ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 38, No. 4, 475–586, August 1967
Completing Volume 38

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.) or to
Dr. A. M. G. MACDONALD, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

Manuscripts

Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (*e.g.*, 2%, 2 ml, 2 g, 2 μl, 2 μg, 2 ng, 2 cm, 200 mμ).

Figures should be drawn in Indian ink on drawing or tracing paper with all lettering in **thin** pencil. Standard symbols should be used in line drawings; the following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◘ ⊖ ⊡ ▪ + ×

Photographs should be submitted as clear black and white glossy prints. Figures and photographs should be of the same size as the typed pages. Legends for figures should be **typed on a separate page**. Figures should be numbered in Arabic numerals in the order in which they are mentioned in the text.

References should be given at the end of the paper and should be numbered in the order of their appearance in the text (**not** arranged alphabetically). Abbreviations of journal titles should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition and supplements. The recommended form for references to journal papers and books is as follows:

1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, SMITH *et al.*, is desirable in the text.

Summaries are published in English, French and German; authors must always provide a summary in the language of the paper, and are encouraged to supply translations where convenient. No summaries are needed for Short Communications.

Reprints

Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta has four issues to the volume, and three volumes appear per year. Subscription prices: $ 17.50 or £ 6.6.— or Dfl. 63.— per volume; $52.50 or £ 18.18.— or Dfl. 189.— per year, plus postage. Additional cost for copies by airmail available on request. For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands


ORGANIC CHEMICALS


Options:
• tropicalization
• digital absorbance readout
• recorders
• standard and short path length flow-through cuvettes
• methods manuals
• microcells
• and many others

1967

THE QUEEN'S AWARD
TO INDUSTRY

BDH THE BRITISH DRUG HOUSES LIMITED

It is with a sense of honest pride of achievement that The British Drug Houses Limited, the main subsidiary of B.D.H. Group Limited, announces that The Queen's Award to Industry, 1967 has been conferred on the company.

The distinction has been earned not only for the export of laboratory chemicals, but also for technological innovation in the discovery and exploitation of steroid compounds.

Firstly, the company was granted the Award for its exports of B.D.H. laboratory chemicals across the world. The products of the B.D.H. Laboratory Chemicals Division are regularly exported to more than a hundred countries.

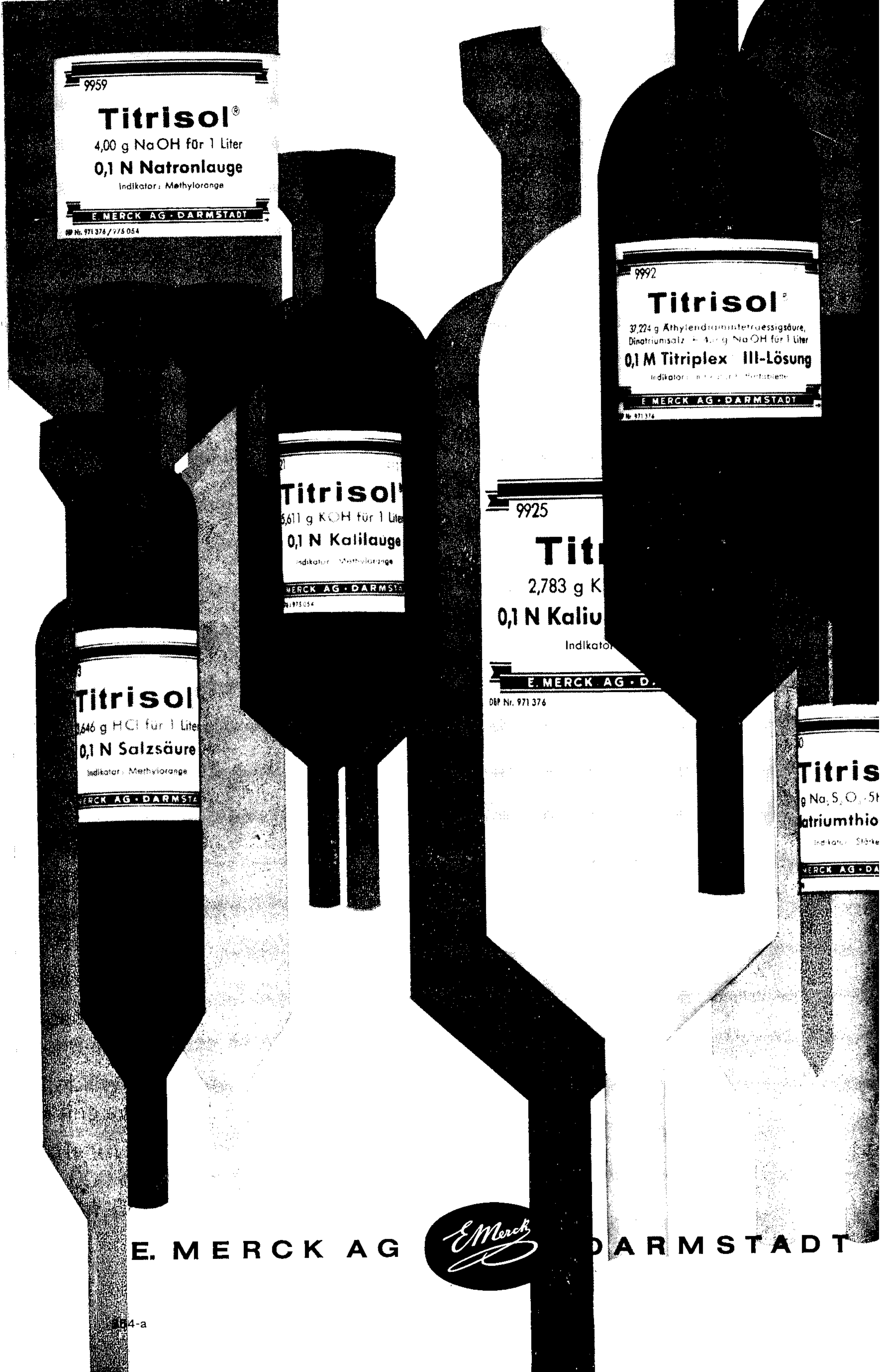
Secondly, the company was granted the Award in the area of technological innovation for the discovery and exploitation, at home and overseas, of its products Dimethisterone and Megestrol Acetate. These progestational steroid compounds are the bases of the B.D.H. oral contraceptives, Volidan* and Serial 28* and are the only steroid compounds discovered in Britain for use in oral contraceptives.

In announcing its success, the company is at the same time very conscious of the constant co-operation it receives from scientists and chemists of many disciplines.

*Trademark

BDH

BDH (INTERNATIONAL) LIMITED
Laboratory Chemicals Division • Poole • England


9959
Titrisol®
4,00 g NaOH für 1 Liter
0,1 N Natronlauge
Indikator: Methylorange
E. MERCK AG · DARMSTADT
DBP Nr. 971 376 / 975 054
Titrisol
5,611 g KOH für 1 Liter
0,1 N Kalilauge
Indikator: Methylorange
MERCK AG · DARMSTA
DBP Nr. 975 054
Titrisol
3,646 g HCl für 1 Liter
0,1 N Salzsäure
Indikator: Methylorange
MERCK AG · DARMSTA
9925
Tit
2,783 g K
0,1 N Kaliu
Indikator
E. MERCK AG · D
DBP Nr. 971 376
9992
Titrisol®
37,224 g Äthylendiamintetraessigsäure, Dinatriumsalz + 4,0 g NaOH für 1 Liter
0,1 M Titriplex III-Lösung
E. MERCK AG · DARMSTADT
Nr. 971 376
Titris
g Na2S2O3 · 5H
Natriumthio
Indikator: Stärke
MERCK AG · DA

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 38, No. 4, August 1967

A STUDY OF SOME PROBLEMS IN DETERMINING THE STOICHEIOMETRIC PROTON DISSOCIATION CONSTANTS OF COMPLEXES BY POTENTIOMETRIC TITRATIONS USING A GLASS ELECTRODE

Possible errors in the measurement of acid dissociation constants by potentiometric titration techniques have been considered, with particular references to nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Unknown junction potentials can arise when pH measurements are carried out using a glass electrode with saturated calomel reference electrode which have been previously calibrated with a standard buffer solution. The magnitude of the influence of these unknown potentials has been demonstrated and an experimental procedure recommended which gives meaningful results.

The precision of calculated acid dissociation constants will also be influenced by the presence of cationic species (*e.g.* H_4L^+), the total acid strength, the absolute values of the constants and the value accepted for the auto-dissociation constant of water (K_w). All these factors have been considered quantitatively and their effect on metal complex formation constants, calculated from these acid dissociation constants, noted. The proton dissociation constant of the cationic species of NTA (*i.e.* H_4L^+) has been found to have the value of $pK_0 = 0.80$ at 20° and $\mu = 0.10\ M$.

H. M. Irving, M. G. Miles and L. D. Pettit,
Anal. Chim. Acta, 38 (1967) 475–488

THE DETERMINATION OF CHROMIUM IN BIOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROSCOPY

Biological samples were mineralized with a mixture of nitric, sulfuric, and perchloric acids. The chromium was oxidized to chromium(VI) followed by extraction into methyl isobutyl ketone in the cold. The ketone extract was aspirated into a fuel-rich hydrogen–air flame, and the absorption recorded using the 357.9 nm line of chromium. The limit of detection for chromium was found to be 10 p.p.b. Tissue chromium levels of normal albino rats were determined. Increased chromium values were observed for animals maintained on a high chromium diet compared to those fed a deficient diet.

F. J. Feldman, E. C. Knoblock and W. C. Purdy,
Anal. Chim. Acta, 38 (1967) 489–497

DETERMINATION OF MANGANESE, IRON, COBALT AND NICKEL IN AIR AND WATER BY ATOMIC ABSORPTION SPECTROSCOPY

Flames of 4 different kinds and of various compositions were studied for their suitability for atomic absorption spectroscopy for the determination of manganese, iron, cobalt and nickel. The effects of various other factors such as lamp current, slit-width and position of the burner were also investigated. Interference effects of a large number of ions and compounds were studied. Very few ions were found to interfere and means of eliminating the interferences noted are described. As a result of the investigation, sensitive and selective procedures for the determination of manganese, iron, cobalt and nickel are reported. Sensitivities are Mn, 0.01 mg/l; Fe, 0.05 mg/l; Co, 0.03 mg/l and Ni, 0.02 mg/l for 1% absorption.

S. L. Sachdev, J. W. Robinson and P. W. West,
Anal. Chim. Acta, 38 (1967) 499–506

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF MIXTURES OF *n*-HEXYL SALICYLATE AND SALICYLIC ACID IN PROPYLENE GLYCOL

Propylene glycol (PG) is proposed as solvent for the collection and analysis of samples of vapors and aerosols, and *n*-hexyl salicylate is suggested as "model" compound for these systems. A UV-spectrophotometric method is described for simultaneous determination of *n*-hexyl salicylate and salicylic acid in pure and aqueous PG solutions, at concentrations of 0–35 μg/ml. The method is based on water content determinations and on absorbance measurements at 305 nm and, after addition of aqueous potassium hydroxide, at 335 nm. Simplifying approximations are proposed for less accurate work, the errors involved are evaluated, and possible improvements are suggested.

M. D. BITRON AND Y. SUZIN,
Anal. Chim. Acta, 38 (1967) 507–516

PHOTOMETRIC TITRATION OF TITANIUM(III) WITH IRON(III)

An oxidimetric titration of titanium(III) with iron(III) with a photometric end-point is proposed. Acetylacetone was used to obtain an intensely coloured titanium(III) complex; titanium(III) was formed by prereduction with chromium(II) or vanadium(II). Amounts of titanium down to 35 μg were determined with fairly good accuracy and precision. Few common elements interfere.

