auf Ionenaustausch-Prozesse wurden Methoden zur Herstellung von Ionenaustausch-Schäumen mit offenen Zellen untersucht. Homogene Ionenaustausch-Schäume wurden hergestellt, indem an vorher hergestellten Schäumen aus Phenol–Formaldehyd, Polyurethan und Polyäthylen Ionenaustausch-Gruppen eingeführt wurden. Die maximale Kapazität der aus sulfonierten Phenol–Formaldehyd bestehenden Kationenaustausch-Schäume war 1.85 mval g^{-1}; bei Anionaustausch-Schäumen aus Styrol–Polyurethan betrug der Wert 2.2 mval g^{-1}. Schwache carboxylische Ionenaustausch-Schäume wurden durch Strahlenbehandlung von Polyurethan- und Polyäthylenschäumen präpariert; die maximale Kapazität dieser Schäume betrug 4.02 mval g^{-1}. Heterogene Ionenaustausch-Schäume wurden hergestellt, indem ein feines Pulver eines handelsüblichen Kationenaustauschers mit den Vorstufen von Polyurethanschaum des offenzelligen Polyäthertyps vermischt wurde. Die Kapazität eines solchen Schaums mit einem Gehalt von 26% Ionenaustausch-Pulver war 1.0 mval g^{-1}. Die Kinetik des Kationenaustausch-Prozesses an den heterogenen Schäumen wurde mit ^{85}Sr untersucht.

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ELECTROCHEMISTRY OF COBALT–PORPHYRIN COMPLEXES IN AQUEOUS SOLUTION

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The electrochemistry of cobalt hematoporphyrin with nitrogen-containing axial ligands has not been reported previously although some complexes with pyridine and cyanide have been investigated by spectrophotometry[1]. Unlike most complexes of cobalt(III) which are not very labile, the hematoporphyrin complex has been shown by stopped-flow methods[2] to be quite labile toward substitution. This lability is caused by some loss of transition metal character when cobalt interacts with the delocalized orbitals of the porphyrins.

Cobalt porphyrins are of great biological interest since they are structurally similar to iron porphyrins, vitamin B_{12} and other cobalamins. Vitamin B_{12} and similar cobalamins have cobalt coordinated to a porphyrin-like structure. It is this resemblance which makes cobalt hematoporphyrin an interesting choice for electrochemical study.

Both cobalt(II) and cobalt(III) can add two further ligands[3], one above and one below the planar porphyrin ring to give an octahedral complex. The prime candidates for these ligands would be water, hydroxide ion, and nitrogenous bases.

Both polarography and cyclic voltammetry were employed to investigate the reaction of cobalt(III) hematoporphyrin in the presence of nitrogenous ligands in aqueous solution; for such methods have proved successful[4,5] for yielding information about metalloporphyrin solution chemistry.

EXPERIMENTAL

Chemicals and procedure

Cobalt(III) hematoporphyrin (Fig. 1) was prepared from hematoporphyrin dihydrochloride (Nutritional Biochemical Corp. or Sigma Chemical Co.) as described by Adler *et al.*[6]. Cobalt(II) acetate was used as the metallic salt and air oxidation of the product[7] yielded the higher oxidation state complex. The course of this reaction was followed by visible spectrometry. Analysis: found 57.9% C, 5.3% H, 8.7% N; calculated (assuming the monoacetate with a dimethylformamide molecule of solvation) 59.7% C, 5.9% H, 8.9% N.

Reagent or comparable grade chemicals were used throughout this work without further purification. All solutions were prepared with distilled water, and if required, reagent-grade absolute ethanol. Triply distilled mercury was used for

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* NDEA Fellow.

dropping mercury electrodes. All electrochemical experiments were carried out under a nitrogen atmosphere after deaerating the solution with prepurified nitrogen which had passed through a vanadium(II) sulfate solution and a chromium(II) sulfate solution to remove traces of oxygen. Finally a portion of solution was studied to minimize evaporation of volatile materials. All measurements were carried out at room temperature.

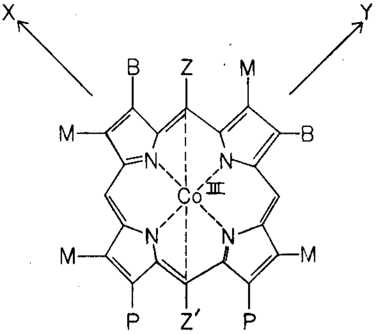


Fig. 1. Cobalt hematoporphyrin: (M) methyl; (B) α-hydroxyethyl; (P) propionic acid; (Z) ligand; (Z′) ligand.

All solutions used for electrochemical studies were 1.0 *M* in sodium nitrate and were buffered with an appropriate buffer (0.25 *M*). Test solutions of cobalt porphyrins were prepared shortly before use by weighing the appropriate quantity of the solid compound directly. The composition of the buffer varied according to the desired pH but the substances used were borax, sodium hydrogencarbonate, sodium monohydrogenphosphate, potassium hydroxide, and potassium dihydrogenphosphate. The pH values were checked with a Beckman Zeromatic pH meter.

Absorption spectra were recorded on a Beckman model DB spectrophotometer. Polarograms were recorded with a standard dropping mercury electrode (D.M.E.) in conjunction with a Sargent Model XV polarograph with a saturated calomel electrode as reference, and all potentials are reported *versus* this reference.

Controlled potential electrolysis, to establish that cobalt(III) hematoporphyrin was reduced by one electron, was performed with an Analytical Instruments potentiostat and current integrator. The control potential was selected by examining polarograms of cobalt(III) hematoporphyrin in the solution of choice. A mercury pool electrode was employed.

All cyclic voltammetric measurements were made with a three-electrode potentiostat circuit constructed from operational amplifiers. The details of the apparatus have been previously described[4].

RESULTS AND DISCUSSION

Unlike hemin and a number of other metalloporphyrins, cobalt(III) hematoporphyrin in the absence of added nitrogenous ligands is not electrochemically reducible in aqueous solution. In the presence of nitrogenous bases such as pyridine and related compounds, a reduction wave is obtained. Figure 2 depicts the polarogram of cobalt(III) hematoporphyrin in buffered electrolyte with excess of pyridine. The reduction of cobalt(III) to cobalt(II) gives rise to the main wave (Part B), while the small prewave (Part A) is due to adsorption of the product of the electrode reaction on the surface of the dropping mercury electrode. The adsorption phenomenon will be discussed later.

There was no effect of pH on the $E_{\frac{1}{2}}$ of the waves in the pH range 7.5–12. Between about 7.5 and 6.0 a shift in half-wave potentials toward the anodic direction was noted, which was due in part to conversion of some pyridine to pyridinium ion at the low pH values. Another effect, probably varying liquid junction potentials, also caused some $E_{\frac{1}{2}}$ shifts. (Data at lower pH values were not obtainable because of solubility problems.) This constancy over a reasonably wide pH range indicates that neither hydrogen nor hydroxide ions are involved in the electrode reaction in this region. Controlled-potential electrolysis proved that the electrode reaction involves one electron.

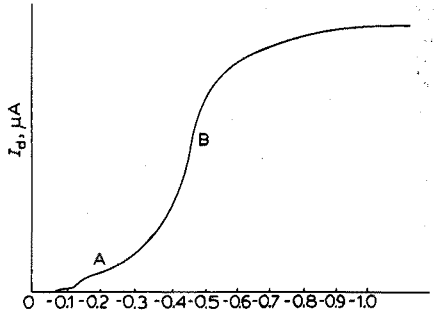


Fig. 2. Typical polarogram: 1.02 mM cobalt hematoporphyrin, 20% pyridine (2.48 M), 1.0 M NaNO$_3$, 0.05 M NaHCO$_3$, pH 8.70.

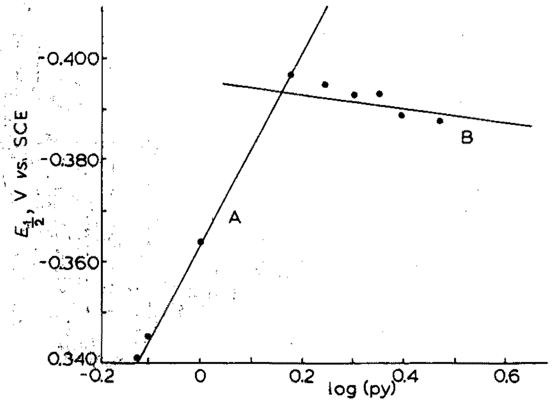


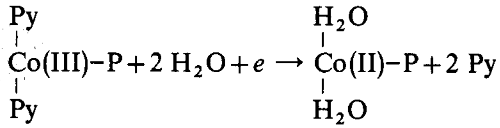
Fig. 3. Variation of half-wave potential with log of pyridine concentration at pH 6.5.

When the concentration of pyridine was varied at pH values of 6.5 and at 11.2, the half-wave potential shifted cathodically as the concentration varied from 0.75 M to about 1.5 M, and then remained fairly constant at higher pyridine concentrations. At low concentrations of pyridine, low currents were obtained, indicating that not all of the cobalt porphyrin was in a complexed state with pyridine, since as previously mentioned, the aquo and hydroxo complexes are not reducible. Figure 3 shows the variation of half-wave potential with log pyridine concentration at pH 6.5. From the slopes of the lines in Fig. 3, one can deduce the number of free ligand molecules involved as 2 for Section A and none for Section B. (These values are based on the polarographic slope value of 0.109 V observed at this pH.) This indicates that at concentrations of pyridine less than 1.5 M, the cobalt(III) hematoporphyrin complex contains two more pyridine ligands than the cobalt(II) hematoporphyrin complex. At pyridine concentrations greater than 1.5 M both cobalt complexes are coordinated with two pyridine ligands. A similar plot for pH 11.5 was also made.

Here the slopes indicate the number of ligands involved as 1 for Section A and none for Section B. (These values are based on the polarographic slope value of 0.082 observed at this pH.) This indicates that when the pyridine concentration is less than 1.5 *M*, the cobalt(III) complex has one more pyridine ligand than the cobalt(II) complex. At pyridine concentrations higher than 1.5 *M*, both cobalt complexes are coordinated with two pyridine ligands. McConnell *et al.*[1] have previously reported a bipyridine complex of cobalt(III) hematoporphyrin in aqueous solution at pH 9.0. Both Walker[8] and Yamamoto and Kwan[9] have reported cobalt(II) tetraphenylporphyrin derivatives having one pyridine coordinated at low pyridine concentrations. Walker[8] also reported cobalt(II) tetra(*p*-methoxyphenyl)porphine being coordinated with two pyridines at high pyridine concentrations. Thus it can be inferred from the data above that cobalt(III) hematoporphyrin is more strongly coordinated than the cobalt(II) complex. Other nitrogenous ligands behave in a similar manner.

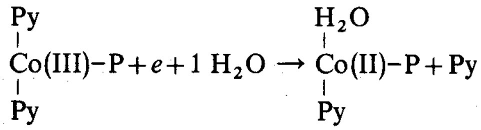
On the basis of these data, the following electrode reactions can be proposed for the pH range 7.5–13.

Low pyridine concentration



$$\underset{\mathrm{Py}}{\overset{\mathrm{Py}}{\mathrm{Co(III)}}}\mathrm{-P} + 2\,H_2O + e \rightarrow \underset{H_2O}{\overset{H_2O}{\mathrm{Co(II)}}}\mathrm{-P} + 2\,\mathrm{Py}$$

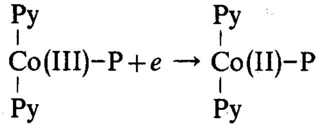
Low pH



$$\underset{\mathrm{Py}}{\overset{\mathrm{Py}}{\mathrm{Co(III)}}}\mathrm{-P} + e + 1\,H_2O \rightarrow \underset{\mathrm{Py}}{\overset{H_2O}{\mathrm{Co(II)}}}\mathrm{-P} + \mathrm{Py}$$

High pH

High pyridine concentration



$$\underset{\mathrm{Py}}{\overset{\mathrm{Py}}{\mathrm{Co(III)}}}\mathrm{-P} + e \rightarrow \underset{\mathrm{Py}}{\overset{\mathrm{Py}}{\mathrm{Co(II)}}}\mathrm{-P}$$

Low pH
and
high pH

Reversibility

The polarographic wave (Fig. 1, Wave B) was carefully investigated and it was concluded that a diffusion-controlled process was involved. Measurements of the diffusion current, i_d, showed that i_d/C was constant for the concentration range 0.253 m*M*–1.523 m*M* at pH 8.70. This also indicated no change in the Stokes'-Einstein radius, *r*, of the diffusion of the complex to the electrode. The diffusion coefficient for cobalt(III) hematoporphyrin was found to be $0.772 \cdot 10^{-6}$ cm^2 s^{-1} in 0.05 *M* sodium hydrogencarbonate and 1.0 *M* sodium nitrate. This can be compared with the value[4] for manganese(III) hematoporphyrin in borax at pH 9.0 which is $0.93 \cdot 10^{-6}$ cm^2 s^{-1}.

It was also found that $i_d h^{-\frac{1}{2}}$, where *h* is the height of the mercury reservoir, was constant, indicating diffusion-control rather than any type of kinetic control.

From the polarograms, the polarographic slope, defined by $E_{\frac{3}{4}} - E_{\frac{1}{4}}$, was found to be dependent on pH. The slope was 109 mV at pH 6.5, 100 mV at pH 8.0, and 82 mV at pH 11.2. These slopes indicate a certain amount of irreversibility, especially at lower pH values.

A number of cyclic voltammograms were recorded at scan rates between 0.06 $V\ s^{-1}$ and 18.0 $V\ s^{-1}$ at pH 8.7. There was no change in the difference between anodic and cathodic peak potentials at the various scan rates, which indicates reversibility. If the electrode process were a typical irreversible one, variations of ΔE_p would be expected[10]. However, the measured ΔE_p values were unusually large.

All the evidence indicates that the electrode reaction is not irreversible in the conventional sense, despite the fact that the polarographic slope is greater than the Nernstian value of 59 mV. Possibly the presence of adsorbed reactant tends to block the electrode surface, thus causing the polarographic slope to be greater than expected and the ΔE_p values to be large[4,11].

Adsorption

Wave B in Fig. 2 may be characterized as an adsorption wave on the basis of the observation that the height of this wave varies linearly with the height of the mercury column above the dropping mercury electrode. As previously stated, for a normal diffusion-controlled reduction wave, the wave height is proportional to the square root of the height of the mercury column. Since this polarographic prewave is indicative of the adsorption of product on the electrode surface, cyclic voltammetry was employed to elucidate the nature of this adsorption process at pH 8.7.

Two functions, which are widely used to elucidate whether the product of this electrode reaction or reactant is being adsorbed, are the cathodic current function, $(i_p)_c/v^{\frac{1}{2}}$, and the ratio of anodic to cathodic peak current function $(i_p)_a/(i_p)_c$. The scan rate is v and $(i_p)_c$ is the cathodic peak current. For a process involving a weak absorption of product, the function $(i_p)_c/v^{\frac{1}{2}}$ is constant and the function $(i_p)_a/(i_p)_c$ increases with the square root of the scan rate[12]. From the data in Table I, it can be said that weak adsorption of product occurs at pH 8.7, because the functions $(i_p)_c/v^{\frac{1}{2}}$ and $(i_p)_a/(i_p)_c$ vary with the square root of the scan rate in the manner previously described.

The presence of product adsorption at this pH can possibly account for the "observed" irreversibility mentioned earlier.

Coupled chemical reactions

The cyclic voltammetric studies showed that at constant concentration at pH 8.7, the ratio of anodic to cathodic peak currents (Table I) increases with scan rate which might also indicate a process in which a reversible chemical reaction precedes the reduction of cobalt(III) to cobalt(II)[13], instead of weak product absorption. However, the invariance of the cathodic current function with scan rate does not verify this hypothesis. This invariance indicates no reaction preceding or following the reduction[13].

A similar study was done at pH 12.0 where the polarographic slope was closest to the reversible slope value of 65 mV (Table I). The ratio of anodic to cathodic current function was found to be approximately constant with scan rate at this pH. Such a relationship suggests either a simple reversible reaction or a reaction in which there is a slow kinetic step following the reduction which regenerates the reactant. The substantial decrease in $(i_p)_c/v^{\frac{1}{2}}$ with increasing scan rate narrows the possibilities to only the case of a catalytic reaction[13]. Precisely what this reaction is has not been determined. Further investigations of this type were not attempted because of adsorption problems.

Ligands other than pyridine

Table II summarizes the polarographic data for the other ligands tested. In general, the concentration of complexing agent was made large enough to assure

TABLE I

CYCLIC VOLTAMMETRIC DATA FOR 1.02 m*M* COBALT HEMATOPORPHYRIN WITH 2.48 *M* PYRIDINE

Scan rate ($V\ s^{-1}$)	$(i_p)_c/v^{\frac{1}{2}}$	$(i_p)_a/(i_p)_c$
pH 8.7		
0.063	3.10	1.08
0.100	3.00	1.00
0.400	3.00	1.37
0.600	3.10	1.10
1.00	3.10	1.23
4.00	4.10	1.35
8.00	3.30	2.27
18.0	3.60	1.85
pH 12.0		
0.072	12.30	0.93
0.090	10.20	0.96
0.270	10.20	0.89
0.450	7.88	0.95
0.720	6.23	1.00

TABLE II

POLAROGRAPHIC DATA FOR NITROGENOUS BASES

(The concentration of cobalt hematoporphyrin was 1.02 m*M*)

Ligand	*Ligand concn. ($mole\ l^{-1}$)*	*$-E_{\frac{1}{2}}$ (V vs. S.C.E.)*		*log $i/i_d - i$ (V)*
Pyridine	2.46	0.436	8.70	0.099
4-Phenylpyridine	0.1	0.384	9.46	0.068
4-Picoline	2.05	0.425	8.80	0.065
4-Acetylpyridine	1.81	0.362	8.50	0.077
Ethyl nicotinate	1.46	0.291	8.78	0.093
4,4′-Bipyridine[a]	0.1	0.300	8.70	0.056
2-Picoline	2.05	0.420	8.80	0.187

[a] Solution prepared from 0.5 *M* stock solution.

complete complexation of both oxidized and reduced forms of the cobalt species. The slopes reported in the last column indicate irreversibility in some cases, but it was shown in the case of pyridine that adsorption was a contributing factor. In any case, it can be said that the various nitrogenous bases tested behave similarly to pyridine.

CONCLUSION

The results of this study have shown that although cobalt(III) hematoporphyrin is incapable of undergoing a reduction in the absence of added ligands, it readily undergoes one in the presence of added nitrogenous bases such as pyridine. Both cobalt(II) and cobalt(III) hematoporphyrin can coordinate two molecules of nitrogenous base ligands, but the reduction of the cobalt(III) hematoporphyrin complex is hampered by the presence of adsorption on the electrode. These findings have prompted a study of cobalt porphyrins in non-aqueous solvents.

This investigation was supported by the National Science Foundation through Grant GP-19749.

SUMMARY

The polarography and cyclic voltammetry of cobalt(III) hematoporphyrin was investigated in buffered aqueous solutions. In the absence of nitrogenous bases, which can act as axial ligands, the cobalt porphyrin is not electroactive. Polarographic waves are found in solutions containing pyridine and similar compounds. Both cobalt(III) and cobalt(II) hematoporphyrin can add two pyridine molecules, although only one ligand may react at lower concentrations. Adsorption problems were encountered.

RÉSUMÉ

Une étude est effectuée sur le comportement de la cobalt(III)–hématoporphyrine en polarographie et voltammétrie cyclique, en milieu aqueux et tampon. En absence de bases azotées, pouvant agir comme ligand axial, la cobalt–porphyrine n'est pas électroactive. Les vagues polarographiques sont obtenues dans des solutions contenant pyridine et composés similaires. On examine également les phénomènes d'adsorption.

ZUSAMMENFASSUNG

Die Polarographie und cyclische Voltammetrie von Kobalt(III)-hämatoporphyrin in gepufferten wässrigen Lösungen wurden untersucht. In Abwesenheit von stickstoffhaltigen Basen, die als axiale Liganden wirken können, ist das Kobaltporphyrin nicht elektroaktiv. Polarographische Stufen treten in Lösungen auf, die Pyridin und ähnliche Verbindungen enthalten. Sowohl Kobalt(III)- als auch Kobalt(II)-hämatoporphyrin kann zwei Pyridinmoleküle anlagern, wenn auch bei niedrigeren Konzentrationen nur ein Ligand reagieren kann. Es traten Adsorptionsprobleme bei dieser Untersuchung auf.

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THE PREPARATION AND ANALYTICAL EVALUATION OF A NEW HETEROGENEOUS MEMBRANE ELECTRODE FOR CADMIUM(II)

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A solid-state electrode for cadmium(II) has been described by Ross[1], who obtained it by pressing a mixture of silver sulfide and cadmium sulfide to form a polycrystalline membrane. A ceramic cadmium sulfide–silver sulfide–copper(I) sulfide electrode selective for cadmium ion has been described by Hirata and Higashiyama[2].

The present paper deals with the preparation of a new heterogeneous membrane electrode for cadmium ion obtained by thermomoulding cadmium sulfide and polythene; its electrochemical properties are evaluated.

EXPERIMENTAL

Preparation of electrodes

The membrane electrodes were prepared as described previously[3] by mixing thoroughly either cadmium sulfide or a mixture of cadmium sulfide and silver sulfide, with polythene in powder, and thermomoulding the mixture in a suitable moulding press on to polythene tubing. The percentage of insoluble salt was about 70%.

Cadmium sulfide and the mixed silver and cadmium sulfides were prepared as follows.

(*a*) Sodium sulfide solution (about 0.1 M) was added to neutral solutions of metal nitrates.

(*b*) Hydrogen sulfide was bubbled into a solution which was 0.1 M in silver nitrate, 0.05 M in cadmium nitrate and 10^{-2} M in perchloric acid. The settled precipitate was washed several times with water and with carbon disulfide and dried at 120°.

(*c*) The salts obtained from the (*a*) or (*b*) procedures were heated to 600°, for 3 h under a stream of hydrogen sulfide. This process is designated in this paper as heat treatment.

The electrochemical behaviour of electrodes made with eight different salt preparations reported by the following numbers has been investigated:

1. Ag_2S–CdS mixture, precipitated with sodium sulfide;
2. Ag_2S–CdS mixture, precipitated from acidic solutions with hydrogen sulfide;

3. Ag_2S–CdS mixture, precipitated with sodium sulfide and submitted to the heat treatment;
4. Ag_2S–CdS mixture precipitated from acidic solutions with hydrogen sulfide and submitted to the heat treatment;
5. CdS precipitated with sodium sulfide;
6. CdS precipitated from acidic solutions with hydrogen sulfide;
7. CdS precipitated with sodium sulfide and submitted to the heat treatment;
8. CdS precipitated from acidic solutions with hydrogen sulfide and submitted to the heat treatment.

Electrode assembly

The cadmium electrodes were assembled in a similar way as other ion-selective electrodes[3]; the internal solution was 10^{-3} *M* cadmium nitrate and 10^{-2} *M* potassium chloride and the internal reference electrode was a silver–silver chloride electrode. The external reference electrode was a saturated calomel electrode. Potentiometric measurements were carried out in the conventional manner with a Beckman Research pH meter 1019.

RESULTS AND DISCUSSION

Response characteristics

The calibration curves were obtained with cadmium nitrate solutions alone or in the presence of 1 *M* sodium nitrate to keep the ionic strength constant. They are plotted in Fig. 1 for electrodes obtained with various salt preparations. No results were obtained with electrodes prepared by method 8, because the membrane

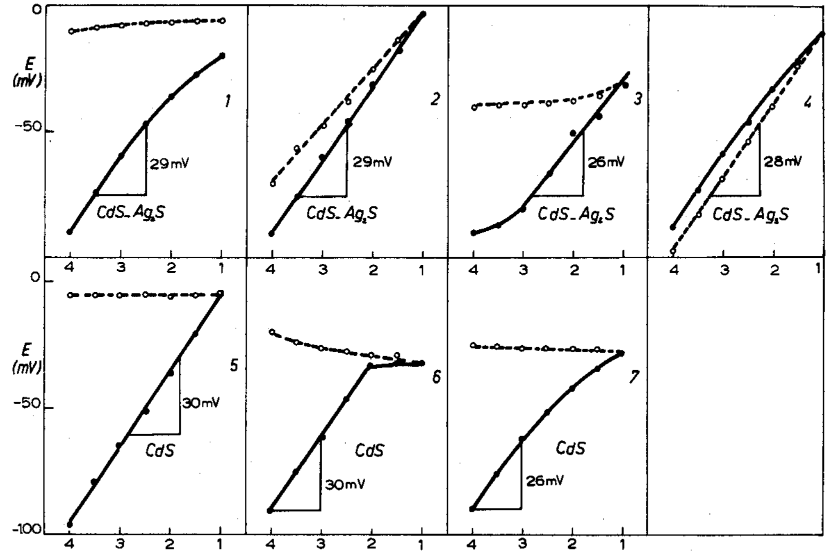


Fig. 1. Calibration curves of electrode types 1–7 for cadmium(II). (●) Pure $Cd(NO_3)_2$ solutions; (○) in the presence of 1 *M* $NaNO_3$.

behaved as an insulator. For each composition at least three electrodes were prepared and the curves reported in Fig. 1 were selected as representative of the behaviour of the electrode. Slight differences among the electrodes of the same kind were observed very likely because of asymmetry effect differences; differences were of the order of 5–10 mV, and the slope difference between two electrodes of the same type was about 2–3 mV.

In solutions of pure cadmium nitrate, the potential varied linearly with log $[Cd^{2+}]$ and the slope in all cases was near to the Nernst value (29.1 mV/decade of concentration).

In the presence of sodium nitrate, the behaviour of the various electrodes was quite different. The electrodes containing only cadmium sulfide in the membrane (5, 6 and 7) became insensitive to variations in cadmium(II) concentration and the measured potential was higher than in pure cadmium(II) solutions. The electrodes containing in the membrane a mixture of silver sulfide and cadmium sulfide had two different behaviours: those obtained by precipitation with sodium sulfide solutions in alkaline conditions (methods 1 and 3) were insensitive to cadmium concentration, while those obtained by methods 2 and 4 again showed Nernstian behaviour. For electrodes prepared by method 4 the calibration curve obtained with pure cadmium nitrate solutions lay above the curve obtained when an inert electrolyte, sodium nitrate, was added. This is in agreement with the Nernst law

$$E = E^0 + (0.059/2)\log[Cd^{2+}]\cdot\gamma_{Cd^{2+}}$$

The addition of an inert electrolyte like sodium nitrate, decreases the activity coefficient, $\gamma_{Cd^{2+}}$, and a lower potential is measured.

Only electrodes made by method 4 showed Nernstian behaviour; the procedure described for its preparation is therefore recommended to obtain an ion-selective cadmium electrode. Electrodes prepared by the other procedures lacked selectivity and exhibited ion-exchanger characteristics with a general cation sensitivity. This behaviour, which has been observed also for lead sulfide electrodes[4], can be explained by assuming the presence of negative free charges on the surface of the crystals, which give rise to a Donnan potential between the internal and external solutions. These negative free charges could be associated with the coprecipitation of polymeric forms between cadmium(II) ions and hydroxide, sulfide or hydrogensulfide at the precipitation stage.

The heat treatment is an effective procedure for the rearrangement of the crystalline structure, as is shown by the behaviour of electrodes made by method 4. In the case of method 8, heat treatment is, however, unsuccessful because cadmium sulfide alone does not exhibit the required conductivity.

This explanation is based on the characteristic of cadmium sulfide single crystals. They are reported[5] as polar solid insulators; small deviations from the stoichiometric composition or the presence of foreign ions greatly affect the electrical properties and the conductivity, which however is always electronic. The heat treatment, which is responsible for a recrystallization process, eliminates lattice defects and as the precipitates tend to acquire a stoichiometric composition a decrease of conductivity is observed.

The addition of silver sulfide to cadmium sulfide in the membrane preparation strongly affected the behaviour of the electrodes. Electrodes made by method 2 (no heat treatment) suffered smaller interfering effects from inert ions such as Na^+ and K^+ and there was no interference at all when the mixture was submitted to heat treatment (method 4).

Silver sulfide is an ionic conductor and the Nernstian behaviour in the presence of inert salts should be related to its presence. It is not clear if the charge transfer in this mixture is electronic or ionic. A silver sulfide membrane electrode is itself insensitive to changes of cadmium ion concentration; the potential of such electrodes in a solution of cadmium(II) is unstable and irreproducible. It seems therefore that cadmium sulfide should be mainly responsible for an exchange mechanism, whereas any charge transfer which may take place either through the Ag_2S itself (ionic) or through crystals doped with cadmium sulfide (electronic) must be attributed to silver sulfide.

An X-ray investigation was made to correlate diffraction patterns with electrochemical behaviour. Only the diffraction lines of silver and cadmium sulfides were observed; the intensities of the lines were similar. This technique does not seem to offer useful indications for characterization of membrane mixtures.

Resistance measurements of the different mixtures were carried out as described in the literature[6]. Large variations in the resistance values (1–100 mΩ) were measured among electrodes of the same batch. These measurements also have a limited utility for the evaluation of the electrodes.

Analytical evaluation of the electrodes

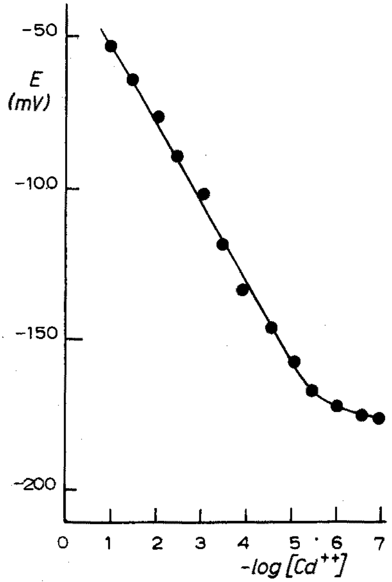
The analytical characteristics of electrodes prepared by method 4 were evaluated as follows:

Limit of detection. The calibration curve (Fig. 2) was plotted to determine the sensitivity limit. The electrode had a linear response to 10^{-5} M but indicated any changes in concentration down to 10^{-7} M; this is the limit of detection for the total concentration of cadmium in solution. As is shown later, the electrode followed the concentration of free cadmium(II) ions at quite low values when cadmium(II) was measured in the presence of complexing species.

Behaviour in mixed solvents. The use of this electrode in mixed solvents was investigated by examining the calibration curves in (1+1) acetone–water and (1+1) dioxane–water (Fig. 3). In these solvents the slope was about 19 mV per decade of concentration. This application is rendered possible by the thermoplastic junction of the membrane to the polythene tubing, which is achieved without adhesives.

pH effect. The E–pH diagram is shown in Fig. 4. The pH was adjusted with nitric acid or sodium hydroxide. The formation of cadmium hydroxide limits the application in the alkaline range.

Interferences. Ions which yield sulfides less soluble than cadmium sulfide (Ag^+, Hg^{2+}, Cu^{2+}) interfere as they react with the membrane material and affect its composition. The interfering effect of other ions which yield sulfides is reported in Table I; it can be predicted from the solubility product value. Iron(III) at low pH interfered quite strongly at fairly low concentrations; this must be attributed to a redox effect[4].



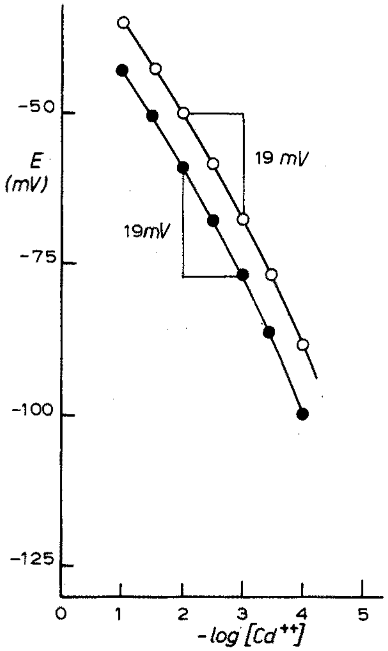


Fig. 2. Calibration curve and limit of detection of electrode type 4.

Fig. 3. Calibration curve in nonaqueous media. (○) 1:4 dioxane 50%; (●) acetone 50%.

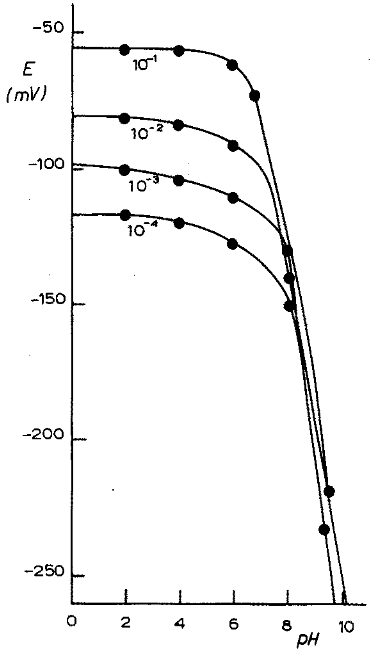


Fig. 4. *E*–pH diagram. The pH was varied by adding either HNO_3 or NaOH.