W. E. VAN DER LINDEN AND G. DEN BOEF,
Anal. Chim. Acta, 38 (1967) 517–522

SEPARATION OF GALLIUM AND IRON IN THE PRESENCE OF EDTA

Macro- or microquantities of gallium can be separated from iron by precipitating the latter with sodium hydroxide in the presence of EDTA. Nearly all the gallium remains in solution. After the separation of iron, gallium is extracted with tributylphosphate from 3 *N* hydrochloric acid medium, and then re-extracted into water. Gallium is finally determined by precipitation with cupferron and ignition to the oxide, or for trace amounts of gallium, by colorimetric determination with rhodamine B. The method was checked with radioactive gallium and iron.

G. LANFRANCO,
Anal. Chim. Acta, 38 (1967) 523–528

THE EXTRACTION OF LANTHANIDES AND ACTINIDES WITH ALKYLPHOSPHINE OXIDES

PART II. THE EXTRACTION OF NITRIC ACID WITH TRI-*n*-HEXYLPHOSPHINE, TRICYCLOHEXYLPHOSPHINE AND TRI-*n*-OCTYLPHOSPHINE OXIDES

(in French)

The distribution of nitric acid between an aqueous phase and a solution of THPO, TcHPO and TOPO in benzene was measured at 25°. The apparent stability constants K_1' were found to be 17.2 ± 1.0 $(M)^{-2}$ for THPO·HNO_3, 7.0 ± 0.8 $(M)^{-2}$ for TcHPO·HNO_3 and 15.2 ± 1.1 $(M)^{-2}$ for TOPO·HNO_3. The stoichiometry of the last complex was confirmed in *n*-octane solution at constant ionic strength in the aqueous phase.

J. GOFFART AND G. DUYCKAERTS,
Anal. Chim. Acta, 38 (1967) 529–536

DETERMINATION OF NITROGEN IN VANADIUM BY VACUUM FUSION

(in French)

A study of the conditions for the determination of nitrogen in vanadium by vacuum fusion in a platinum bath has shown that (*a*) the amount of nitrogen extracted depends on the ratio (*R*) of the weights of platinum and vanadium, and (*b*) the amount extracted passes through a maximum value for a particular *R* value depending on the temperature. With *R* values of *ca.* 2 and extraction temperatures above 1900°, results were in reasonable agreement with those obtained by the Kjeldahl method, the reproducibility being 2–3%.

G. BAUDIN, J. DESREUMAUX AND R. FONTAINE,
Anal. Chim. Acta, 38 (1967) 537–545

EXTRACTION OF COBALT(II) FROM AQUEOUS THIOCYANATE SOLUTIONS BY TRI-*n*-OCTYLAMINE

The distribution of cobalt(II) between acidic thiocyanate solutions and tri-*n*-octylamine dissolved in various diluents has been measured for several cobalt(II) loadings and amine concentrations. Diluents investigated included *n*-hexane, cyclohexane, benzene, xylene, carbon tetrachloride, chloroform, chlorobenzene, *o*-dichlorobenzene and nitrobenzene. In all cases, the species extracted is bis(tri-*n*-octylammonium)tetrathiocyanatocobaltate(II). The ability of each diluent to extract cobalt(II) from acidic thiocyanate solutions is approximately correlated with the dielectric constant of the pure diluent, *i.e.*, the smaller the dielectric constant, the larger the distribution ratio, with the exception of nitrobenzene and chloroform.

H. WATANABE AND K. AKATSUKA,
Anal. Chim. Acta, 38 (1967) 547–552

POLAROGRAPHIC BEHAVIOR OF URANIUM(VI) IN MALONIC ACID MEDIA

DETERMINATION OF URANIUM IN PLUTONIUM

The polarographic behavior of the uranium–malonate complex was investigated over the pH range 1.1–6.5. A reversible, one-electron wave was obtained. Below pH 4.9, the rate of disproportionation is nearly instantaneous and gives rise to a pseudo uranium(VI)–uranium(IV) reduction. Above pH 4.8 the concentration of uranium(V) is stable with respect to disproportionation. The half-wave potential is pH-dependent below pH 4.9, but it is independent of the malonate concentration above 0.1 *M*. The diffusion current constant is 2.78 for the conditions described. A procedure for the determination of uranium in plutonium was developed for uranium concentrations greater than 225 p.p.m. Of 21 common impurities found in plutonium metal, only Cu, Fe, Pb, Sb and Ti cause significant interference; titanium can be removed by ion exchange, and the other interferences by mercury cathode electrolysis.

C. E. PLOCK AND F. J. MINER,
Anal. Chim. Acta, 38 (1967) 553–562

CHARACTERIZATION OF LINEAR POLYURETHANES

Methods are described for the qualitative analysis of linear polyurethanes of unknown composition. Based on the type of polymer, determined from the I.R.-spectrum of a polymer film, the products obtained on alkaline hydrolysis under pressure in a Parr bomb are separated by means of ion-exchangers, the course of the analysis being dependent on the type of polymer to be examined. Identification of the isolated hydrolysis products is accomplished by I.R. analysis or thin-layer chromatography.

J. L. Mulder,
Anal. Chim. Acta, 38 (1967) 563–573

DETERMINATION OF ALKANES IN TECHNICAL FATTY ALCOHOLS

(Short Communication)

G. W. Van Galen, H. Dronkers and P. W. Hendrikse,
Anal. Chim. Acta, 38 (1967) 575–577

THE MOHR TITRATION OF CHLORIDE WITHOUT CORRECTION

(Short Communication; in German)

F. L. Hahn,
Anal. Chim. Acta, 38 (1967) 578–579

APPLICATION OF VARIOUS METHODS IN ACTIVATION ANALYSIS FOR IRON AND COBALT

(Short Communication)

C. Bondy,
Anal. Chim. Acta, 38 (1967) 579–580

JAROSLAV HEYROVSKÝ, 1890–1967

On March 27, 1967, Professor JAROSLAV HEYROVSKÝ died in his native city of Prague, ending an illustrious career in science, which had been capped by the award in 1959 of the Nobel Prize in Chemistry for his discovery of polarography.

The measure of Professor HEYROVSKÝ's contribution to science—and more particularly to analytical chemistry—is emphasized by the fact that, whereas many physical methods of measurement have been developed to a useful form by the independent or joint efforts of many scientists with sometimes even the attribution of priority being questionable, the discovery of polarography is the achievement of one person, who, furthermore, strongly influenced the subsequent development of the method into one of the important techniques of contemporary electrochemistry and analytical chemistry. One need only point to the development, particularly in the United States, of the area frequently referred to as "electroanalytical chemistry" to realize the impact of Professor HEYROVSKÝ's contribution. There is general agreement that polarography caused a renaissance in electrochemistry, e.g., polarographic studies of transport phenomena revived interest in important areas of electrochemistry which had been considered to be closed. The great activity in the investigation of heterogeneous electrode kinetics during the past twenty years has been largely based on the experimental use of polarography and techniques derived from it.

Professor HEYROVSKÝ was born on December 20, 1890, in Prague, where he began his study of science at the University in 1909. In 1910, he transferred to University College in London where he was strongly influenced by F. G. DONNAN, under whom he started doctoral research. His stay in London interruped by World War I, he completed his research in Prague where he began to teach after the War at the Charles University. The researches which led to the development of polarography, have been described (P. ZUMAN AND P. J. ELVING, *J. Chem. Education*, 37 (1960) 562), as well as his subsequent scientific activities, which, in a sense, culminated in the founding in 1950 of the Polarographic Institute as a statesupported research center with Professor HEYROVSKÝ as its Director. In 1952, the Institute was incorporated into the Czechoslovak Academy of Sciences and, subsequently, was formally designated as the Jaroslav Heyrovský Institute of Polarography.

Professor HEYROVSKÝ's scientific works included some two hundred research papers, a considerable number of authoritative books on various aspects of polarography and, last but not least, a large number of former students and collaborators who have contributed greatly to the development of polarography. His accomplishments were recognized by his election to many foreign academies of science and to honorary membership in many chemical societies, and by his receipt of numerous honorary degrees and prizes.

On behalf of the Editorial Board of *Analytica Chimica Acta*, which Professor HEYROVSKÝ joined in 1953, the writer expresses the sorrow and regret of the Board on his passing and extends its sympathies to his family: Madame MARIE HEYROVSKÝ, his wife and long-time secretary, and MICHAEL and JITKA, his children.

PHILIP J. ELVING

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A STUDY OF SOME PROBLEMS IN DETERMINING THE STOICHEIOMETRIC PROTON DISSOCIATION CONSTANTS OF COMPLEXES BY POTENTIOMETRIC TITRATIONS USING A GLASS ELECTRODE

H. M. IRVING, M. G. MILES AND L. D. PETTIT
School of Chemistry, The University, Leeds 2 (Great Britain)

(Received January 20th, 1967)

Qualitative measurements of the stabilities of complexes, $ML_j^{(m-jp)+}$, formed from a cation M^{m+} and a ligand L^{p-} received a great impetus when J. BJERRUM published his thesis *Metal Ammine Formation in Aqueous Solution*[1]. The most significant advance came from his demonstration that, provided the ligand is the conjugate base of a weak acid, measurements of the pH of a series of solutions, containing known total concentrations of the metal salt and the ligand acid, would permit a full evaluation of the step-wise equilibrium constants. BJERRUM showed that the glass electrode was especially suitable for measuring the pH of many systems and later developments, in which his procedure was simplified by adaptation to a titration technique and extended to non-aqueous solvents[2-5], added nothing new in principle.

The apparent simplicity of the procedure has made it attractive to an increasing number of workers and the object of the present paper is to indicate some fundamental difficulties that appear to be commonly overlooked and which can lead to unreliable results.

ERRORS RESULTING FROM JUNCTION POTENTIAL AND ACTIVITY EFFECTS

The first problem arises when relating the pH of the solution to the concentration of the free ligand L^{l-} and its various protonated forms $H_jL^{(l-j)-}$ through their relevant acid dissociation constants. The thermodynamic dissociation constant of the acid HL (here and subsequently formal charges will be omitted on the grounds of simplification and generality) is defined by:

$$K^{T} = \frac{\{H\}\{L\}}{\{HL\}} = \frac{[H][L]f_{H}f_{L}}{[HL]f_{HL}} \tag{1}$$

where $\{L\}$, $[L]$, and f_L denote the activity, the concentration and the activity coefficient respectively of the species L. Other terms in current use are the stoicheiometric dissociation constant defined by:

$$K^{S} = [H]\,[L]/[HL] \tag{2}$$

and the "mixed" or Brønsted dissociation constant often defined by:

$$K^{B} = \{H\}\,[L]/[HL] \tag{3}$$

The values of K^T, K^S and K^B will not normally be identical and the appropriate value must be used when calculating the stability constant of the metal complex ML_j, which may be similarly defined by:

$$\beta^{T}_{ML_j} = \{ML_j\}/\{M\}\{L\}^j \tag{4}$$

$$\beta^{S}_{ML_j} = [ML_j]/[M][L]^j \tag{5}$$

Some authors[5-9] have sought to obtain K^T and the corresponding thermodynamic metal–ligand stability constants, but the majority have adopted the procedure of measuring stoicheiometric constants in a medium of known ionic strength, deliberately chosen to be large in comparison with the concentration of M, L and H. Although such results are meaningful only with respect to the actual ionic strength at which they were measured (and sometimes to the nature of the medium), it is generally accepted that, with these reservations, intercomparison of data is profitable and justifiable.

However the calculated values of β^S, K^S and K^B all depend on a knowledge of the concentration terms [L] and [HL] and a calculation of these magnitudes requires a knowledge of the hydrogen ion concentration $[H^+]$. Errors will obviously be introduced if the latter are derived from readings of a pH meter on the assumption, so often made, that $pH \equiv -\log_{10}[H^+]$.