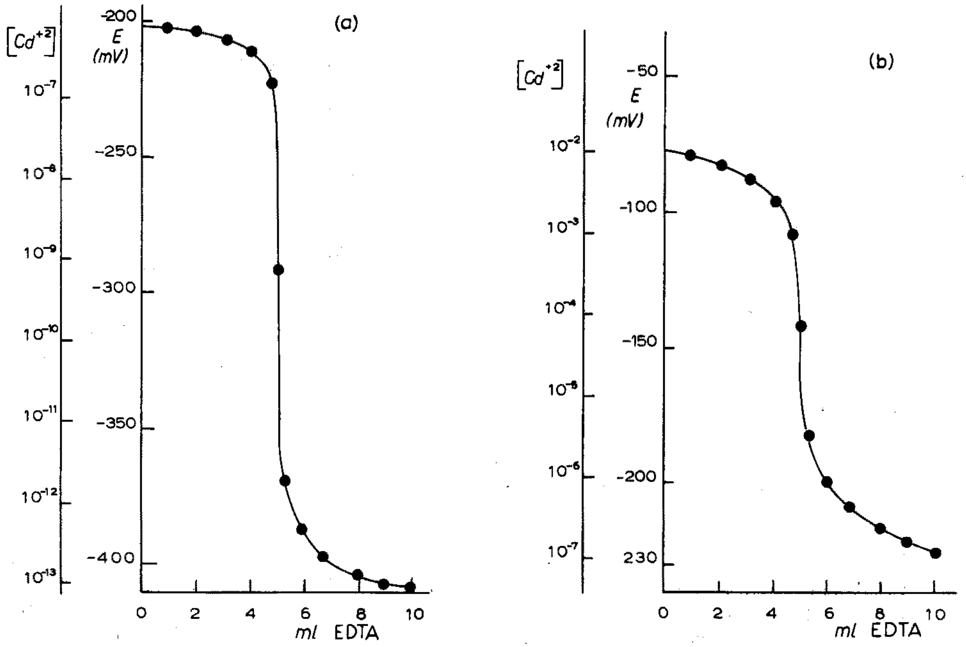


Fig. 5. EDTA titration. 50 ml of 0.01 M $Cd(NO_3)_2$, 0.1 M in buffer, are titrated with 0.1 M EDTA. (a) Ammonia buffer; (b) acetic buffer.

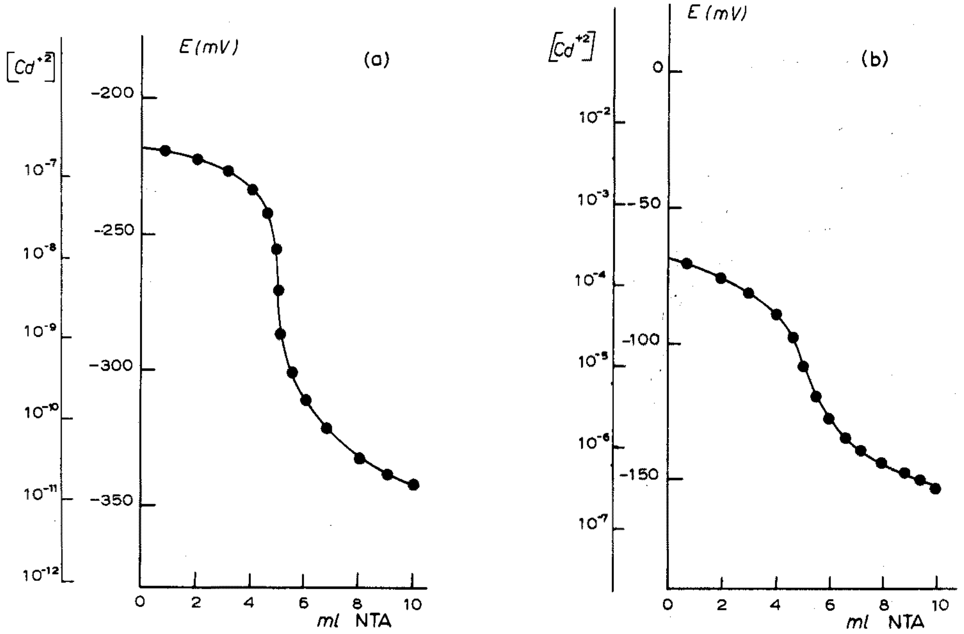


Fig. 6. Nitrilotriacetic titration. 50 ml of 0.01 M $Cd(NO_3)_2$, 0.1 M in buffer, are titrated with 0.1 M NTA. (a) Ammonia buffer; (b) acetic buffer.

TABLE I

INTERFERING EFFECT OF VARIOUS IONS ON THE CdS ELECTRODE BEHAVIOUR

Interfering ion (M)		pK_{s_0}[a]	K_{CdX}[b]
H^+	10^{-2}	7; 13.1	$5 \cdot 10^{-4}$
Pb^{2+}	10^{-2}	27.9	$5 \cdot 10^{-1}$
Zn^{2+}	10^{-1}	23.8	10^{-4}
Co^{2+}	10^{-1}	20.4	$5 \cdot 10^{-5}$
Ni^{2+}	10^{-1}	18.5	$5 \cdot 10^{-6}$
Fe^{3+}[c]	10^{-3}	—	$3 \cdot 10^{-2}$
	10^{-4}		$4 \cdot 10^{2}$

[a] Solubility product of metal sulfide.

[b] K_{CdX} was calculated by measuring the e.m.f. in solutions containing a fixed amount of interfering ion with varying amounts of the cadmium ion, and calculating K_{CdX} by eqn. (4) of the paper of Moody and Thomas[7]:

$$K_{CdX} = (10^{(E_2 - E_1)/\text{slope}} - 1)/(a_X{}^{2/x}/a_{Cd})$$

where E_1 is the e.m.f. with only cadmium ions, E_2 is the e.m.f. in the presence of interfering and cadmium ions, X is the interfering ion and x its charge.

[c] The solution was at pH 0 (perchloric acid).

Complex formation studies. In Figs. 5 and 6 are shown the potentiometric titration curves of cadmium solution with EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid) under different experimental conditions (ammonia and acetate buffer). The concentration of cadmium(II) ion reported on the ordinates,

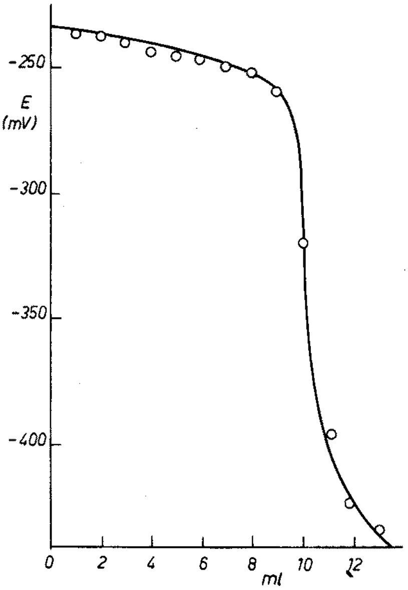


Fig. 7. Precipitation titration with 8-hydroxyquinoline. 50 ml of 10^{-2} M Cd^{2+} are titrated with 0.1 M 8-hydroxyquinoline in ammonia buffer in (1 + 1) water–1,4-dioxane medium.

was calculated from the potential values by applying the Nernst law. It is clear that the free concentration is far lower than the detection limit calculated for Fig. 3 by dilution.

The electrode can also be used in nonaqueous medium; Fig. 7 shows the precipitation titration of cadmium(II) with 8-hydroxyquinoline in the presence of ammonia buffer in a (1+1) dioxane–water medium.

SUMMARY

The preparation of a new cadmium-selective heterogeneous membrane electrode obtained by hot-pressing a mixture of cadmium and silver sulfides with polythene in a moulding press is described. Nernstian response to cadmium ion was achieved only when the mixture of salts was purified by heat treatment at 600° in an atmosphere of hydrogen sulfide for several hours. This behaviour is discussed in terms of the purity of the salts. Interferences and analytical applications in aqueous and nonaqueous solvents are described.

RÉSUMÉ

On décrit la préparation d'une nouvelle électrode à membrane sélective hétérogène, obtenue par compression à chaud d'un mélange de sulfures de cadmium et d'argent, avec du polythène. La réponse nernstienne au cadmium n'est obtenue qu'après purification du mélange de sels par traitement thermique à 600°, dans une atmosphère de sulfure d'hydrogène, pendant plusieurs heures. On examine les interférences et applications analytiques en milieu aqueux et non-aqueux.

ZUSAMMENFASSUNG

Es wird eine neue cadmiumselektive heterogene Membranelektrode beschrieben, für deren Herstellung ein Gemisch von Cadmiumsulfid und Silbersulfid mit Polythene in einer Formpresse unter Wärmeeinwirkung zusammengepresst wird. Nernstsches Verhalten gegenüber Cadmiumionen wurde nur erhalten, wenn das Gemisch der Salze gereinigt wurde, indem es für mehrere Stunden bei 600° einer Atmosphäre von Schwefelwasserstoff ausgesetzt wurde. Dieses Verhalten wird hinsichtlich der Reinheit der Salze diskutiert. Störungen sowie analytische Anwendungen in wässrigen und nichtwässrigen Lösungen werden beschrieben.

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REVERSED-PHASE FOAM CHROMATOGRAPHY

REDOX REACTIONS ON OPEN-CELL POLYURETHANE FOAM COLUMNS SUPPORTING TETRACHLOROHYDROQUINONE

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Work on the application of foamed supports in reversed-phase partition chromatography has been carried out in this laboratory[1,2]. It was found that polyurethane foam retains a considerable amount of organic extractant more efficiently than Kel-F powder (polytrifluorochloroethylene), which is considered as one of the best granular support for reversed-phase extraction chromatography. Also, the hydrodynamic properties and the kinetics of adsorption, exchange and partition[2] on foam-packed chromatographic columns proved to be extremely favourable. As a further extension, the application of polyurethane foam as a support for chloranil (tetrachloro-*p*-benzoquinone) in redox columns was investigated in the present study.

Cerrai and Testa[3] suggested the use of water-insoluble substituted hydroquinones coated on an inert support as a redox system suitable for column operation. They recommended the application of columns packed with tetrachlorohydroquinone supported on Kel-F powder as a practical analytical tool.

In a critical study, Belcher *et al.*[4] examined a wide variety of substituted hydroquinones supported on various supports. They proved that the water-insolubility of the redox compound is the most important factor and that adsorptive forces play little or no part in a stationary phase–support system. Finally, they also recommended the use of tetrachlorohydroquinone coated on Kel-F powder as an advantageous redox column. It was reported[4] that this redox column was superior to the Jones reductor column for the determination of iron and vanadium.

Although the results obtained by applying columns packed with tetrachlorohydroquinone-loaded Kel-F powder were very promising, yet the slowness of operation of these columns is still a serious disadvantage. This may be due to the fact that only relatively low flow-rates (max. 2–4 ml min^{-1}) can be achieved with columns packed with Kel-F powder or any other granular support.

In the present work, the use of elastic polyurethane foam as the support for chloranil was examined.

EXPERIMENTAL

Reagents and materials

"Pure" grade chloranil was recrystallized from chlorobenzene or by sublimation under vacuum.

All metal salts and inorganic acids were of reagent grade and were used without further purification. Flexible polyurethane foam, a polyether of open cell-type (North Hungarian Chemical Works, Sajóbábony, Hungary), was used as the supporting material.

Iron, vanadium and cerium solutions were standardized by the usual standard methods.

Apparatus

Glass columns of 15 mm diameter and 15 cm long were used. A separating funnel was fitted at the top of the column as a reservoir of the eluting solution.

Column preparation

The polyurethane foam was washed 3 times with acetone and then dried at 80°. The chloranil solution was prepared by dissolving 1 or 3 g of the pure recrystallized substance in 50 ml of chlorobenzene or methyl isobutyl ketone (hexone) at *ca.* 80°. The dried foam material (3 g) was placed in a glass dish, which was kept in a drying oven at 80°, and the chloranil solution was added to it in successive 10-ml aliquots. After each 10-ml addition, the solvent was removed by thoroughly mixing the foam material with a glass rod. After the addition of the 50 ml of chloranil solution, the solvent was removed until a dry loaded foam was obtained. The dried loaded foam material was then packed as described previously[2]. Ascorbic acid (100 ml of 0.2 *N*) was used for the reduction of the column at a flow-rate of 2–4 ml min^{-1} and at room temperature.

Experiments at controlled temperature were performed with jacketed columns in which thermostated water was circulated.

Procedures

Determination of cerium(IV). The foam column in the reduced form was washed with 1 *M* sulfuric acid and 2 ml of cerium(IV) sulfate solution in 1 *M* sulfuric acid were allowed to pass through it at the flow-rate mentioned in the text. The column was then washed with 50 ml of 1 *M* sulfuric acid and finally with distilled water. Ascorbic acid (4 ml of 0.2 *N*) was then passed through the column at a flow-rate of 2–4 ml min^{-1}. The column was washed with 60 ml of distilled water and the combined eluate was titrated with 0.1 *N* iodine solution. The amount of cerium(IV) reduced was considered to be equivalent to the difference between the original quantity of ascorbic acid added to the column and that determined in the effluent[3,4].

Determination of vanadium(V). The column was washed with 1 *M* sulfuric acid and 2 ml of ammonium vanadate solution in 1 *M* sulfuric acid were passed through it. After washing with 50 ml of 1 *M* sulfuric acid and distilled water, 4 ml of 0.2 *N* ascorbic acid were then added followed by 60 ml of distilled water as eluant. The combined eluate was then titrated with 0.1 *N* iodine solution.

Determination of iron(III). The foam column was washed with 0.03 *M* hydrochloric acid and 2 ml of iron(III) chloride solution in 0.03 *M* hydrochloric acid were passed through it. The column was then washed with 50 ml of 0.03 *M* hydrochloric acid and distilled water. Ascorbic acid (4 ml of 0.2 *N*) was added and the column was finally washed with 60 ml of distilled water. The combined eluate was titrated with 0.1 *N* iodine solution.

RESULTS AND DISCUSSION

The application of foamed inert support in reversed-phase extraction chromatography is based on the relatively high available surface area of the foam material which is responsible for the high uptake of the organic extractant[1,2]. In previous work[2] on reversed-phase partition chromatography, the rate of extraction of palladium–thiourea complex by polyurethane foam loaded with tri-*n*-butyl phosphate, as investigated by batch technique, was found to be fast, and the equilibrium adsorption of the palladium complex was attained rapidly. Furthermore, columns packed with foam material showed better hydrodynamic properties than columns filled with other known reliable granular supports, even on applying the recently recommended[5] vacuum technique of packing.

Polyurethane foam was found to hold chloranil in a finely divided state and so it may be used in column operation, in place of Kel-F powder, keeping all the advantages of foam-filled columns. In order to examine the possibility of using polyurethane foam as a support for chloranil or tetrachlorohydroquinone in column operation a detailed study of various factors had to be carried out. These factors are illustrated below.

Effect of the amount of the loaded redox reagent on the capacity of the column

The practical usefulness of a column packed with foam material loaded with chloranil can be tested by measuring its break-through capacity. Two columns were prepared in which the amount of the dry foam material was the same, but the chloranil loading solution was of different concentration. The first column was packed with 3 g of polyurethane foam which had previously been loaded with 1 g of chloranil in 50 ml of chlorobenzene, and the second with the same amount of foam material but the loading solution contained 3 g of chloranil. Aliquots (5 ml) of 0.1 *M* cerium(IV) sulfate solution were allowed to pass through the columns at a flow-rate of 4 ml min^{-1} at room temperature. After washing with 75 ml of 1 *M* sulfuric acid, the combined eluate after each addition was titrated with 0.1 *N* sodium thiosulfate solution in presence of excess of potassium iodide. Plots of the percentage of reduced cerium(IV) against the volume of cerium(IV) sulfate solution added to the column are shown in Fig. 1, which shows that the break-through curve of the first column (1 g of chloranil/3 g of foam) is sharper than that of the second column (3 g of chloranil/3 g of foam). Presumably, the crystals of redox reagent loaded on the foam material from dilute solution will be finer than those from the more concentrated solution; in the latter case, the redox reagent would have more chance to form bigger crystals. Clearly, the reaction between cerium(IV) and the finely divided chloranil would be more rapid than that with the coarse crystals. It was also noticed that a significant amount of the redox reagent was crystallized on the internal surface of the glass dish, which was used as a container, when the concentrated solution was used to load the foam material.

Effect of temperature and flow-rate on the reduction efficiency of the column

The effect of temperature and flow-rate on column efficiency was tested by the reduction of cerium(IV), vanadium(V) and iron(III) at a wide range of flow-rates and at 35° and room temperatures.

Figure 2 represents the variation of the amount of cerium(IV) reduced on the foam-filled column as a function of the flow-rate over the range 2–11 ml min^{-1} at room temperature. It is clear from the curve that 2 ml of 0.0851 *M* cerium(IV) sulfate were completely reduced at all the flow-rates applied.

In case of vanadium(V), on the other hand, the reduction of 2 ml of 0.0853 *N* ammonium vanadate was quantitative only at flow-rates in the range 2–4 ml min^{-1}. Flow-rates higher than 4 ml min^{-1} gave incomplete reduction (*cf.* Fig. 3). This suggests that the reaction rate of tetrachlorohydroquinone with vanadium(V) is slower than that with cerium(IV). The application of relatively low flow-rates in the reduction of vanadium(V) and iron(III) on columns packed with tetrachlorohydroquinone held on Kel-F powder by Cerrai and Testa[3] supports this conclusion. However, when the temperature of the foam-filled column was increased

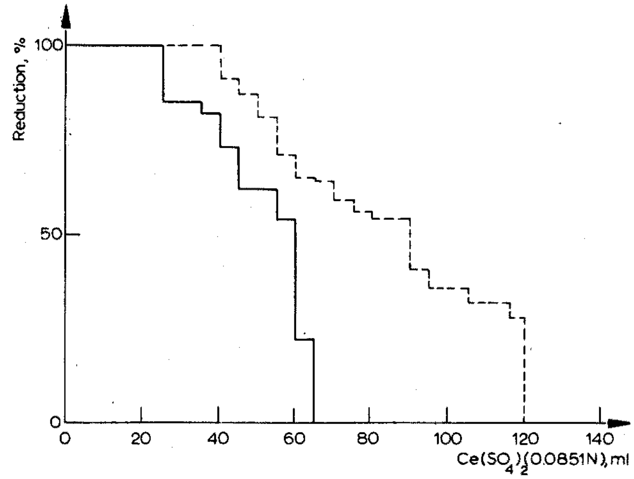
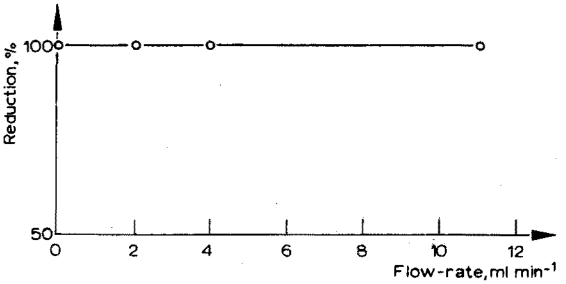


Fig. 1. Break-through capacity curve of cerium(IV) reduction on columns packed with open-cell polyurethane foam loaded with various amounts of chloranil. (——) 1 g chloranil/3 g dry foam; (–––) 3 g chloranil/3 g dry foam.



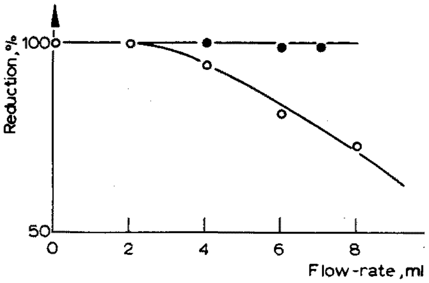


Fig. 2. Effect of the flow-rate on the reduction of cerium(IV). Ce: 0.1702 meq; eluent: 1 *M* H_2SO_4; room temperature.

Fig. 3. Effect of the flow-rate and temperature on the reduction of vanadium(V). V: 0.1706 meq. (○) Room temperature; (●) 35°. Eluent: 1 *M* H_2SO_4.

to 35°, quantitative reduction of vanadium(V) was obtained even when a flow-rate as high as 7 ml min^{-1} was applied (Fig. 3).

The curves of Fig. 4 show the reduction efficiency for iron(III) on the foam-filled column at various flow-rates and at 35° and room temperature. At room temperature the reduction was only complete at a flow-rate up to 2 ml min^{-1}. As is clear from the curves, reduction of iron(III) was quantitative at flow-rates of 1–6 ml min^{-1} on applying a temperature of 35°.

Applying the developed foam column for the reduction of cerium(IV), vanadium(V) and iron(III) gave quantitative results. It was also possible to make a further measurement of the amount of the ion reduced, by determining the amount of tetrachlorohydroquinone oxidized on the column by passing a known volume of standard solution of ascorbic acid through it and titrating the effluent with standard iodine solution. The results using this column "memory"[3] method are given in Table I.

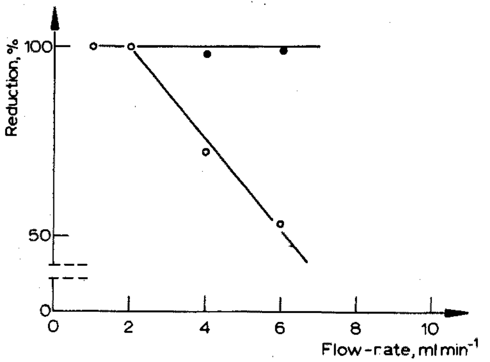


Fig. 4. Effect of the flow-rate and temperature on the reduction of iron(III). Fe: 0.1975 meq; eluent: 0.03 *M* HCl. (○) Room temperature; (●) 35°.

TABLE I

DETERMINATION OF CERIUM(IV), VANADIUM(V) AND IRON(III) BY COLUMN "MEMORY"

Ion determined	*Amount (mg)*		*Average* $(\bar{X})$	*Deviation* $(X-\bar{X})$	*Variance*[a]	*Standard deviation* (σ)	*Standard error* $\sigma/\sqrt{n}$
	Present	*Found*					
Ce(IV)	76.57	78.15		+1.47			
		77.38		+0.70			
		76.21	76.68	−0.47	1.1576	1.076	0.481
		76.21		−0.47			
		75.44		−1.24			
V(V)	21.22	21.27		−0.08			
		21.83	21.35	+0.48	0.2025	0.45	0.260
		20.94		−0.41			
Fe(III)	54.06	52.13		−1.46			
		54.33	53.59	+0.74	1.6134	1.27	0.734
		54.33		+0.74			

[a] $\sigma^2 = \Sigma(X-\bar{X})^2/(n-1)$.

The standard deviations obtained in the determinations of cerium(IV), vanadium(V) and iron(III) were 1.076, 0.45 and 1.27, respectively, with a standard error of 0.48, 0.26 and 0.73. This recommends the use of foam redox columns for the reduction of these ions. The packed columns could be used over 30 reduction cycles without losing their efficiency.

SUMMARY

The use of elastic polyurethane foam as a support for chloranil was proved successful. Reductions of cerium(IV), vanadium(V) and iron(II) on foam-filled columns were carried out quantitatively and rapidly. The effect of flow-rate and temperature on the reduction of each metal ion was examined in detail. Cerium(IV) was reduced quantitatively on passing through the foam-redox column at flow-rates of 2–11 ml min^{-1} at room temperature. The reduction of vanadium(V) and iron(III) was slower; complete reduction occurred only at flow-rates up to 4 and 2 ml min^{-1} for V(V) and Fe(III), respectively. At 35°, however, it was possible to use flow-rates of 7 and 6 ml min^{-1} for the quantitative reduction of V(V) and Fe(III), respectively.

RÉSUMÉ

On a utilisé avec succès une mousse de polyuréthane élastique comme support de la tétrachlorohydroquinone. Des réductions de cérium(IV), vanadium(V) et fer(III) ont été effectuées sur ces colonnes de mousse, quantitativement et rapidement. On examine l'influence de la vitesse de débit et de la température.

ZUSAMMENFASSUNG

Elastischer Polyurethan-Schaum wurde mit Erfolg als Träger für Chloranil verwendet. Die Reduktion von Cer(IV), Vanadin(V) und Eisen(III) in Säulen mit Schaumpackungen verlief quantitativ und schnell. Der Einfluss der Fliessgeschwindigkeit und der Temperatur auf die Reduktion wurde für jedes Metallion im einzelnen untersucht. Cer(IV) wurde beim Durchgang durch die Schaum-Redox-Säule bei Fliessgeschwindigkeiten von 2–11 ml min^{-1} bei Raumtemperatur quantitativ reduziert. Die Reduktion von Vanadin(V) und Eisen(III) verlief langsamer; eine vollständige Reduktion von V(V) und Fe(III) wurde nur bei Fliessgeschwindigkeiten unterhalb 4 bzw. 2 ml min^{-1} erzielt. Bei 35° waren jedoch für die quantitative Reduktion von V(V) und Fe(III) Fliessgeschwindigkeiten von 7 bzw. 6 ml min^{-1} möglich.

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REVERSED-PHASE FOAM CHROMATOGRAPHY

SEPARATION OF TRACE AMOUNTS OF COBALT FROM NICKEL IN THE TRI-*n*-OCTYLAMINE–HYDROCHLORIC ACID SYSTEM

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Tri-*n*-octylamine was first used by Cerrai and Testa[1] as a stationary phase in hydrochloric acid medium for the extraction chromatographic separation of cobalt from nickel. To separate 5 mg of the two metals from each other, they used a column filled with cellulose as support and eluted the metals with 8 *M* and 3 *M* hydrochloric acid, respectively. Their investigation has not been extended to other concentration ratios. In later experiments, Krefeld *et al.*[2] proved that the trioctylamine-loaded cellulose deteriorated under the action of 8 *M* hydrochloric acid, and the column could not be used for more than two elutions.

Smułek and Zelenay[3] loaded tri-*n*-octylamine on Kieselguhr (Hyflo Supercell) support to study more thoroughly the separation of cobalt from nickel in hydrochloric acid medium. They separated cobalt from nickel, but still in a restricted range of concentrations. A considerable drawback of their method is that it requires pressurized columns and even so the maximum flow rate is about 0.09 ml min^{-1}. The total capacity of their column is also relatively low (about 4 mg of cobalt).

It seemed of interest to investigate the applicability of the recently described foam chromatographic method[4,5] to the tri-*n*-octylamine–hydrochloric acid system. These experiments were thought to be useful, in particular, because the reports published to date on extraction chromatographic experiments do not cover the cobalt–nickel separation in a wide range of concentrations; moreover, because cobalt is a frequent contaminant of nickel salts, the determination of cobalt in the presence of nickel presents a current analytical problem. Similarly, the post-irradiation separation of ^{58}Co produced from ^{58}Ni activated in nickel metal or salts by irradiation with fast neutrons is an important radiochemical preparative method[6] for the production of carrier-free ^{58}Co.

Tri-*n*-octylamine reacts with hydrochloric acid according to the equation:

$$[R_3N]_o + H^+ + Cl^- \rightleftharpoons [R_3NH^+Cl^-]_o \quad \text{where } R = -CH_2-(CH_2)_6-CH_3.$$

The amine salt thus formed acts as a liquid anion exchanger and reacts with the metal chloride complex present in the aqueous phase[7] in the sequence

$$m(R_3NH^+Cl^-)_o + (MCl^{m-}_{m+n})_{aq} \rightleftharpoons (R_3NH)_m(MCl_{m+n})_o + m(Cl^-)_{aq}$$

where o and aq stand for the organic and aqueous phase, respectively. This mechanism is also valid in the case of extraction chromatography[8].

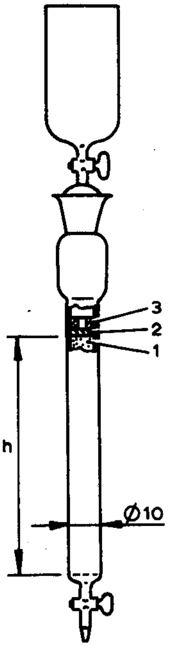
The separation of cobalt from nickel by extraction with tri-*n*-octylamine from hydrochloric acid medium is made possible by the tendency of cobalt to form chlorocomplexes and depends on the stability of the complexes thus formed. It has been shown that cobalt forms with hydrochloric acid predominantly the $CoCl_4^{2-}$ species and is extracted in this form in the organic phase[9]. Nickel, on the other hand, is not extractable from hydrochloric acid solutions with long-chain amines[10]. On this principle cobalt can be separated from nickel.

This paper describes an experimental study of the preparation and applicability of chromatographic columns filled with the open-cell polyether-type polyurethane foam as inert support[4,5], loaded with tri-*n*-octylamine as stationary phase, for the separation of traces of cobalt from nickel in hydrochloric acid medium.

EXPERIMENTAL

Reagents and materials

All chemicals were of reagent grade, unless otherwise stated. Tri-*n*-octylamine (Fluka, Switzerland) was of technical grade, and was found to contain 97% trioctylamine, as titrated with hydrochloric acid. The open-cell polyether-type foam was produced by the North Hungarian Chemical Works, Sajóbábony, Hungary. Carrier-free ^{58}Co (cobalt(II) chloride) was supplied by the Institute of Isotopes of the Hungarian Academy of Sciences.



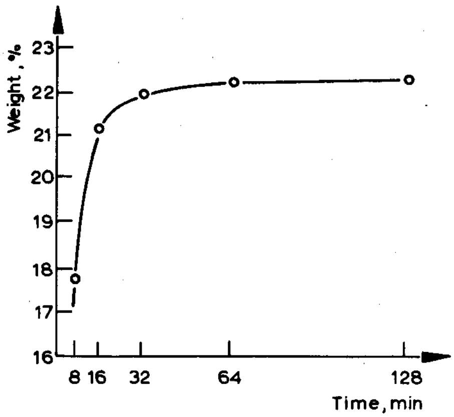


Fig. 1. Foam chromatographic column. (1) Foam packing; (2) polyethylene net; (3) polycarbonate ring.

Fig. 2. Time dependence of the tri-*n*-octylamine hydrochloride uptake by polyurethane foam.

Equipment

The chromatographic columns were 10 mm in diameter and about 20 cm long. Stoppered jars and mechanical shakers were used in the batch experiments. For activity measurements, a NaI(Tl) scintillation detector and a 1024-channel analyser (Type KFKI, Hungary) were used.

Column preparation

The column was filled as described previously[5]. In order to reduce the dead volume, the earlier form of the column was modified as shown in Fig. 1.

Analytical methods

A given quantity of the test solution was evaporated to dryness in a Teflon cup on a sand bath, and then diluted with water to about 10 ml. The pH of the solution was adjusted to 4–5 with the addition of concentrated ammonia solution and 60% acetic acid. Copper was titrated with 0.01 *M* EDTA in the presence of PAN indicator. Nickel, cobalt and iron was determined by back-titration of excess of 0.01 *M* EDTA with copper(II) solution (PAN indicator)[11]. Cobalt was measured radiometrically.

RESULTS AND DISCUSSION

"Batch" experiments

Foamed polyurethane as support for tri-n-octylamine. Before use the polyurethane foam was washed with benzene which was then removed at 85°. About 0.2 g of dry foam was cut to small cubes with 3–6 mm edges and shaken for various periods with a solution of 0.1 *M* tri-*n*-octylamine in benzene equilibrated with 6.0 *M* hydrochloric acid. After shaking, the foam was dried between two sheets of filter paper, and then the benzene was left to evaporate for 2 h in a drying oven at 85°. The amount of the amine fixed was determined gravimetrically and plotted as a function of the shaking time (Fig. 2). The loaded foam turned brownish and became less elastic. The curve shows that the maximum load (22.4 wt.%, saturation value) which could be taken up by the foam under these conditions was reached in about 30 min.

The dependence of the tri-*n*-octylamine load on the concentration of tri-*n*-octylamine hydrochloride (TOA–HCl equilibrated with 6.0 *M* hydrochloric acid dissolved in benzene) was also measured. As the TOA–HCl uptake increased, the elasticity of the foam gradually decreased. This phenomenon was already observed on a foam treated with a solution of 0.2 *M* TOA·HCl in benzene.

The uptake of tri-*n*-octylamine hydrochloride could not be increased by repeated treatment with a 1.0 *M* solution of TOA–HCl in benzene, the load remaining around 55% for any number of treatments. However, when a 1.0 *M* solution of tri-*n*-octylamine in benzene previously equilibrated with the stoichiometric amount of 1.0 *M* hydrochloric acid was used, instead of a solution of TOA·HCl equilibrated with 6.0 *M* hydrochloric acid in benzene, the uptake of tri-*n*-octylamine hydrochloride could be increased to about 67 wt.%.

The subsequent batch experiments and part of the column experiments were performed with a foam loaded to 67% with tri-*n*-octylamine hydrochloride.