The procedure usually adopted in potentiometric titrations using a glass electrode is to calibrate the electrode by means of a standard buffer using either a silver/silver chloride or a saturated calomel reference electrode, with or without an intervening salt bridge. Standardisation may be carried out with either a solution of known hydrogen ion concentration (*e.g.* $HClO_4$)[6] or, more commonly, of known hydrogen ion activity (*e.g.* 0.05 *M* potassium hydrogen phthalate, phth)[10]. In the latter case two major problems may arise. Activity effects, resulting from differences between the solution under investigation and the standardisation solution, may influence the potential to be measured to an unknown extent. Furthermore, in cells incorporating liquid junctions, junction potentials may introduce further errors whose magnitude may not always be calculable. Errors resulting from both of these factors have been considered in detail by Feldman[11] for both aqueous and nonaqueous solvents.

The following cells were studied to illustrate the effect that such errors may have on calculated acid dissociation constants.

(1) Hg_2Cl_2/Hg | sat. KCl || titration soln. in 0.1 *M* KCl | G.E.

(2) Hg_2Cl_2/Hg | sat. KCl || 0.1 *M* KCl bridge || titration soln. in 0.1 *M* KCl | G.E.

(3) Ag/AgCl | titration soln. in 0.1 *M* KCl | G.E.

The pH was measured with a Radiometer 4 pH meter using a Radiometer glass electrode G202B and a Radiometer calomel electrode. The Ag/AgCl electrode was prepared by Brown's method[12]. Readings were found to be reproducible to 0.005 pH units.

Two procedures were adopted for the standardisation of cells (1) and (2). The pH meter was standardised *either* with 0.05 M potassium hydrogen phthalate ($\mu \cong 0.050$) for which $p[H] = 4.000$ or with a solution of 0.05 M potassium hydrogen phthalate in 0.05 M potassium chloride ($\mu \cong 0.10$) for which $p[H] = 3.960$[13]. As soon as the assembly had been standardised with the one buffer (underlined in Table I) the pH value of the other buffer solution was measured with the results shown in Table I.

TABLE I

RESULTS OF MEASUREMENTS WITH STANDARD BUFFERS

	0.05 M KHphth in 0.05 M KCl	ΔE_j	*0.05 M KHphth*	ΔE_j
	$\underline{3.960}$		$\underline{4.000}$	
Cell (1)		0.023		0.022
	3.937		4.022	
	$\underline{3.960}$		$\underline{4.000}$	
Cell (2)		0.061		0.060
	3.899		4.060	

Since $p\{H\} = (E - E_0 - E_j)/2.303\ RT/nF$, where E is the measured EMF and E_j the total junction potential, the differences noted in Table I (ΔE_j) must relate to the differences in the junction potentials caused by differences in the ionic strength (0.05 M and 0.10 M respectively) of the two buffer solutions. Specifically

$\Delta E_j^{(1)} = 0.022_5$ pH units for cell (1) and

$\Delta E_j^{(2)} = 0.060_5$ pH units for cell (2),

where $\Delta E_j = (E_j^{(a)} - E_j^{(b)})/(2.303\ RT/nF)$; $E_j^{(a)}$ is the junction potential between 0.05 M potassium hydrogen phthalate in 0.05 M KCl and $E_j^{(b)}$ is the junction potential between 0.05 M potassium hydrogen phthalate alone and the saturated calomel electrode respectively.

To illustrate what effect these differences in standardisation procedure may have on calculated acid dissociation constants, a series of titrations of nitrilotriacetic acid, NTA (10^{-3} M in 0.1 M KCl) and of ethylenediaminetetraacetic acid, EDTA (10^{-3} M in 0.1 M KCl) were carried out with cells (1) and (2) after each had been standardised with one or other of the two standard buffers. (The acids were titrated with 0.1 M carbon dioxide-free potassium hydroxide prepared by SCHWARZENBACH's method[20].) Table II shows values of "experimental" constants, *i.e.* values calculated by using the relationship:

$(H) = 1/\text{antilog}$ (pH-meter reading)

Here (H) cannot be identified precisely with either $\{H\}$ or $[H]$ but must be regarded solely as an experimentally determined value relevant to titration of NTA and EDTA under the specific experimental condition used. The values reported by SCHWARZENBACH[5], for the stoicheiometric acid dissociation constants, K_j^s referred to 0.1 M KCl, are also given in the Table. The value $K_w^c = [H^+][OH^-] = 1.14 \cdot 10^{-14}$ was used in calculating K_4^s.

TABLE II

EXPERIMENTAL ACID DISSOCIATION CONSTANTS AT 20.0° AND $\mu = 0.10\ M$

pK_n	*Cell (1)*		*Cell (2)*		*Schwarzenbach* pK_n^s
	0.05 M phth	*0.05 M phth /0.05 M KCl*	*0.05 M phth*	*0.05 M phth /0.05 M KCl*	
EDTA					
pK_1	2.49	2.59	2.00	2.32	1.99
pK_2	2.94	3.04	2.67	2.89	2.67
$pK_1 + pK_2$	5.43	5.63	4.67	5.21	4.66
pK_3	6.28	6.30	6.18	6.24	6.16
pK_4	10.36	10.40	10.22	10.30	10.26
NTA					
pK_1	2.28	2.43	(0.0)[a]	2.14	1.89
pK_2	2.73	2.79	2.48	2.69	2.49
$pK_1 + pK_2$	5.01	5.22	(2.48)	4.83	4.38
pK_3	9.78	9.80	9.71	9.75	9.73

[a] Methods for calculating the values of the successive dissociation constants produced a physically unacceptable negative value for pK_1. The reason for this is discussed later (p. 484 *et seq.*).

The constants obtained would not be expected to agree with SCHWARZENBACH's results, and this is found to be the case. For instance, if a buffer solution of known hydrogen ion activity, p{H}, is used to standardise a cell, the measured p(H) of the test solution will only be equal to p{H} if the solutions are of comparable ionic strength[10,11] and composition, so that there is no difference in the junction potentials of the two systems. A difference in ionic strength between the buffer and test solutions will give a pH meter reading which is given by

$$
\begin{aligned}
p(H) &= p\{H\} - \Delta E_j = p[H] + \log f - \Delta E_j \\
&= p[H] + A \qquad (6)
\end{aligned}
$$

The quantity A may be compared to the factor R used by VAN UITERT AND HAAS when discussing acid–base equilibria in mixed solvents[14].

It is difficult to calculate accurately the ionic strength of a solution containing NTA (or EDTA) and varying amounts of alkali, since the complex mixture of zwitter-ions can hardly be regarded as point charges[15], and the appropriate values of Z, the ionic charge, to be used in the calculation of $\mu = {}^1/_2\ CZ^2$ are in doubt. Hence ΔE_j cannot be eliminated merely by choosing a suitable buffer solution. The appropriate value for A was therefore obtained by calibrating cells (1), (2) and (3) in terms of [H] by titrating perchloric acid ($10^{-3}\ M$ in 0.1 M KCl) against CO_2-free potassium hydroxide (0.1 M) and the titrations of NTA and EDTA with alkali were then repeated. The corrected p(H) readings were now, by definition, equal to p[H]. The calculated stoicheiometric dissociation constants are given in Tables III and IV.

The values obtained for EDTA are seen to be in close agreement with those obtained by SCHWARZENBACH[16]. Comparatively little weight should be attached to the value reported for pK_1^s for NTA since, in dilute solution, the acid is already strongly dissociated and only about 1.1% is present in the form H_3L in a $10^{-3}\ M$ solution. Small errors in p[H] will therefore cause disproportionately large errors in calculated values for pK_1^s. These errors are discussed in more detail later.

Experiments were next carried out to find the differences between titration curves of a given complexone (pH meter readings against volume of titrant) when both cells (1) and (2) were used after the pH meter had been "calibrated" (a) in terms of either (*i*) 0.05 *M* potassium hydrogen phthalate or (*ii*) 0.05 *M* potassium hydrogen phthalate in 0.05 *M* KCl, and (b) by titration of perchloric acid of known concentration so as to read p[H] directly. The curves obtained lie parallel to one another and can be made to superimpose exactly by a small displacement along the pH axis. The extent of the displacement of the curves after standardisation by method (a) from those obtained after using method (b) was found to be the same in the case both of NTA and EDTA and gives an exact measure of A for each cell and for each method of standardisation. The values obtained are given in Table V.

TABLE III

STOICHEIOMETRIC ACID DISSOCIATION CONSTANTS OF NTA

pK_j^s	*Schwarzenbach*[3]	*Present work*	
		10^{-3} M	*8·10^{-3} M*
pK_0^s		—	0.80±0.2
pK_1^s	1.89	(0)	1.71±0.10
pK_2^s	2.49	2.50±0.04	2.47±0.01
pK_3^s	9.73	9.71±0.01	9.71±0.01

TABLE IV

STOICHEIOMETRIC ACID DISSOCIATION CONSTANTS OF EDTA

pK_j^s	*Schwarzenbach*[16]	*Present work*
pK_1^s	1.99	1.9±0.1
pK_2^s	2.67	2.67±0.02
pK_3^s	6.16	6.16±0.01
pK_4^s	10.26	10.23±0.02

TABLE V

Cell	*Cell (1)*		*Cell (2)*	
Buffer	0.05 phth	0.05 phth/0.05 KCl	0.05 phth	0.05 phth/0.05 KCl
A	0.08±0.01	0.10±0.01	0.00±0.01	0.06±0.01

For cell (1), when standardised with 0.05 *M* potassium hydrogen phthalate in 0.05 *M* potassium chloride, $A=0.10$ and ΔE_j is zero. Substituting in eqn. (6) this gives $f_H=0.794$ which is in reasonable agreement with the value, $f_H=0.776$, calculated by GRIMES *et al.*[17], from the expression:

$$-\log f_H = AZ_H^2\sqrt{\mu}/(1+Ba_H\sqrt{\mu})$$

where a_H, A and B are assigned the values used by the National Bureau of Standards. MAJER AND DVORAKAVA[18] have used the value of $f_H = 0.782$. This gives [H] accurate to within 0.01 p[H] units only if a buffer solution of an ionic strength $\mu = 0.10$ is used with a cell of type (1).

It appears to be quite fortuitous that cell (2), standardised with 0.05 *M* potassium hydrogen phthalate, gives p[H] directly. It follows from eqn. (9) that in this case $\log f_H = {}^{-}\Delta E_j$. Authors[9,19] who have used this cell have offered no explanation for this.

Recommended procedure

To obtain values of hydrogen ion concentration from measurements on a cell containing a liquid junction the following procedure is recommended.

Adjust the pH meter using a primary standard buffer solution. Use a standardised solution of a strong base to titrate a solution of a strong acid, of comparable concentration, ionic background, and ionic strength to that of the test solution. Determine *A* by subtracting the value of p[H], calculated at various points on the titration curve, from the p(H) values as read on the meter. Add the correction factor (*A*) to all values of p(H) obtained with the cell subsequent to standardisation: this will then give $p[H] = -\log_{10}[H^+]$. It should be noted that this correction factor will be applicable only to the particular cell and the experimental conditions in use.

ERRORS RESULTING FROM CONCENTRATION AND OTHER FACTORS

Assuming that the hydrogen ion concentrations are known reasonably accurately, the accuracy with which the successive dissociation constants of polybasic acids can be determined by pH titration techniques depends on their magnitude: any errors in these determinations will cause concomitant errors in calculating the stability constants of metal complexes formed from these ligands. Particularly large errors can arise if the acid has a high dissociation constant ($pK<3$) or low one ($pK>11$), although only in the latter case is there considerable influence on the calculation of formation constants of the metal complexes. We have investigated the behaviour of NTA and EDTA, with a particular study of the first two dissociation constants and have examined the behaviour in alkaline solution of some analogues of NTA which have lower values of K_3 than NTA itself. The influence of the precision of pH measurement, errors resulting from neglecting cationic species and errors in the chosen value of K_w, have been studied and concomitant errors in the formation constants of metal complexes computed from the resulting calculated dissociation constants have also been considered.