Distribution ratios of cobalt, nickel, iron and copper in hydrochloric acid medium. The distribution ratios were determined for cobalt, nickel, iron(III) and copper ions at different concentrations of hydrochloric acid. The foam loaded with tri-*n*-octylamine hydrochloride was first equilibrated with hydrochloric acid of the required concentration by shaking for 20 min, then dried between two sheets of filter paper, and put into the shaker to be shaken until the equilibrium distribution with the solution containing the metal was achieved.

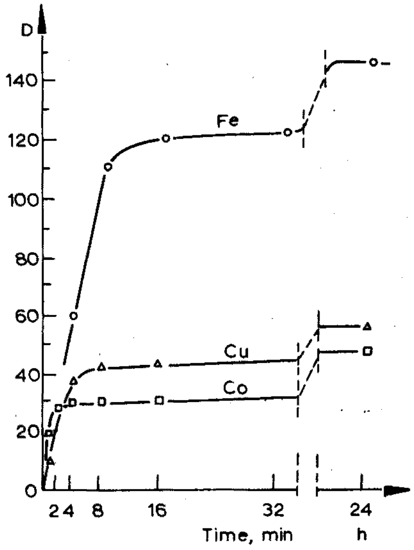
The equilibrium distribution ratio of the metal at the given acid concentration was calculated from the measured values as

$$D = \frac{g_o/V_o}{g_{aq}/V_{aq}}$$

where g_o and g_{aq} are the quantities of metal measured on the foam and in the aqueous phase, and V_o and V_{aq} are the volumes of the organic phase (retained on the foam) and the aqueous phase, respectively.

The starting metal concentration of the experimental solution was of the order of 1 mg ml^{-1}. The time dependence of the equilibrium distributions shown in Fig. 3 was plotted from the values measured at the acid concentration which gave the maximum distribution ratio for the metal in question.

The distribution ratio *vs.* hydrochloric acid concentration curves for cobalt, iron and copper are presented in Fig. 4. The distribution ratio of nickel was found to be negligible at any acid concentration. It can be seen that higher acid concentrations favour the separation of cobalt from nickel.



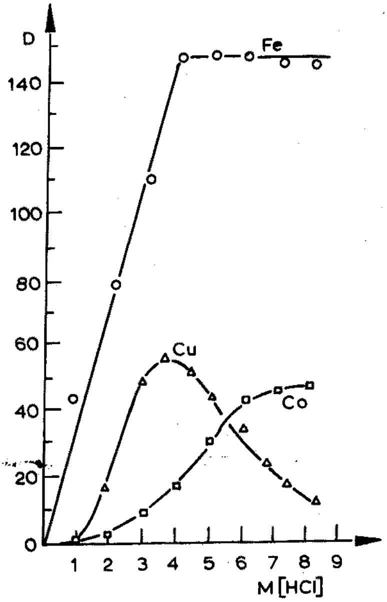


Fig. 3. Cobalt, copper and iron distribution ratios *vs.* shaking time.

Fig. 4. Cobalt, copper and iron distribution ratios *vs.* hydrochloric acid concentration of the aqueous phase.

Column experiments

Evaluation of interstitial volume. To evaluate the interstitial volume, the breakthrough curve for nickel, which showed zero retention, was measured. A nickel chloride solution was fed to the column until the effluent showed the same concentration as that of the feed solution. The latter was then left to sink to the top level of the packing before the column was washed with nickel-free 2 *M* hydrochloric acid until no nickel could be detected with PAN indicator in the effluent upon neutralization. From the nickel concentration of the collected effluent, compared with that of the feed solution, the total of the interstitial plus dead volume was calculated from the amount of nickel present on the column and in the lower capillary. The interstitial volume of the columns varied in these experiments from 60 to 80% of the total column volume.

Investigation of support inertness. Elution tests for cobalt, nickel, iron and copper were carried out on columns filled with unloaded polyurethane foam, to see whether the support was completely inert or not, *i.e.*, to check the zero retention in hydrochloric acid medium for each of the four metals. The results of the elution tests (Table I) showed nearly zero retention of the four metal ions; thus the support can be regarded as essentially inert.

TABLE I

ELUTION OF COBALT, NICKEL AND COPPER ON UNLOADED POLYURETHANE COLUMN

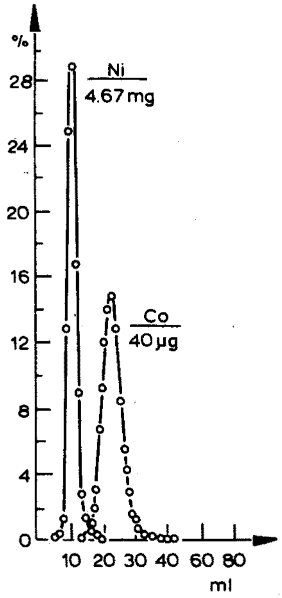
(The eluent volume was 30 ml in all cases)

Taken (mg)		*Eluent*	*Eluted*	
			mg	%
Ni	4.67	1 *M* HCl	4.70	100.6
(1 *M* HCl)	4.67	1 *M* HCl	4.68	100.2
Fe	2.0	0.02 *M* HNO_3	1.98	99.0
(4 *M* HCl)	2.0	0.02 *M* HNO_3	2.02	101.0
Cu	4.88	1 *M* HCl	4.84	99.2
(4 *M* HCl)	4.88	1 *M* HCl	4.86	99.6
Co	3.72	1 *M* HCl	3.79	101.9
(8 *M* HCl)	1.00	1 *M* HCl	1.03	103.5

Separation of cobalt from nickel on TOA·HCl–polyurethane column

The first experiments with polyurethane columns loaded (to about 67%) with tri-*n*-octylamine hydrochloride showed that, in spite of the reasonably symmetrical elution peaks, only 85–88% of the metal placed on the column (about 1.0 mg) could be eluted at the applied flow rate of 1.0 ml min^{-1}. This is probably due to retardation of the kinetic processes in the thick tri-*n*-octylamine hydrochloride layer loaded on the foam. Experiments were therefore carried out on columns with three different lower percentage loads (3.8%, 11.4%, and 17.7%).

The results of the separations on the column loaded with 3.8% tri-*n*-octylamine hydrochloride (Fig. 5) showed that with this low load, separation was incomplete.



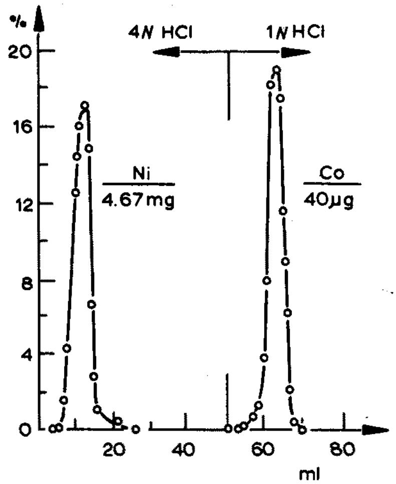
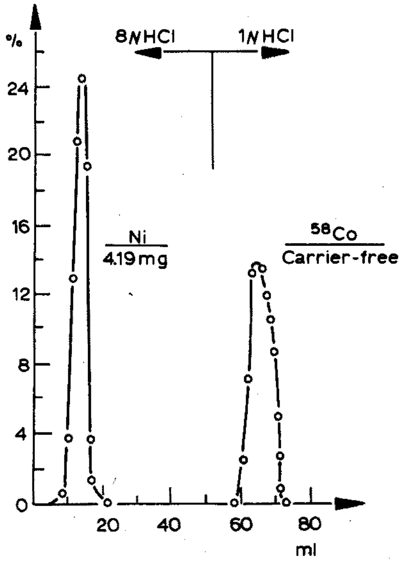


Fig. 5. Nickel–cobalt separation. Support: polyether-type polyurethane foam; stationary phase: 3.8% TOA · HCl; flow-rate: 1 ml min^{-1}; nickel elution: 99.9%; cobalt elution: 100.7%.

Fig. 6. Nickel–cobalt separation. Stationary phase: 11.4% TOA · HCl. Support and flow-rate as for Fig. 5. Nickel elution: 94.5%; cobalt elution: 99.5%.



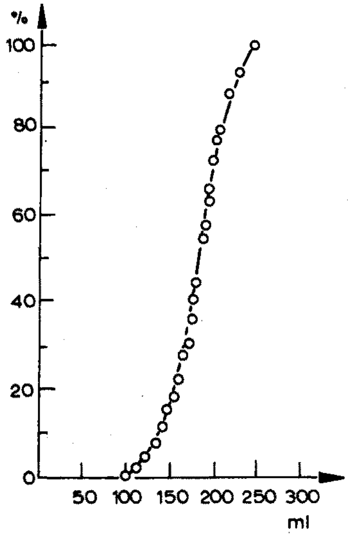


Fig. 7. Separation of carrier-free ^{58}Co from nickel. Stationary phase: 17.7% TOA · HCl. Support and flow-rate as for Fig. 5. Nickel elution: 99.6%; cobalt elution: 101.6%.

Fig. 8. Break-through curve for cobalt. Weight of packing: 2.4323 g. Support and flow-rate as in Fig. 5. Stationary phase: 17.7% TOA · HCl. Cobalt concentration: 0.07 mg ml^{-1}.

The results for the column with a load of 11.4% (Fig. 6) showed that nickel passed through the column without any retention, and that the cobalt retained on the column could be subsequently eluted with 1 *M* hydrochloric acid solution; thus a column with this load provided a satisfactory separation of cobalt from nickel. Good results were also obtained with a 17.7% load; Fig. 7 shows the separation of carrier-free ^{58}Co from nickel.

Measurement of the break-through curve for cobalt

The column capacity was evaluated as 12.075 mg from the break-through data (Fig. 8) obtained on a column loaded to 17.7% for a cobalt feed solution with a concentration of 0.07 mg ml^{-1}.

Analytical application

It was thought of interest to establish the relative quantities at which cobalt can be successfully separated from nickel. This parameter is often omitted from reports on extraction chromatographic separation, though it is obvious that the range of separable quantities is an important characteristic of the performance of a method.

The measurements to this end were performed by using feed solutions containing cobalt and nickel at various relative concentrations. The column was loaded to 17.7%; nickel was eluted with 8 *M* hydrochloric acid, and cobalt with 1 *M* hydrochloric acid, and the volume of the eluate was kept in both cases at 30 ml. The results of the measurement are listed in Table II.

TABLE II

NICKEL–COBALT SEPARATION

Ni:Co ratio	*Taken*		*Found*			
	Ni (mg)	*Co (mg)*	*Ni (mg)*	*Co (mg)*	*Ni (%)*	*Co (%)*
1	0.537	0.500	0.558	0.509	103.9	101.7
	0.537	0.500	0.542	0.498	100.9	99.6
	0.537	0.500	0.531	0.510	98.7	102.0
10	0.537	$5\cdot10^{-2}$	0.547	$4.97\cdot10^{-2}$	101.9	99.1
	0.537	$5\cdot10^{-2}$	0.540	$5.04\cdot10^{-2}$	100.6	100.8
	0.537	$5\cdot10^{-2}$	0.551	$4.99\cdot10^{-2}$	102.6	99.7
10^2	0.537	$5\cdot10^{-3}$	0.547	$4.93\cdot10^{-3}$	101.9	98.6
	0.537	$5\cdot10^{-3}$	0.527	$5.05\cdot10^{-3}$	98.1	100.9
	0.537	$5\cdot10^{-3}$	0.542	$5.06\cdot10^{-3}$	100.9	101.2
10^3	0.537	$5\cdot10^{-4}$	0.532	$5.04\cdot10^{-4}$	99.0	100.7
	0.537	$5\cdot10^{-4}$	0.539	$4.96\cdot10^{-4}$	100.4	99.1
	0.537	$5\cdot10^{-4}$	0.544	$5.15\cdot10^{-4}$	101.3	102.9
10^8	4.19	$4\cdot10^{-8}$	4.17	$4.06\cdot10^{-8}$	99.5	101.6
	4.19	$4\cdot10^{-8}$	4.22	$4.04\cdot10^{-8}$	100.7	100.9
	4.19	$4\cdot10^{-8}$	4.23	$3.99\cdot10^{-8}$	101.0	99.8

SUMMARY

The separation of cobalt and nickel in hydrochloric acid media by reversed-phase chromatography on open-cell polyether-type polyurethane foam columns loaded with tri-*n*-octylamine hydrochloride has been studied. The results showed that good results are obtained with 11.4 and 17.7% loadings of the amine. The separation was studied in the Ni:Co range from 1 to 10^8.

RÉSUMÉ

Une étude est effectuée sur la séparation cobalt–nickel, en milieu acide chlorhydrique, par chromatographie sur colonnes de mousse de type polyuréthane. Le rapport Ni:Co est de l'ordre de 1 à 10^8.

ZUSAMMENFASSUNG

Kobalt und Nickel werden in salzsaurem Medium durch Chromatographie mit umgekehrten Phasen getrennt, wobei Säulen verwendet werden, in denen offenzelliger Polyurethan-Schaum vom Polyäther-Typ mit Tri-*n*-octylaminhydrochlorid beladen ist. Gute Ergebnisse wurden bei 11.4 und 17.7%-iger Aminbeladung erhalten. Die Trennung wurde untersucht in dem Ni:Co-Bereich von 1 bis 10^8.

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THE INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF THE SULPHATE ION WITH 2-AMINOPERIMIDINE

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The determination of small amounts of sulphate ion by simple spectrophotometric procedures depends on a few well-tried methods, such as the conversion of sulphate to hydrogen sulphide and thence methylene blue[1], the liberation of chloranilic acid from barium chloranilate[2], or the precipitation and dissolution of benzidine sulphate[3]. Each method has its own distinct drawbacks and recent work has been directed towards spectroscopic analysis for sulphur ions[4]. This does not, however, solve the immediate problem of providing the analyst with a simple process for the determination of this very common anion.

Over twenty years ago, studies of the analytical chemistry of benzidine and related compounds led to the development of the compound 4-amino-4′-chlorobiphenyl hydrochloride as a highly sensitive precipitant for the sulphate ion[5]. The precipitated sulphate was then determined by direct alkalimetry and the reagent found application for the determination of sulphur in a variety of materials. Jones and Letham[6], also in this Department, were able to apply the reagent in a submicro procedure for the determination of sulphur in nucleic acid residues after Carius oxidation. The high molar absorptivity (*ca.* 23,000) of the amine cation in dilute aqueous acidic solution at 254 nm provided an accurate determination of the amount of amine remaining in solution after precipitation of the test sample containing 5–30 μg of sulphate. Ahmed and Lawson[7] later adapted the procedure to deal with milligram amounts of sulphate. Unfortunately, it was assumed quite erroneously that, in common with its parent, 4-aminobiphenyl, the amine was carcinogenic, and its manufacture was stopped by most chemical supply houses, with the result that the reagent is now virtually unobtainable.

The great sensitivity of this precipitation reaction was further exploited in turbidimetry by Martin and Stephen[8], whose method enabled amounts of sulphate in the range 1–25 μg ml^{-1} to be determined. This remained the most sensitive procedure for sulphate until Stephen[9] introduced the novel reagent 2-aminoperimidine hydrochloride in a simple nephelometric method. During development of 2-aminoperimidine as a reagent for the precipitation of the sulphate ion, the amine cation was examined spectrophotometrically and found to absorb quite strongly in the ultraviolet region. This suggested that a simple spectrophotometric procedure might be developed which would provide a useful alternative to the nephelometric method[10,11].

Spectrophotometry of 2-aminoperimidine cation

The u.v. absorption spectrum (Fig. 1) of an aqueous solution of 2-aminoperimidine hydrochloride shows a double peak in the u.v. (200–230 nm) and a rather broad peak at 305 nm. This latter peak is very suitable for analytical work; it is broad enough to minimize the effect of small errors in wavelength setting and it occurs in a region of the spectrum where measurements are reliable. A solution of the amine salt in the concentration range 10^{-4}–10^{-5} *M* shows complete conformity with Beer's law and gives a value for the molar absorptivity of the reagent of 7230.

Preliminary quantitative studies

The high sensitivity of the precipitation reaction of 2-aminoperimidine with sulphate ions can be used to the full in procedures which do not require the isolation of the precipitate. In common with other amine salts, 2-aminoperimidine sulphate is much less soluble in a solution of the precipitant than in water; errors arising from losses of material either mechanically or from enhanced solubility in wash liquids are completely eliminated if no isolation is involved. Initial work indicated that in order for an amount of sulphate in the p.p.m. range to cause an easily measurable change in the absorbance of the reagent, only a small volume of 0.5% reagent could be used. For the range 10–80 p.p.m. of sulphate, it proved suitable to treat the sulphate solution with no more than 0.25 ml of a saturated solution of 2-aminoperimidine hydrochloride. Complete precipitation occurred

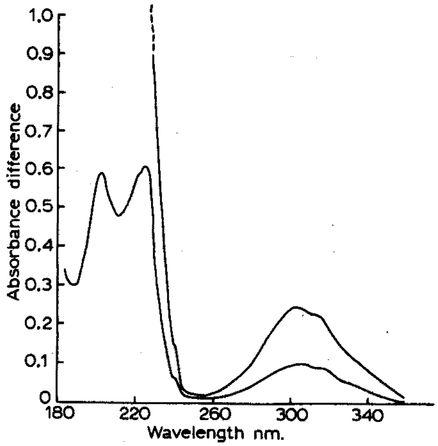

Fig. 1. Ultraviolet spectrum of 2-aminoperimidine hydrochloride.

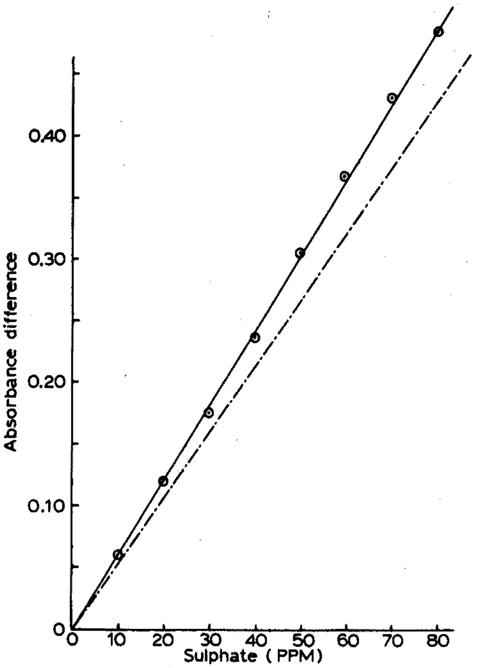

Fig. 2. Plot of difference in absorbance between sample and blank *vs.* sulphate concentration at 605 nm. (——) Practical calibration; (–·–) theoretical calibration.

immediately, but the precipitates were stored for 30 min before being centrifuged. A 1-ml portion of the clear supernatant liquid was then diluted to 25 ml for subsequent measurement of absorbance.

The results of the calibration are shown in Fig. 2, where the differences between the absorbances of the reagent blank and the sample solutions are plotted against concentration of sulphate. This procedure eliminates errors arising from day-to-day variation in the strength of the reagent. However, when the theoretical sulphate concentrations were calculated on the basis of the absorbances recorded in Fig. 1, from the relationship

$$SO_4^{2-} \text{ concn. (p.p.m.)} = \text{absorbance difference} \cdot 186.8$$

(calculated on the molar absorptivity, dilution factors, etc.), a constant positive error of 10–15% was incurred. This error is shown by the difference from the broken line in Fig. 2 which describes the theoretical calibration.

It had been hoped that recoveries of reagent could be made very close to theory, so that a simple calculation could be used instead of calibration. These findings required an investigation into the cause of this quite significant error and how it might be eliminated.

STUDIES OF THE PRECIPITATION REACTION

Although Stephen[9] had established the best conditions for the formation of a stable suspension of 2-aminoperimidine sulphate for purposes of nephelometry, the requirements for the spectrophotometric method were not necessarily similar. However, the large positive errors obtained following the procedure described above were quite unexpected. Indeed, a process such as this involving a precipitation reaction is much more likely to lead to negative errors because of incomplete precipitation. The constant positive error over a wide range of sulphate concentrations seemed to indicate either that the reaction of the amine with sulphuric acid is not stoicheiometric, or that the reagent coprecipitates strongly under the experimental conditions.

Mole ratio measurements resulted in the discovery that the ratio of reagent to sulphate does not correspond to the assumed theoretical value of 2, but is nearer to 2.3, and when this value is used in the calculations, the results are no longer at variance with the expected values.

Similar mole ratio experiments with iodate, sulphite and phosphate as examples of mono-, di- and trivalent ions which provide sparingly soluble salts with 2-aminoperimidine were carried out. Results with iodate and sulphite indicated normal stoicheiometries for the 2-aminoperimidine–anion reaction, *i.e.* 1:1 and 2:1 respectively; but even with fairly concentrated solutions of phosphate, the reaction was incomplete and no mole ratio data were obtained. Results with the selenate ion, the ion most likely to resemble sulphate, were even more striking. The deviation from theory was very much greater than in the case of sulphate, and indicated a mole ratio of 2.7:1.

During the course of these experiments, the various precipitates were observed to behave differently. The iodate and sulphite salts flocculate quite rapidly, particularly in the presence of an excess of reagent. This is in marked contrast to the behaviour of the sulphate and selenate salts which show little tendency to settle out even after long periods of time. This stability of its suspensions is, after all, the main advantage of 2-aminoperimidine sulphate in the nephelometric procedure[9].

These results would indicate that the errors in the spectrophotometric procedure for the sulphate ion are probably caused by reagent coprecipitation. However, direct gravimetric analyses on 10-mg amounts of sulphate, which should give a theoretical yield of 48.4 mg of 2-aminoperimidine sulphate, gave actual yields of 48.9, 48.6 and 49.5 mg. Elemental analyses of the precipitates obtained gave acceptable values for carbon, hydrogen, nitrogen and sulphur, based on the 2:1 stoicheiometry, with no evidence for the presence of chlorine in the samples. These results indicate that the high molar ratio obtained in the spectrophotometric method is probably caused by surface adsorption of the reagent in solution, and not by mixed crystal formation or non-stoichiometric reaction.

Attempts to reduce or eliminate the supposed adsorption of reagent included the use of a weaker solution of the reagent, a wider range of pH for the precipitation (as low as 2.2 and as high as 8.0), and the addition of ethanol in amounts up to 30% of the final volume of solution. In every case, results remained as before and the differences from the theoretical values were still 10–15%.

Development of empirical method

As all attempts to bring the yield nearer to 100% led to no improvement, the empirical method was examined to see if its range and reproducibility were good enough for general use. Few, or no, problems were experienced in extending the general procedure to deal with three ranges of sulphate concentration, namely 4–20 p.p.m., 10–60 p.p.m., 20–120 p.p.m. All that is necessary is the adjustment of reagent volume and final dilution for the different ranges. Calibration curves are completely linear for the individual ranges. The relative standard deviations are shown in Table I and indicate a very satisfactory precision for the analytical procedure.

TABLE I

PRECISION AND ACCURACY DATA

Concn. of sulphate (p.p.m.)	*No. of detns.*	*Mean value of absorbance difference*	s	s_r
50.0	20	0.3031	0.0112	3.7
10.0	20	0.167	0.0084	5.0

Interferences

The effect of phosphate ions on the determination was studied in more detail than that of other ions, particularly because of its frequent association with sulphate in organic and biochemical analysis. In isolation, phosphate is precipitated by 2-aminoperimidine at concentrations of 1 mg ml^{-1}, but with 100 μg ml^{-1}, no precipitation is evident even after some hours of storage. With 50 p.p.m. of

TABLE II

EFFECT OF INTERFERENCES

Concn. of sulphate taken (p.p.m.)	*Added ion (p.p.m.)*		*Absorbance difference at 305 nm*	*Concn. of sulphate found (p.p.m.)*
50.0	—		0.303±0.011	50.0±1.8
50.0	PO_4^{3-}	50.0	0.306	50.5
50.0	PO_4^{3-}	75.0	0.304	50.0
50.0	PO_4^{3-}	100.0	0.318	52.5
50.0	PO_4^{3-}	200.0	0.333	54.5
10.0	—		0.167±0.008	10±0.5
10.0	PO_4^{3-}	25.0	0.170	10.2
10.0	PO_4^{3-}	50.0	0.165	9.8
10.0	PO_4^{3-}	100.0	0.200	12.0
50.0	F^-	100.0	0.295	48.0
50.0	F^-	500.0	0.330	54.0
50.0	NO_3^-	100.0	0.310	51.0
50.0	NO_3^-	500.0	0.510	84.0

sulphate, 100 $\mu g\ ml^{-1}$ of phosphate showed only a marginal effect (results only a little above one standard deviation higher than the mean); with 200 $\mu g\ ml^{-1}$, the interference was 9%. The effects were similar at the 10 p.p.m. sulphate level (Table II). This interference is considerably less than in the nephelometric procedure. The presence of 500 p.p.m. of acetate, chloride, bromide and iodide had no significant effect on the determination of 50 p.p.m. of sulphate, but fluoride, nitrate and carbonate did interfere. The effect of fluoride was not too serious; even when 500 p.p.m. were present, the error was only +4%. Nitrate at the same concentration resulted in a positive 60% error; but at 100 p.p.m., there was no adverse effect. Carbonate affected the determination mainly through its effect on the pH of the solution. Provided that the pH was not greater than 8, results were not unduly affected. Because of its ready elimination, carbonate is not considered a serious interference. Ions such as iodate, sulphite and selenate which react quite sensitively with the reagent must be absent. A fuller list of such interferences is given in the account of the nephelometric method[9].

Cations such as lead and barium which precipitate sulphate should be absent, but copper, iron, magnesium and calcium can be tolerated in amounts much greater than those normally associated with sulphate in surface and rain waters.

EXPERIMENTAL

Reagents

2-Aminoperimidine hydrochloride was prepared as described previously[9]. The reagent was further purified by boiling a saturated aqueous solution with charcoal, filtering and leaving the salt to crystallize. A 0.5% (saturated) solution in water was used as reagent solution. Amounts were prepared as required and stored in a dark coloured bottle. The solution was stable for some days if stored in a tightly closed container in a dark place.

A standard sulphate solution was prepared from freshly dried A.R. potassium sulphate; 0.9071 g dissolved in water and diluted to 500 ml gave a stock solution containing 1 mg SO_4^{2-} ml^{-1}.

Apparatus

Precipitation reactions were performed in 3-ml Pyrex centrifuge tubes which were sealed with "Parafilm" to prevent contamination during storage time. Centrifuging was done in a small bench electric centrifuge operating at 2000 r.p.m. A Beckman DB spectrophotometer was used with 1-cm matched silica cells for absorbance measurements.

Procedures

10–60 p.p.m. of sulphate. To a 2-ml volume of standard sulphate solution or test solution containing 10–60 p.p.m. of sulphate in a centrifuge tube, add exactly 0.25 ml of the 2-aminoperimidine solution. Mix well, cover the mouth of the tube with "Parafilm" and leave for 30 min. Centrifuge the precipitate of 2-aminoperimidine sulphate for 2 min, remove a 1.0-ml portion of the clear supernatant liquid to a 25-ml calibrated flask, and dilute to volume. Transfer sufficient solution to a 1-cm silica cell and measure the absorbance at 305 nm against water in the reference cell. Repeat the procedure with 2 ml of pure water to obtain the blank reading.

20–120 p.p.m. of sulphate. As above, but use 0.50 ml of the 2-aminoperimidine solution, and dilute 0.50 ml of the supernatant liquid to 25 ml.

4–20 p.p.m. of sulphate. As above, but use 0.10 ml of the 2-aminoperimidine solution and dilute 1.0 ml of the supernatant liquid to 10 ml.

DISCUSSION

The new method enables the indirect spectrophotometric determination of sulphate to be carried out simply and accurately. With calibration graphs, satisfactory results are obtained for sulphate concentrations in the range 4–120 p.p.m. with a relative standard deviation of 5% or less. The empirical mole ratio of 2.3 can be used with the molar absorptivity to calculate the concentration of sulphate without recourse to calibration graphs, but this may not prove to be entirely satisfactory for general analysis, because the value may change under different conditions. Nevertheless, the new method is ideally suited to the determination of sulphate in raw or treated natural waters of low mineral content, particularly rain and surface waters. It is not suitable for untreated sea water because the high chloride concentration would lead to precipitation of the reagent by common ion effect. The method could also be used for organic analysis after combustion of the sample in a tube or oxygen flask, or for biochemical determinations where the presence of possible interfering species is minimal. Although phosphate begins to interfere at concentrations above 100 p.p.m., it is still not too significant at 200 p.p.m., but if the error is unacceptably high for the required determination, it could be eliminated by first precipitating the phosphate as magnesium ammonium phosphate. Jones and Letham found this satisfactory in the 4-amino-4′-chlorobiphenyl procedure[6].

Compared with this earlier method, which it most closely resembles, the present method is simpler and more sensitive.

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SUMMARY

A new spectrophotometric determination of the sulphate ion is described which uses 2-aminoperimidine hydrochloride as a precipitating reagent. The excess of the reagent is measured at 305 nm. The procedure deals with sulphate in the range 4–120 p.p.m., and relies on simple calibration. The relative standard deviation for 50 p.p.m. of sulphate is 3.7%. The interference of 100 p.p.m. of phosphate, fluoride and nitrate is only slight in the determination of 50 p.p.m. of sulphate. The method is recommended for the determination of sulphate in rain and surface waters.

RÉSUMÉ

On propose une nouvelle méthode de dosage spectrophotométrique des sulfates, au moyen de chlorhydrate d'amino-2-perimidine comme réactif de précipitation. Le réactif en excès est mesuré à 305 nm. Ce procédé permet l'analyse de quantités de l'ordre de 4 à 120 p.p.m. La déviation standard relative est de 3.7% pour 50 p.p.m. de sulfate. 100 p.p.m. de phosphate, de fluorure et de nitrate ne présentent qu'une faible interférence sur le dosage de 50 p.p.m. de sulfate. Cette méthode est recommandée pour le dosage des sulfates dans les eaux de pluie et de surface.

ZUSAMMENFASSUNG

Es wird eine neue spektrophotometrische Bestimmungsmethode für Sulfationen beschrieben, bei der 2-Aminoperimidinhydrochlorid als Fällungsreagenz verwendet wird. Der Überschuss des Reagenzes wird bei 305 nm gemessen. Das Verfahren ist auf Sulfat im Bereich 4–120 p.p.m. anwendbar und beruht auf einer einfachen Eichung. Die relative Standardabweichung für 50 p.p.m. Sulfat ist 3.7%. Die Störung durch 100 p.p.m. Phosphat, Fluorid und Nitrat bei der Bestimmung von 50 p.p.m. Sulfat ist nur gering. Die Methode wird für die Bestimmung von Sulfat in Regen- und Oberflächenwasser empfohlen.

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THE DETERMINATION OF MANGANESE IN URINE BY ATOMIC ABSORPTION SPECTROMETRY*

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Manganese is an essential element for all organisms studied. The functions of manganese are varied. Brain symptoms accompanying manganese poisoning resemble those of Parkinson's disease, and both conditions have responded to administration of L-dihydroxyphenylalanine (DOPA)[1]. Elevation of serum manganese is claimed as one of the more accurate indicators of myocardial infarction[2]. An elevated urine manganese has been associated with schizophrenia[3]. Although manganese promotes the synthesis of liver cholesterol[4], data suggest that it can also reduce the cholesterol content of atherosclerotic lesions of aortic tissue[5]. Preliminary evidence hints that urinary excretion of manganese does not follow a diurnal variation[6].

Confirmation and interrelation of the biochemical manifestations of manganese require improvement of analytical methodology for this element. In trace analysis, the sensitivities by colorimetry cannot be surpassed except by neutron activation[7]. However, several of the recommended colorimetric and catalytic methods for manganese lack reliability[8–12]. Few of these techniques are applicable to the region 0.6–6.0 p.p.b. Mn, which includes the reported ranges for serum[13], whole blood[13], and urine[14,15].

Several authors[16–18] have proposed atomic absorption as an alternative to neutron activation for manganese analysis of bio-fluids. These procedures appear either to involve fairly extensive sample preparation or to have inadequate detection limits. Ebdon *et al.*[19], in using a carbon filament atom reservoir for manganese determination by atomic absorption, found severe interferences from substances which would appear in biological material at high concentrations. Delaughter[20] and Takeuchi *et al.*[21] have briefly investigated the cupferron–methyl isobutyl ketone system for manganese extraction. For the elimination of organic matter in urine, Simon *et al.*[22] have adapted a wet-digestion procedure[23] utilizing HNO_3–H_2SO_4–$HClO_4$ (about 10:5:1) with addition of molybdate as catalyst.

The present paper describes the development of an atomic absorption procedure for the determination of urine manganese. A catalytic wet digestion of the urine is followed by cupferron extraction into methyl isobutyl ketone to yield

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stable extracts of urine manganese at concentration levels quantifiable by atomic absorption spectrometry. The catalytic digestion and the cupferron extraction contribute to a shorter and more direct manganese analysis of urine samples. Readily available reagents and commercial equipment are specified, and the technique is not limited by contamination problems. A modified standard-addition technique insures optimal accuracy. The testing of extraction systems and the investigation of possible interferences are both described.