The stoicheiometric acid dissociation constants for EDTA and NTA, calculated from potentiometric titrations, were reproducible within "experimental" error if values for pK_1^s and pK_0^s are excepted (see Tables III and IV). Values for pK_1^s, particularly for NTA, differed from one titration to another and in some cases gave physically meaningless results (*viz.* negative values of *K*).

The general expression for the stoicheiometric constants of an acid of basicity *n*, in terms of experimentally determinable quantities, is:

$$\sum_{0}^{n}(R-j)\,[H]^{n-j}\beta_j = 0 \qquad (7)$$

where $\beta_j = K_1K_2K_3\ldots K_j$, $R = (aC_a + [H] - [OH])/C_a$ and *a* is the degree of neutralisation of the acid of total concentration C_a. Since in acid solution (pH<4) the only species of the acids studied present in quantities detectable by potentiometric techniques are the ions H_nL, $H_{n-1}L^-$ and $H_{n-2}L^{2-}$, together with the possibility of the cation $H_{n+1}L^+$, eqn. (7) may be written thus:

$$(R-2)K_0K_1K_2+[H](R-1)K_0K_1+[H]^2RK_0+[H]^3(R+1)=0 \tag{8}$$

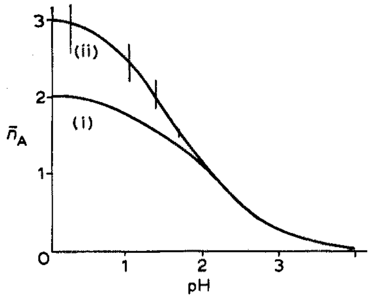
where $K_0=[H_nL]\,[H^+]/[H_{n+1}L^+]$. Titration curves for each ligand of the complexones studied were examined to ensure that the influence of K_3 could be neglected as assumed in eqn. (8). This was found to be the case so that, in acid solution pH⩽4, both NTA and EDTA could be considered to behave essentially as dibasic acids, H_2L, which can accept protons to form H_3L^+.

The formation curve of an acid is obtained by plotting $\bar{n}_A$ (the degree of formation of the acid, defined as the average number of protons bound to each acid ion) against pH. If the acids are both considered to be dibasic acids of formula H_2L then:

$$\bar{n}_A = \frac{2C_A-[H]-aC_A+[OH^-]}{C_A} = (2-R) \tag{9}$$

Since the formation curve illustrates, in the most fundamental form, the behaviour of the acid as a function of pH, this curve should always be the basis for the interpretation and calculation of acid dissociation constants.

The influence of cationic species on calculated values of pK_1 becomes immediately apparent when calculated formation curves, assuming various values for pK_0, are compared with the experimental curve. It should be noted that for the acid H_2L the formation curve will range through $2 \geqslant \bar{n} \geqslant 0$ but for the species H_3L^+ through $3 \geqslant \bar{n} \geqslant 0$ (as shown in Fig. 1) where differences in the formation curves become inappreciable at high pH.



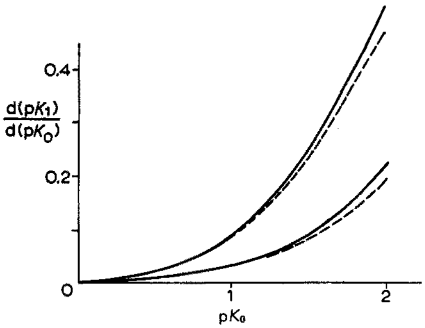


Fig. 1. Formation curves for NTA assuming dibasic behaviour (*i.e.* H_2L). (i) Calculated curve for $pK_0 = 0$, $pK_1 = 1.71$, $pK_2 = 2.47$; (ii) calculated curve for $pK_0 = 0.80$, $pK_1 = 1.71$, $pK_2 = 2.47$. Vertical lines show possible range of experimental points.

Fig. 2. The reliability of calculated pK_1 values as a function of pK_0. ——— NTA, -------- EDTA. Lower lines, 10^{-3} *M*; upper lines, $4 \cdot 10^{-3}$ *M*.

Figure 1 shows the influence of K_0 on the formation curve for NTA. It will be noticed that, up to $\bar{n}_A=0.9$, the value of K_0 has little or no effect on the calculated curve (provided that $pK_0 < 0.8$). However, if the formation curve is extended experimentally to $\bar{n}_A=1.5$ the existence of a cationic species is demonstrated beyond doubt.

Calculations based on a limited range of observations can, therefore, be surprisingly misleading.

The extent of the influence of pK_0 on pK_1 is best demonstrated by plotting the rate of change of calculated values of pK_1 for small changes in assumed values of pK_0, *viz.* $d(pK_1)/d(pK_0)$ against pK_0. Figure 2 demonstrates this for NTA and EDTA at the start of their titration curves in 10^{-3} M solution and $4 \cdot 10^{-3}$ M soln., with no mineral acid present.

Values for dpK_1/dpK_0 were calculated from a modified form of eqn. (8), using the values $pK_2 = 2.47$ for NTA and 2.67 for EDTA. Alternatively, by using measured values for pK_0, $d(pK_1)/d(pK_0)$ may be plotted as a function of C_A, as shown in Fig. 3 where $pK_0(\text{NTA}) = 0.80$ (Table III) and $pK_0(\text{EDTA}) = 1.55$[21]. If $dpK_1/dpK_0 < 0.1$, it is reasonable to ignore the influence of pK_0 on pK_1. With NTA this condition is realised only when the solution is strongly supersaturated ($C_A > 7 \cdot 10^{-3}$ M) so that, for normal considerations, the influence of cationic species may be ignored. With EDTA, however, these cationic species will measurably influence the value for pK_1 when the total acid concentration exceeds a value as low as $1.5 \cdot 10^{-3}$ M.

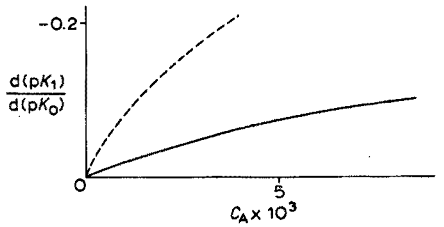


Fig. 3. The influence of pK_0 on calculated pK_1 values as a function of total acid strength. Upper curves, $C_A = 4 \cdot 10^{-3}$ M; lower curves, $C_A = 10^{-3}$ M. ——— NTA, -------- EDTA.

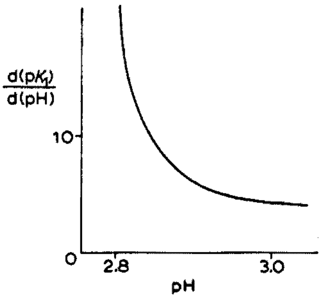


Fig. 4. The reliability of calculated pK_1 values as a function of pH for NTA.

The measurement of pK_0

Values of pK_0 for EDTA have previously been calculated from data obtained by the titration of the acid with a strong mineral acid[21], and by solubility measurements in the presence of mineral acid[22-24]. No attempts to determine pK_0 for NTA have so far been reported. In the present work, the determination of pK_0 for EDTA by both methods gave substantially the same results as those previously reported. No evidence was found in solution for a dicationic species, other than that offered by the apparent symmetry of the graph of solubility against pH. The solid diperchlorate and difluoborate were, however, prepared by BECK AND GÖRÖG's method[22] and provided evidence for the existence of this species in strongly acid media. The solubility curve obtained indicated a slightly higher solubility than that obtained by other workers. This results from the differences in ionic strengths and is in agreement with the findings of YOSHINO *et al.*[24].

The cationic species derived from NTA (H_3L^+ if NTA is considered for the moment to behave as a dibasic acid H_2L) was more readily detected in spite of the adverse indications of Fig. 3, because the solubility of this complexone is higher than that of EDTA and supersaturated solutions are more readily obtained. By titration with an alkaline solution of strength $8.65 \cdot 10^{-3}$ M, the departure of the experimental curve from the theoretical curve ((i) in Fig. 1) could just be detected experimentally. Higher $\bar{n}_A$ values were obtained by measuring the solubility of NTA as a function of pH. The pH of a saturated solution of NTA in the presence of excess mineral acid was measured and the total acid and complexone concentrations were determined by titration. Unfortunately, the precision of the calculated $\bar{n}_A$ value decreases as its absolute value increases as shown in Fig. 1. However, it proved possible to calculate a formation curve that fitted the experimental data (solid line in Fig. 1) using the value $pK_0=0.8$, $pK_1=1.71$, $pK_2=2.47$; this clearly approaches the value $\bar{n}=3$.

The measurement of pK$_1$

The precision with which pK_1 can be calculated is, like that of pK_0, dependent on the range of $\bar{n}_A$ values available. Assuming that the presence of cationic species can be neglected in titrations of acid of concentration 10^{-3} M, and considering the complexone as H_2L, eqns. (7) and (9) may be combined to give, at the start of the titration before any alkali is added,

$$K_1 = \frac{C_A{}^2\,(2-\bar{n}_A)^3}{\bar{n}_A K_2 + (2-\bar{n}_A)\,(\bar{n}_A-1)C_A}$$

whence, assuming that calculated K_1 values are not dependent on the value of K_2,

$$\frac{d(pK_1)}{d\bar{n}_A} = \frac{2K_2(\bar{n}_A+1)+\bar{n}_A C_A(2-\bar{n}_A)}{(2-\bar{n}_A)\,[\bar{n}_A K_2+(2-\bar{n}_A)\,(\bar{n}_A-1)C_A]} \qquad (10)$$

Equation (10) gives the sensitivity of pK_1 to small charges in $\bar{n}_A$. The quantity $d(pK_1)/d\bar{n}_A$ can be shown to reach infinity only when $\bar{n}_A(K_2/C_A+3)=\bar{n}_A{}^2+2$ (*i.e.* somewhere between $\bar{n}_A=0$ and 1), since a value of $\bar{n}_A=2$ can only be reached if both K_1 and K_2 are zero. When $\bar{n}_A$ is smaller than this, the calculated value of pK_1 is influenced to an unreasonable extent by the value chosen for pK_2 and eqn. (10) no longer holds. Above this value, as $\bar{n}_A$ increases, the precision of a calculated value for pK_1 increases although it decreases again as $\bar{n}_A$ approaches two. The function $dpK_1/d\bar{n}_A$ approaches infinity when $\bar{n}_A=0.330$ in the case of NTA and $\bar{n}_A=0.425$ for EDTA. A 10^{-3} solution of NTA has an initial $\bar{n}_A$ value of 0.311 and, as the titration with alkali proceeds, $\bar{n}_A$ decreases. Hence, from no points on the titration curve can one expect to be able to calculate reliable values for pK_1. A similar solution of EDTA, however, has an $\bar{n}_A$ value of 0.485 (*i.e. above* the value for which the precision is a minimum) hence a value for pK_1 can be quoted with some confidence.

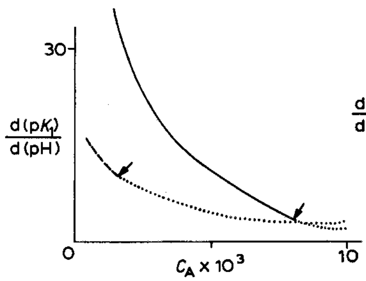
Alternatively, the sensitivity of calculated pK_1 values to small errors in measured pH may be considered. This is demonstrated for NTA ($C_A=10^{-3}$ M) in Fig. 4 where dpK_1/dpH is plotted against pH.

For the situation before the addition of the alkali, eqn. (8), neglecting K_0, gives the relationship:

$$\frac{d(pK_1)}{dpH} = \frac{(2C_A-[H])\;(2K_2+[H])+2C_A K_2}{(2C_A-[H])K_2+(C_A-[H])\;[H]} \qquad (11)$$

This expression approaches infinity as pK_1 approaches infinity. A 10^{-3} M solution of NTA has a calculated pH of 2.787 (taking the values $pK_1 = 1.71$ and $pK_2 = 2.47$) and at this pH, $d(pK_1)/dpH = 4.43$. The value for $d(pK_1)/dpH$ reaches infinity when $pH = 2.777$ and if the measured $pH < 2.777$, the value calculated for K_1 will be negative. Hence an error as small as 0.011 pH units is sufficient actually to change the sign of K_1 to give a calculated value for K_1 that will be negative; this is a physically meaningless result. With EDTA the function reaches infinity at a pH of 2.802 whereas a 10^{-3} M solution has a pH of 2.823, hence an error of 0.021 pH units is required to change the sign of K_1. This again indicates a much higher precision for pK_1 for EDTA than for NTA.

The precision with which pK_1 can be calculated may be increased by increasing the acid concentration, C_A, provided that complications are not introduced by making the concentration of cationic species appreciable. The quantity dpK_1/dpH can be evaluated for a range of values for C_A, using values for [H] calculated from eqn. (7) when the most accurate values for K_1 and K_2 are employed. Graphs of dpK_1/dpH against C_A for both NTA and EDTA are shown in Fig. 5.



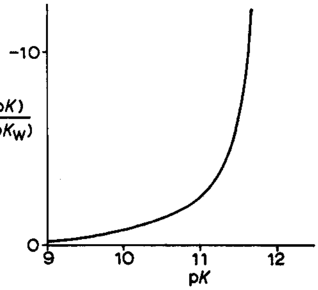


Fig. 5. The reliability of calculated pK_1 values as a function of total acid concentration. ——— NTA, -------- EDTA. Saturation concentrations at 20° indicated by arrows.

Fig. 6. The dependence of calculated acid dissociation constants on the value taken for pK_w as a function of the pK value.

It will be noticed that precise values for pK_1 (NTA) cannot be expected unless the acid concentration is at least $5 \cdot 10^{-3}$ M; however reliable values for pK_1 (EDTA) can be found when $C_A > 1.5 \cdot 10^{-3}$ (*i.e.* just before the effect of cationic species is important).

In strongly alkaline solution ($pH > 10$) there will be a similar dependence on the precision of measurement of pH. In dilute solutions of extremely weak acids (*e.g.* α-amino-isobutyric acid-N,N-diacetic acid and cycloheptane-1-amino-1-carboxylic acid-N,N-diacetic acid), the values of $\bar{n}_A$ will be found to be always too large to obtain the complete formation curves between $\bar{n}_A = 0$ and 1, so that the reverse of the situation described earlier will be found. Similar reasoning to that used earlier will demonstrate the dependence of the precision with which the acid dissociation constant, K, for the reaction $HL = H + L$ can be calculated from the total acid strength, C_A, and the measurements of pH of varied precision.

A further complication arises in alkaline solution in that the auto-dissociation of water must also be considered since this will influence the calculated value for $[OH^-]$ in eqn. (7). Errors in K_{HL} arising from errors in the value taken for K_w, the auto-dissociation constant for water, will decrease the precision with which acid dissociation constants can be calculated in strongly alkaline solution making them even less reliable than those calculated in strongly acidic solution. Since it is the smallest dissociation constants that have the greatest influence on calculated metal complex formation constants, it is essential that these are known with the highest possible reliability. The dependence of the values calculated for K_{HL} on the value taken for K_{w} is illustrated in Fig. 6. Considering the dissociation $\mathrm{HL} \rightleftharpoons \mathrm{H} + \mathrm{L}$ when the acid is half neutralised, the following relationships are obtained: $C_{\mathrm{A}} = [\mathrm{HL}] + [\mathrm{L}]$ and, for electroneutrality, $0.5\, C_{\mathrm{A}} + [\mathrm{H}] - [\mathrm{OH}] = [\mathrm{L}]$. In alkaline solution these can be combined to give

$$K_{\mathrm{HL}} = \frac{[\mathrm{H}]\,[\mathrm{L}]}{[\mathrm{HL}]} = \frac{C_{\mathrm{A}}[\mathrm{H}] - 2K_{\mathrm{w}}}{C_{\mathrm{A}} + 2K_{\mathrm{w}}/[\mathrm{H}]} \tag{12}$$

Measurements of K_{w} in 0.1 M KCl at 20° have been made by several workers[25,26] who report values between 10^{-14} and $1.14 \cdot 10^{-14}$. From eqn. (12) [H] may be calculated for a given value of K_{HL} taking $K_{\mathrm{w}} = 1.14 \cdot 10^{-14}$ and assuming $C_{\mathrm{A}} = 10^{-3}\ M$. If, using this value for [H], K_{HL} is recalculated using the value $K_{\mathrm{w}} = 10^{-4}$, the quantity $\mathrm{d}pK/\mathrm{d}pK_{\mathrm{w}}$ can be evaluated approximately by numerical differentiation. This can be repeated for a range of K values to give the relationship illustrated in Fig. 6. It will be noticed that when the value for pK exceeds 12, the dependence on pK_{w} is too great to allow a very accurate value for pK to be calculated.

Stability constants of metal complexes are frequently measured by the potentiometric titration technique originated by CALVIN AND WILSON[2]. In this technique the competition equilibrium between protons and metal ions for coordination with the ligand is followed by means of pH measurements.

$$\mathrm{HL} + \mathrm{M} \rightleftharpoons \mathrm{ML} + \mathrm{H}$$

The equilibrium constant for this reaction, K_{e}, may be expressed as the product of the acid dissociation constant, K, and the metal complex formation constant, K_{ML}

$$i.e.\ K_{\mathrm{e}} = \frac{[\mathrm{ML}]\,[\mathrm{H}]}{[\mathrm{HL}]\,[\mathrm{M}]} = K_{\mathrm{ML}} \cdot K_{\mathrm{HL}}$$

Any errors in the value taken for K will therefore introduce, to a first approximation, an equal error in the value calculated for K_{HL}, assuming that the overall equilibrium constant, K_{e}, can be measured exactly.

EXPERIMENTAL

Solubility measurements

Solutions containing an excess of the complexone and various known concentrations of HCl and KCl such that the total ionic strength of the background was 0.100 M (except at pH values below 1) were equilibrated by shaking in a thermostat at 20±0.05° for 48 h. The concentration of total acid present was found by pH titration with 0.1 M potassium hydroxide, the end-point being determined by GRAN's method[27], and the concentration of complexone from the difference between this end-point and that obtained in the presence of excess zinc sulphate. The pH of the solution was determined with the assembly used for the titrations. The solubility, C_{A}, of NTA is given by

$$C_A = \sum_{0}^{4}[H_nL^{(3-n)-}] \qquad (13)$$

Neglecting terms in K_3, as they are negligible in the region under investigation, and incorporating equations for electroneutrality and mass balance, eqn. (13) may be modified to give an equation identical to eqn. (8). Hence an $\bar{n}_A$/p[H] curve can be constructed and the constants calculated as indicated later.

Titration procedure

pH-metric titrations of supersaturated solutions of the complexone in 0.1 M KCl with CO_2-free potassium hydroxide (0.1 M) were performed using a Radiometer 4 pH meter with a glass electrode and a saturated calomel reference electrode. The titration assembly was calibrated in terms of hydrogen ion concentration by means of titration of 10^{-3} M perchloric acid in KCl (0.1 M). A graph of $\bar{n}_A$ against pH was then constructed using eqn. (8). It was found that this curve could be exactly superimposed on the curve constructed from solubility measurements (Fig. 1). In the case of EDTA the experimental results agreed with those of other workers[21–24] within the precision of the measurements and have therefore been omitted from this paper.

Table VI shows the experimental data found for NTA.

TABLE VI

Solubility measurements of NTA at 20.0°, μ = 0.1 M KCl

pH	0.288[a]	1.041	1.322	1.682	2.123	2.608	2.793
$\bar{n}$	2.76±0.4	2.39±0.3	2.03±0.2	1.44±0.05	0.995±0.01	0.508±0.001	0.387±0.002
C_A	$12.83\cdot10^{-3}$	$3.785\cdot10^{-3}$	$3.241\cdot10^{-3}$	$3.550\cdot10^{-3}$	$7.497\cdot10^{-3}$	$29.95\cdot10^{-3}$	$53.93\cdot10^{-3}$

Titration measurements at 20.0°, μ = 0.1 M KCl, $C_A = 8.653\cdot10^{-3}$ M

pH	2.080	2.230	2.334	2.413	2.558	2.664	2.881	3.091	3.239	3.448	3.602	3.828	4.006
$\bar{n}$	1.039	0.871	0.757	0.675	0.548	0.456	0.311	0.208	0.154	0.0994	0.0716	0.0434	0.0290

[a] μ clearly greater than 0.1 M.

Approximate values for pK_1 and pK_2 were obtained from a linear plot of $(1-\bar{n})[H]/\bar{n}$ against $(2-\bar{n})[H]^2/\bar{n}$. From eqn. (8), ignoring K_0, combined with eqn. (9) it can be seen that the slope of the line will give $1/K_1$ and the intercept will give K_2. The values of $\bar{n}$ used were in the range 1.0 to 0.2, assuming the acid to be H_2L. pK_2 was found to be 2.469, in good agreement with SCHWARZENBACH *et al.* (see Table III) and pK_1 was found to be 1.72. The $\bar{n}$ (pH) curve was then constructed (Fig. 1) from those values neglecting K_0. This value of pK_2 was then substituted into eqn. (13) (obtained by rearranging eqn. (8) after substituting with eqn. (9)),

$$\frac{-(2-\bar{n})\,[H]^2}{(1-\bar{n})\,[H]-\bar{n}[H]^2} = \frac{[H]^3(3-\bar{n})}{(1-\bar{n})\,[H]-\bar{n}[H]^2}\cdot\frac{1}{K_0} + K_1 \qquad (14)$$

Values for K_0 and K_1 were obtained from a plot of $\dfrac{(2-\bar{n})\,[H]^2}{(1-\bar{n})\,[H]-\bar{n}[H]^2}$ against $\dfrac{[H]^3(3-\bar{n})}{(1-\bar{n})\,[H]-\bar{n}[H]^2}$ taking values of $\bar{n}$ between 1.2 and 2.7.

The value obtained for pK_1 (1.70) differed only very slightly from the value obtained when K_0 was neglected and gives a value of much higher accuracy than that obtained by other workers[28].

SUMMARY

Possible errors in the measurement of acid dissociation constants by potentiometric titration techniques have been considered, with particular references to nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Unknown junction potentials can arise when pH measurements are carried out using a glass electrode with saturated calomel reference electrode which have been previously calibrated with a standard buffer solution. The magnitude of the influence of these unknown potentials has been demonstrated and an experimental procedure recommended which gives meaningful results.

The precision of calculated acid dissociation constants will also be influenced by the presence of cationic species (*e.g.* H_4L^+), the total acid strength, the absolute values of the constants and the value accepted for the auto-dissociation constant of water (K_w). All these factors have been considered quantitatively and their effect on metal complex formation constants, calculated from these acid dissociation constants, noted. The proton dissociation constant of the cationic species of NTA (*i.e.* H_4L^+) has been found to have the value of $pK_0=0.80$ at 20° and $\mu=0.10$ *M*.

RÉSUMÉ

Les auteurs ont effectué une étude sur les erreurs possibles lors de la mesure des constantes de dissociation acides par titrage potentiométrique; ils ont examiné en particulier l'acide nitrilotriacétique (NTA) et l'acide éthylènediaminotétracétique (EDTA), en utilisant une électrode de verre avec électrode de référence au calomel, saturé. La précision des constantes de dissociation acide calculées est influencée par la présence de particules cationiques (ex. H_4L^+), la force acide totale, les valeurs absolues des constantes et la valeur de la constante d'auto-dissociation de l'eau (K_w). La constante de dissociation des particules cationiques de NTA (ex. H_4L^+) est de $pK_0=0.80$ à 20° et $\mu=0.1$ *M*.