EXPERIMENTAL

Reagents

All chemicals used were reagent grade except for tris(hydroxymethyl)aminomethane (TRIS), which was Calbiochem A-grade. Chemicals were used as received without further purification. All deionized water was obtained by allowing tap water to pass through a carbon-particle filter followed by a mixed-bed ion-exchange column (Corning, Ultra-High Purity). This two-component purification apparatus yielded water which could not be further reduced in manganese content by distillation through a Corning AG-lb still. The water from the exchanger contained organic matter, as evidenced by frothing. This organic material, perhaps plasticizer from the exchange resin, could not be completely removed by distillation. The deionized water usually contained less than 1 p.p.b. manganese as determined by a standard addition–extraction technique similar to that described for the Recovery studies.

Standard manganese(II) stock solutions containing 1.0–4.8 p.p.m. (μg ml^{-1}) were prepared by dissolving the appropriate weight of manganese metal (99.9%) in nitric acid. Contained in a polyethylene bottle with 0.1 *M* nitric acid, a 1.0 p.p.m. manganese(II) solution showed no change in atomic absorption over a period of one year.

Preparation of the modified Cummins' reagent (MCR) was patterned after the formulation of Simon *et al.*[22]. For an approximately 330-ml portion, dissolve 6 g of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) in 150 ml of deionized water, add 150 ml of concentrated sulfuric acid with cooling, then add 30 ml of 70% perchloric acid.

Apparatus

All atomic absorption measurements were made with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. A Boling burner head was employed with an air–acetylene flame. A manganese hollow-cathode lamp (Perkin-Elmer, Intensitron) served as light source. The absorption measurements were recorded on a Servo/Riter II Potentiometric Recorder (Texas Instruments, Inc.) coupled to the Perkin-Elmer Recorder Readout Accessory. Increased noise accompanying scale expansion of the recorder was counteracted by adjusting the filter circuit (shifting the noise suppression control) of the accessory to provide an increased time constant.

The Kjeldahl digestion flasks (Pyrex) were cleaned by boiling in each flask 100 ml of 1 *M* sodium hydroxide. Boiling time was 5 min; the boiling was accompanied by occasional rotation of the flask. After the alkali cleaning, the flasks were thoroughly rinsed with tap water followed by 4–6 rinses with deionized water. All other glassware and utensils were cleaned by tap- and deionized-water rinses after an ordinary soap-and-water washing. Each of the Kjeldahl flasks contained a tooled pouring lip with a groove opposite the lip to facilitate quantitative pouring.

Recommended procedure

Clean the 500-ml Kjeldahl flasks and glass beads as described above. For each replicate add to each of two 500-ml Kjeldahl flasks, each containing three glass boiling beads: 100 ml of urine, 10 ml of concentrated nitric acid, and 20 ml of MCR. Rapidly bring the contents of the flasks to a boil over Meker burners or heating mantles. After about 35 min, foaming and dense white fumes appear. Digestion may be considered finished about 1 min later, when foaming subsides. At this point the digests will have turned colorless and clear. After the digests are cool, proceed with each flask as follows:

Add carefully, to avoid spattering, 20.0 ml of concentrated ammonia solution. Add 10.0 ml of 1 *M* TRIS (which yields 0.04 *M* final solution). Add sufficient concentrated ammonia solution to raise the pH to 7 as estimated with pH paper.

The following step is optional: to reduce turbidity or the extent of precipation, add 3.0 g of sodium citrate dihydrate to each digestion flask, and warm to dissolve the citrate and to facilitate clarification; this provides a 0.04 *M* citrate solution.

Transfer, with three small rinsings, the contents of each digestion flask into separate 250-ml volumetric flasks. (The procedure may be interrupted overnight at this step, but should be carried straight through after adding cupferron, due to the instability of aqueous cupferron.) To one of the volumetric flasks add 1.0 ml of 2.5 p.p.m. manganese(II) solution; and to the other flask add 2.0 ml of 2.5 p.p.m. manganese(II) solution. These amounts will constitute standard additions of 10.0 and 20.0 p.p.b. (ng ml^{-1}), respectively, in the final aqueous solutions. Add 1.6 g of cupferron dissolved in a small quantity of water (which yields 0.4 *M* solution). Dilute to volume. Pipet 150.0 ml of each preparation into a separate 250-ml separatory funnel fitted with a Teflon stopcock and a glass stopper.

With the solution containing the 10.0 p.p.b. standard addition, perform a 5-stage extraction by extracting with five 6-ml portions of MIBK (methyl isobutyl ketone). Shake the funnel for 1 min after each 6-ml addition of solvent. Collect the six portions of MIBK in a small polyethylene bottle. The aqueous phase, for re-extraction, should be collected in a polyethylene beaker, which requires no rinsing. Allow 5 min for phase separation after the fifth shaking.

With the solution containing the 20.0 p.p.b. standard addition, perform a three-stage extraction in similar manner, but utilizing three 10-ml portions of MIBK.

Set the instrument controls of the atomic absorption spectrophotometer to the values recommended in Table I or as previously determined for the instrument available. To measure percent absorption, solutions can conveniently be aspirated from small, disposable, polyethylene tubes.

Perform a blank determination by repeating the above procedure without addition of urine or any substitute for it.

If desired, perform extractions from deionized water, according to the method described in the Recovery studies, of 10.0 and 20.0 p.p.b. manganese(II) to use as comparison solutions. Occasional aspiration of a comparison solution, between samples, provides a correction factor for evaluating the true sample absorbance in the event of instrumental drift (which often occurs). The comparison solutions also can be used to verify the linearity of sample absorbance *vs.* concentration by the procedure described under Recovery studies.

TABLE I

ATOMIC ABSORPTION SPECTROMETER SETTINGS RECOMMENDED FOR DETERMINING MANGANESE

Instrument	Perkin-Elmer Model 303	
Wavelength setting	279.7 nm	
Slit	Position 4 (1.0 mm)	
Source	15 mA	
Burner height	Position 0	
Flow rate positions[a]		
	MIBK extracts	*Aqueous solutions*
air	7–9 (about 18 l min^{-1})	9 (20 l min^{-1})
acetylene	4 (2 l min^{-1})	9 (4 l min^{-1})
Gas pressures		
air	30 p.s.i.	
acetylene	8 p.s.i.	

[a] Flow rates in l min^{-1} interpolated from graph supplied by manufacturer.

Calculate the concentration of urinary manganese, C_x, (uncorrected for blank) as follows:

$$C_x = \frac{25(2.0\,A_1 - A_2)}{A_2 - A_1}$$

where A_1 is percent absorption of the extract containing the 10.0 p.p.b. manganese(II) addition and A_2 is the percent absorption of the extract containing the 20.0 p.p.b. manganese(II) addition. (Percent absorption is very nearly proportional to concentration in the region below about 10% absorption.)

The manganese concentration in the blank can be obtained by dividing the result calculated from eqn. (1) by the factor 2.5.

Instrumental parameters

The optimal spectrophotometer adjustments determined in this study are listed in Table I. The settings agree with recommendations of other authors and with the instruction manual for the spectrophotometer used in this study. A slit width of 1.0 mm at a wavelength setting of 279.7 nm admits a manganese triplet in the 279.5- to 280.1-nm region. With the burner height at position 0, the optical path passes through the base of the flame.

RESULTS AND DISCUSSION

Measurement of limits of determination

In order that an instrumental finish contributes only a small fraction to the overall random error of the analysis, a sufficient signal-to-noise ratio must be available for measuring concentrations in the range expected for the samples. The question of including a preconcentration step to achieve an adequate signal can be resolved after comparing the measured *determination limit* with the expected analyte concentration. The determination limit, as defined by Parsons[24], is the concentration of analyte which provides a signal-to-noise ratio, S/N, sufficient for analysis at a pre-assigned relative standard deviation, s_r. Parsons' equation (eqn. 2) relates the requisite S/N to the desired s_r value and the chosen number of measurement pairs, n. For peak-to-peak noise, this relation is

$$S/N = 28.28/s_r n^{\frac{1}{2}} \tag{2}$$

For a more complete specification of the determination limit, one includes a statement of the electronic-readout response time (noise suppression), which carries an inverse relation to the noise.

The limits of determination were measured at a ten-times scale expansion and with noise suppression at position 4. Other instrument controls were set as recommended in Table I. Under these conditions a 0.09-p.p.m. aqueous manganese-(II) solution registered a signal (average of three) at 16.0% A with peak-to-peak noise of 1.5% A. For a s_r value of 1% and for three measurement pairs, eqn. (2) gives a value of 16.4 as the S/N for the chosen precision. As calculated by proportion from the data for the 0.09-p.p.m. solution (assuming constant noise), this signal-to-noise ratio would be exhibited by a concentration of 0.14 p.p.m. manganese(II), the limit of determination (aqueous).

For the investigation of sensitivity in MIBK solution, an extract of 7.5 p.p.b. manganese(II) (in aqueous phase before extraction) was prepared by the Recommended procedure. With the instrument conditions described above, this MIBK extract showed 25.5% A with peak-to-peak noise of 1.3% A. The calculated limit of determination (MIBK) is 6.3 p.p.b. manganese(II) in aqueous phase before extraction. Urine manganese was expected to range as low as 2 p.p.b.

Analysis of aqueous urine digests containing standard additions

Direct aspiration of urine digests provided further evidence for the need for a preconcentration step. To five urine aliquots, digested and buffered according to the Recommended procedure, were added amounts of stock manganese(II) solution giving the final addition concentrations and absorptions as indicated below (all absorptions measured at 3-times scale expansion).

Neutralized digestion	1.8%
Neutralized digestion	1.4
Neutralized digestion with 10 p.p.b. Mn(II)	2.0
Neutralized digestion with 20 p.p.b. Mn(II)	2.2
Neutralized digestion with 40 p.p.b. Mn(II)	2.9

These absorptions, compared to absorptions of cupferron–MIBK extracts of the same aqueous concentrations, are somewhat high and erratic. (The organic solvent effect, of course, must be considered in making these comparisons. This enhancement, observed with extracts obtained by the Recommended procedure, amounts to a factor of 3.9.) A combination of ionization interference and scattering (or molecular absorption) may help explain this erratic and nonlinear pattern.

Choice of solvent extraction system

As a preconcentration technique with atomic absorption, solvent extraction has the advantages of the well-known "organic solvent effect" and of simplicity. There are at least five experimental criteria governing the choice of extraction system used before an atomic abosption finish:

(*a*) The system should have a high percent extraction into a solvent amenable to atomic absorption. An analyte not quantitatively extracted in two or three shakings will be unpredictably influenced at low concentrations by variations in matrix hold-up or salting-out. Systems involving the common extraction solvents, chloroform or carbon tetrachloride, may have different extraction characteristics when the solvent is replaced by one of the ketones or esters used in conjunction with atomic absorption.

(*b*) The system should not be conducive to erratic aspiration nor to unstable flame behavior. This criterion may depend on such factors as matrix composition and ligand concentration.

(*c*) The system should form an extract which is stable with time.

(*d*) The system should extract optimally over a wide pH range.

(*e*) The system ideally should simultaneously extract several analytes and hold them in stable solution.

In this work data were obtained pertaining to three of the above factors.

Efficiency of extraction systems for preconcentration of manganese(II) into MIBK. Table II lists the solvent-extraction systems tested for extracting manganese(II)

TABLE II

EFFICIENCY OF EXTRACTION SYSTEMS FOR PRECONCENTRATION OF MANGANESE(II) INTO MIBK

Procedure (conditions)	*Percent extraction*
1. Sodium diethyldithiocarbamate (0.01 *M*, pH 8.6)	80
2. As (1) with 1.0 mg potassium hexacyanoferrate(III)	90
3. As (2) with 2% sodium potassium tartrate	88
4. Thenoyltrifluoroacetone (0.15 *M*, pH 8.6)	88
5. Sodium diethyldithiocarbamate (0.01 *M*, pH 7.8, 2 extractions)	98
6. Oxine (1%, pH 7.8, 2 extractions)	41
7. Thenoyltrifluoroacetone (0.15 *M*, pH 7.8, 2 extractions)	106
8. Tetraphenylarsonium chloride (0.02 *M*, pH 6.3, periodate oxidation, 2 extractions)	0
9. Cupferron (0.1 *M*, pH 7.1)	103
10. 1-(2-Pyridylazo)-2-naphthol (PAN) (0.1%, pH 7.0)	5
11. As (10) at pH 8.9	97
12. Isonitrosoacetophenone (0.1%, pH 7.2)	0
13. As (12) at pH 9.0	0
14. Dibenzoylmethane (0.1 *M*, pH 9.0)	Anomalously high
15. Benzoylacetone (0.1 *M*, pH 9.0)	Anomalously high
16. Acetylacetone (0.1 *M*, pH 8.9)	43
17. Salicylaldoxime (0.1%, pH 9.1)	24
18. Oxine (0.1 *M*, pH 9.1)	3
19. Oxine (0.5 *M*, pH 9.1)	70
20. 2-Nitroso-1-naphthol (0.02%, 6 *N* H_2SO_4, pH 1.0)	0
21. As (20) without H_2SO_4 (pH 9.0)	12
22. 8-Hydroxyquinaldine (0.02%, pH 9.1)	60
23. As (22) but at pH 11.8	115
24. *N*-Phenylbenzohydroxamic acid (1.0%, pH 6.0)	0
25. Dithizone (0.1%, pH 9.0)	Anomalously high
26. Dithizone (0.01%, pH 9.0)	75
27. 8-Mercaptoquinoline hydrochloride (saturated, pH 8.9)	31
28. PAN (0.002%, pH 9.0, 2 extractions)	11

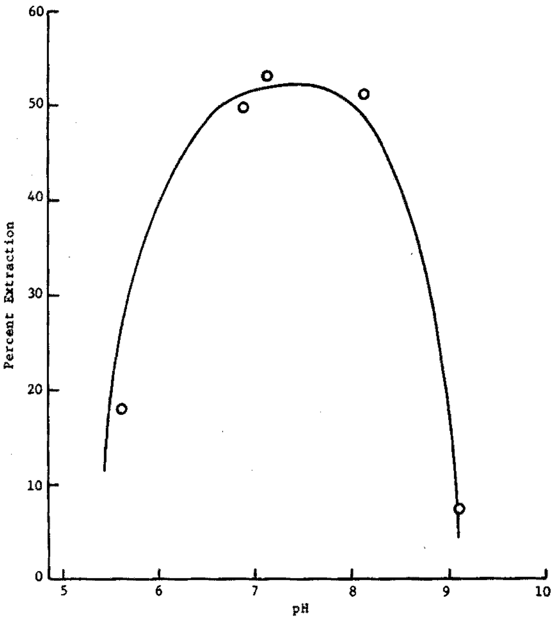

Fig. 1. Diethyldithiocarbamate–MIBK extraction of manganese(II) *vs.* pH.

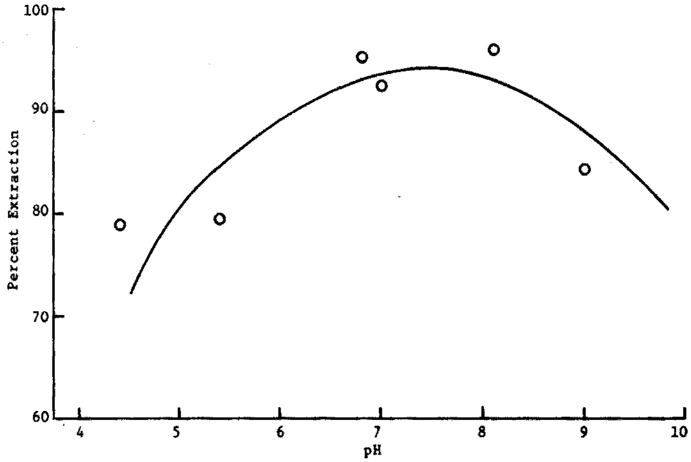

Fig. 2. Cupferron–MBK extraction of manganese(II) *vs.* pH.

into MIBK. Many of the systems chosen are from a list recommended by Starý[25] specifically for manganese extraction. Where the literature recommendations did not require otherwise, the procedure was as follows. Portions (100 ml) of 0.2 p.p.m. aqueous manganese(II) solution were shaken with 20 ml of MIBK. TRIS buffer (ionic strength 0.05 *M*) was employed for adjusting pH, which was measured after extraction. Unless indicated differently, extractions were performed with one shaking of 2-min duration. Standard manganese(II) in MIBK was prepared as described by Feldman *et al.*[26] by dissolving the requisite weight of manganese sulfate in a minimum amount of concentrated hydrochloric acid, and then diluting with MIBK. The anomalously high absorbance for three of the systems is possibly a result of unspecific matrix effects.

Percent extraction vs. pH for manganese chelates. Extraction as a function of pH was investigated for several systems which, according to Table II, had favorable extraction efficiency, and which did not tend to form emulsions or to show erratic or anomalous absorption, etc. The data for two of the systems are shown in Figs. 1 and 2. Solutions used and procedures followed are described in the paragraph above. Below pH 6.9 an acetate buffer served for pH adjustment; while above pH 9.1 the pH adjustment was made with sodium hydroxide and perchloric acid. Single extractions were accomplished with 2-min shakings.

Stability of manganese chelates in MIBK. Investigation of solution stability for several favorable manganese chelates in MIBK, determined by atomic absorption, is reported in Table III. The extracts were prepared as described above for the respective chelates. Manganese in the diethyldithiocarbamate complexes is considered[27] to be manganese(III), while the other complexes are assumed to be chelates of manganese(II).

TABLE III

STABILITY OF MANGANESE CHELATES IN MIBK EXTRACTS

Chelating agent	*pH*	*Duration of stable absorption*
Dithizone	9.02	Decreased 29% in 1 h
Diethylammonium diethyldithiocarbamate	6.90	2 h; color stable for 50 min
Sodium diethyldithiocarbamate	6.80	2 h; color stable for 30 min
	7.67	Decreased 5% in 17 min
1-(2-Pyridylazo)-2-naphthol	8.01	Over 4 h
Cupferron	7.40	Over 3 days

TABLE IV

EXTRACTION INTERFERENCE TESTS

Test species	*Weight ratio of test atom to Mn*	*% Decrease in extract absorbance*
Bi(III)	800.0	30.0
Fe(III)	500.0	0.0
Cu(II)	500.0	0.0
Mo(VI)	(0.07 g l^{-1} as $Na_2MoO_4 \cdot 2H_2O$)	0.0
$SbCl_4^-$	400.0	>8.0 (decomposition)
$TlCl_4^-$	100.0	11.0
Hg(II)	12.0	0.0
Pb(II)	12.0	0.0
Cd(II)	0.4	0.0
$SnCl_6^{2-}$	0.3	0.0

Investigation of possible interferences

Extraction interferences. There are several biologically significant cations among those listed by Starý and Smizanska[28] that are more completely extracted than manganese(II) at pH 7 by cupferron in chloroform. In Table IV are listed for these ions the results of individual tests for interference on a two-stage extraction, similar to the extraction in the Recommended procedure. Aqueous manganese(II) solution at 24.0 p.p.b., in the presence of the indicated weight ratio of test atom to manganese(II), was extracted by cupferron–MIBK from aqueous solutions buffered with TRIS buffer at ionic strength 0.05 *M*. For comparison solutions, identical extractions were performed in the absence of the test ion. The weight ratios of test atoms were chosen, where data were available, to provide test-element concentrations commensurate with urine toxicological values. Most of the toxicological values are from Patty[29]. Gross precipitation prohibited the use of full toxicological concentration values in several cases. Molybdenum was studied at its concentration in the diluted digest of the Recommended procedure.

Test for scattering or molecular absorption. A 100-ml urine sample containing additions of 0.040 g of calcium nitrate tetrahydrate and 0.028 g of magnesium chloride hexahydrate was digested and prepared for extraction by a two-stage extraction as above. The aqueous phase contained a 48-p.p.b. manganese(II) addition and 0.05 *M* trisodium citrate. The resulting extract showed no significant difference in absorbance at the 279.1-nm line of tungsten when compared to a similar extract from a solution containing no added calcium, magnesium, or citrate.

The lack of absorbance close to the manganese line tends to show absence of scattering or molecular absorption measured by this technique. The aqueous calcium and magnesium concentrations were chosen to represent high normal values for these ions in urine.

Verification of quantitative extractions at low concentrations

Figure 3 presents evidence of quantitative extraction of manganese(II) from buffered aqueous solutions. With a three-stage extraction, quantitative extraction can be effected in the concentration range of at least 0.025–0.90 p.p.m. manganese in MIBK. (This statement does not imply quantitative extraction from biological digests in this range by a three-stage procedure.)

The curve in Fig. 3 includes the atomic absorbances of solutions of tris-(acetylacetonato)manganese(III), $Mn(acac)_3$, dissolved in MIBK. The parent solution for these dilutions contained 2320 p.p.m. manganese as determined titrimetrically after destruction of the ketone vehicle by digestion with a mixture of nitric, sulfuric, and phosphoric acids. The titration, with standard arsenite–nitrite mixture, of the permanganate produced by persulfate oxidation was patterned after the method of Sandell *et al.*[30].

For the MIBK extracts the concentrations of manganese in MIBK were calculated by applying the factor 5.6 to manganese-concentration values of the prepared aqueous phases, diluted from standard stock solutions. The factor 5.6 accounts for the volume ratio and for the solubility[31] of MIBK in water.

Collinearity of the data for the standard extracts with the data for the titrimetrically analyzed solutions provides evidence for quantitative extraction. The slope of the curve in Fig. 3 is 1.14 absorbance units per p.p.m. manganese in

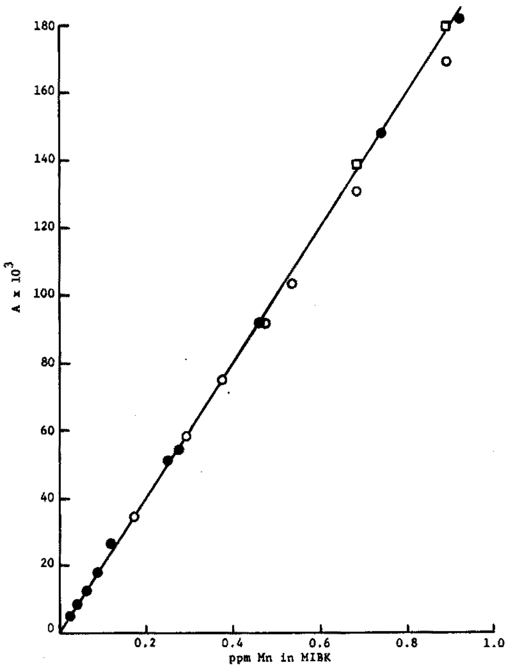

Fig. 3. Linearity of atomic absorbance of manganese in MIBK. Verification of quantitative extraction. (○) 2-stage extraction; (□) 3-stage extraction; (●) solution of Mn(acac)$_3$ analyzed titrimetrically.

MIBK. This is the same sensitivity obtained by Takeuchi *et al.*[21], who used a similar extraction system for manganese with an atomic absorption finish.

Clarification of digest solutions

Without clarifying agent, the urine-digest residues exhibited turbidity or insoluble matter upon final dilution at pH 7.0. Reduction of the sulfate content of the modified Cummins' reagent to about half strength did not significantly reduce the amount of insoluble residue. Dissolution of this intractable matter, however, occurred by warming the neutralized digest with 3 g of sodium citrate (0.04 *M* in final aqueous dilution). Although complete clarification was thus effected in digest solutions containing both calcium and magnesium at the upper end of the normal urine range, this clarification technique was not used routinely. The citrate appeared to contribute somewhat to erratic recovery or to unstable extracts. Moreover, it was observed that when the digestion flasks had been cleaned by the recommended alkali-cleaning procedure, very little insoluble matter remained at final dilution without citrate. Any further solubilization efforts seemed superfluous. It is possible that elimination of this very small solid material, occasionally evident, would have obviated the need for extra extraction stages [illegible] the "low-addition" aliquots of urine samples. The situation, however, deserves further investigation.

Recovery studies and precision of extraction at the two addition concentrations

Determinations of urine manganese are presented in Table V. The procedure

TABLE V

RESULTS OF URINE MANGANESE DETERMINATIONS

Sample no.	*p.p.b. Mn(II)*	*Percent recovery at addition points*	
		10 p.p.b.	*20 p.p.b.*
1	3.8 3.0	107	105
2	4.2 3.8	119	117
3	3.0 2.2	124	125
4	2.0 2.5	109	110
5	2.5 2.8	111	112

was slightly modified to include pipetting the standard additions to the sample before digestion, rather than as in the Recommended procedure. This variation in procedure, together with the concomitant analysis of a comparison solution for each of the two addition concentrations, gave data which allowed comparison of the relative percent recovery, *i.e.*, relative to the comparison-extract absorptions, at the two addition points. The comparison extracts for each addition concentration were obtained by two-stage extractions based on the recommended procedure, from standard manganese solutions buffered with TRIS.

For each digestion extract (prepared in duplicate) the measured percent absorptions (averages of three aspirations) at each addition point were corrected for the calculated urine manganese(II) "originally present" by subtracting the absorption corresponding to the manganese(II) originally present. The factor for converting concentration to percent absorption was obtained from the concomitant comparison-extract data at the 20-p.p.b. addition. The five comparison extracts of Table V contained "contaminations" (calculated as described at the end of the Recommended procedure) ranging from −0.3 to 0.3 p.p.b. Mn(II) and averaging 0.1 p.p.b. In Table V is listed, for both the 10- and 20-p.p.b. addition concentrations, the ratio (average of duplicates) of the corrected digestion-extract absorption to the corresponding comparison-extract absorption. These ratios are listed as percent recovery. The difference in percent recovery between addition points remains small for all five analyses. The daily differences are possibly a result of matrix variations previously discussed. The fact that all recoveries, relative to the comparison extracts, are over 100% is probably due to a net combination of solvent salting-out and ionization interference.

The urine manganese(II) values listed in Table V are duplicate determinations of five different urine samples obtained from the same subject during a two-week period. A value of 1.1 p.p.b. manganese(II) (average of two) resulted from a blank determination. Corrected for this blank, the average of ten urine manganese(II) concentrations is 3.0 p.p.b. with a range of 2.0–4.2 p.p.b.; the average deviation is 0.6 p.p.b.

It is suggested that the validity of the urine manganese results reported here be judged by comparison with results obtained with similar samples by an alternative technique. By neutron activation analysis, Cotzias[15] measured urine manganese at 2.1 p.p.b.

Notes on technique

Development of a procedure having some feasibility as a clinical method required efforts at simplification. For this reason all investigations were conducted with commercial equipment. Ordinary reagent-grade chemicals, realistic sample sizes, minimal sample preparation, and minimal precaution against contamination were employed. No reason was found to doubt the usefulness of this approach.

Water was obtained sufficiently pure only with some difficulty. Reagent purity, however, should also receive further attention. Overall blank values for the determination averaged 1.1 p.p.b. Blank values were also calculated for extraction of the standards used in conjunction with the five urinalysis and recovery runs. These values, averaging 0.1 p.p.b. with a range of −0.3 to 0.3 p.p.b., do not include contamination from the digestion acids or ammonia solution. They are, therefore, an indication of the manganese contribution from the water and extraction reagents. By comparison of these two sets of blank values, it is concluded that the digestion acids and/or the ammonia should be considered the major sources of contamination.

Blank values obtained by following the Recommended procedure, when using the alkali-treated flasks, did not differ significantly from values obtained with the same procedure but omitting the 35-min boiling. This fact tends to show an insignificant contribution of manganese from the Kjeldahl flasks during the digestion. The use of alkali cleaning solution, suggested by Moore and Leddicotte[32] for trace manganese clean-up, had two advantages over the sulfuric–nitric acid soaking treatment often recommended. The alkali treatment seemed to decrease the apparent tendency for manganese to accrete to the flasks or to be mobilized from the flasks. Secondly, it reduced tendencies for digests to show turbidity or insoluble matter when diluted. These two observations deserve further investigation.

SUMMARY

Urine samples were digested with a mixture of nitric, sulfuric, and perchloric acids containing molybdate as catalyst. A two-point standard addition technique involved extracts of buffered, digested aliquots containing 10- and 20-p.p.b. manganese(II) in the aqueous phase. The extraction system was MIBK–cupferron. Of the substances tested only bismuth, antimony, and thallium interfered. From the same subject, five morning urine samples averaged 3.0 p.p.b. of manganese with a range of 2.0–4.2 p.p.b.; the average deviation was 0.6 p.p.b.

RÉSUMÉ

Une méthode est proposée pour le dosage du manganèse dans l'urine, par spectrophotométrie d'absorption atomique. L'échantillon à analyser est traité par un mélange d'acides nitrique, sulfurique et perchlorique, en présence de molybdate comme catalyseur. On procède à une extraction en système cupferron–méthylisobutylcétone. Parmi les produits testés, seuls bismuth, antimoine et thallium peuvent gèner. On a dosé ainsi des quantités de manganèse allant de 2.0 à 4.2 p.p.b., avec déviation moyenne de 0.5 p.p.b.

ZUSAMMENFASSUNG

Urinproben wurden mit einem Gemisch von Salpeter-, Schwefel- und Perchlorsäure behandelt, das Molybdat als Katalysator enthielt. Nach einem Zweipunkt-Standardzumischverfahren wurden gepufferte aliquote Anteile der wässrigen, 10 und 20 p.p.b. Mangan(II) enthaltenden Lösungen mit MIBK–Cupferron extrahiert. Von den untersuchten Elementen störten nur Wismut, Antimon und Thallium. Fünf Morgen-Urinproben von derselben Person enthielten im Durchschnitt 3.0 p.p.b. Mangan in einem Bereich von 2.0–4.2 p.p.b.; 0.6 p.p.b. war die mittlere Abweichung.

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THE ALKALINE DECOMPOSITION OF HEXAMMINOCOBALT(III) CHLORIDE

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It has become fashionable in recent years to have students in undergraduate laboratory courses prepare and analyze transition metal complexes, notably various chloro-ammine complexes of cobalt(III)[1–4]. In typical procedures the halide is determined gravimetrically, the ammonia is determined by a simplified Kjeldahl method, in which ammonia is evolved when the complex is decomposed in boiling strong base, and the cobalt is determined either spectrophotometrically as the tetrathiocyanato complex of cobalt(II), or titrimetrically by an iodimetric method.

It has been known for more than a century that simple alkaline decompositions yield ammonia analyses for cobalt(III) ammines which are systematically low[5]. Horan and Eppig[6] suggested that the low values resulted from some uninvestigated reaction between ammonia and cobalt(III). They also showed that if arsenic(III) oxide was added to the distillation flask, ammonia could be recovered quantitatively.

What seems not to have been appreciated, is that an iodimetric "cobalt" assay which is done on the alkaline reaction mixture which remains after the ammonia has been expelled, must be affected by the oxidation–reduction chemistry which has already taken place between cobalt(III) and ammonia. The present work reports experiments designed to identify the principal reactions which occur during the alkaline decomposition and iodimetric analysis of hexamminocobalt(III) chloride.

EXPERIMENTAL

Analytical reagent-grade chemicals were used throughout. Sodium thiosulfate and potassium permanganate solutions were prepared and standardized by textbook methods[7].

Hexamminocobalt(III) chloride was synthesized by the method of Palmer[8]. The pooled results of over 1200 student analyses give $\%\mathrm{Cl}=39.8\pm0.2$; $\%\mathrm{NH_3}=37.8\pm0.5$ (theoretical: $\%\mathrm{Cl}=39.78$; $\%\mathrm{NH_3}=38.20$). When the oxidizing power of the compound was determined by a method similar to that described by Palmer (decompose in boiling alkali, acidify, add excess of iodide, allow to stand, and titrate with standardized thiosulfate), it was found that the results based on cobalt(III) were *ca.* 5% low, and the starch end-point was very unstable. The blue color returned repeatedly, often within 10 s.

An unstable starch end-point in an iodimetric analysis of a system open to the air suggests the presence of nitric oxide, the precursor of which is nitrous acid[9].

A Griess–Ilosvay test[10] confirmed the existence of nitrite ion in a sample of the complex which had been boiled in strong base in air and then was made strongly acidic. The oxidizing power of the system was then studied systematically. Identical 25.00-ml aliquots of a stock solution of $Co(NH_3)_6Cl_3$, each containing 0.4627 g (1.732 millimoles) of complex, were taken for analysis. The cobalt(III) content of each aliquot is equivalent to 17.32 ml of 0.1000 *M* sodium thiosulfate. Four procedures, which differ mainly in the point at which an argon atmosphere was introduced, were employed as follows.

Procedure A

To a 25-ml aliquot of complex stock solution add 10 ml of 6 *M* sodium hydroxide. Boil in an argon atmosphere for 10 min. All further operations are also performed under a blanket of argon. Remove the solid by filtration, preserving the filtrate. Transfer the solid and filter paper to a 300-ml Erlenmeyer flask. Add 25 ml of boiled, deionized water, 2 g of potassium iodide and 7 ml of 6 *M* hydrochloric acid. Allow the flask to stand for 5 min. Add 100 ml of boiled water and titrate with 0.1000 *M* thiosulfate to a starch end-point. To the alkaline filtrate, add 2 g of potassium iodide and 17 ml of 6 *M* hydrochloric acid. After 5 min add 100 ml of boiled water and titrate.

Procedure B

This is similar to Procedure A, except that the complex is decomposed in a flask open to the atmosphere. After the filtration step has been done in air, every subsequent manipulation is performed under a blanket of argon.

Procedure C

This is similar to Procedure B, except that the complex is decomposed with 5 ml of 6% hydrogen peroxide and 10 ml of 6 *M* sodium hydroxide.

Procedure D

This is similar to Procedure C, except that the argon is not introduced until the reaction flasks are ready to be titrated. The flasks are stoppered during the 5-min waiting periods.

RESULTS AND DISCUSSION

The results of experiments performed using Procedures A–D are summarized in Table I. The reproducibility of the titration volumes is ±0.05 ml of 0.1000 *M* thiosulfate.

Procedure D is very similar to a procedure contrived in this laboratory to produce the "right" answer for students. They do not separate the phases, and the inert atmosphere is generated by adding a small piece of dry ice to the titration vessel. Table I shows that the success of this procedure is purely fortuitous.

The entries for Procedure A in Table I show that nearly 25% of the cobalt(III) is reduced by ammonia when the complex is decomposed in base in an inert atmosphere. Given the N:Co ratio of 6:1 in the complex, together with the fact that 0.12 millimoles of nitrogen fail to appear as ammonia, it follows that 3.5 moles of

TABLE I

TITRATION VOLUMES

Procedure	*ml of 0.100 M thiosulfate required*		
	Solid phase	*Liquid phase*	*Total*
A	13.12	0.02	13.14
B	14.60	0.32	14.92
C	15.80	0.40	16.20
D	15.87	1.63	17.50
Theoretical	17.32	0.00	17.32

cobalt(III) are reduced to cobalt(II) per mole of unrecovered nitrogen.

The results of Procedure B show that atmospheric oxygen serves both to reoxidize some cobalt(II) to cobalt(III) and to cause 1/4 of the unrecovered nitrogen to appear as nitrite. In Procedure C the added hydrogen peroxide acts principally on the hydroxide of cobalt(II), but the reaction is incomplete.

Procedure D shows that almost 10% of the total oxidizing power of the system found when everything but the titration is done in air, may be attributed to nitrogen chemistry, according to the reactions

$$2\,H^+ + NO_2^- + I^- \rightarrow \tfrac{1}{2}\,I_2 + NO + H_2O \tag{1}$$

$$NO + \tfrac{1}{2}\,O_2 \rightarrow NO_2 \tag{2}$$

$$2\,H^+ + NO_2 + 2\,I^- \rightarrow I_2 + NO + H_2O \tag{3}$$

According to the results of Procedures A and B, the presence of oxygen is essential to the production of nitrite in the system. The results of Procedure A are most readily interpreted by postulating that the oxidation of ammonia by cobalt(III) occurs in two successive 2-electron steps. It is suggested that the initial oxidation product is hydroxylamine, which forms by a reaction which may be written schematically as

$$\overset{\diagdown}{\underset{\diagup}{-}}Co^{3+}\text{–}NH_2^- + {}^-HO\text{–}Co^{3+}\overset{\diagup}{\underset{\diagdown}{-}} \rightarrow H_2NOH + 2\,Co^{2+} \tag{4}$$

There is ample precedent for suggesting the deprotonation of ammonia molecules bound to cobalt(III) in strongly basic solution[11], and the precipitation of the hydrated cobalt(III) oxide almost certainly occurs by a series of stepwise substitutions of hydroxide for ammonia.

Strong evidence for the initial production of hydroxylamine comes from a series of experiments in which 0.12 millimoles of hydroxyammonium chloride in 35 ml of 1.7 *M* sodium hydroxide was boiled in air for 10 min, with and without the presence of solid hydrated cobalt(III) oxide. This amount of hydroxylamine is equivalent to the ammonia loss from an aliquot of the $Co(NH_3)_6Cl_3$ stock solution.

In the first set of experiments, the boiled solutions were cooled and filtered, and the volumes were readjusted to 35.00 ml by adding water. A 25.00-ml portion was withdrawn, to it was added 25.00 ml of 0.020 *M* potassium permanganate and, after 10 min, 11 ml of 3.6 *M* sulfuric acid and 2 g of potassium iodide were added.

After 5 min, the liberated iodine was titrated with standard thiosulfate solution. It was found that when cobalt(III) oxide was absent, 25 ml of the boiled reaction mixture reduced an amount of permanganate equivalent to 2.7 ± 0.1 ml of 0.1000 *M* thiosulfate. This may be compared with the value of 3.7 ± 0.1 ml found when 25 ml of the reaction mixture was not boiled, but rather was assayed immediately after it had been prepared. When cobalt(III) oxide was added and the mixture was boiled, the permanganate consumption was equivalent to 1.5 ± 0.1 ml of 0.1000 *M* thiosulfate.

In a second set of experiments, in which the sulfuric acid was added to the 25.00-ml portions of boiled, reconstituted solutions before the permanganate was added, the permanganate losses were equivalent to 3.1 ± 0.1 ml of thiosulfate when cobalt(III) oxide was absent, and 0.5 ± 0.1 ml when it was present. Cobalt-free reaction mixtures assayed in acidic solution without boiling, consumed permanganate equivalent to 4.3 ± 0.1 ml of thiosulfate.

The two different titration volumes which were found when cold hydroxylamine was reacted with permanganate in acidic or basic solution both agree well with the permanganate consumptions found by Kurtenacker and Neusser[12] under similar conditions. Since the same ratio of permanganate consumptions in acidic and basic media was found for both the cold and the boiled (cobalt-free) reaction mixtures, it can be concluded that in boiling alkaline solution, hydroxylamine partially decomposes to form volatile products, possibly nitrous oxide and ammonia[13]. When hydroxylamine and cobalt(III) oxide were boiled together in alkali, not only were the amounts of permanganate consumed by the reaction mixtures greatly reduced, but more importantly, the consumption in acidic solution was only one-third of the consumption in basic solution. Thus the hydroxylamine must have reacted essentially completely with the trivalent cobalt oxide. Nitrite could be detected in the acidified reaction mixture, but the marked nonequivalence of the titration volumes found after permanganate treatments in acidic and basic media showed that nitrite cannot be the sole non-volatile oxidation product of the reaction, since permanganate and nitrite do not react in alkaline solution[9]. This system obviously merits further study.

In the present study, 25-ml aliquots of $Co(NH_3)_6Cl_3$ were next decomposed according to Procedure B. The solids were filtered away, the solutions were reconstituted to 35 ml, and 25-ml portions were subjected to permanganate oxidations under both acidic and basic conditions as above. The permanganate consumptions were equivalent to 0.5 ± 0.1 and 1.5 ± 0.1 ml of 0.1000 *M* thiosulfate, respectively. Since these volumes are identical to those found for the corresponding cobalt oxide–hydroxylamine systems, hydroxylamine is almost certainly the initial oxidation product in the alkaline oxidation of ammonia by cobalt(III).

Since the results of Procedure A show that a total of 3.5 electrons are involved in nitrogen–cobalt redox chemistry, and since nitrite must derive from at least one non-volatile oxidation product of hydroxylamine, it can be presumed that much of the hydroxylamine then reacts with cobalt(III) in another 2-electron process. The most probable reaction product is nitroxyl (NOH), or its anion (NO^-), for the reason that many repeated attempts to detect hyponitrite ($N_2O_2^{2-}$) in the alkaline filtrates from Procedure A all produced negative results. The hyponitrite ion has an intense ultraviolet absorption maximum ($\lambda_{max} = 247$ nm, $\varepsilon = 3980$)[14]. According to the kinetic data of Buchholz and Powell[15], at pH 14 and 25° the half-life for the decomposition of hyponitrite is *ca.* 15 days. If the activation energy for the decomposition is *ca.* 25 kcal, then at 100° its half-life would be *ca.* 5 min, and the species should be detectable in the present reaction mixtures. In no instance was absorption found at wavelengths above 225 nm.

It is noteworthy that nitroxyl has also been postulated as an intermediate in the alkaline oxidation of hydroxylamine by either $Cu(OH)_2$[16] or pertungstate[17] at room temperature. In these systems in the presence of oxygen, nitrite yields of 30–50% based on hydroxylamine were obtained.

SUMMARY

When hexamminocobalt(III) chloride is boiled in 1.7 *M* sodium hydroxide, 3.5 moles of cobalt(III) are reduced to cobalt(II) per mole of unrecovered ammonia. In air, nitrite is produced. The oxidation of ammonia probably proceeds by two 2-electron steps to produce first hydroxylamine, and then nitroxyl.

RÉSUMÉ

On examine la décomposition du chlorure d'hexamminocobalt(III), en milieu hydroxyde de sodium 1.7 *M*, à ébullition: 3.5 moles de cobalt(III) sont réduites en cobalt(II) par mole d'ammoniac. À l'air il y a formation de nitrite. L'oxydation de l'ammoniac se fait probablement en deux stades (de 2 électrons): d'abord formation d'hydroxylamine, puis de nitroxyle.

ZUSAMMENFASSUNG

Wenn Hexamminkobalt(III)-chlorid mit 1.7 *M* Natronlauge zum Sieden erhitzt wird, werden pro Mol umgewandelten Ammoniaks 3.5 Mol Kobalt(III) zu Kobalt(II) reduziert. In Luft wird Nitrit gebildet. Die Oxidation von Ammoniak verläuft wahrscheinlich über zwei 2-Elektronenstufen unter Bildung von zunächst Hydroxylamin und dann Nitroxyl.

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TITRATION OF MIXTURES OF ACIDS OF NEARLY EQUAL STRENGTHS

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Since the introduction of electronic computers, a considerable amount of work has been devoted to the development of versatile computer programs for evaluating stability constants from experimental data. Since no computer can yield results that are better than the input data, many workers found it worthwhile to devote some effort to the improvement of the techniques used to acquire the experimental data. Considerable success has been achieved, and in particular potentiometric techniques have been developed to a very high degree of refinement. Sillén and his coworkers, among others, have been occupied in this field.

With reference to what has been said above, the question arises whether the analyst could benefit from the results of the solution chemists. The present paper describes an investigation of how the high-quality experimental data provided by glass electrode measurements can be utilized to evaluate the individual concentrations of a complex mixture of weak acids. The stability constants of the acids should preferably be known, but need not differ much from each other, which gives the technique an analytical interest.

First, the theoretical foundation of the titrations will be summarized. In the second part, the experimental techniques are described and, finally, a computer program designed for the evaluation of the data is discussed. Some examples of the use of the computer program with actual data are also given.

THEORY

The theory of precision potentiometric techniques has been elucidated by several authors. However, since the analyst and the inorganic or physical chemist do not always speak in the same terms, we feel that a repetition in some detail is justified here.

The cell used for pH measurement may be written

– ref. half cell | sample solution | glass electrode +

The e.m.f. of the cell may be described by an equation consisting of three terms, thus

$$E = E_0' + (RT/nF)\ln[\mathrm{H}^+] + E_j' \tag{1}$$

The division into three terms is perhaps somewhat artificial but nevertheless very practical. E_0' is a constant depending only on the type of cell. The second term could be called the "Nernst term" and accounts for the variation of E with the concentration of hydrogen ions, $[\mathrm{H}^+]$. The third quantity E_j' includes the liquid junction potential and terms for the variation of the activity factors with changing acidity of the solution. It should be stressed that, although the glass electrode in principle responds to hydrogen ion *activity*, it may nevertheless be *calibrated* with solutions of known hydrogen ion *concentration*. Moreover, if the activity factors can be kept constant throughout the experiment, and if E'_j is negligible or known, $E-E'_j$ will be a linear function of the logarithm of the hydrogen ion concentration $[H^+]$. As it is the concentration that is of interest to the analyst and not the activity, calibration with known concentrations instead of activities would simplify the analytical work.

One well-known method for keeping the activity factors constant is provided by Debye–Hückel theory. This implies that the activity factors remain constant if the total ionic strength of the solution is constant throughout the experiment. Figure 1 shows the calculated variation of the activity coefficients with increasing ionic strength for ions of different charge[1]. It can be clearly seen from the Figure that when the ionic strength attains a certain value—which is different for ions of different charge—the activity factors are not appreciably affected by small changes in the total ionic strength. The activity factor of the hydrogen ion remains essentially constant at all ionic strengths upwards of 0.05. Doubly and triply charged ions show a stronger dependence but in general it can be stated that the effect of small variations in the ionic strength upon the activity factors is negligible, provided that the total ionic strength is greater than, say, about 0.5.

There is, however, a reason for working in more concentrated ionic media than this; which is preferably discussed in terms of the liquid junction potential. In cells with liquid junction, *i.e.* in practically all cells of interest to the analytical chemist, there is a liquid junction potential which, at constant ionic strength, can be taken to depend only on the hydrogen ion concentration in the solution. The lower the ionic strength, the greater, in principle, is the liquid junction potential. This last-mentioned fact means that if the liquid junction potential is known with poor accuracy, it is advantageous to use a concentrated ionic medium. The analyst, however, is not likely to accept a method requiring addition of large amounts of neutral salt to the solution before analysis since very pure salt must then be used in order to avoid contamination. The liquid junction potential has been shown to have an approximately linear dependence on the free hydrogen ion concentration and we can thus write

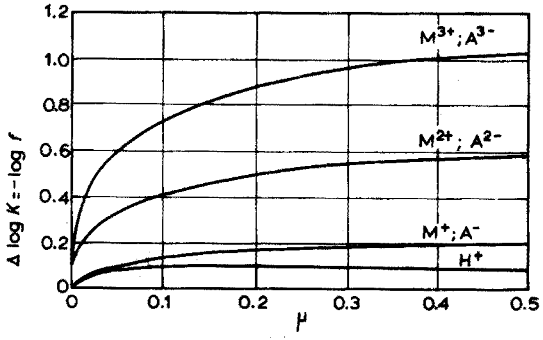

Fig. 1. Diagram permitting approximate conversion of activity constants into concentration constants. The correction is positive for ions in the numerator and negative for ions in the denominator. From A. Ringbom, *Complexation in Analytical Chemistry*, Wiley–Interscience, New York, 1963.

TABLE I

VALUES OF j IN EQN. (2) IN SOME IONIC MEDIA

Medium	*Concentration (moles l^{-1})*	j *($mV/(mole\ l^{-1})$)*	*Ref.*
$NaClO_4$	3.0	16.5	3
	1.0	63.5	3
	0.1	440	4
NaCl	3.0	18	2
KCl	2.0	20.25	This work
	0.5	90.5	This work

$$E_j' = j \cdot [H^+] \qquad (2)$$

Values of the quantity j have been determined experimentally by Dunsmore and Sillén[2], by Rossotti and Rossotti[3] and by Dyrssen[4] among others. Some of them are listed in Table I. It may be noted that the shape of the liquid junction is not without effect at high acidity but in the range normally used in analytical work ($-\log[H] > 1$), no significant effect has been observed[5]. The Table shows that the junction potential of a 0.01 *M* hydrochloric acid solution will be 1 mV in an ionic medium of 0.5 mole l^{-1} of potassium chloride, but only 0.2 mV if the concentration of the ionic medium is 2 moles l^{-1}.

The present authors have, for a compromise, chosen to run most of their experiments in 0.5 *M* potassium chloride as the ionic medium. Since, however, according to a recent recommendation[6] to the International Union of Pure and Applied Chemistry, determination of stability constants should preferably be made in 2 *M* media, some of the experiments were carried out in potassium chloride of this molarity. No significant effect was noted.

Since E_0' is known by experience to change when the electrodes are removed from one solution and immersed in another, the usual way of calibrating the electrode system with standard buffer solutions cannot be used in precision titrations. Instead, a so-called E_0'-titration should be made. A known amount of strong acid is titrated with strong base and E is measured after each addition of titrant. The equivalence volume is determined according to known principles[7] and a plot of $E-(RT/F)\ln[H^+]$ *vs.* $[H^+]$ yields j as the slope and E_0' as the intercept with the y-axis. If j has been determined in a separate experiment (and this is, in our opinion, the best practice), several values of E_0' can be calculated from

$$E_0' = E-(RT/F)\ln[H^+]-j\cdot[H^+]$$

and E_0' is then obtained as the mean of all the individual values calculated for the experimental points. A least-squares computer program designed for processing the data obtained in an E_0'-titration is available.

When the E_0'-titration has been completed, the sample is added to the solution in the titration vessel and the titration is continued. The electrodes remain in the solution during all these operations.

EXPERIMENTAL

Equipment and chemicals

A thermostated bath was used in order to maintain the titration vessel at a temperature of 25±0.05°. The titration vessel was a Metrohm 200-ml glass vessel equipped with a no. EA 880 cover having 5 necks for electrodes, buret and gas inlet tubes, etc.

The electrodes were a Beckman no. 39303 glass electrode and an Orion no. 90-02-00 double-junction reference electrode. The outer sleeve of the reference electrode was filled with the ionic medium being used in the titration. No adverse effect of the (very slow) leaking of ionic medium from the outer sleeve into the titration vessel could be observed. The e.m.f. values were read to the nearest 0.1 mV by using a digital voltmeter Type S 1016 H (Systemteknik, Lidingö, Sweden). Magnetic stirring of the solution was employed and nitrogen gas was passed through the solution in order to prevent dissolution of atmospheric carbon dioxide.

Additions of titrant were made with pneumatically operated reagent pipettes (AGA, Lidingö, Sweden). The pipettes can be adjusted to deliver any volume between about 0.5 ml and 5 ml, have a very high degree of repeatability, and are well suited to deliver titrant in automatic titrations[8].

Only reagent-grade chemicals were used. The sodium hydroxide solution used as titrant was prepared in such a way that it had the same total concentration of ions as the solution in the titration vessel.

Procedure

To 50.0 ml of exactly known 0.01 *M* hydrochloric acid containing enough potassium chloride to give the desired total ionic concentration, nine successive 0.5-ml portions of 0.1 *M* sodium hydroxide solution were added and the E_0' value of the electrode system was obtained as outlined above. The sample solution containing various weak acids was then added and the titration was continued by adding successive portions of the sodium hydroxide solution.

EVALUATION OF THE DATA

A computer program called "TITRA", based on the method of non-linear least squares has been designed to evaluate data obtained by titration of a mixture of acids with a strong base. The program is based on the following equation that was derived from the electroneutrality condition[7,9]:

$$U = \Sigma\, V_0 C_{0i}/\{1+K_i\cdot[\mathrm{H}^+]\} + (V_0+V)(K_w/[\mathrm{H}^+]-[\mathrm{H}^+]) - V\cdot C_B \tag{3}$$

where C_{0i} is the concentration and K_i the stability constant of acid i; K_w is the ionic product of water, V_0 the volume at the start of the titration and V the volume of added titrant; C_B is the concentration of the titrant.

The program accepts $[\mathrm{H}^+]$ data in the form of pH or E (mV) and refines optionally C_{0i}, K_i and K_w.

The problem is to evaluate the unknowns of a series of equations obtained by inserting the observations into eqn. (3). The equations are reduced to the corresponding normal equations which are then solved by Gauss elimination procedures. The IBM routine SIMQ is used.

Since eqn. (3) is nonlinear with respect to K_i, the program requires that values of the stability constant K_i be given to the computer with the input data. The more complicated is the mixture titrated, the more accurate should be the values of K_i. If a mixture of two acids with very nearly equal K_i values is titrated, the values of the constants should be accurately known. In such a case, only the concentrations should be refined.

Polybasic acids are satisfactorily treated as a mixture of monobasic acids with the same concentration but with different stability constants. It is possible to handle bases or mixtures of bases and acids if a sufficient and known amount of strong acid is added to the solution before titration with a strong base. Bases and mixtures of bases may also be titrated with a strong acid. The program then automatically converts the pH or E data into pOH and $[OH^-]$. In that case, K_i is the stability constant of the base i. No other modification is necessary.

In order to check the results, log $[H^+]$ values are computed from the found values of concentrations and stability constants in the following way: $-\log[H^+]$ is assumed to be within a specified interval, *e.g.* 0–14. The interval is divided in half and U is computed from eqn. (3). Since U is a single valued function of $[H^+]$, the polarity of U will decide in which one of the two halves of the interval the actual log $[H^+]$ is.

The performance of the program was tested by using synthetic "titration" data calculated from assumed concentrations and stability constants for a mixture of up to four acids (formic, acetic, propionic and oxalic acid). The results show that the log $[H^+]$ data should be correct to the second decimal place to ensure an analytical accuracy of 1%, assuming approximately equal concentrations of two acids. When more complex mixtures are analysed, the data should be correct to the third decimal if the accuracy required is 2.5%. The error is largest for acetic and propionic acids. The results can be improved by increasing the amount of data used in the calculation. In other words, the greater the number of additions of titrant, the better will the results be.

RESULTS AND DISCUSSION

A mixture of known, approximately equal, molar quantities of the acids was titrated with sodium hydroxide solution, and the computer program was used to refine the constants instead of the concentrations during the evaluation. The values so determined can be considered as being conditional, in the sense that the effects of possible interactions between the two acids are included in the constants[10]. Table II lists the values used in the evaluation of the titrations summarized in Table III.

Table III summarizes the results of a few determinations of the individual acids in binary mixtures of formic acid, acetic acid and propionic acid. The precision is remarkably good, considering that the stability constants differ by only

TABLE II

STABILITY CONSTANTS USED IN EVALUATION

	Logarithm of stability constant		
In mixt. with	*Formic acid*	*Acetic acid*	*Propionic acid*
Formic acid	3.486	4.510	4.630
Acetic acid	3.492	4.501	4.649
Propionic acid	3.492	4.489	4.681

TABLE III

RESULTS OF SOME TITRATIONS OF MIXTURES OF ACIDS

(Nineteen pairs of data (volume of titrant e.m.f.) were used for the evaluation of the first six titrations. For the last nine, ten more pairs were used. To reach the second equivalence point, about twenty additions of titrant were required)

I	*II*	*Amount of acids taken (mmole)*		*Amount of acids found (mmole)*				*Total amount (mmole)*		
		I	*II*	*I*	*Rel. error (%)*	*II*	*Rel. error (%)*	*Taken*	*Found*	
Formic	Acetic	0.5091	0.5012	0.5078	−0.25	0.5027	+0.30	1.0103	1.0105	+0.02
Formic	Acetic	0.5091	0.5012	0.5089	−0.04	0.5013	+0.02	1.0103	1.0102	−0.01
Formic	Acetic	0.5091	0.5012	0.5098	+0.14	0.5010	−0.03	1.0103	1.0108	+0.05
Formic	Propionic	0.5091	0.4988	0.5089	−0.04	0.4993	+0.10	1.0079	1.0082	+0.03
Formic	Propionic	0.5091	0.4988	0.5094	+0.06	0.4992	+0.08	1.0079	1.0086	+0.07
Formic	Propionic	0.5091	0.4988	0.5090	−0.01	0.4988	±0	1.0079	1.0078	−0.01
Formic	Propionic	0.4039	1.6010	0.4061	+0.54	1.6091	+0.51	2.0049	2.0152	+0.51
Formic	Propionic	0.4039	1.6010	0.3909	−3.22	1.6193	+1.14	2.0049	2.0102	+0.26
Formic	Propionic	0.4039	1.6010	0.4037	−0.05	1.6079	+0.43	2.0049	2.0116	+0.33
Formic	Propionic	1.6135	0.4008	1.6302	+1.03	0.3858	−3.74	2.0143	2.0160	+0.08
Formic	Propionic	1.6135	0.4008	1.6259	+0.77	0.3871	−3.42	2.0143	2.0130	−0.06
Formic	Propionic	1.6135	0.4008	1.6159	+0.15	0.3861	−3.66	2.0143	2.0020	−0.61
Acetic	Propionic	0.2007	0.7981	0.1981	−1.30	0.8003	+0.27	0.9988	0.9984	−0.04
Acetic	Propionic	0.2007	0.7981	0.2147	+6.98	0.7828	−1.92	0.9988	0.9975	−0.13
Acetic	Propionic	0.2007	0.7981	0.2162	+7.72	0.7823	−1.98	0.9988	0.9985	−0.03

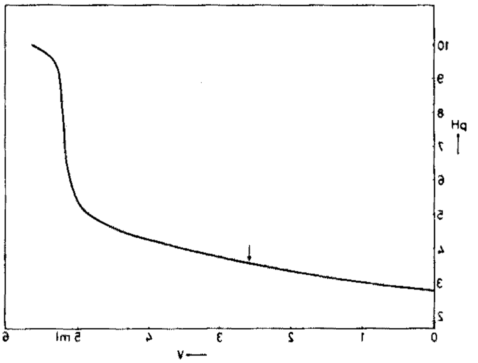

Fig. 2. Titration of 100 ml of a solution that was 0.02500 *M* with respect to both formic and acetic acids with 0.0967 *M* sodium hydroxide. The ionic strength was 0.5. The equivalence point for formic acid is indicated by an arrow.

about one logarithmic unit. For comparison, a titration curve recorded with a Metrohm Potentiograph E 336 is shown in Fig. 2. The equivalence volume for formic acid is indicated by an arrow. It is seen from the Table that the accuracy of the titrations is affected by altering the ratio of the concentrations of the acids. Points obtained after the second equivalence point were used in the evaluation to refine the value of the sum of the acids and of K_w.

In order to stretch the technique to the limits of acceptable performance, some titrations of a solution of acetic acid and propionic acid were also made. Here, the stability constants differ by only some 0.2 logarithmic units, but it nevertheless seems quite possible to attain a precision of about 2% in the determination of the individual acids, provided that the concentrations of the acids do not differ too much from each other.

It is interesting to note that if an electrode, selective to ethylenediaminetetraacetate (EDTA) ions could be devised—and some partly successful efforts have been reported—this would make it possible to analyse quite complicated mixtures of metal ions in solution. The effect of side reactions can be taken into consideration by introducing the concept of conditional constants. It should, however, be borne in mind that titrations of the kind described here require that the conditional constants remain truly constant during the entire course of the titration. This is not always the case.

A universal tool for solving analytical problems of the kind discussed in this paper is offered by the large computer programs that have been designed to evaluate stability constants from titration data, *e.g.* the "Letagrop" program by Sillén *et al.*[11]. The program is then used to evaluate the concentrations by using known stability constants. The use of such programs in practice is somewhat complicated, however, and requires considerable experience. These programs often require a very large amount of computer memory space. It might therefore often prove easier to design a special program—in this case "TITRA"—to solve a particular analytical problem.

The authors wish to express their gratitude to Mrs. Karin Lindgren for valuable technical assistance. Financial aid from the Swedish board of technical development is gratefully acknowledged.

SUMMARY

Accurate and precise experimental methods that were developed for the purpose of determining stability constants in aqueous solutions are employed in titrations of acids which have nearly equal strengths. A computer program capable of handling five acids simultaneously has been designed to evaluate the titration data. The results show that it is possible to determine two acids which have stability constants differing by only about one logarithmic unit with an accuracy better than 1%. If the conditions are favourable, it is even possible to analyse a mixture of two acids with about 2% accuracy when the constants differ by as little as 0.2 logarithmic units.

RÉSUMÉ

Des méthodes expérimentales exactes et précises, développées pour la détermination de constantes de stabilité, sont utilisées pour des titrages d'acides de forces voisines. Un programme d'ordinateur capable de traiter cinq acides simultanément est proposé pour évaluer les valeurs de titrage. Les résultats montrent qu'il est possible de doser deux acides, dont les constantes de stabilité ne diffèrent que d'environ une unité logarithmique, avec une précision supérieure à 1%; il est même possible d'obtenir une précision de 2% pour des constantes différent de 0.2 unités logarithmiques.

ZUSAMMENFASSUNG

Genaue und reproduzierbare experimentelle Methoden, die für die Bestimmung von Stabilitätskonstanten in wässrigen Lösungen entwickelt worden sind, werden bei Titrationen von Säuren angewendet, die nahezu gleiche Säurestärken haben. Für die Auswertung der Titrationsergebnisse wurde ein Computerprogramm aufgestellt, mit dem fünf Säuren gleichzeitig behandelt werden können. Die Ergebnisse zeigen, dass zwei Säuren bestimmt werden können, deren Stabilitätskonstanten sich nur um eine Logarithmische Einheit voneinander unterscheiden; die Genauigkeit ist hierbei besser als 1%. Unter günstigen Bedingungen ist es sogar möglich, mit etwa 2% Genauigkeit ein Gemisch zweier Säuren zu analysieren, deren Konstanten sich nur um 0.2 Logarithmische Einheiten unterscheiden.

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SHORT COMMUNICATION

A programmer for cyclic voltammetry

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In cyclic voltammetric studies it is frequently desirable to examine the current–potential curve on the second, third or later potential cycles in order to gain information about intermediates, unstable products or follow-up chemical reactions giving rise to electroactive products. At slow sweep rates (500 mV s^{-1} or less) it is possible to record only the cycles of interest by manual switching of either the recorder or in some instances the potentiostatic instrumentation. However, at higher sweep rates some type of electronic switching becomes necessary and the voltammograms must be recorded on an oscilloscope.

Reported here is such an electronic switching device which, when used in conjunction with the function generator described by Myers and Shain[1], permits display of any selected potential cycle (or cycles) through the fifth cycle at sweep rates of up to 1000 V s^{-1}. It is our experience that after the fifth cycle the vast majority of voltammograms exhibit a steady-state form, *i.e.*, they change very little upon further cycling.

In order to keep circuit design and construction to a minimum, printed circuit modules and integrated circuits were used extensively.

Circuit design and operation

A block diagram of the circuit is shown in Fig. 1. Briefly, each time the output of the function generator crosses zero volts, a pulse is produced by the zero crossing detector. This pulse is counted by counters I and II, and the number of counts accumulated by the counters is compared to the numerical values set on the thumbwheel switches I and II. When the value accumulated by the counter equals the value set on the thumbwheel switch the output of the respective comparator goes from 0 V to 5 V. In the case of comparator I this change of state is used to switch the function generator into the "hold" mode, while the output of comparator II is used to turn the electronic switch "on", thus allowing the current to be recorded. In operation, therefore, thumbwheel switch II is set to an appropriate number corresponding to the beginning of the trace to be recorded. Thumbwheel switch I is set to a number corresponding to the end of the trace to be recorded. In other words, if thumbwheel switch II is set at 4 and thumbwheel switch I at 6, the cycle recorded is between the fourth time zero is crossed and the sixth time zero is crossed, *i.e.*, the third potential cycle.

A more detailed description of each of the block modules is given below.

Zero crossing detector. The zero crossing is made up of two integrated circuit operational amplifiers, contained on a single chip, wired as analog

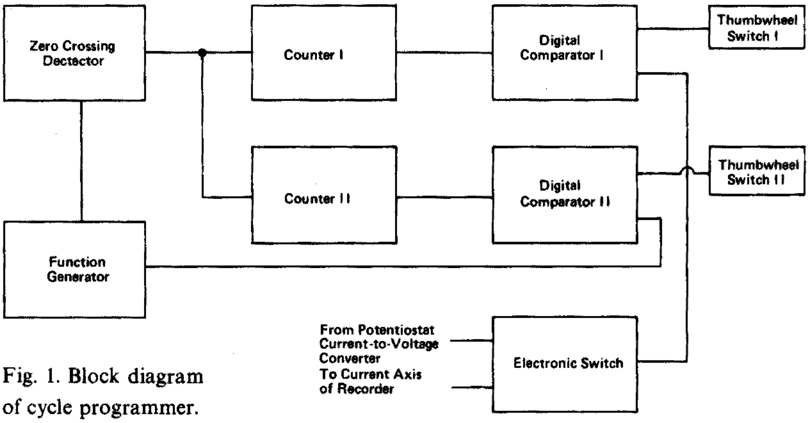


Fig. 1. Block diagram of cycle programmer.