ZUSAMMENFASSUNG

Mögliche Fehler bei der Messung von Säuredissoziationskonstanten mittels potentiometrischer Titration werden diskutiert unter besonderer Berücksichtigung der Nitrilotriessigsäure (NTA) und der Aethylendiamintetraessigsäure (AeDTE). Zu diesen Fehlermöglichkeiten gehören: Unbekannte Berührungspotentiale, wenn Glaselektroden und gesättigte Kalomelelektroden verwendet werden; die Gegenwart von Kationen, wie z.B. H_4L^+; die totale Säurestärke; die absoluten Werte der Konstanten und der Wert, der für die Selbstdissoziationskonstante des Wassers angenommen wird. Alle diese Faktoren wurden quantitativ betrachtet und ihr Einfluss auf die aus den Säuredissoziationskonstanten berechneten Metallkomplexbildungskonstanten angegeben. Die Protonendissoziationskonstante der kationischen Spezies von NTA beträgt $pK_0=0.80$ bei 20° und $\mu=0.10$ *M*.

REFERENCES

1 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, P. Haase and Son, Copenhagen, 1941.
2 M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 67 (1945) 2003.
3 G. Schwarzenbach and co-workers, *e.g. Helv. Chim. Acta*, 34 (1961) 1492.
4 H. Irving and J. H. H. Griffiths, *J. Chem. Soc.*, (1954) 213; H. Irving and H. Rossotti, *J. Chem. Soc.*, (1954) 2904, 2910; D. P. Mellor and L. Maley, *Nature*, 159 (1947) 370; W. C. Fernelius and co-workers, *J. Am. Chem. Soc.*, 76 (1954) 375, 1696.
5 *Chem. Soc. Special Publ.*, No. 17, 1964; and refs. therein.
6 G. Schwarzenbach *et al.*, *Helv. Chim. Acta*, 28 (1945) 828; 29 (1946) 364; 31 (1948) 456.
7 F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, 76 (1954) 2153.
8 (a) W. P. Evans and C. B. Monk, *Trans. Faraday Soc.*, 47 (1951) 292, 297; 51 (1955) 1244; (b) R. Izatt, C. Haas, B. Block and W. Fernelius, *J. Phys. Chem.*, 58 (1954) 1133; 59 (1955) 80, 170, 235.
9 H. Irving and J. da Silva, *J. Chem. Soc.*, (1963) 458.
10 R. G. Bates, *Determination of pH, Theory and Practice*, Ch. 4, John Wiley, New York, 1964.
11 I. Feldman, *Anal. Chem.*, 28 (1956) 1859.
12 A. S. Brown, *J. Am. Chem. Soc.*, 56 (1934) 646.
13 W. J. Hamer and S. F. Acree, *J. Res. Natl. Bur. Std.*, 32 (1944) 215.
14 L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 75 (1953) 451.
15 J. G. Kirkwood, *J. Chem. Phys.*, 2 (1934) 351.
16 G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 30 (1947) 1798.
17 J. H. Grimes, A. J. Huggard and S. P. Wilford, *J. Inorg. & Nucl. Chem.*, 25 (1963) 1225.
18 J. Majer and E. Dvorakava, *Chem. Zvesti*, 18 (1963) 402.
19 H. Irving and M. H. Stacey, *J. Chem. Soc.*, (1961) 2019.
20 G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 331.
21 M. Tillotson and L. A. K. Staverley, *J. Chem. Soc.*, (1958) 3613.
22 M. Beck and S. Görög, *Magy. Tud. Akad. Kem. Tud. Oszt. Kozlemen.*, 12 (1959) 265.
23 P. Mechelynck and W. Schietecatte, *Anal. Chim. Acta*, 19 (1958) 577; D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, 82 (1960) 5602; G. S. Tereshin and I. V. Tananaev, *Zh. Analit. Khim.*, 16 (1961) 523; A. E. Klygin, I. D. Smirnova and H. A. Nikolskay, *Zh. Neorgan. Khim.*, 4 (1959) 2766.
24 Y. Yoshino, A. Iquchi, M. Kojina and K. Mizumachu, *Bull. Chem. Soc. Japan*, 31 (1958) 892.
25 G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 30 (1947) 1798.
26 H. S. Hanard and W. J. Hamer, *J. Am. Chem. Soc.*, 55 (1933) 2194.
27 R. Gran, *Acta Chem. Scand.*, 1 (1950) 559.
28 G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta*, 38 (1955) 1147 and refs. therein.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF CHROMIUM IN BIOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROSCOPY*

FREDRIC J. FELDMAN AND EDWARD C. KNOBLOCK
Division of Biochemistry, Walter Reed Army Institute of Research, Walter Reed Army Medical Center, Washington, D.C. 20012 (U.S.A.)
AND
WILLIAM C. PURDY
University of Maryland, College Park, Md. (U.S.A.)

(Received December 16th, 1966)

In 1959 SCHWARZ AND MERTZ[1] identified chromium(III) as the active ingredient of the glucose tolerance factor, a dietary agent required for maintenance of normal glucose tolerances in the rat. Further work by MERTZ and others[2-9] indicates that chromium should be considered an essential trace element. In order to understand fully the metabolic role played by chromium, its physiological concentration must be known. Thus, a need developed in our laboratory for an accurate and sensitive determination of chromium at the parts-per-billion level.

Colorimetric procedures have been used to determine chromium[10]. However, the drawbacks of these procedures at such low levels, such as stability of color, interferences, etc., are well known.

Atomic absorption spectrophotometry is rapidly becoming the method of choice for trace metal analysis. High sensitivity, ease of sample preparation, and reduction of interferences are among the reasons for this trend. WILLIAMS *et al.*[11] studied the determination of chromium in feces by atomic absorption spectrophotometry. They used a phosphoric acid–manganese sulfate–potassium bromate digestion mixture with an acetylene–air flame and worked over a chromium range of 0.8–70 p.p.m., using aqueous solutions.

DELAUGHTER[12] recently determined p.p.b. concentrations of chromium in brines by atomic absorption, after chelation with diphenylthiocarbazone and extraction with methyl isobutyl ketone. Since the limit of detection was 1 p.p.b., the method appeared to be extremely sensitive. However, the minimum sample weights were 800 g.

The optimum conditions for the determination of trace amounts of chromium by atomic absorption spectrophotometry have been described by FELDMAN AND PURDY[13]. Solution matrix, flame composition, and extraction procedures were the variables studied. A detection limit of 0.006 p.p.m. of chromium was observed with an air–hydrogen flame and methyl isobutyl ketone as the solvent.

The present paper describes the application of this method to the deter-

---

* Taken in part from the Ph.D. dissertation of FREDRIC J. FELDMAN, University of Maryland, College Park, Maryland, 1966.

mination of chromium in biological materials. Interference studies of a wide number of cations are described. Chromium levels in human serum are reported. Chromium tissue levels of albino rats were studied. Some average values found in p.p.b. were: whole blood, 24; serum, 29; liver, 130; spleen, 360; and heart, 90. Groups of animals were maintained on a high chromium diet and on a chromium-deficient diet, and their chromium levels compared.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade. In some cases, purified mineral acids were used for the ashing. Concentrated sulfuric acid and perchloric acid, which had been distilled and stored in Vycor, were obtained from the G. Frederick Smith Chemical Company. Nitric acid (Mallinckrodt AR) was distilled before use.

Standard stock solutions containing 50 and 100 μg of chromium(VI) per ml were prepared from primary standard potassium dichromate. Standard chromium(III) stock solutions containing 50 μg/ml were prepared by dissolving chromium metal (99.9%) in a minimum amount of concentrated hydrochloric acid and making up to volume with water or by weighing out reagent-grade chromium nitrate. Working standards containing 0.1–10 μg of chromium per ml were prepared by dilution of the above stock solutions. The water used was as previously described.

Apparatus

Radioactive tracers in the form of ^{51}Cr were used to check on the recoveries of chromium during digestion. A Nuclear-Chicago Scaler Model 186 was used to count the radioactive chromium.

All atomic absorption measurements were made with a Jarrell-Ash atomic absorption spectrophotometer (Model 83-000). This model was equipped with 3 Beckman flame spectrophotometer burners to increase the path length and was designed to allow 5 light passes through the flame. A fuel-rich air–hydrogen flame was used for these studies. The light source was a Westinghouse, neon-filled, hollow-cathode lamp. All absorption measurements were recorded on a Bristol Dynamaster recorder supplied with the instrument. The 357.9 nm resonance line of chromium was used for these measurements. The instrument was operated at maximum sensitivity, using scale-expansion techniques to increase the signal.

Biological samples

Human serum, plasma, and whole blood were obtained from the Walter Reed Blood Bank. Urine samples were obtained from laboratory personnel.

The white albino rats that were used were the Walter Reed Sprague–Dowly strain. Three groups of rats were used for the experiments. The first two groups were kept on a synthetic diet for 6 months. The diet consisted of 30% Torula yeast, 5% stripped lard, 4% salt mix, 1% vitamin powder, and 60% sucrose. The first group received ordinary distilled water while the second received distilled water that contained 5 p.p.m. of chromium as chromium(III) chloride. The third group received a diet of Purina Rat Chow and distilled water.

The rats were anesthetized with Nembutal sodium and blood was removed from the heart. After the blood was removed, the liver and other tissues were extracted and stored in a freezer for subsequent analysis.

Rabbits of the Walter Reed strain were handled in a similar manner. The principles of animal care as promulgated by the National Society for Medical Research were observed.

PROCEDURES

Preparation of sample

Dry ashing. Samples consisting of blood, urine, and diet, were ashed in Corrs #1 porcelain crucible. The samples were placed in a furnace and kept at 550° for 4–5 h until all that remained was a white powder. ^{51}Cr was added to the samples to check recoveries during the ashing.

Wet decomposition. The biological samples were mineralized with a mixture of nitric, sulfuric, and perchloric acids in the ratio of 3:1:1. The material (1–10 g) was added to a 30-ml Kjeldahl flask, followed by 10 ml of the acid mixture. The mixture was heated gently at first (avoid charring) to allow the protein to go into solution. The heat was then increased until dense fumes of sulfuric trioxide appeared, indicating that the digestion was complete. The flask was cooled and 5 ml of distilled water and 1 ml of 0.01 M permanganate were added. The solution was then boiled gently for 5 min to allow the oxidation of Cr(III) to Cr(VI) to take place. If the pink color disappeared, more permanganate was added until the color finally persisted. The solution was cooled to 5° in an ice bath and transferred to a 30-ml separatory funnel. The flask was washed twice with 1-ml portions of distilled water, after which the washings were added to the funnel. Two ml of concentrated hydrochloric acid were added, followed by 5 ml of methyl isobutyl ketone. (The acid and the ketone were also kept at 5° before addition.) The mixture was shaken for 30 sec and the ketone layer separated. The ketone solution was then aspirated into the flame.

Reagent blanks were run in the same manner. The difference in the absorption between the sample and the blank was taken as the per cent absorption. The concentration of chromium was determined from a calibration curve (see below) or by the method of standard additions.

Preparation of standards

Known amounts of chromium, ranging from 50 to 500 ng were run through the above procedure and a calibration curve prepared. A calibration curve was also prepared by adding the same amounts of chromium to pooled human serum and running through the above procedure. Both curves were parallel and the latter curve was displaced from the initial curve by the amount of chromium that was present in the pooled serum.

Instrumental

The optimum conditions were the same as previously described by FELDMAN AND PURDY[13].

RESULTS AND DISCUSSION

Wet and dry mineralization procedures were studied in order to ascertain the most efficient method to use. Although some losses of chromium during dry ashing have been reported in the literature, the thorough study of dry ashing done by GORSUCH[14] indicated almost complete recovery of chromium. Blood, urine, and diet samples, to which ^{51}Cr had been added, were dry ashed (after evaporation in a steam bath), and the recovery of chromium determined. In all cases, as tabulated in Table I, practically complete recovery was obtained.