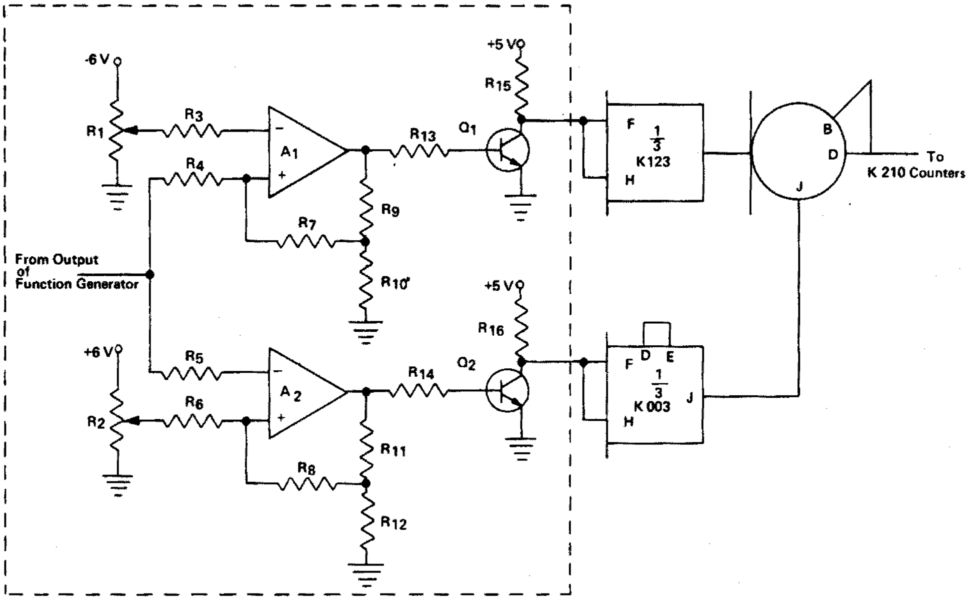
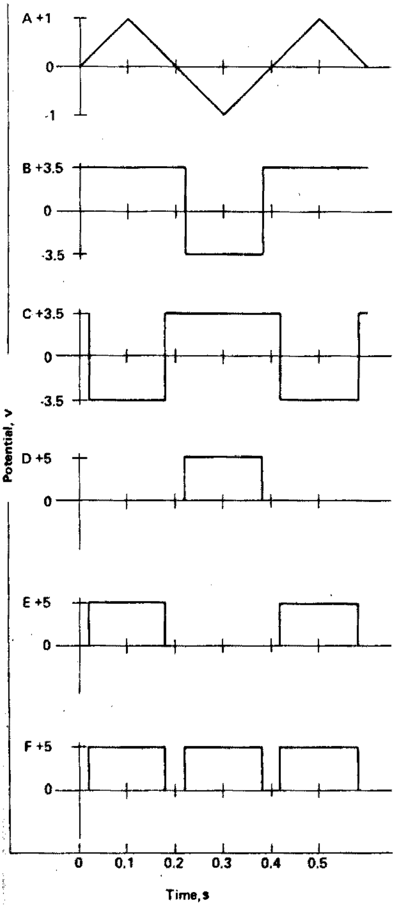


Fig. 2. Schematic diagram of zero crossing detector. (R_1, R_2) 10K trimpot; (R_3–R_8) 100K, 1%; (R_9, R_{11}) 47K, 10%; (R_{10}, R_{12}) 220K, 10%; (R_{13}, R_{14}) 10K, 5%; (R_{15}, R_{16}) 1K, 5%; (A_1, A_2) 1/2 Motorola MC1435 IC; (Q_1, Q_2) 2N718A. The K123 module is modified by removal of D_8 and D_{14} and by replacement of C_1 with switch-selected 0.01, 0.1 and 1.0 μF capacitors (see DEC schematic for K123). The portion of the circuit enclosed with the dotted line was constructed on a printed circuit card.

voltage comparators whose outputs are connected to inverters which in turn are connected to an OR gate (Fig. 2). The reference voltages for voltage comparators A_1 and A_2 are set by potentiometers R_1 and R_2, typically at values of about −50 mV and +50 mV respectively. Thus, when the non-inverting input to operational amplifier A_1 is more positive than −50 mV (*i.e.*, from the function generator) its output is at its positive limit (+3.5 V) and when the non-inverting input is more negative than −50 mV its output is at its negative limit (−3.5 V). Similarly, for amplifier A_2 when the inverting input is more negative (*i.e.*, from function generator) than +50 mV, a positive limit output is produced and an inverting input more positive than +50 mV produces a negative limit output. The output signals of the analog voltage comparators are shown in Figs. 3B and 3C. In order to obtain clean, transient-free switching of the comparators it was found necessary to introduce a small amount of hysteresis *via* resistors R_7–R_{12}. The outputs of the inverters (Figs. 3D and E) are connected to the OR gate which consists of 1/3 of a Digital Equipment Corporation (DEC) K 123 Logic Gate and 1/3 of a DEC K003 Gate Expander. The output of the OR gate is shown in Fig. 3F. In order to obtain proper counting at slow sweep rates, capacitor C_1 of the K123 module was replaced with switch-selected capacitors of 0.01, 0.1 and 1.0 μF.

Counters, comparators and thumbwheel switches. The circuit diagram is shown in Fig. 4. The counters used were DEC K210 modules which count up each time the input steps to logic 0 (0 V). This occurs each time the function



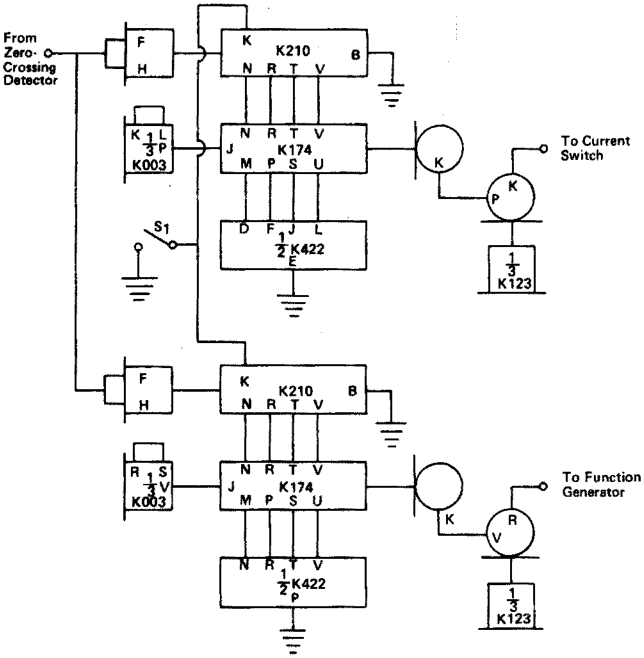


Fig. 3. Waveforms at various points in the zero crossing detector. For the purpose of illustration, a voltage sweep rate of 10 V s^{-1} between +1 and −1 V was chosen. (A) Output of function generator. (B) Output of A_1. (C) Output of A_2. (D) Collector of Q_1. (E) Collector of Q_2. (F) Output of OR gate (pin D of K123 module). This is also the input to the counters.

Fig. 4. Connection of counters, comparators, and thumbwheel switches. Letters refer to module connections. S_1 is a normally open push-button switch which clears the counters when closed.

generator output crosses 0 V (*i.e.*, see Figs. 3A and F). The DEC K174 Digital Comparators compare the counter outputs with the numerical values set on the thumbwheel switches (DEC K422). When the counter output equals the value set on the thumbwheel switches, the comparator output goes from 0 V to 5 V.

Function generator. Addition of an inverter, the output of which is connected directly to the collector of Q_3 of the function generator of Myers and Shain[1] (Fig. 5, and Fig. 1 of ref. 1), permits switching of the function generator into the "hold" mode when the comparator output goes from 0 V to +5 V.

Electronic switch. The heart of the electronic switch (Fig. 6) is an RCA CA3019 diode array which, when connected as shown[1,2], acts as a very effective electronic switch. As long as the potentials at pins 3 and 9 of G1 (Fig. 6) are positive and negative respectively, the output at pin 2 is the same as the input at pin 6 which is connected to the current-to-voltage amplifier of the potentiostat. When the polarity of the potentials at pins 3 and 9 is reversed, the output at pin 2 remains at 0 V.

Construction

The DEC printed circuit cards were mounted in a DEC H800F Connector Block, which has space for eight circuit boards. The zero crossing detector and electronic switch were constructed on printed circuit cards. Power for the DEC modules was supplied by an Elasco Model LIC5-1A ± 5 V power supply (Elasco-Eastern, Inc., Bloomfield, Conn.). Power for the operational amplifiers integrated circuits was furnished by an Acopian 6J40D-6540D supply (Acopian Technical Co., Eastern, Pa.). Other voltages were obtained from these supplies by appropriate resistive dividers.

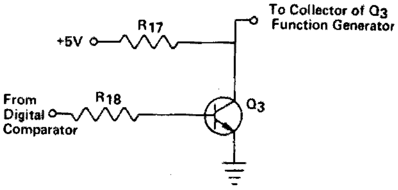


Fig. 5. Schematic diagram of inverter which is connected to the function generator. (R_{17}) 1K, 5%; (R_{18}) 12K, 5%; (Q_3) 2N718A.

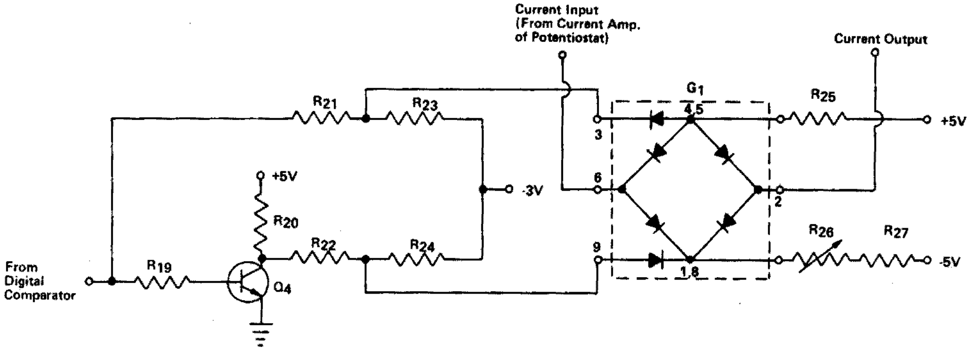


Fig. 6. Schematic of electronic switch. (R_{19}) 12K, 5%; (R_{20}) 1.8K, 5%; (R_{21}, R_{22}) 5K, 5%; (R_{23}, R_{24}) 10K, 5%; (R_{25}) 100K, 5%; (R_{26}) 20K Trimpot; (R_{27}) 91K, 5%; (Q_4) 2N718A; (G_1) RCA CA3019.

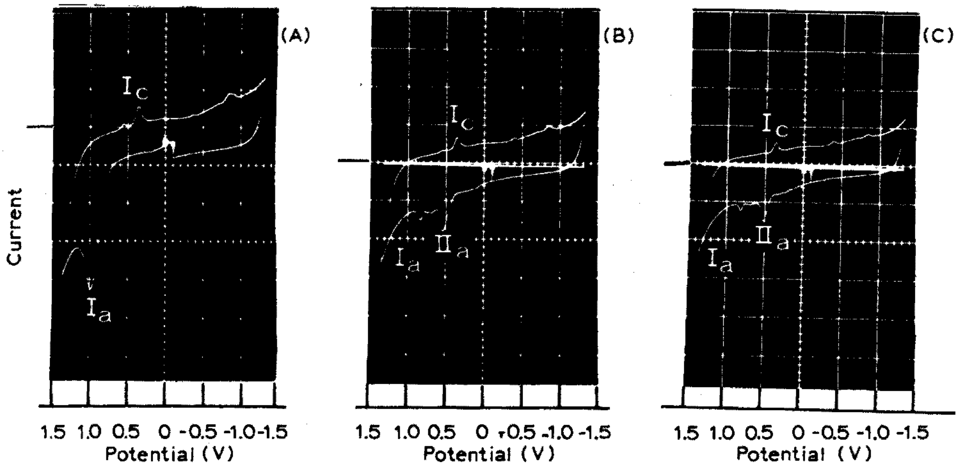


Fig. 7. Cyclic voltammetry of xanthine, saturated solution in pH 4.7 acetate buffer, at the pyrolytic graphite electrode. Voltage sweep rate, 10 V s^{-1}. All voltammograms begin at 0 V (*vs.* S.C.E.) and the initial scan is in the positive direction. Current sensitivity is 500 μA/division. Current above axis marker is cathodic, below axis marker is anodic. (A) First cycle at a clean electrode, (B) second cycle, (C) fourth cycle. Traces were recorded from a Tektronix Type 502A dual-beam oscilloscope with a Tektronix type C-27 oscilloscope camera.

Performance

The programmer was found to operate well at scan rates up to 1000 V s^{-1} (the limit of the function generator). When the electronic switch is "on", the output follows the input within ±1%.

A typical use of the programmer can be demonstrated by the electrochemical oxidation of xanthine at a pyrolytic graphite electrode (P.G.E.) in acetate buffer pH 4.7. On the first sweep at a clean P.G.E. (0.0 V→+1.40 V→0.0 V→1.3 V→0.0 V), xanthine shows a single anodic peak, $E_p = 0.95-1.0$ V, peak I_a[3]. Once peak I_a has been scanned, on the subsequent sweep in the negative direction a small cathodic peak (peak I_c; $E_p = 0.35$ V) is observed if the scan rate is fast enough (>500 mV s^{-1}). On the second and subsequent sweeps in the positive direction, peak II_a ($E_p = 0.55$ V) is observed. The cyclic programmer was used in recording the first sweep (Fig. 7A), the second sweep (Fig. 7B) and the fourth sweep (Fig. 7C).

Should it be required to record cyclic voltammograms where the potential never crosses zero volts, it should be an easy matter to adjust the circuits shown in Fig. 2 appropriately.

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SHORT COMMUNICATION

A polythene graphite electrode for voltammetry

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A variety of carbon electrodes such as impregnated graphite[1], carbon paste[2], pyrolytic graphite[3], glassy carbon[4], and recently silicon rubber graphite[5] electrodes have been developed and applied in voltammetry. The primary interest of these electrodes is for the investigation of oxidation and reduction processes in the anodic polarization range; in this range, pyrolytic graphite, glassy carbon and silicon rubber graphite electrodes exhibit low residual currents and highly reproducible current values, so that they are valuable for analytical purposes.

In the present paper the preparation of a different type of electrode made with spectral graphite and a thermoplastic polymer and its behaviour in voltammetry are described.

Electrode preparation

Spectral graphite (type GPO, 230 mesh; Electrocarbonium S.P.A., Milan) was mixed with finely powdered thermoplastic polymer, *e.g.* polythene or methacrylic esters. The mixture was placed in a suitable mould and thermosealed to a rigid polythene tube.

This procedure gave electrodes with good mechanical properties and chemical durability; as neither adhesive nor sealing of any materials was required for their preparation[6]. Though any thermoplastic polymer could probably be used, polythene was preferred and the electrode is described as the polythene graphite electrode (Pth. G. E.). When the percentage of graphite in the mixture with polythene was 70%, the resistance of the electrodes was about 1 Ohm; when the percentage was decreased to 50%, the resistance rose to about 50 Ohm and for a percentage of 30% the resistance was about 1000 Ohm. The electrodes with the smaller graphite content showed lower values of current and were less reproducible in their voltammetric behaviour.

Internal electrical contact was ensured by mercury. No problems of permeability of mercury, such as have been found with pyrolytic graphite electrodes[3], were observed.

Electrodes having two types of surface were prepared (Fig. 1). Type A had a 2.5 cm^2 electrode surface which was both planar and cylindrical, whereas type B had a planar surface of 0.5 cm^2. Planar diffusion was achieved with the latter design

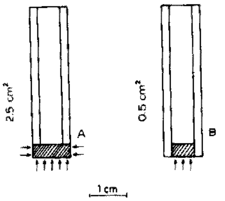

Fig. 1. Polythene graphite electrodes. (type A) Planar–cylindrical surface 2.5 cm^2; (type B) planar surface 0.5 cm^2.

TABLE I

CHANGE OF i WITH TIME AT CONSTANT POTENTIAL

(Supporting medium 1 M KCl; applied potential +0.8 V *vs.* S.C.E.; electrode area (measured): type A 2.5 cm^2, type B 0.5 cm^2)

t (s)	*Type A:* $4\cdot10^{-5}$ *M* $Fe(CN)_6^{4-}$		*Type A:* $2\cdot10^{-4}$ *M* $Fe(CN)_6^{4-}$		*Type B:* $2\cdot10^{-4}$ *M* $Fe(CN)_6^{4-}$	
	i (μA)	$i\cdot t^{\frac{1}{2}}$	i (μA)	$i\cdot t^{\frac{1}{2}}$	i (μA)	$i\cdot t^{\frac{1}{2}}$
10	4.15	13.1	17.8	56.5	4.38	13.8
15	3.42	13.2	15.4	59	3.75	14.5
20	3.08	13.8	13.6	61	3.32	14.8
25	2.81	14.1	12.6	63	3.06	15.3
30	2.60	14.2	11.6	63	2.84	15.5
35	2.43	14.3	10.9	64.5	2.68	15.8
40	2.30	14.5	10.3	65	2.50	15.8
45	2.18	14.6	9.82	66	2.40	16.1
50	2.04	14.4	9.43	66.5	2.35	16.6
55	1.97	14.6	9.10	67.5	2.08	15.5
60	1.89	14.6	8.82	68	1.94	15.0
		14.1		63.5		15.3
	Surface area calcd. = 2.56 cm^2		Surface area calcd. = 2.33 cm^2		Surface area calcd. = 0.55 cm^2	

and the diffusion law was followed; as the former, however, behaved similarly (Table I), this type of electrode, which was more easily made, was mainly used.

Method of measurement

Current–voltage curves were obtained with an Amel (Milan) polarograph. In all experiments a polarisation rate of 0.1 V min^{-1} was used. The Pth. G.E. was immersed in the solution contained in an open cell and a saturated calomel reference electrode with large surface was connected to the cell by an agar salt bridge. The total resistance of the cell and of the electrode was about 2000 Ohms.

All standard solutions were prepared from reagent-grade chemicals. Dilutions were made with an appropriate supporting electrolyte.

Results and discussion

Examination of the polarisation range. Current–potential curves were recorded in various supporting electrolytes, with the type A electrode. The results are

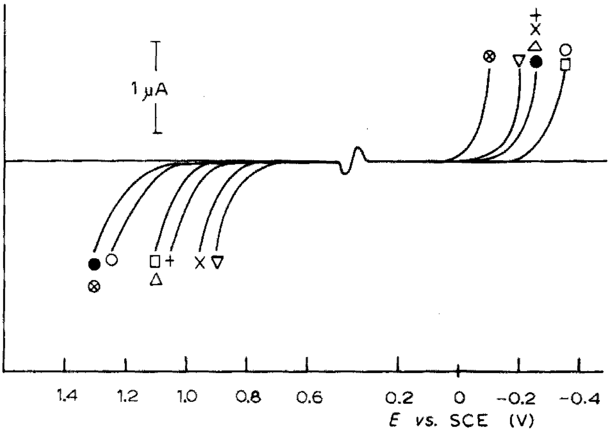

Fig. 2. Potential range for polythene graphite electrodes in various supporting media. (○) KNO_3 0.1 M (+1.25 to −0.32), (×) KCl 0.1–1 M (+0.95 to −0.24), (+) Na_2SO_4 0.1 M (+1.05 to −0.24), (●) H_2SO_4 0.1 M (+1.3 to −0.25), (⊗) H_2SO_4 1 M (+1.3 to −0.10), (□) HCl 0.1 M (+1.1 to −0.30), (△) HNO_3 0.1 M (+1.1 to −0.25), (▽) $HClO_4$ 0.1 M (+0.92 to −0.20).

plotted in Fig. 2. The residual current was very low and generally did not exceed 0.1 μA over much of the range.

Diffusion current. In order to demonstrate that the measured currents were diffusion-controlled, the oxidation of hexacyanoferrate(II) was studied with the type A and B electrodes, by recording the current over a period of time, at constant potential. The results (Table I) showed that the type A electrode yielded a higher current than the type B electrode owing to its larger working area; in both cases, however, the $it^{\frac{1}{2}}$ values were fairly constant. The electrode area can be calculated if the average value obtained is used in the expression[7]:

$$A = \frac{it^{\frac{1}{2}}\pi^{\frac{1}{2}}}{FCD^{\frac{1}{2}}} \tag{1}$$

where i is the current (A), t the time (s), F the faraday, C the concentration (moles cm^{-3}), and D the diffusion coefficient ($cm^2\ s^{-1}$). As shown in Table I, the agreement between calculated and geometrical surface is quite good.

The hexacyanoferrate(III)/(II) system was chosen in order to compare the results obtained with those of other carbon electrodes. The Pth.G.E. compared very favorably with the glassy carbon and with the pyrolytic graphite in almost all phases of this work.

Current–voltage curves. Representative curves for cathodic and anodic reactions are shown in Figs. 3 and 4. In general, the wave form is the one expected for linear-sweep voltammetry with a solid planar electrode. The voltammetric characteristics for reduction and oxidation of several inorganic ions are given in Table II; Fig. 5 shows the peak height (i_p) *versus* concentration. The peak height with the Pth.G.E. is higher than with other electrodes in the same media, and as it has a low residual current this electrode seems to have higher sensitivity.

Reproducibility and storage of electrodes. The reproducibility of the reported curves was better than 1% even from day to day for the same electrode; no pretreatment was needed before or during a series of measurements. The surface of the

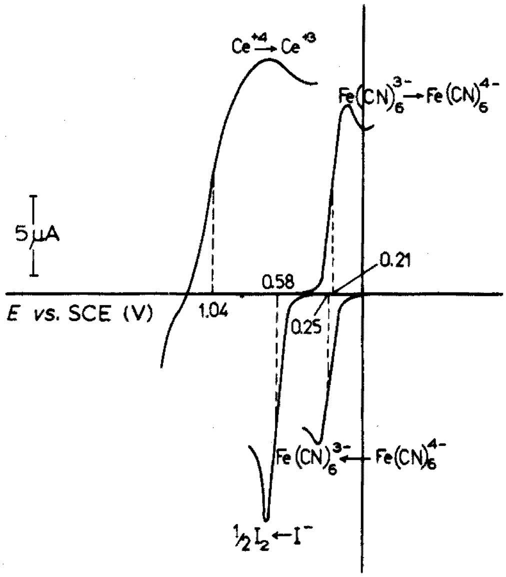

Fig. 3. Typical voltammetric cathodic and anodic curves taken with the polythene graphite electrode. Voltage scan rate, 0.1 V min^{-1}.

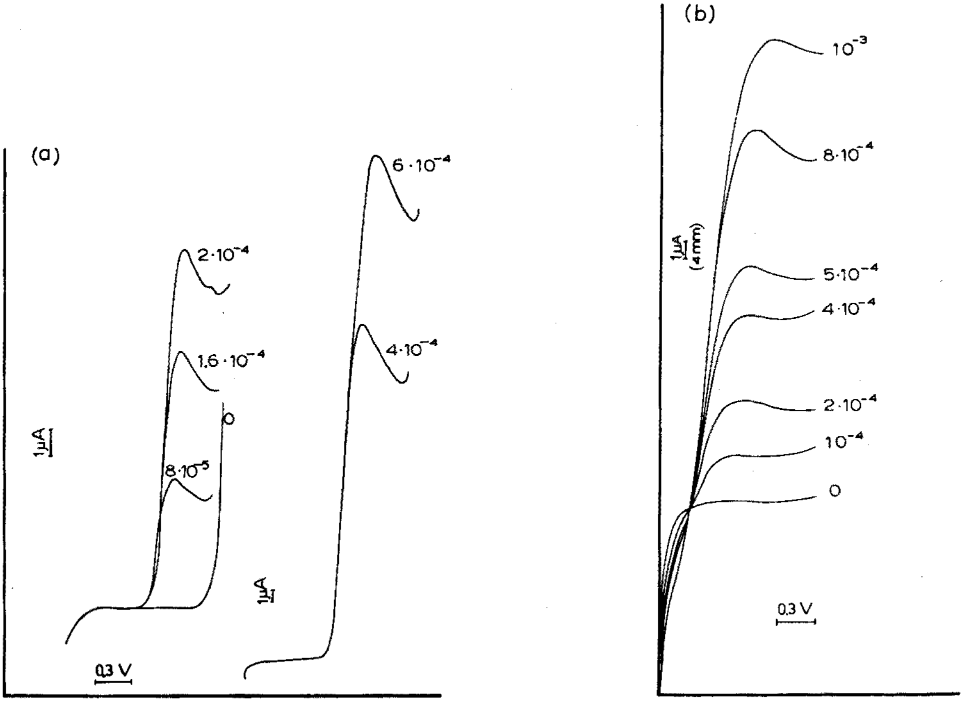

Fig. 4. Voltammograms of hexacyanoferrate(II) oxidation (a) and of cerium(IV) reduction (b). Supporting media: (a) M KCl; (b) M H_2SO_4. Concentrations are in M.

TABLE II

RESULTS OF VOLTAMMETRY AT A POLYTHENE GRAPHITE ELECTRODE

(Electrode type A; scan rate 0.1 V min^{-1})

Concentration of ion[a] *($M \cdot 10^4$)*	*i_p (μA)*	*i_p/C ($\mu A/mM \cdot 10^2$)*	*$E_{p/2}$ (V vs. S.C.E.)*	*Concentration of ion*[a] *($M \cdot 10^4$)*	*i_p (μA)*	*i_p/C ($\mu A/mM \cdot 10^2$)*	*$E_{p/2}$ (V vs. S.C.E*
Iodide				*Hexacyanoferrate(II)*			
0.20	2.30	1.15	0.585	0.40	2.50	6.25	0.245
0.40	4.30	1.08	0.585	0.75	4.70	6.25	0.255
0.80	8.9	1.11	0.580	1.50	9.30	6.20	0.245
1.00	11.3	1.13	0.575	3.00	18.6	6.20	0.263
1.20	14.0	1.16	0.575	5.00	31.0	6.20	0.255
1.50	17.0	1.13	0.570	*Cerium(IV)*			
Hexacyanoferrate(III)				1.00	1.60	1.60	1.05
0.80	4.4	0.55	0.23	2.00	3.40	1.70	1.05
1.60	8.95	0.56	0.23	4.00	6.40	1.60	1.04
2.00	12.3	0.61	0.21	5.00	8.10	1.60	1.04
4.00	22.5	0.56	0.19	8.00	12.7	1.60	1.03
6.00	33.75	0.56	0.18	10.00	15.9	1.59	1.025

[a] Supporting electrolyte: 0.1 *M* KNO_3 for iodide, 1 *M* KCl for hexacyanoferrate(III) and (II), and 1 *M* H_2SO cerium(IV).

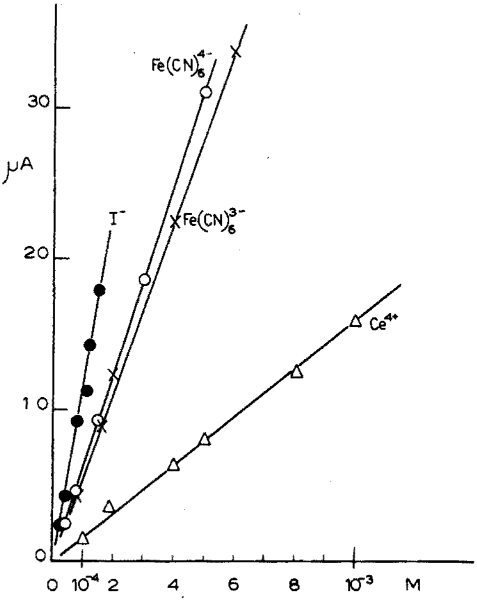

Fig. 5. i_p–C curves for some oxidation and reduction reactions at the polythene graphite electrode. Supporting media listed in Table II.

electrode obtained from the mould was shiny and remained so after several months of use.

It is well known that voltammetry at noble metal electrodes with ions of high positive potential results in ill-defined curves; this behaviour is generally attributed to a coating with oxide or hydroxide at the surface of the noble-metal electrodes.

It is interesting to compare the behaviour of graphite electrodes in the voltammetry of cerium(IV) solutions. With the pyrolytic graphite electrode[8] the reduction of cerium was found to be reversible; the peak current was calculated from the following equation, which is valid for a reversible reaction

$$i_p = (2.72 \cdot 10^5) \cdot n^{\frac{3}{2}} A D^{\frac{1}{2}} C^0 V^{\frac{1}{2}} \qquad (2)$$

where i_p is the peak current (A), A the electrode area (cm^2), C^0 the concentration of electroactive species (moles cm^{-3}), D the diffusion coefficient (cm^2 s^{-1}), V the voltage scan rate (V s^{-1}), and n the electron charge.

The agreement between the calculated and measured i_p values was about 20% for the P.G.E.; with the glassy carbon electrode the reduction of cerium(IV) is not reversible[4]; whereas on the silicon rubber graphite electrode no data are available. With the Pth.G.E., eqn. (2) can be applied and the agreement between calculated and measured i_p values for the cerium(IV) reduction was about 10%. The behaviour of other ions with a high positive charge which yield ill-defined voltammetric waves at glassy carbon or pyrolytic graphite electrodes, is under investigation.

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SHORT COMMUNICATION

Determination of cadmium in uranium and thorium compounds by atomic fluorescence spectrometry

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Cadmium in reactor materials is often determined by the dithizone method[1], which is rather tedious and time-consuming. To apply atomic absorption spectrometry for this analysis, very long-path burners[2] were necessary. Winefordner *et al.*[3,4] and Dagnall *et al.*[5] have shown the superiority of atomic fluorescence (a.f.s.) over atomic absorption (a.a.s.) spectrometry for the determination of cadmium. This note describes the application of a.f.s. for the determination of cadmium in uranium and thorium compounds at sub-p.p.m. level.

Experimental

Cadmium solution. 1.000 g of zone-refined metal (Chemistry Division of this Centre) was dissolved in analytical-grade hydrochloric acid and made up to 100 ml; the final acidity was 1 *M*. This solution was suitably diluted with 0.01 *M* acid to give a working solution of 0.10 μg Cd ml^{-1}.

Dithizone solution. A 0.02% solution in carbon tetrachloride was prepared after the reagent had been purified from the degradation products.

All other reagents were purified from cadmium either by dithizone extraction or distillation, whenever necessary.

Equipment. A Techtron AA-4 spectrophotometer with FE-1 burner and HTV-R106 ultraviolet-sensitive photomultiplier was used for a.f.s. measurements. A Microtron-200, modulator unit Mark II (285 Hz) and a 214-L $\frac{1}{4}$-wave cavity (Electromedical Supplies, U.K.) were used to provide r.f. power to the electrodeless discharge lamp.

Preparation and operation of discharge lamp. The cadmium lamps were prepared as described by Dagnall *et al.*[6]. They contained 10 mg of cadmium metal sealed under an argon pressure of 3–4 torr in a quartz tube of 8 mm i.d. and 3–4 cm length. When operated at 75 W (incident power), after an initial run-in period of a few hours, the instability of the output differed by less than 2% from the mean over a period of 30 min. The intensity was adequate to give a full-scale fluorescence signal for 0.1 p.p.m. cadmium with an air–acetylene flame.

Calibration curve. A 0.1-p.p.m. cadmium solution (in *ca.* 0.01 *M* acid) was aspirated into an air–acetylene flame. With a slitwidth of 300 μm, the fluorescence signal was adjusted to 100% transmittance. Under these conditions a linear calibration curve was obtained between 0.01 and 0.1 p.p.m. cadmium.

Application

Cadmium in uranium and thorium compounds was quantitatively separated and then determined by the procedure given below. The extraction procedure with dithizone was included in order to avoid direct atomisation of uranium or thorium solutions. The reliability of the method was tested by comparing the results on diuranate samples with those obtained by the dithizone method, as well as by the method of standard additions. The results are given in Table I.

TABLE I

DETERMINATION OF CADMIUM IN URANIUM AND THORIUM COMPOUNDS[a]

Sample	*Cd added (p.p.m. on the sample taken)*	*Cd obtained (p.p.m.)*	
		Present method	*Dithizone method*[1]
MDU Composite 1	—	0.28	0.28
		0.29	
MDU Composite 1A	—	0.19	0.25
		0.19	
MDU Composite 2	—	0.25	0.28
		0.27	
Uranyl nitrate	—	~0.012	
	0.030	0.044	
	0.060	0.074	
	0.12	0.13	
	0.18	0.20	
	0.24	0.25	
	0.30	0.30	
Thorium nitrate	—	~0.007	
	0.020	0.030	
	0.040	0.050	
	0.080	0.090	
	0.12	0.13	
	0.16	0.17	
	0.20	0.20	

[a] Sample weight taken for the separation was 2.5 g for the proposed method and 5 g for the dithizone method[1].

Procedure

Weigh about 10 g (accurate to 10 mg) of uranium or thorium compound into a 250-ml beaker. Dissolve it in dilute nitric acid and make upto 250 ml. Transfer by pipette a suitable aliquot, containing 0.1–1.0 μg of cadmium, into a separating funnel. Add 20 ml of 50% (w/v) ammonium citrate solution, make the mixture just alkaline with 10% (v/v) ammonia solution and then add 5 ml in excess; finally add 5 ml of 1% (w/v) potassium cyanide solution*. Extract the cadmium with 5-ml

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* Cyanide is useful, particularly in the case of diuranate samples, to mask other extractable cations.

portions of dithizone solution until the organic phase has a pure green colour. Collect the organic extracts in another separating funnel and wash twice with 10-ml portions of water. Reject the washings. Strip cadmium with 10 ml of 0.01 *M* hydrochloric acid and aspirate it into the air–acetylene flame. Measure the fluorescence signal and compute the cadmium content from a calibration graph.

Conclusions

The results in Table I show that the proposed method is quite satisfactory for the determination of cadmium in materials of nuclear purity. The standard deviation for the determination of cadmium at 0.06 p.p.m. level was 7% (8 determinations). The blank value varied from 0.01 to 0.02 μg in different experiments.

The authors are grateful to Dr. M. Sankar Das, Head of the Analytical Chemistry Division, for his keen interest in the work. Our thanks are due to Ss. S. Ganapathy Iyer and P. V. Pandit for the results by the dithizone method on MDU samples.