The recoveries of chromium during wet combustion were obtained in a similar manner. Table II summarizes the results.

TABLE I

RECOVERIES OF ^{51}Cr AFTER DRY ASHING

Sample	*Counts/min (·10³)*			*% Recovery*
	Before ashing	*After evaporation*	*After ashing*	
Blank	12.1	12.2	12.2	101
Whole blood	12.5	12.3	12.6	101
Whole blood	12.8	12.9	12.5	97.7
Urine	11.6	11.3	11.4	98.3
Urine	11.2	11.3	11.0	98.2
Diet	12.6	12.8	12.8	102
Diet	12.2	12.2	12.1	99.2
Control[a]	11.8	11.9	11.8	100

[a] Did not go through ashing procedure.

TABLE II

RECOVERIES OF ^{51}Cr AFTER WET DECOMPOSITION

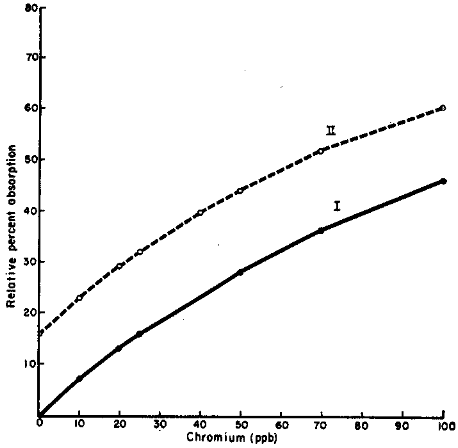
Sample	*Counts/min (·10³)*		*% Recovery*
	Before ashing	*After ashing*	
Blank	15.2	15.5	102
Plasma	12.3	12.2	99.2
Plasma	11.6	11.2	96.6
Urine	12.9	12.6	97.7
Urine	10.1	10.2	101
Control[a]	13.1	13.0	99.2

[a] Did not go through mineralization procedure.

The drawbacks of the dry ashing procedure were the time involved (4–5 h) and the difficulty in removing the ash. Since the wet method was rapid and left the chromium in solution, it was used almost exclusively. The ketone extract of the reagent blank gave a 4–5% absorption above the pure ketone. It was thought that this was due to trace amounts of chromium present in the acids used.

The amount of chromium introduced into the final ketone extract by the acid mixture was investigated. The reagent-grade acids and the "pure" acids that were double distilled and stored in Vycor, were run through the decomposition and extraction procedure and the ketone extracts of both gave the same absorption. It seemed, therefore, that the small difference in absorption between the ketone and ketone extract was probably not caused by chromium but by small traces of water dissolved in the ketone.

The calibration curve prepared by adding known amounts of chromium(III) to distilled water and running through the entire mineralization and extracting procedure, is illustrated in Fig. 1. Also illustrated is the curve prepared from pooled human serum. The difference in the group corresponds to 24 ng of chromium per milliliter, which is due to the serum chromium concentration.



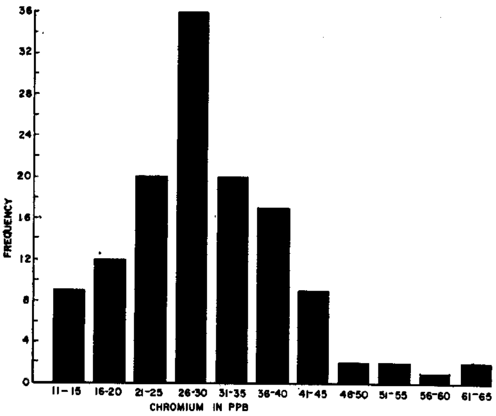


Fig. 1. Calibration curves of chromium(III): (1) in water, (II) in pooled human serum.

Fig. 2. Frequency distribution of chromium in human plasma.

The extent of interference from other cations and anions was studied. It was expected that very little, if any, interference would be noted, since a selective extraction procedure was used and since atomic absorption is a specific method. The results (Table III) indicate that this is so.

TABLE III

THE EFFECT OF ADDED IONS ON THE RECOVERY OF CHROMIUM

Ion added (1.0 mg)	*% Chromium recovered*	*Ion added (1.0 mg)*	*% Chromium recovered*
—	97	Mg	99
—	96	Li	98
K	94	Mn	94
Pb	96	V	98
Co	97	Al	97
Ni	96	Zn	93
Fe	94	Cu	95
Ca	97	Cd	96

The chromium concentration of human serum, plasma, and cells, was determined. Table IV compares the values obtained with those reported by other workers. Figure 2 illustrates the frequency distribution of chromium in these samples.

Chromium values previously reported in the literature generally agreed with those of the present study. In some cases, the values were considerably higher. These extremely high values may possibly be due to an unusually high chromium concen-

TABLE IV

CHROMIUM CONTENT OF HUMAN BLOOD

Sample	*Chromium (p.p.b.)*	*Range (p.p.b.)*	*Investigation*
Plasma	29	11–64	Present study[a]
Cells	26	21–36	Present study[b]
Plasma	29	—	MILLER AND YOE[15]
Cells	23	—	MILLER AND YOE[15]
Plasma	24	16–39	PAIXAO AND YOE[16]
Cells	22	11–41	PAIXAO AND YOE[16]
Serum	47	—	HERRING *et al.*[17]
Plasma	22	7–52	KOCH *et al.*[18]
Serum	520	—	SCHROEDER *et al.*[2]
Whole blood	12	—	URONE AND ANDERS[19]

[a] = 132 samples.
[b] = 23 samples.

TABLE V

PRECISION OF CHROMIUM DETERMINATION IN POOLED HUMAN SERUM

No. of determinations	*Cr p.p.b. mean*	*Range*	*S.D.*
14	36	32–40	2.4
10	25	20–31	3.7
10	14	9–20	4.3

TABLE VI

CHROMIUM CONTENT IN TISSUES OF ALBINO RATS[a]

Tissue	*No. of animals*	*p.p.b. Cr*
Serum	13	29
Liver	12	130
Spleen	12	360
Heart	12	90
Lung	12	< 10
Brain	12	15

[a] Rats were maintained on a normal diet (Rat Chow).

tration in the drinking water or to some contamination which occurred during analysis.

The precision of the chromium determination was found by running a number of replicate samples (Table V). Pooled human serum was used rather than whole blood since the mineralization of the former proceeded more rapidly. It is evident that at higher chromium concentrations, the method is more precise. This is mainly due to the low signal-to-noise ratio when measuring smaller amounts.

The amount of chromium(VI) in human serum was also determined. This was done by mineralization, eliminating the oxidation step. Some previous work on the metabolism of chromium in the body has shown that the hexavalent form is more rapidly excreted than chromium(III)[20]. Since chromium(VI) is an oxidizing agent, it can react with reducing agents present in the body. Thus, it is to be expected that the concentration of chromium(VI) would be very small. Serum samples were analyzed and the amount of chromium(VI) was found to be undetectable.

The chromium levels of various tissue in normal albino rats were determined. The rats were kept on a normal diet (Rat Chow) and were sacrificed when they were about six months old. Some serum, liver, spleen, heart, lung, and brain were removed and analyzed for chromium content (Table VI). The serum levels approximate those of humans, but the liver and spleen values appear to be unusually high. However, some recent work on the distribution of ingested ^{51}Cr by HOPKINS[21] shows that the spleen concentrates chromium with time. The chromium in the liver also seems to increase (after an initial decline) with time. A possible mechanism for this was suggested by KRAINTZ *et al.*[22], who proposed that the spleen captures the chromium by colloidal trapping.

Two groups of albino rats were maintained on different chromium diets for a period of about six months. The diets, which were composed of a synthetic preparation (see EXPERIMENTAL), were the same in both groups. However, one group drank distilled water containing 5 p.p.m. chromium as chromium chloride. The rats were then sacrificed and the tissue chromium levels determined (Table VII). The rats that were on a chromium-deficient diet had much lower chromium levels than normal ones. However, the ratios of chromium in the different tissues appear to remain approximately the same. The rats on the high chromium diet showed extremely elevated chromium levels although the levels of all tissues did not increase at the same rate. Table VIII illustrates the percent increase or decrease of the chromium levels compared to the normal group, and the ratios of the chromium levels of the tissues to serum among the 3 groups.

TABLE VII

CHROMIUM LEVELS OF ALBINO RATS

Tissue	*Group A*[a]		*Group B*[b]	
	No. of animals	*p.p.b. Cr*	*No. of animals*	*p.p.b. Cr*
Serum	6	18	6	111
Liver	6	60	6	214
Heart	6	42	6	190
Spleen	6	165	6	[illegible]3

[a] Chromium deficient diet.
[b] High chromium diet.

TABLE VIII

RATIOS OF TISSUE CHROMIUM LEVELS IN ALBINO RATS

Tissue	*% Increase from normal*	*% Decrease from normal*	*Ratios of tissue chromium levels to serum*		
			Group		
			Normal	*High*	*Low*
Serum	65.5	24.1	1.0	1.0	1.0
Liver	33.1	6.15	4.48	3.60	5.50
Heart	36.7	30.0	3.10	2.56	2.86
Spleen	26.7	13.3	12.4	9.50	14.2

Similar studies were made with a group of rabbits. The diets (Chow) of all the rabbits were the same, but the water of one group contained 50 p.p.m. of chromium. After 45 days, the rabbits were sacrificed and the tissue chromium levels determined. Table IX summarizes the results which are similar to those obtained in the rats. Thus, it appears that a sensitive method has been developed for the determination of chromium in biological materials. The method is rapid (< 1.5 h) and can be used to detect chromium at physiological levels.

TABLE IX

CHROMIUM LEVELS OF RABBIT TISSUES

Tissue	*Group A*[a]		*Group B*[b]	
	No. of animals	*p.p.b. Cr*	*No. of animals*	*p.p.b. Cr*
Serum	2	22	2	48
Liver	2	122	2	173
Heart	2	63	2	123
Spleen	2	312	2	456

[a] Normal laboratory diet.
[b] High chromium diet.

SUMMARY

Biological samples were mineralized with a mixture of nitric, sulfuric, and perchloric acids. The chromium was oxidized to chromium(VI) followed by extraction into methyl isobutyl ketone in the cold. The ketone extract was aspirated into a fuel-rich hydrogen–air flame, and the absorption recorded using the 357.9 nm line of chromium. The limit of detection for chromium was found to be 10 p.p.b. Tissue chromium levels of normal albino rats were determined. Increased chromium values were observed for animals maintained on a high chromium diet compared to those fed a deficient diet.

RÉSUMÉ

Les échantillons biologiques sont minéralisés à l'aide d'un mélange d'acides nitrique, sulfurique et perchlorique. Le chrome est ensuite oxydé en chrome(VI) et extrait au moyen de méthylisobutylcétone à froid. Le dosage s'effectue par spectroscopie par absorption atomique. L'extrait cétonique est aspiré dans une flamme hydrogène–air; l'absorption est enregistrée à la ligne 357.9 nm du chrome. La limite de détection est de 10 p.p.b.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Chrom in biologischen Materialien beschrieben. Die Probe wird mit einem Gemisch aus Salpeter-, Schwefel- und Perchlorsäure verascht und das Chrom nach Oxydation zur sechswertigen Stufe mit Methyl-Isobutylketon extrahiert. Im Extrakt wird das Chrom mittels seiner Linie bei 357.9 nm flammenabsorptionsanalytisch bestimmt. Die Nachweisgrenze beträgt 10 p.p.b. Cr. Der Chromgehalt von Knochen normaler Albinoratten wurde in Abhängigkeit vom Chromgehalt der Nahrung verfolgt.