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SHORT COMMUNICATION

Graphite rod atomization and atomic fluorescence for the simultaneous determination of silver and copper in jet engine oils

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Considerable research efforts have been recently directed towards development of multichannel spectrometers for the simultaneous determination of a number of elements in samples. The multichannel spectrometers have been used in conjunction with atomic emission spectrometry, atomic absorption and flame emission spectrometry, X-ray fluorescence spectrometry, spark-source mass spectrometry, and atomic fluorescence spectrometry with a sequential measurement system. All these have required the use of multiple slits or apertures and one or more photomultiplier detectors[1–6]. In a recent article, Winefordner *et al.*[7] have described the use of a single spectrometer (one entrance and one exit slit) and one photomultiplier for atomic absorption determination of copper and silver by sequential atomization. Proximity of the second most sensitive copper line at 327.40 nm and the most sensitive silver line at 328.07 nm was advantageously utilized by setting the monochromator at a wavelength between 327.4 nm and 328.1 nm and using a monochromator spectral bandwidth of about 0.7 nm and a multielement hollow cathode. The determinations were carried out by atomizing copper and silver sequentially with different atomizing conditions for each element. This, however, required critical control of atomizing conditions for each element.

This paper describes a simplified atomic fluorescence technique, whereby both silver and copper can be determined *simultaneously* without altering any conditions for sample atomization. Both the elements are atomized simultaneously from a heated graphite rod at an intermediate temperature (1800°K), and the two separate atomic fluorescence peaks resulting for silver and copper are employed for their analysis in used jet engine oils provided by the U.S. Air Force Spectrochemical Oil Analysis Program (S.O.A.P.).

Experimental

The experimental arrangements for atomic fluorescence measurements with the graphite rod atomizer, described previously[8], were used. The multiple-element electrodeless discharge lamp light source containing the elements Ag–Co–Cr–Cu–Fe–Mn–Ni–Pb–Sn was used[9] in the "simultaneous mode" at a controlled tem-

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perature of 450°C. The spectrometer and electronics were similar to those described elsewhere[8,9]. The monochromator was set at a wavelength of 327.75 nm with a 1-mm entrance slit. Standard solutions containing 0–20 μg ml^{-1} of silver 2-ethylhexanoate and bis(1-phenyl-1,3-butanediono)copper(II) in a synthetic oil (Phillips Condor 105) were used for the construction of the analytical curves.

Atomic fluorescence measurements for both the standards and the used jet engine oils were performed by placing 0.5-μl samples in the cavity on the top of

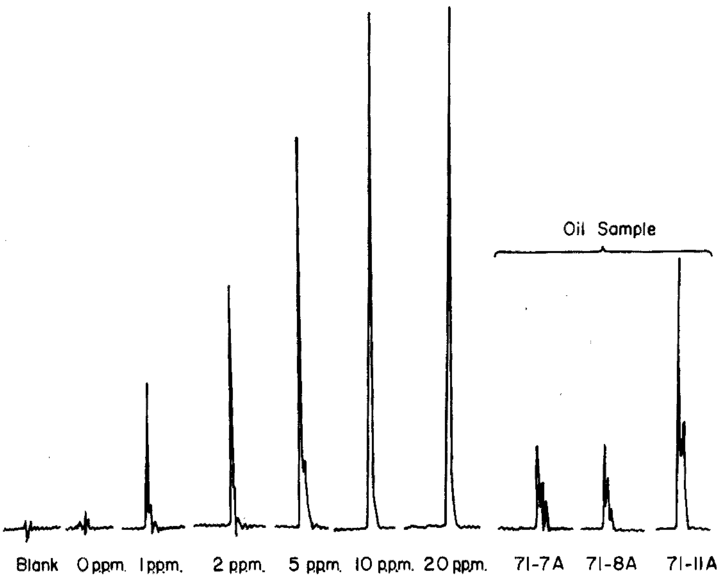

Fig. 1. Examples of atomic fluorescence signals from simultaneous atomization of silver and copper for standard solutions containing 1, 2, 5, 10, and 20 μg ml^{-1} of both silver and copper and for jet engine oils 71-7A, 71-8A, and 71-11A from S.O.A.P.

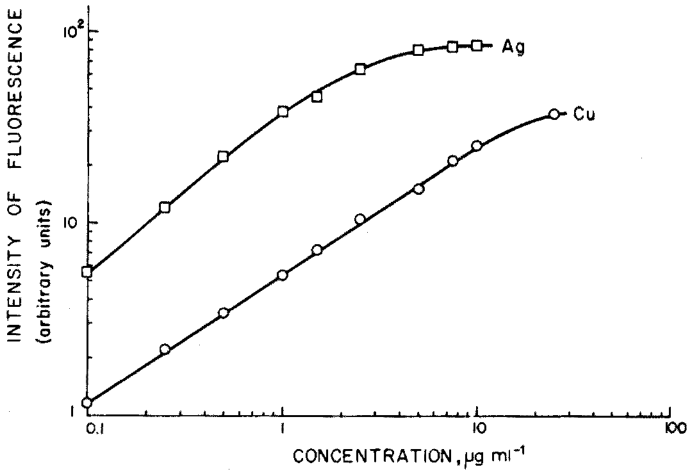

Fig. 2. Atomic fluorescence analytical curves for simultaneous atomization of silver and copper.

TABLE I

COMPARISON OF SILVER AND COPPER DETERMINATION IN ENGINE OIL SAMPLES BY DIFFERENT METHODS

Sample	*Element*	*Concentration ($\mu g\ ml^{-1}$)*		
		Emission[a] *Air Force* *Mean, S. D.*	*Atomic absorption*[b] *Air Force* *Mean, S. D.*	*Atomic fluorescence*[c] *This work* *Mean, S. D.*
72-1A	Ag	0.5±0.8	0.7±0.3	1.4±0.1
	Cu	10.5±3.6	7.2±0.8	7.0±0.8
72-4A	Ag	0.9±0.4	0.6±0.7	0.7±0.1
	Cu	5.6±0.7	2.3±0.6	1.9±0.4
71-3A	Ag	0.3±0.5	0.7±0.2	1.0±0.1
	Cu	1.8±0.7	1.8±0.3	3.0±0.7
71-7A	Ag	0.3±0.5	0.4±0.2	0.5±0.1
	Cu	9.1±7.4	4.4±0.4	5.1±0.6
71-8A	Ag	0.0	0.3±0.1	0.6±0.1
	Cu	6.8±2.1	4.2±0.4	5.2±1.4
71-10A	Ag	0.3±0.5	0.5±0.2	0.8±0.1
	Cu	12.6±1.9	8.1±0.7	7.2±1.2
71-11A	Ag	1.0±0.8	1.2±0.2	2.3±0.2
	Cu	22.7±6.1	14.2±0.9	12.2±1.0
70-2A	Ag	0.0	0.6±0.5	0.8±0.1
	Cu	2.9±0.5	2.2±0.6	4.1±1.4
70-3A	Ag	0.0	0.2±0.2	0.3±0.2
	Cu	1.6±0.7	1.0±0.1	3.8±0.5
70-5A	Ag	0.4±0.4	0.6±0.1	1.0±0.3
	Cu	10.0±2.1	5.3±0.4	6.1±1.8
69-6A	Ag	4.9±1.3	4.9±0.4	5.9±0.5
	Cu	10.8±1.5	6.8±0.6	7.8±0.9
69-7A	Ag	6.2±1.1	5.2±0.4	5.8±1.1
	Cu	11.3±2.7	6.2±0.5	7.2±1.1
69-8A	Ag	1.4±0.5	1.9±0.3	3.9±0.4
	Cu	22.8±2.4	18.9±1.8	16.6±2.2
69-12A	Ag	0.4	1.0±0.1	1.3±0.1
	Cu	6.9±1.0	4.4±0.3	4.0±0.8

[a] U.S. Air Force S.O.A.P. Laboratories, emission (Central Labs.) values.
[b] U.S. Air Force S.O.A.P. Laboratories, flame atomic absorption values.
[c] Present work, simultaneous atomic fluorescence technique.

a Poco FX91 graphite rod with a 1-μl syringe (Hamilton Co. Inc., Whittier, Calif.). The samples were ashed at 42 A (645°K) for 18 s. Silver and copper were simultaneously atomized by suddenly increasing the current to 98 A for 3 s to give a temperature of about 1800°K. The resulting atoms produced two resolved atomic fluorescence peaks. An atmosphere of argon and hydrogen (with flow rates 6.4 l min^{-1} and 1.2 l min^{-1}, respectively) was maintained around the graphite rod atomizer[7–9].

Results and discussion

Atomic fluorescence signals resulting from the simultaneous atomization of silver and copper from the graphite rod are shown in Fig. 1 for different standard solutions containing 1, 2, 5, 10, 20 μg ml^{-1} of both silver and copper, and the S.O.A.P. oil samples 71-7A, 71-8A, and 71-11A. In Fig. 2, analytical curves following simultaneous atomization are given for silver and copper. The analytical curve for silver shows curvature at concentration higher than 1 p.p.m. However, in the case of copper, the analytical curve is linear over the entire concentration range studied. Furthermore, linearity and slopes of the analytical curves remained constant from day to day.

The results for silver and copper in used jet engine oil samples, determined by the simultaneous atomic fluorescence technique, are compared with the mean values from the U.S. Air Force S.O.A.P. laboratories by emission and flame atomic absorption methods in Table I. It can be seen that there is reasonable agreement among the values, and that results from the simultaneous atomization technique usually fall within the standard deviations of the results from the S.O.A.P. laboratories.

The relative standard deviations calculated from 10–15 determinations for different oil samples by this technique were between 6 and 12%. This is certainly not as satisfactory as can be obtained by separate determinations for both elements. However, the slight loss in precision is compensated by the saving in time achieved.

With the development of sophisticated optical multichannel analyzers, the technique of simultaneous atomization from the graphite rod might be very useful in the simultaneous determination of other combinations of elements by judicious choice of the atomization conditions. The principle of simultaneous atomization from the graphite rod atomizer may be advantageously utilized for quick trace elemental analysis of several elements in a wide variety of samples.

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SHORT COMMUNICATION

Separation of matrix absorption and enhancement effects in the determination of sulfur in sea water by X-ray fluorescence*

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A recent report[1] described the use of X-ray fluorescence analysis for the determination of total sulfur in sea water. Large variations in salinity were found to have a marked effect on the observed intensity of SK_α fluorescence. An apparent correction for this matrix effect was achieved by using the scattered radiation method of internal standardization[2]. Other studies[3,4] have demonstrated that scattered bremsstrahlung measured in the soft region is less useful than is short-wavelength bremsstrahlung or Compton bands associated with scattered X-ray tube lines in compensating for matrix absorption effects in aqueous systems. These studies have shown that the degree of internal standardization afforded by the scattered radiation method is poor if the "peak-to-background" approach is used in the solft region, as it was in the case of Gallo *et al.*[1]. These findings have prompted an investigation into the relationship between matrix absorption and enhancement effects as observed in the determination of sulfur in sea water.

Experimental

Apparatus and equipment. X-Ray measurements were made with the equipment and operating conditions described previously[1] except that an improved thin-window, high-intensity chromium target X-ray tube (Machlett FAAQ 60/3.5) operated at 60 kV and 25 mA was used.

Reagents. Solutions were prepared with deionized distilled water, from reagent-grade chemicals. Sulfate standards were prepared from lithium sulfate monohydrate. Sodium and chlorine were added to the primary sulfate standards as matrix variants in various forms: sodium and chlorine together, as sodium chloride; sodium alone, as borax; chlorine alone, as lithium chloride. The composition of the resulting solutions is shown in Table I.

Analysis. The intensity of SK_α fluorescence (I_F) at a wavelength of 5.372 Å as well as the intensity of scattered bremsstrahlung (I_{SR}) at 5.299 Å were measured. Solutions 1, 2 and 3 were used to establish calibration curves based upon sulfur

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TABLE I

COMPOSITION OF SOLUTIONS

Solution	*S (p.p.m.)*	*Na (%)*	*Cl (%)*	*Solution*	*S (p.p.m.)*	*Na (%)*	*Cl (%)*
1	800	—	—	7	400	2.00	—
2	400	—	—	8	400	1.00	—
3	200	—	—	9	400	0.50	—
4	400	2.00	3.08	10	400	—	3.08
5	400	1.00	1.54	11	400	—	1.54
6	400	0.50	0.77	12	400	—	0.77

TABLE II

INTENSITIES, RATIOS AND APPARENT COMPOSITIONS

Sample	*SK_α (counts s^{-1})*	*I_{SR} (counts s^{-1})*	*I_F (counts s^{-1})*	*I_F/I_{SR}*	*Apparent composition I_F only:*	*I_F/I_{SR}*
1	391	55	336	6.11	—	—
2	231	57	174	3.05	—	—
3	142	55	87	1.58	-	—
4	204	51	153	3.00	368	392
5	223	56	167	2.98	402	390
6	216	53	163	3.07	392	402
7	216	62	154	2.48	370	322
8	209	57	152	2.66	366	346
9	210	56	154	2.75	370	358
10	270	55	215	3.91	516	514
11	260	55	205	3.73	492	486
12	229	53	176	3.32	422	434

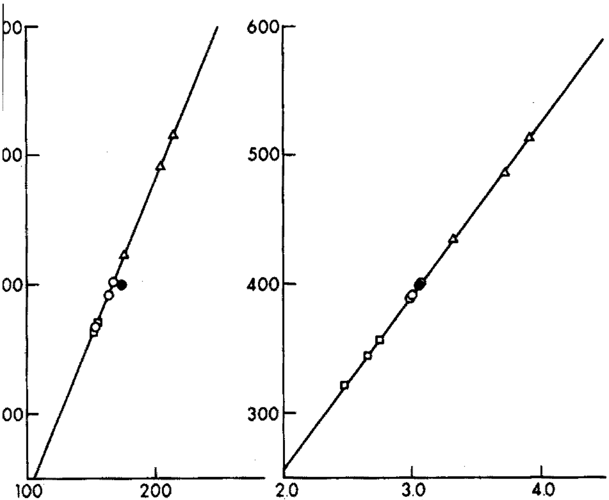
concentration (p.p.m.) plotted *vs.* I_F and also *vs.* I_F/I_{SR}. The intensity of SK_α fluorescence, I_F, was defined as the total intensity at 5.372 Å minus the background intensity (I_{SR}) at 5.299 Å.

Results

Measurements of the SK_α fluorescence and the scattered continuum at 5.299 Å for the test solutions are shown in Table II; also shown are the apparent compositions of solutions 4–12 based on the calibration curves (Fig. 1). This allows for the comparison of analytical results based upon I_F alone as opposed to I_F/I_{SR}.

Discussion

Spectroscopic behavior of the solutions is determined by the locations of absorption edges and emission lines, as well as the magnitude of the X-ray mass absorption coefficients (μ) of the constituents. This is illustrated in Fig. 2, which shows that the ClK_α radiation is strongly absorbed by sulfur, which in turn enhances the emission of SK_α. On the other hand, sodium strongly absorbs SK_α, which depresses the intensity. The ionic species lithium(I) and borate were chosen for



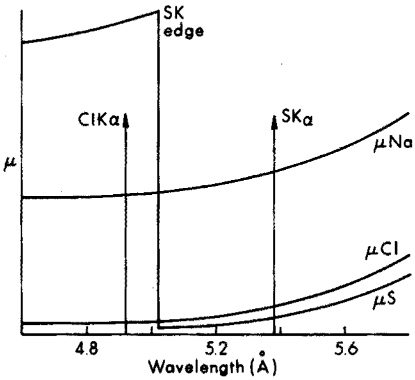


Fig. 1. Calibration curves for sulfur in sea water. (●) S only (standards); (○) S, Na, Cl; (□) S, Na; (△) S, Cl.

Fig. 2. X-Ray absorption coefficients of sulfur, chlorine, and sodium in the region of the absorption edge of sulfur.

their "transparent" nature. The X-ray mass absorption coefficients of lithium and boron are very small, compared with those of heavier elements present, so that these two elements have essentially no effect upon the observed SK_α intensity in these experiments. Thus, individual effects of sodium and chlorine can be isolated and evaluated.

Solutions containing identical concentrations of sulfur (No. 2, 4–12) but with various combinations of sodium and chlorine concentrations are expected to display a range of SK_α intensities. Relative concentrations of sodium and chlorine may be such that enhancement and absorption effects cancel.

Ordinary sea water contains concentrations of sulfur, sodium, and chlorine in the approximate ratio 1:12:22[5]. Of the samples used in this study, solution 6 most closely resembled sea water, with an approximate ratio of concentrations of 1:12:19. The sodium-to-chlorine concentration ratio in samples 4, 5, and 6 is slightly greater than that found in natural sea water.

The analytical data (Fig. 1, Table II) are not easily interpreted if I_F alone is considered. Irregularities in the results could arise from several causes, such as bubble formation in the liquid specimens, wrinkles in the Mylar cell windows, etc., which were unnoticed during the experiment. When I_F/I_{SR} ratios are used, the interpretation is simpler. Data points of the calibration curve are slightly more collinear, and the trends in the enhancement and absorption of the SK_α fluorescence are displayed much more uniformly as a function of the amount of matrix variant used.

The use of soft scattered continuum as an internal standard has little effect on the matrix absorption effect of sodium (solutions 7, 8 and 9). This result confirms predictions of previous soft-region studies[3,4] with aqueous solutions. Also, it clearly shows that matrix enhancement effects (solutions 10, 11 and 12) are not compensated for by the scattered radiation method, which has been pointed out previously[6]. An apparent compensation for variations in salinity shown in the case of solutions 4, 5 and 6, is therefore interpreted as a fortuitous combination of matrix effects which obtains because of the unique character of sea water.

Conclusions

The scattered radiation method with soft scattered bremsstrahlung affords only slight compensation for matrix effects in X-ray analysis for sulfur in sea water. The technique offers an effective means by which the effects of instrumental variations and sample inhomogeneities may be diminished.

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SHORT COMMUNICATION

Rapid determination of heavy elements in organometallic polymers by X-ray fluorescence

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In organometallic polymer chemistry, chemical analysis of the metal content of the polymers is not only a convenient approach to characterize the polymer composition[1–5], but frequently it represents the only practical method of obtaining the M_1/M_2 ratio in organometallic copolymers. This situation results because many organometallic monomers are difficult or impossible to analyze by g.l.c. Thus, an analysis of the unreacted monomers from the reaction mixture is tedious, and it is more efficient to analyze the resulting polymers directly. A knowledge of the mole ratio of the metal atoms in bimetallic copolymers[6] permits the calculation of the relative reactivity ratios[7], r_1 and r_2, which define the copolymerization. In cases in which the polymer is prepared from only one organometallic monomer[1–3], the knowledge of the metal content still permits the calculation of the percent of each monomer in the copolymer. Furthermore, analysis of the metal content is often far more sensitive in indicating the M_1/M_2 ratio than a carbon–hydrogen analysis would be.

When these samples are submitted to commercial analytical laboratories, the analyses are usually performed by conventional techniques after wet-ashing the sample. X-Ray fluorescence has already been shown to provide a rapid and in many cases a nondestructive method for the determination of the central metal atoms in organometallic compounds[8]. A major advantage of this procedure is that more than one element may be determined on a single sample. The technique is rapid, requiring only about 20 min for duplicates of a sample if standards are previously prepared. This technique has been applied to organometallic polymers and the results compared with those obtained by commercial analytical laboratories.

Experimental

Apparatus. The instrument used was a Philips-Norelco PW-1410 X-ray spectrometer. A LiF 200 analyzing crystal and a molybdenum target tube were used for all analyses. The spectrograph was equipped with scintillation and gas flow proportional counters, the latter using P-10 gas. For each element the detector giving the largest peak to background ratio was determined, and used for subsequent analysis.

Before each set of samples was analyzed, a check for any possible spectral interferences was made. A scan of 2θ was conducted in the vicinity of the angle to be used for the analysis to check for overlapping peaks. Also a pulse height scan was made at the selected 2θ angle to ensure correct setting of the counter voltage, and to check for higher-order components in the radiation being counted.

The spectrometer is equipped with an ASR-33 teletype unit for data output. A switch was added to provide a circuit modification so that the teletype could double as a remote terminal to a CDC 6400 time-shared computer. Calibration and sample data were taken on paper tape in the instrument mode. After completion of a run, the teletype was switched to the computer mode and a program called which prepared a least-squares working curve from the calibration data, and computed the results including statistical parameters for the unknowns. All results were displayed at the teletype a few minutes after the run was completed.

Reagents. Standards were analytical reagent-grade chemicals and were used without further purification. Iron wire and manganese dioxide dissolved in hydrochloric acid were used as the iron and manganese standards. Whatman no. 40 filter paper was used for paper discs which were punched out with a die with a diameter of *ca.* 0.5 in. The paper discs were mounted on aluminum (for manganese samples) or copper (for iron samples) discs of 0.625 in. diameter with double adhesive tape.

Procedure. The samples were prepared as follows. First, a series of aqueous solutions of the standards was carefully prepared such that exactly 5 μl of each solution could be used to prepare a series of discs containing amounts of the element ranging from 0.1–0.5 μmole. The 5-μl portions were added slowly so as to saturate the paper disc but not allow the solution to overrun the paper. The standard discs were then dried at room temperature and sprayed with a very light coating of 10% (v/v) collodion in acetone to protect them. With care these discs can be used as permanent standards. The compounds to be analyzed were prepared in like manner, with the amount used selected to fall within the range of the standard discs. Usually, 25–50 mg samples in 2 ml were used. Solvents were selected by the solubility of the particular compound; either tetrohydrofuran or ethyl acetate was used in all cases. Six discs for each example were prepared. The sample was supported in the X-ray beam by a mylar window in the bottom of the sample holder provided with the instrument. An aluminum washer was used to keep the sample from shifting out of the X-ray beam. The samples were rotated in the beam to ensure even irradiation. A vacuum path in the spectrometer was utilized. The samples were irradiated until 10^5 or greater counts were accumulated. In all cases, the relative standard deviation in the net counts was maintained below 1.0%.

Copolymers. The organometallic copolymers used in these studies were prepared as described elsewhere[9,10].

Results and discussion

Table I shows the results of the analyses performed on eleven organometallic polymers as well as comparison of these values with those obtained by two commercial analytical laboratories. The abbreviations for the sample labels were made by combination of the abbreviations in the legend for the monomers. For example, VCM-VF-140 is a sample of a copolymer of vinylcyclopentadienyl man-

TABLE I

RESULTS OF METAL ANALYSIS OBTAINED BY X-RAY FLUORESCENCE AND COMMERCIAL LABORATORIES

Sample no.[a]	*Element*	*X-ray (%)*	*Commercial laboratory (%)*	*Mole % M_2 in copolymer*		*Mole% VCM in copolymer (M_1)*		*Total wt.% of polymer made up of M_1 and M_2 according to analysis*		*Mole ratio M_1/M_2 in copolymer*	
				X-ray	*Comm.*	*X-ray*	*Comm.*	*X-ray*	*Comm.*	*X-ray*	*Comm.*
VCM-VF-140	Fe	18.3±0.4	16.9	70.31	71.15	29.68	28.85	101.35	92.43	0.42	0.42
	Mn	7.6±0.2	6.7								
VCM-VF-146	Fe	20.6±0.3	18.5	76.86	79.61	23.14	20.38	103.80	89.79	0.30	0.26
	Mn	6.1±0.2	4.66								
VCM-VF-155	Fe	4.5±0.5	5.1	16.69	21.61	83.31	78.39	109.66	95.60	4.99	3.62
	Mn	22.1±0.1	18.2								
VCM-VF-156	Fe	4.5±0.3	5.3	17.07	22.85	82.93	77.15	107.14	93.85	4.86	3.38
	Mn	21.5±0.4	17.6								
VCM-AN-112[b]	Mn	21.6±0.1	19.3	37.34	39.95	62.66	60.05	102.8	94.09	1.68	1.51
	N	—	3.28								
VCM-AN-128[b]	Mn	21.8±0.2	19.3	39.26	42.49	60.74	57.50	104.8	94.15	1.55	1.35
	N	—	3.59								
VCM-MA-232[c]	Mn	13.6±0.3	11.9	66.9[c]	72.8[c]	33.1	27.2	100[c]	100[c]	0.49	0.37
VCM-MA-235[c]	Mn	22.1±0.3	21.6	11.2[c]	22.39[c]	88.8	77.61	100[c]	100[c]	7.98[b]	3.46
VF-VP-A006[d]	Fe	22.1±0.5	21.3	27.1	31.1	72.9	68.9	100[d]	100[d]	2.66	2.17
VF-VP-A010[d]	Fe	24.6±0.5	22.3	12.7	25.7	87.3	74.3	100[d]	100[d]	7.16[e]	2.62
VF-VP-B001[d]	Fe	15.8±0.5	14.9	59.0	59.6	41.0	40.4	100[d]	100[d]	0.68	0.67

[a] VCM = vinylcyclopentadienyl manganese tricarbonyl, VF = vinylferrocene, AN = acrylonitrile, MA = methylacrylate, VP = N-vinylpyrrolidone.

[b] The X-ray analysis of N was not performed. Thus, calculations of (1) the mole % M_2 in copolymer and (2) the total wt.% of polymer made up of M_1 and M_2 (for the X-ray analyses) were done using the commercial % N.

[c] Mole % of M_2 was not measured directly; thus, it was determined by 100 − % M_1. Thus, the total wt.% of polymer must be 100%.

[d] Vinylferrocene is defined as M_1, N-vinylpyrrolidone is M_2. All calculations are based on the % Fe as nitrogen analyses were not performed. Thus, the mole % of M_2 is 100 − mole % M_1. For this reason the total wt.% of polymer made from M_1 and M_2 had to come to 100%.

[e] The mole ratio is very sensitive to the analysis as the % $M_1 \rightarrow 100$ and % $M_2 \rightarrow 0$. Thus, moderate or small differences in analyses make a large difference in M_1/M_2 in appropriate cases.

ganese tricarbonyl with vinylferrocene[9]. The most obvious comparison is that the results obtained by X-ray are in nearly all cases higher than those obtained by the commercial laboratories. The most likely possibility is that sample loss occurred during the ashing process used by the commercial laboratory. In the case of the first four copolymers, the X-ray results accounted for 101.4–109.7% of the sample, whereas the commercial results accounted for 89.8–93.9% of the sample. The X-ray values are the average and standard deviation of six replicates and show excellent precision. The commercial values are at best duplicates and nothing is known of the precision.

One difficulty was encountered with the polymers which was not encountered with compounds analyzed earlier. The calibration curves were prepared by dispensing an aqueous solution onto the filter paper disc. The samples, however, were dissolved in either tetrahydrofuran or ethyl acetate. These solvents did not penetrate the paper as well as aqueous solutions, and there was some possibility of a molecular weight gradient of the polymer developing on the paper. The result was that the count rate obtained was dependent upon the solvent and which side of the disc was facing the X-ray beam and detector. A study showed that this effect was reproducible and that a correction factor could be applied if the side of the disc to which the sample was applied was placed facing the X-ray beam and detector.

The mole ratio calculations shown in the last column in Table I range from excellent agreement between our results and those obtained by commercial laboratories to very poor agreement. However, those showing poor agreement are cases of large mole ratios, which are inherently sensitive to variations in the analyses.

The technique of the paper disc as a support matrix for X-ray fluorescence analysis of organometallic monomers and polymers should prove to be of considerable value. The relatively inexpensive, nondispersive X-ray fluorescence units now available should encourage the use of this technique as a rapid, nondestructive method of analysis of metallic elements in these compounds. With the use of multichannel analyzers, several elements may be determined simultaneously.

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SHORT COMMUNICATION

The fluorimetric determination of phosphate with thiamine

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Trace amounts of phosphorus play important roles in various chemical, physical or biological systems and there is an increasing interest in analytical methods capable of its determination at levels of less than 1 p.p.m.; fluorimetric methods based upon ion-association complexes of molybdophosphate with organic molecules have recently been reported[1,2]. A method for the fluorimetric determination of phosphate at the p.p.b. level is described here; phosphate is converted to hexadimolybdatophosphate which is then reacted with non-fluorescent thiamine to produce the highly fluorescent thiochrome[3].

Experimental

Apparatus and reagents. All fluorimetric measurements were made with an Aminco-Bowman Spectrofluorimeter in 1-cm quartz cells with a xenon arc source. The instrument was standardized with a 1 p.p.m. solution of quinine sulphate; slit widths for all measurements were 1, 4, 5, 5, 4, 3, 5 mm for slits 1–7, respectively.

Solutions of the desired concentration were freshly prepared daily by dilution of the following stock solutions: 0.01 *M* thiamine chloride hydrochloride (USP, Aldrich), 0.01 *M* (in terms of Mo) molybdate from $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (AR, Mallinckrodt), and 0.01 *M* phosphate from potassium dihydrogenphosphate (ACS, Fisher).

The buffer was a 0.1 *M* solution of borax.

Procedure. To 1 ml of 1:100 sulphuric acid, add 5 ml (or less) of an approximately neutral unknown solution containing 0.050–1.00 μg of phosphate, 0.8 ml of 0.01 *M* ammonium molybdate, and 0.8 ml of 0.001 *M* thiamine. Add 2 ml of 0.1 *M* borax and dilute to 10 ml with twice-distilled water. Measure the fluorescence intensity at 440 nm using an excitation wavelength of 375 nm. Determine the amount of phosphate from a calibration curve, in the preparation of which the volume of phosphate standard used was approximately the same as the unknown.

Results and discussion

Figure 1A shows a calibration curve obtained without subtraction of the blank; it is a straight line up to 30 p.p.b. of phosphate but does not pass through the origin because of background fluorescence. A straight line through the origin is obtained by subtraction of the blank (Fig. 1B), and even 1 p.p.b. of phosphate can be determined at higher instrument sensitivity. The standard deviation of seven determinations of 50 p.p.b. of phosphate was 3%; for 5 p.p.b. the deviation was less than 10%.

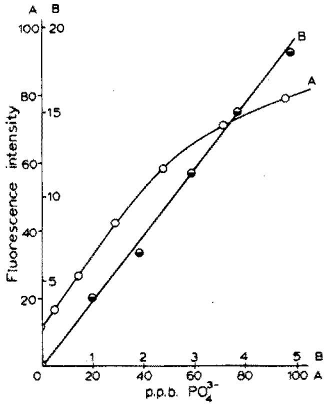

Fig. 1. Calibration curves. (A) 5–100 p.p.b. phosphate at meter multiplier (MM) setting of 0.1 and sensitivity (s) of 0; (B) 1–5 p.p.b. phosphate at MM of 0.03 and s of 0.

The method was successfully applied to the determination of phosphate in sodium chloride by standard addition; a sample of reagent-grade Baker & Adamson salt was found to contain 0.5 p.p.m. of phosphate. The well established molybdenum blue photometric method could not be used because no colour formed at the sodium chloride concentrations (2%) allowable in the fluorimetric procedure, and lower salt concentrations did not have sufficient phosphate present to be determined colorimetrically. The fluorimetric method is more sensitive than the colorimetric one and time is not a critical factor in the formation of the product used for measurement; except for mercury and iron, most common ions can be tolerated at substantially higher concentrations than in the colorimetric one.

Effect of anions and cations. Fifty p.p.b. of phosphate was successfully determined in the presence of a 10,000-fold molar amount of acetate, chloride, nitrate, perchlorate or thiocyanate, or a 1,000-fold amount of bromide, fluoride, or tartrate. Results were also satisfactory with a 100-fold amount of citrate, EDTA, iodide or persulphate. A 10-fold amount of silicate or hexacyanoferrate(III) could be present but larger amounts increased the fluorescence intensity; an equivalent amount of sulphide strongly quenched the fluorescence.

A 10,000-fold molar amount of Ni(II), Mn(II), or Cd(II), and a 1,000-fold amount of Cu(II), Co(II), Ca(II), Zn(II) or Al(III) did not interfere. A 10-fold amount of iron(III) and an equivalent amount of iron(II) could be present, but an order of magnitude increase in concentration decreased the fluorescence. Mercury(II) and mercury(I) markedly increased the fluorescence even at equimolar ratios.

The fluorescence intensity depends, of course, upon the amount of thiochrome obtained by oxidation of thiamine by the dimolybdatophosphate formed from phosphate on reaction with molybdate in acid solution. Provided that there are no other species in solution capable of oxidizing* thiamine to thiochrome, the same fluorescence intensity would be observed for the same phosphate concentration if there are no interferences in (*a*) the formation of dimolybdatophosphate, (*b*) the oxidation of thiochrome, or (*c*) the fluorescence output of thiochrome. Thus silicate interferes because it forms a heteropoly acid capable of oxidizing thiamine, and hexacyanoferrate(III) also oxidizes thiamine to thiochrome; sulphide interferes with the oxidation of thiamine. Iron(II) interferes in the oxidation step; the interference of iron(III) is due to the absorption or scatter of fluorescent light by nuclei of the hydrous oxide. Mercury(I) and (II) increase the amount of thiochrome formed either through direct or catalytic oxidation of thiamine.

Factors affecting fluorescence. For analytical purposes reaction conditions must be such as to maintain a constant fluorescence intensity difference between the required ion and the blank (for the same concentration). The ratio of the intensity of sample (I_s) to blank (I_b) fluorescence is also important because the ratio I_s/I_b is a measure of the practical sensitivity of the method. Thus if, for the same sample concentration, I_s increases with a change in pH from 20 to 30 and I_b increases from 10 to 20, $I_s - I_b$ remains constant but I_s/I_b decreases and the sensitivity also decreases.

Important factors in the determination of phosphate with thiamine are the starting acidity, the thiamine concentration, the molybdenum concentration and the final pH.

For phosphate concentrations of 5–100 p.p.b., I_s/I_b was a maximum when 1 ml of (1+99) sulphuric acid was initially present; the amount of molybdophosphate formed is highly acid-dependent[4]. I_b was unchanged when more acid was present but I_s decreased rapidly; I_b increased with decreasing acidity whilst I_s decreased slightly. For example, the I_s/I_b ratio was 1.4, 2.1 and 1.6 for 0.25, 1.0 and 2 ml of (1+99) sulphuric acid added, respectively; similar results were obtained on replacing sulphuric with hydrochloric or nitric acids.

The I_s/I_b ratio remained unchanged for final thiamine concentrations of $6–10 \cdot 10^{-5}$ *M* and molybdenum concentrations of $5–10 \cdot 10^{-4}$ *M*. I_s decreased for higher or lower thiamine concentrations (I_b did not change appreciably over the range studied); for higher molybdenum concentrations I_b increased faster than I_s whilst the reverse was true with lesser amounts of molybdenum present. Molybdenum concentrations of *ca.* $8 \cdot 10^{-4}$ *M* and thiamine concentrations of *ca.* $8 \cdot 10^{-5}$ *F* are recommended for best sensitivity.

A final pH of *ca.* 8 is necessary for maximal sensitivity. Above pH 8 the absolute increase in I_s and I_b was the same but I_s/I_b decreased; from pH 2–8 the blank fluorescence was constant but I_s increased. For example, the I_s/I_b ratio was 1.0, 6.5 and 2.0 for respective pH values of 2.3, 8.0 and 12.0; $I_s - I_b$ was constant from pH 8 up, but the sensitivity decreased as a result of the high blank reading.

With increasing temperature, both I_s and I_b increased to the same degree. For example, 47.5 p.p.b. of phosphate gave I_s and I_b values of 54 and 5, respectively, at 24°, and readings of 79 and 27 at 95°. Again the $I_s - I_b$ figure was essentially unchanged, whilst I_s/I_b decreased.

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* Oxidizing agents, before formation of molybdophosphate, can be destroyed by treatment with sulphite; excess of sulphite must be removed by heating before addition of molybdate.

No change in fluorescence intensity was observed for solutions allowed to stand for various time periods before measurement (up to 30 min before adjustment to pH 8, and up to 330 min after adjustment). The fluorescence measurement can therefore be performed immediately after mixing the reactants and the fluorescence reading is stable for several hours at least.

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SHORT COMMUNICATION

A radioreagent method for the determination of traces of bismuth

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Bismuth is one of the few elements which is insensitive to nuclear methods of trace analysis. Both neutron activation analysis[1] and charged particle activation analysis[2] have been proved to be either insensitive or inapplicable in the determination of traces of bismuth. The atomic-absorption technique provides rather poor sensitivity[3]. In the past, bismuth has been determined mostly by colorimetric methods, of which the widely used techniques have been discussed by Sandell[4], but the sensitivities of these methods are not very good, and the interferences are such that masking and extraction techniques are essential.

Kenney and Menon[5,6] have recently demonstrated that radioreagent methods of analysis have certain advantages over other methods of analysis for phosphorus and boron. This communication describes a similar method for the determination of traces of bismuth with radioiodide. Lisicki and Boltz[7] and others[4] have reported that the addition of excess of soluble iodide to an acidic solution of bismuth produces tetraiodobismuthic acid, which is extractable by higher alcohols and esters. The present method makes use of this reaction to convert bismuth ion to radioactive tetraiodobismuthic acid by treatment with excess of iodide labelled with ^{131}I. The active product is extracted into *n*-butyl acetate and the γ-ray activity of a portion of the extract is determined.

Experimental

Equipment. The equipment used has already been described[5]; a single-channel analyzer, amplifier, pre-amplifier, high-voltage power supply, scaler and a 3″ × 3″ NaI(Tl) well-type scintillation detector were needed.

Reagents. A solution of bismuth nitrate (1 mg Bi ml^{-1}) was prepared by dissolving an appropriate amount of bismuth in 250 ml of water containing a little 6 M nitric acid. Standardization against EDTA by the thiourea method[8] showed an actual content of 0.96 mg Bi ml^{-1}.

Iodine-131 (*ca.* 10 mCi) was used as sodium iodide (Union Carbide). The radioreagent was prepared by dissolving 2.5 g of potassium iodide in 250 ml of water and mixing it with the appropriate amount (1–2 mCi) of the tracer.

A complexing mixture containing 12.5 g of EDTA (disodium salt) and 12.5 g of sodium cyanide in 250 ml of 1.5 M ammonia solution was also prepared. All of the chemicals used were of reagent-grade quality.

Formation and separation of tetraiodobismuthic acid. Since the success of the proposed method depends on the effective separation of the active product from excess of reagent[5], the minimal amount of reagent should be used. For the separation, the extractability of tetraiodobismuthic acid and of the reagent itself was tested with various higher alcohols and esters[7]. In each case, a 25-μg Bi standard and a blank were treated with 5 ml of the radioreagent solution (the activity of the added reagent was $3.35 \cdot 10^6$ c.p.m.), 2 ml of aqueous 2.5% ascorbic acid and 1 ml of aqueous 1% sodium sulfite, and diluted to 25 ml. The mixture was shaken with 10 ml of the extractant for 1 min and 5 ml of the extract was counted.

Of the solvents tried, only butyl acetate in the presence of acid separated the product from the reagent satisfactorily (Table I).

TABLE I

EFFECT OF VARIOUS SOLVENTS ON THE EXTRACTION OF ACTIVE TETRAIODOBISMUTHIC ACID

Extractant	*% Activity observed*	
	25 μg of Bi standard	*Blank*
Isobutanol	16.1	16.1
Amyl alcohol–ethyl acetate (1:1, v/v)	11.2	11.4
Butyl acetate (25%, v/v)–amyl alcohol	0.62	0.75
Butyl acetate	0.092	0.025
Butyl acetate (in the presence of 0.5 *M* H_2SO_4)	0.120	0.030

Although the stoichiometric ratio for the reaction between bismuth and iodide is 1:4, a very large excess of iodide is required for this reaction with trace concentrations of bismuth[7]. A study of the effect of different concentrations of labelled iodide reagent on the formation of the active $HBiI_4$ from 25 μg of bismuth showed that at least 5 ml of the 1% radioreagent solution was required to obtain maximal activity in the reaction product.

Analytical procedure. For standards, and samples which do not have significant amounts of the interfering elements, the following procedure may be employed. Add 5 ml of 3 *M* sulfuric acid, 2 ml of 2.5% ascorbic acid and 1 ml of 1% sodium sulfite to a 25-ml volumetric flask containing the bismuth solution, and mix the contents with 5 ml of the radioreagent solution. (The ascorbic acid and sulfite reduce any oxidizing impurities such as iron(III), which might liberate iodine from iodide.) Dilute the mixture to 25 ml with water and transfer the contents to a 125-ml polypropylene separatory funnel. Shake the mixture with 10 ml of *n*-butyl acetate for 1 min and, after equilibration, discard the aqueous phase and about 2 ml of the organic phase. Collect the remaining extract in a small polypropylene beaker and dry the extract with about 0.5 g of sodium sulfate. Pipet 5 ml of the dried extract into a test tube and measure the ^{131}I γ-ray activity (0.364 MeV) above 0.2 MeV. Prepare a blank solution under the same conditions and determine the activity in a 5-ml extract. Correct all activities for decay and background activity before comparison. Plot the net activity against the concentration of bismuth in the standards to obtain a calibration graph.

Effect of specific activity of the radioreagent. The detection limit of the radioreagent method is largely governed by the variable specific activity of the radioreagent. The activity of the product, and so the sensitivity, may be enhanced by increasing the specific activity of the reagent. This effect was studied with radioreagents of different specific activities; the results (Table II) showed that the activity in the reaction product increases with the specific activity of the reagent, and is also in general agreement with the expected activity.

Interference studies. In the spectrophotometric determination of bismuth, several elements interfere[4]. Although interference by color formation does not exist in the proposed method, elements such as Pb, Ag, Cu, Cd, etc. which form either precipitates or complexes with iodide may interfere. Possible interferences were investigated by mixing a known amount of the diverse ion with 25 μg of bismuth and measuring the activity of the reaction product as outlined above. Table III shows the results.

TABLE II

EFFECT OF THE SPECIFIC ACTIVITY OF THE RADIOREAGENT ON THE ACTIVITY OF TETRAIODOBISMUTHIC ACID

Specific activity of the reagent, (counts min^{-1} $mmole^{-1}$)	*Net activity of the isolated $HBiI_4$[a] (counts min^{-1})*	*Expected activity for 100% chemical yield (counts min^{-1})*
$1.12 \cdot 10^7$	2767	2700
$1.28 \cdot 10^7$	3030	3070
$2.41 \cdot 10^7$	5893	5800
$3.65 \cdot 10^7$	9360	8800

[a] Relative activities after correction for decay and blank for an original sample containing 25 μg Bi.

TABLE III

INTERFERENCE OF SELECTED CATIONS

(25 μg Bi taken)

Amount of cation added	*Observed activity (counts min^{-1})[a]*	*Percentage interference*
—	2951	—
100 mg Fe^{3+}	3096	5.0
100 mg Cr^{3+}	2953	0.0
100 mg Cd^{3+}	52530	High
100 mg Ni^{2+}	3013	2.0
100 mg Cu^{2+}	Precipitate	—[b]
100 mg Hg^{2+}	Precipitate	—[b]
1 mg Sb^{5+}	927	−68.5
100 μg Pb^{2+}	3502	18.7
100 μg Ag^{+}	5310	80.0
100 μg V^{5+}	1096	−63.0

[a] Activity corrected for decay and blank.

[b] Analysis impossible.

Analysis of N.B.S. reference standards. Two N.B.S. reference standards, tin metal (SRM 432) and tin-base bearing metal (SRM 54D), were analyzed by the proposed method. Samples of about 2 g were dissolved in a hot (3+1) mixture of concentrated hydrochloric and nitric acids, and the solutions were diluted with deionized water to 100 ml in a volumetric flask. Attempts to determine bismuth directly in these solutions failed because of interference from other metals such as Cu, Pb, Sb, Cd, etc. The use of diethyldithiocarbamate for complexation of bismuth and its extraction into carbon tetrachloride has been reported by Cheng *et al.*[9]; moreover, diethyldithiocarbamic acid is rapidly decomposed by hot mineral acid. The following procedure was therefore developed.

Add about 1 g of tartaric acid to a 10-ml portion of the sample solution and adjust the pH to *ca.* 1. Add 10 ml of the EDTA–cyanide complexing mixture and mix it well with 2 ml of aqueous 0.2% sodium diethyldithiocarbamate solution. Dilute to 25 ml and extract the bismuth–diethyldithiocarbamate complex with 10 ml of carbon tetrachloride. Collect the organic phase and evaporate the carbon tetrachloride by heating the extract with 8 ml of 3 *M* sulfuric acid. Transfer the solution to a 25-ml flask, add 2 ml of 2.5% ascorbic acid and 1 ml of 1% sodium sulfite followed by 5 ml of the radioreagent. Then proceed as described earlier. The amount of bismuth in the sample was determined by comparing the measured activity from the sample with that obtained from bismuth standards.

Results and discussion

The relationship between the net activity of the reaction product and the concentration of bismuth was linear over the range 1–25 μg of bismuth. The sensitivity of the proposed method appears to be better than that of any other method except the dithizone method, which has been applied only to biomaterials[4]. In establishing the sensitivity limit of 0.04 μg Bi ml^{-1} in the solution before extraction, the specific activity of the reagent used was $2.33 \cdot 10^8$ counts min^{-1} per mmole of iodide.

Elements such as Cd, Pb, Cu, Ag, Hg, Sb and V interfere with the direct determination of bismuth (Table III), but bismuth can still be determined directly

TABLE IV

ANALYSIS OF N.B.S. REFERENCE STANDARDS FOR BISMUTH

Standard	*Measured activity in an aliquot (counts min^{-1})*[a]	*% Bismuth*	
		Proposed method	*Certificated value*
Tin metal (SRM 432)	17500	0.0097	0.0098
	16500	0.0092	
Tin-base bearing metal (SRM 54D)	13500	0.041	0.044[b]
	12500	0.038	

[a] Corrected for decay and blank activity. The activities measured without the diethyldithiocarbamate extraction were *ca.* 40000 counts min^{-1}.

[b] Average of 9 values; range 0.037–0.050.

in solutions containing iron, nickel or chromium, or in most biological samples. For the analysis of alloys, metals and ores, a preliminary diethyldithiocarbamate extraction is recommended. The results of the analyses of the N.B.S. reference standards with the preliminary extraction (Table IV) are in fairly good agreement with the values certified by N.B.S.

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SHORT COMMUNICATION

Photometrische Bestimmung von Tellur in unlegiertem und niedrig legiertem Automatenstahl

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Im Rahmen der Produktion von Automatenstählen muss laufend neben Blei[1–4] und Wismut[5] auch der Gehalt an Tellur im Stahl bestimmt werden. Wegen der hohen Zahl der täglich anfallenden Analysen ist hierzu die Anwendung einer einfachen Methode mit geringem Zeitaufwand notwendig. In unserem Laboratorium wurde deshalb vor zehn Jahren eine hierzu geeignete Methode ausgearbeitet, bei der das Tellur nach dem Lösen der Stahlprobe ohne Vorisolierung direkt in der Probelösung als Tellursol[2] photometrisch bestimmt wird. Die Methode ist nachfolgend beschrieben.

An anderer Stelle[3] wird ein Verfahren zur Bestimmung von Tellur in Stahl angegeben, bei dem das Tellur zum Metall reduziert, abfiltriert und anschliessend als Tellur(IV)bromid photometrisch bestimmt wird. Weiterhin erschien in letzter Zeit eine Arbeit[6] mit einer Vorschrift zur Bestimmung von Tellur in Gusseisen und Stahl, bei der das Tellur ebenfalls zuerst durch Reduktion zum Metall ausgefällt und nach dem Lösen des Niederschlages als Tellursol photometrisch bestimmt wird. Wegen des grösseren Arbeitsaufwandes und des Zeitbedarfes von 2–3 Stunden für eine Bestimmung eignen sich diese Methoden nicht für die oben erwähnten Routineanalysen in grossen Serien.

Experimentelles

Apparatur. Alle Messungen wurden mit dem Elko II-Photometer (Zeiss, Oberkochen/Germany) mit Filter S 42 (420 nm), Filter S 53 (530 nm) und 5 cm-Küvette durchgeführt.

Zinn(II)chlorid-Lösung. 175 g $SnCl_2 \cdot 2\,H_2O$ werden in 200 ml Salzsäure (1,19) unter Erwärmen gelöst und mit Wasser auf 500 ml aufgefüllt.

Arbeitsvorschrift

(a) Unlegierter Stahl. 1.0 g Probematerial wird in einem 250 ml-Becherglas mit 20 ml Mischsäure (1 Teil Salpetersäure (1.40) wird mit 1 Teil Perchlorsäure (70%) gemischt) unter Erwärmen gelöst, nach vollständigem Lösen mit 5 ml Phosphorsäure (85%) versetzt und bis zum starken Rauchen der Perchlorsäure-Nebel erhitzt. Nach dem Abkühlen fügt man 20 ml Salzsäure (1.19) hinzu, erwärmt bis zum vollständigen Lösen und füllt nach dem Abkühlen in einem 50 ml-Messkolben mit

Wasser zur Marke auf. Ein aliquoter Teil von 10.0 ml wird in einen 50 ml-Messkolben übergeführt, mit 5.0 ml Salzsäure (1.19), 5.0 ml Phosphorsäure und 5.0 ml Zinn(II)-chlorid-Lösung versetzt, mit Wasser zur Marke aufgefüllt, geschüttelt und innerhalb 5–30 min nach dem Auffüllen in einer 5 cm-Küvette bei 420 nm (Filter S 42) gegen einen Blindwert photometriert. Den Blindwert stellt man nach der Arbeitsvorschrift mit Ferrum reductum oder einem Te-freien Stahl her. Die Auswertung erfolgt mit Hilfe einer Eichkurve (s. Tabelle I) oder nach Gleichung (1).

$$\% \text{ Te} = E \cdot 0.1163 \quad (E = \text{Extinktion}) \tag{1}$$

Die Eichkurve wird nach der Arbeitsvorschrift unter Verwendung von Ferrum reductum oder tellurfreiem Stahl und Zusatz von Tellur-Standardlösung aufgestellt.

(b) Niedrig legierter, Cr- und/oder Mo-haltiger Stahl. Die Analyse wird nach Arbeitsvorschrift (*a*) durchgeführt, die erhaltene Farblösung jedoch davon abweichend in einer 5 cm-Küvette bei 530 nm (Filter S 53) gegen einen analog hergestellten Blindwert photometriert. Die Auswertung erfolgt mit Hilfe einer Eichkurve (s. Tabelle I) und die für anwesendes Chrom und/oder Molybdän erforderliche Korrektur entnimmt man Korrekturkurven oder -tabellen. Auswertung und Korrektur können auch nach Gleichung (2) durchgeführt werden:

$$\% \text{ Te} = [E - (0.040 \cdot \% \text{ Mo}) - (0.013 \cdot \% \text{ Cr})] \cdot 0.1351 \tag{2}$$

Ergebnisse und Diskussion

Die Farbreaktion wird in $\sim$2.8 N HCl/$\sim$5.3 N H_3PO_4/$\sim$0.47 N $HClO_4$-Lösung durchgeführt. Da die Methode für Serienanalysen im Schichtbetrieb eingesetzt wird, wurden die Wellenlängen nach den verfügbaren Filtern des Photometers ausgewählt. Die nach der Arbeitsvorschrift aufgestellten Eichkurven sind linear (s. Tabelle I).

Bei den angewandten Wellenlängen betragen die molaren Extinktionskoeffizienten $\varepsilon_{420} = 5490$ l Mol^{-1} cm^{-1} und $\varepsilon_{530} = 4720$ l Mol^{-1} cm^{-1}, die Empfindlichkeit[2] (für eine Extinktion von $E = 0.001$) $S_M = 0.023$ μg Te ml^{-1} cm^{-1} (bei 420 nm) und $S_M = 0.027$ μg Te ml^{-1} cm^{-1} (bei 530 nm) und die Bestimmungsgrenze[2] (für eine Extinktion von $E = 0.025$) $L_Q = 0.58$ μg Te ml^{-1} cm^{-1} (bei 420 nm) und $L_Q = 0.67$ μg Te ml^{-1} cm^{-1} (bei 530 nm).

TABELLE I

MESSWERTE DER EICHKURVEN

Te-Gehalt		*Extinktion*[a]	
im Stahl (%)	*in der Messlösung (µg/ml)*	*420 nm*	*530 nm*
0.010	0.40	0.085	0.075
0.030	1.20	0.260	0.220
0.050	2.00	0.430	0.370
0.070	2.80	0.600	0.520
0.100	4.00	0.860	0.740

[a] Mittelwerte aus jeweils fünf Messwerten.

Nickel, Blei und Vanadin stören nicht. Auch die in der Regel im Stahl auftretenden Gehalte an Arsen von $\sim$0.05% As führen zu keiner Störung. Eisen wird durch die zugesetzte Phosphorsäure entfärbt. Chrom- und Molybdänionen hingegen stören infolge Eigenfärbung. Zur Herabsetzung der Störung wird in Anwesenheit von Chrom und/oder Molybdän bei 530 nm photometriert. Bei dieser Wellenlänge sind die Messwerte um 14% niedriger im Vergleich zu jenen bei 420 nm, doch fällt dies im Hinblick auf die Aufgabenstellung nicht ins Gewicht. Aus Tabelle II ist ersichtlich, dass die Störung dem Chrom- bzw. Molybdängehalt linear proportional und additiv ist. Die Störung lässt sich daher durch eine Messwertkorrektur nach den Tabellenwerten oder nach der in der Arbeitsvorschrift angegebenen Gleichung (2) beseitigen.

TABELLE II

STÖRUNG DURCH CHROM UND MOLYBDÄN

(Messbedingungen: nach Arbeitsvorschrift *b*)

Gehalt im Stahl			*Gefunden*		*Störung*	
% Te	*% Cr*	*% Mo*	*Extinktion*	*%Te*	*Extinktion*	*% Te*
0.050	—	—	0.370	0.050	0.000	0.000
0.050	1.00	—	0.383	0.051_8	+0.013	$+0.001_8$
0.050	2.00	—	0.398	0.053_6	+0.027	$+0.003_6$
0.050	3.00	—	0.410	0.055_4	+0.040	$+0.005_4$
0.050	—	0.50	0.390	0.052_7	+0.020	$+0.002_7$
0.050	—	1.00	0.410	0.055_4	+0.040	$+0.005_4$
0.050	3.00	1.00	0.450	0.061	+0.080	+0.011

Die beschriebene Methode eignet sich zur Bestimmung von 0.003–0.120% Te in unlegiertem und niedrig legiertem Automatenstahl mit $\leqq$3% Cr, $\leqq$1.2% Mo, $\leqq$3% Ni, $\leqq$0.5% Pb und $\leqq$0.6% V. Das Verfahren weist eine mittlere Standardabweichung von $s = \pm 0.001$–0.002% Te auf. Der Zeitbedarf für eine Einzelbestimmung beträgt $\sim$40 min. Die Bestimmungsgrenze[2] (für eine Extinktion von $E = 0.025$) liegt bei $L_Q = 0.003$% Te.

Die Methode wird in unserem Laboratorium seit zehn Jahren mit befriedigendem Erfolg eingesetzt, wobei täglich 50–200 Proben analysiert werden.

Herrn G. Schmitt danke ich für die sorgfältige Durchführung der Versuche.

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SHORT COMMUNICATION

Standardization of sulfatoceric acid solutions against sodium oxalate in the presence of perchloric acid and manganese(II) sulfate

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Sulfatoceric acid solutions are conveniently standardized against arsenic trioxide. Sodium oxalate can also be used as a primary substance for the same purpose, but the usual procedures are somewhat critical.

The stoichiometry of the cerium(IV)–oxalate reaction in acidic solution is given by

$$2Ce^{4+} + H_2C_2O_4 \rightarrow 2Ce^{3+} + 2CO_2 + 2H^+$$

The oxidation of oxalate ions to carbon dioxide is a two-stage process:

$$C_2O_4^{2-} \rightarrow C_2O_4^{-} + e^- \tag{1}$$

$$C_2O_4^{-} \rightarrow 2CO_2 + e^- \tag{2}$$

Reaction (1) is considered to be the rate-determining step. The nature of the acid used to acidify the oxalate solution may affect considerably the rate of the cerium(IV)–oxalate reaction, because of the formation of complexes between cerium(IV) ions and the anions of the acid.

The oxidation of sodium oxalate by sulfatoceric acid in either sulfuric acid or hydrochloric acid medium is very slow at room temperatures, hence the solution must be heated to at least 75° [1]; oxidation–reduction indicators can not then be used and the titration must be followed potentiometrically, or visually without an indicator.

In view of these limitations, an indirect procedure[1] based on back-titration of excess of cerium(IV) with iron(II) solution is often preferred.

According to Smith and Getz[2], sodium oxalate in 2 *M* perchloric acid solution can be titrated at room temperature with perchloratoceric acid, but not with sulfatoceric acid. This is because the formal potential of cerium(IV)–cerium(III) couple in 2 *M* perchloric acid is 1.71 V, against 1.44 V in 1 *M* sulfuric acid. Nitroferroin serves as indicator, because its transition potential is 1.25 V.

The oxidation of oxalic acid in hydrochloric acid by sulfatoceric acid is catalyzed by iodine monochloride[3]. The direct titration can be performed potentiometrically at room temperatures, but with ferroin as indicator, the temperature must be maintained at 45–50°, which is impractical.

Some procedures which use the catalytic effect of manganese(II) on the oxidation of oxalate by cerium(IV) have been recommended. The various reactions during the oxidation may be summarized as follows[4]:

$$Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+} \qquad (3)$$

$$Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+} + C_2O_4^{-} \qquad (4)$$

$$Ce^{4+} + C_2O_4^{2-} \rightarrow Ce^{3+} + C_2O_4^{-} \qquad (5)$$

$$Mn^{3+} + C_2O_4^{-} \rightarrow 2CO_2 + Mn^{2+} \qquad (6)$$

$$Ce^{4+} + C_2O_4^{-} \rightarrow 2CO_2 + Ce^{3+} \qquad (7)$$

Reaction (4) is much faster than (5). The appearance of the manganese(III) color suggests that reaction (3) is faster than either (4) or (5). The reaction rate is considerably hindered by phosphoric acid or fluoride, which form stable complex ions with manganese(III), so that the manganese(III) color slowly disappears; the oxidation of low oxalate concentrations is slow enough to cause early end-points. The same effect must be caused to some extent by sulfate.

Wheatley[5] used 25 ml of 10% manganese(II) sulfate solution as a catalyst for the titration of 0.005 *M* oxalate solution with 0.01 *M* cerium(IV) solution at room temperatures with ferroin as indicator. The procedure is unsatisfactory at higher concentrations because ferroin turns blue with the first addition of cerium(IV); the original red color slowly returns, and it is necessary to wait after every addition of cerium(IV). Watson[6] recommended similar conditions except that the mixture was heated to 45–50° before titration.

More recently, the catalytic effect of manganese(II) in the oxidation of oxalate was utilized by Siefker and Singh[4]. In their method, *ca.* 6 g of solid manganese(II) sulfate is added to 3–4 milliequivalents of sodium oxalate dissolved in 25 ml of 2 *M* sulfuric acid. The mixture is heated to 70° to dissolve the manganese(II) sulfate, and titrated with the sulfatoceric acid solution. The final appearance of a yellowish-brown or light amber color produced by the addition of a single drop marks the end-point.

The present paper describes a procedure for the standardization of 0.1 *M* cerium(IV) sulfate solutions in 0.5 *M* sulfuric acid based on the direct titration of the sodium oxalate in perchloric acid medium containing manganese(II) sulfate as catalyst. The catalytic effect of manganese(II) and the higher formal potential of the cerium(IV)–cerium(III) couple in perchloric acid, acting together, make it feasible to titrate at room temperatures.

Experimental

Reagents. Exclusively analytical-grade reagents were used, solutions being prepared by the usual techniques.

Recommended procedure. Transfer 50.00 ml of 0.04 *M* sodium oxalate to a 250-ml conical flask. Add 20 ml of 70% perchloric acid and 10 ml of aqueous 0.2 *M* manganese(II) sulfate solution. Dilute to 100 ml with distilled water, add 2 drops of 0.025 *M* nitroferroin indicator and, finally, titrate with the 0.1 *M* sulfatoceric acid solution in 0.5 *M* sulfuric acid at room temperature until the solution becomes pale blue in color and the pink does not return within 1 min. Perform a blank by mixing 20 ml of 70% perchloric acid, 10 ml of manganese(II) sulfate, 70 ml of distilled water, 40 ml of 0.05 *M* sulfuric acid and 2 drops of nitroferroin, and titrating to the same end-point.

Comparison procedure. Transfer 50.00 ml of 0.04 *M* sodium oxalate to a 500-ml conical flask. Dilute to 300 ml with distilled water. Add 5 ml of concentrated sulfuric acid and heat to 75°. Titrate with the sulfatoceric acid solution to a permanent, faint yellow. Prepare a blank with the same amounts of water and sulfuric acid, heat to 75° and titrate to the same end-point.

Results and discussion

The volume of perchloric acid (20 ml) used in the recommended procedure was fixed, preliminarily, in order to ensure, throughout the titration, a concentration of hydrogen ions around 2 *M*; however, this volume can be reduced by half without effect. The volume of 0.2 *M* manganese(II) sulfate solution (10 ml) was found to be the minimum required for satisfactory catalytic action. Nitroferroin was used, instead of ferroin, because it is more suitable under the conditions prescribed; the indicator precipitates when first added, but dissolves after stirring.

The acidity of the sodium oxalate solution prepared for titration with sulfatoceric acid is initially due only to the perchloric acid added; the conditions are then most favorable for the cerium(IV)–oxalate reaction. The titration can be performed at an initial rate of 2 drops per s. As titration proceeds, sulfuric acid (from the sulfatoceric acid solution) is gradually introduced, but even at the end-point the concentration of sulfuric acid is considerably smaller than in the titration of sodium oxalate dissolved in sulfuric acid. Conditions would be even more favorable if 0.1 *M* cerium(IV) sulfate in 0.025 *M* sulfuric acid were used as titrant; such solutions are still stable with regard to hydrolysis.

TABLE I

ACCURACY AND PRECISION OF THE RESULTS

Recommended procedure, 0.1 M $Ce(SO_4)_2$ (ml)	*Comparison procedure 0.1 M $Ce(SO_4)_2$ (ml)*
40.42	40.40
40.44	40.44
40.40	40.46
40.42	40.40
—	40.38
Mean: $m=40.42$	$m=40.42$
$s=0.016$	$s=0.033$
$s/m \cdot 1000=0.4$ p.p.m.	$s/m \cdot 1000=0.8$ p.p.m.

Table I presents results by the recommended and comparison procedures. Blank corrections were applied in both cases. The blank of the recommended procedure amounted to 0.07 ml of 0.1 *M* sulfatoceric acid, of which no more than 0.04 ml can be considered as correction for the indicator. The recommended procedure shows a better precision than the comparison method.

In conclusion, it is practicable to standardize 0.1 *M* cerium(IV) sulfate solutions in 0.5 *M* sulfuric acid against sodium oxalate, in dilute perchloric acid, in the presence of manganese(II) sulfate, at room temperatures. The procedure is simpler than usual ones.

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BOOK REVIEWS

I. M. Kolthoff, P. J. Elving and F. H. Stross (Editors), *Treatise on Analytical Chemistry. Part III. Analytical Chemistry in Industry*, Vol. 2, Wiley–Interscience, New York, 1971, xxiv+597 pp., price £12.00.

This continuation of the Kolthoff–Elving Treatise into *Part III. Analytical Chemistry in Industry* deals with various aspects of *Industrial Toxicology and Environmental Pollution and Its Control* (Section B). This second volume contains seven monographs by specialist authors, most of whom have industrial backgrounds or are associated with public laboratories whose main concerns are industrial analytical problems.

The topics discussed here are Industrial Health Hazards (167 pp.), Odours (20 pp.), Analysis of Air for Pollutants (44 pp.), Analytical Chemistry in the Control of Water Treatment Plants (84 pp.), Potable and Sanitary Water (63 pp.), Analysis of Industrial Wastewaters (134 pp.), Sewage, Effluents and Sludge Analyses (22 pp.).

The great awareness of the problems of industrial hygiene and environmental pollution will help to make this an important and popular volume. Each monograph is well written and documented with copious references to current literature and practices, and the result is a volume well up to the high standards set by the earlier parts of this well-known work.

With the existence of competing publications of a more encyclopaedic nature, the editors have wisely limited the objectives of Part III of the Treatise, to deal essentially with those areas and topics of industrial analytical practice not readily accommodated in Parts I and II. The present volume exemplifies this quite admirably and encourages one to look forward to the subseqent volumes in this concluding part of the Treatise.

W. I. Stephen (Birmingham)

Progress in Separation and Purification, Vol. 3, Edited by E. S. Perry and C. J. van Oss, Interscience–J. Wiley, New York, 1971, xi+316 pp., price £9.35.

One is reluctant to use hackneyed phrases in reviewing a specialist publication with a specialist price, but this book *does* take over where many books on separation and purification leave off! The editors have assembled eight chapters dealing with less common separation and purification methods. The subjects treated are: vapour-programmed t.l.c.; "dry-column" chromatography; ultrafiltration membranes; high-pressure gas chromatography; the plasticizing effects of permeates on membrane permeation and separation; separation and purification by reverse osmosis; inorganic t.l.c.; and the electrolytic separation of nickel and cobalt. Incidentally, the t.l.c. chapters together comprise about 40% of the total contents.

As in any book which is composed of contributions from several authors, the style, balance and size of each chapter vary considerably. Generally, however, the contents are extremely readable because the authors take the trouble to bring a reader up-to-date gently. Also, subsequent discussions are pitched at a level that should make most of the information readily assimilable by a prospective user or student, and yet still be appealing to a specialist. Most of the chapters are thoughtfully illustrated and a great many helpful photographs have been used. What a pity, therefore, that in an otherwise commendable thirty-page text, the chapter on ultrafiltration membranes includes not a single diagram, although there seem to be opportunities to clarify the presentation of information in this way.

I consider the book to be very worthwhile and recommend it highly.

C. L. Graham (Birmingham)

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