REFERENCES

1 K. Schwarz and W. Mertz, *Arch. Biochem. Biophys.*, 85 (1959) 292.
2 H. A. Schroeder, J. J. Balassa and I. H. Tipton, *J. Chronic Diseases*, 15 (1961) 941.
3 H. A. Schroeder, W. H. Vinton and J. J. Balassa, *J. Nutr.*, 80 (1963) 39.
4 W. Mertz, E. E. Roginski and H. A. Schroeder, *J. Nutr.*, 86 (1965) 107.
5 W. Mertz, E. E. Roginski and R. C. Reba, *Am. J. Clin. Pathol.*, 209 (1965) 489.
6 W. H. Glinsmann and W. Mertz, *Metab.*, 15 (1966) 510.
7 L. L. Hopkins, Jr. and A. S. Majaj, *Federation Proc.*, 25 (1966) 303.
8 R. A. Levine, R. J. Doisy and D. H. P. Streeben, *Proc. 26th Annual Meeting of The American Diabetes Assoc.*, 36 (1966).
9 W. H. Glinsmann, F. J. Feldman and W. Mertz, *Science*, 152 (1966) 1243.
10 B. F. Saltzman, *Anal. Chem.*, 24 (1952) 1016.
11 C. H. Williams, D. J. David and O. Iismaa, *J. Agr. Sci.*, 59 (1962) 381.
12 B. Delaughter, *Atomic Absorption Newsletter*, 4 (1965) 273.
13 F. J. Feldman and W. C. Purdy, *Anal. Chim. Acta*, 33 (1965) 273.
14 T. T. Gorsuch, *Analyst*, 84 (1959) 135.
15 D. O. Miller and J. H. Yoe, *Clin. Chim. Acta*, 4 (1958) 378.
16 L. M. Paixao and J. H. Yoe, *Clin. Chim. Acta*, 4 (1959) 507.
17 W. B. Herring, B. S. Leavell, L. M. Paixao and J. H. Yoe, *Am. J. Clin. Nutr.*, 8 (1960) 846.
18 H. J. Koch, Jr., E. R. Smith and J. Conner, *Cancer*, 9 (1956) 499.
19 P. F. Urone and H. K. Anders, *Anal. Chem.*, 22 (1950) 1317.
20 A. M. Baetjer, C. Damron and V. Budacz, *Arch. Industr. Hyg.*, 20 (1959) 124.
21 L. L. Hopkins, *Am. J. Physiol.*, 209 (1965) 731.
22 L. Kraintz and R. V. Talmadge, *Proc. Soc. Exptl. Biol. Med.*, 81 (1952) 490.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF MANGANESE, IRON, COBALT AND NICKEL IN AIR AND WATER BY ATOMIC ABSORPTION SPECTROSCOPY

SHAM L. SACHDEV, J. W. ROBINSON AND PHILIP W. WEST
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

(Received December 12th, 1966)

Atomic absorption spectroscopy has been used for the determination of manganese, iron, cobalt and nickel in a variety of materials such as steel[1-3], plants[4], geological materials[5] and biological fluids[6], etc. However, the methods developed up to the present are not sensitive enough for the direct determination of trace quantities of these metals present in air and water. A detailed study of flames of various compositions and other factors affecting the atomic absorption methods was undertaken and as a result of the study, sensitive and selective procedures for the direct analysis of very dilute solutions were developed. The sensitivity ranges from 0.01 mg/l for manganese to 0.05 mg/l for iron (for 1% absorption).

EXPERIMENTAL

Equipment

Atomic absorption spectrophotometer (Perkin-Elmer Model 303); Perkin-Elmer's premix type air–acetylene burner; large bore oxy–hydrogen and oxy–acetylene total consumption burners (Beckman Instruments, Inc.) fitted on a three-

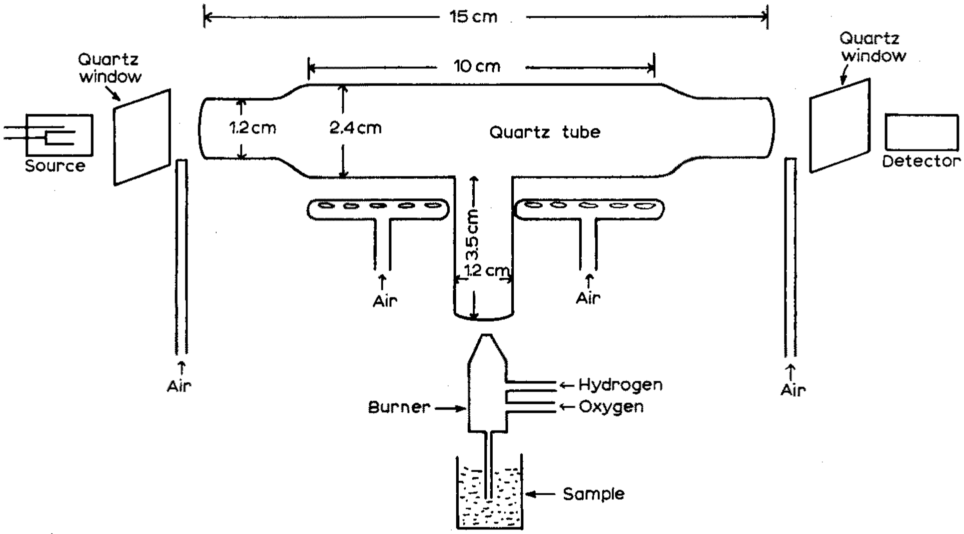


Fig. 1. Quartz T-piece adapter (schematic).

dimensional positioning device; hollow-cathode lamps for manganese, iron, cobalt and nickel; a quartz T-piece adapter (described in Fig. 1).

Relative sensitivities of absorption lines

Because of certain advantages of the oxy–hydrogen flame over other flames, which will be discussed later, relative sensitivities for several absorption lines were determined in such a flame. The results are shown in Table I. The following lines were found to be most sensitive for absorption studies: Mn, 2795 Å; Fe, 2483 Å; Co, 2407 Å and Ni, 2320 Å. Their respective sensitivities were then examined in 4 different kinds of flames; and the results, as shown in Table II, indicate that an air–acetylene flame from a premix type burner provides the best conditions for manganese and iron whereas an oxy–acetylene flame from a total consumption burner provides the best sensitivity for cobalt and nickel. The flame-path, in the case of

TABLE I

RELATIVE SENSITIVITIES FOR SOME INTENSE ABSORPTION LINES

(Flame conditions: *oxy–hydrogen flow rates* $O_2 = 5$ l/min, $H_2 = 20$ l/min)

Manganese		*Iron*		*Cobalt*		*Nickel*	
Wave-length (Å)	*mg/l for 1% absorption*	*Wave-length (Å)*	*mg/l for 1% absorption*	*Wave-length (Å)*	*mg/l for 1% absorption*	*Wave-length (Å)*	*mg/l for 1% absorption*
2795	0.25	2483	0.8	2407	0.5	2302	0.6
2799	0.30	2488	1.2	2412	0.8	2320	0.4
2801	0.50	2523	1.25	2425	0.6	2345	1.4
4031	3.0	2524	4.4	2521	1.2	3002	1.6
		2719	3.5	3405	10.0	3012	8.0
		2721	16.0	3412	9.0	3038	5.7
		2967	9.0	3455	10.0	3054	2.0
		3021	2.8	3463	14.0	3058	10.0
		3441	8.0	3474	9.0	3102	5.0
		3720	3.3	3527	10.0	3393	5.7
		3735	10.0			3415	1.2
		3737	6.1			3434	5.3
		3758	14.0			3437	4.5
		3816	25.0			3446	10.0
		3860	6.0			3525	1.6

TABLE II

SENSITIVITIES FOR THE MOST SENSITIVE ABSORPTION LINES IN 4 DIFFERENT TYPES OF FLAMES

(Spectral slit-width 2 Å)

Metal	*Wave-length (Å)*	*Lamp current (mA)*	*Total consumption burner*		*Premix type burner*	
			Oxy–hydrogen flame (mg/l for 1% absorption)	*Oxy–acetylene flame (mg/l for 1% absorption)*	*Air–acetylene flame (mg/l for 1% absorption)*	*N_2O–acetylene flame (mg/l for 1% absorption)*
Mn	2795	10	0.25	0.18	0.15	0.5
Fe	2483	17	0.6	0.35	0.3	0.6
Co	2407	12	0.6	0.25	0.4	0.7
Ni	2320	12	0.4	0.2	0.3	0.8

air–acetylene flame, is about 5 times longer than that of an oxy–hydrogen or oxy–acetylene flame from a total consumption burner. Thus, if sensitivities per unit length of flame-path be considered, both oxy–hydrogen and oxy–acetylene flames provide better sensitivities than the air–acetylene flame. ROBINSON[7] described the use of a flame adapter to extend the oxy–hydrogen flame and was able to increase the sensitivity for platinum by a factor of 10. Subsequently, such an adapter was used for the determination of lead, copper, zinc and cadmium[8,9]. The original flame adapter, however, could not be successfully used for the determination of nickel and some of the other transition metals; and it was necessary to introduce slight modifications in the dimensions of the T-piece adapter. The modified adapter is illustrated in Fig. 1. The adapter is held in the path of the light beam by means of a clamp. It was observed that by blowing air around the adapter, precision in measuring the absorption could be improved.

TABLE III

SENSITIVITIES IN OXY–HYDROGEN FLAME USING A T-PIECE ADAPTER

Metal	*Wave-length (Å)*	*Lamp current (mA)*	*Spectral slit-width (Å)*	*Oxygen flow rate (l/min)*	*Hydrogen flow rate (l/min)*	*Sensitivity by the use of T-piece adapter (mg/l for 1% absorption)*
Mn	2795	10	6.5	5	22	0.01
Fe	2483	16	2.0	5	22	0.05
Co	2407	10	2.0	5	24	0.03
Ni	2320	12	2.0	5	19	0.02

The use of the flame adapter

The T-piece flame adapter was used with oxy–hydrogen as well as oxy–acetylene flames. The use of a reducing oxy–acetylene flame caused the adapter to glow brilliantly which resulted in erratic absorption readings. The use of the flame adapter was, therefore, confined to investigations with the oxy–hydrogen flame. Ten to 15-fold increase in sensitivities was obtained by the use of the adapter.

TABLE IV

OPTIMUM FLAME CONDITIONS

Oxygen flow rate (l/min)	*Hydrogen flow rate (l/min)*	*Percentage absorption*			
		Mn^{2+} (5 mg/l)	*Fe^{3+} (10 mg/l)*	*Co^{2+} (10 mg/l)*	*Ni^{2+} (10 mg/l)*
5	10	8.5	4.0	5.2	4.8
5	12	13.2	5.2	6.5	13.0
5	14	16.5	8.7	9.2	17.0
5	16	20.4	10.4	10.7	18.2
5	18	22.0	13.0	12.0	18.5
5	20	22.6	14.8	13.7	18.5
5	22	22.0	15.0	14.4	18.5
5	24	—	—	15.2	—
5	26	—	—	15.2	—

Optimization of flames

Various ratios of oxygen to hydrogen were studied to find the best flame composition in all the 4 cases. Results are given in Table IV. The absorption for each of the 4 metals was noted in various parts of the flame. The tip of the burner when placed in the light beam was taken as zero and the absorption in various cases was studied by lowering the burner in increments of 0.5 cm. The results are listed in Table V.

Effect of lamp current

The effects of variations in lamp current on the absorption for the metals (Mn, Fe, Co and Ni) were studied at a constant spectral slit-width of 6.5 Å. As shown

TABLE V

FLAME PROFILE

Distance between light beam and tip of the burner (cm)	*Percentage absorption*			
	Mn^{2+} *(5 mg/l)*	*Fe*$^{3+}$ *(10 mg/l)*	*Co*$^{2+}$ *(10 mg/l)*	*Ni*$^{2+}$ *(10 mg/l)*
1.0	2.0	1.0	1.3	3.0
1.5	—	1.8	2.8	4.2
2.0	7.8	5.8	4.8	6.8
2.5	—	8.5	8.2	12.5
3.0	17.4	10.5	9.8	14.0
3.5	21.0	11.8	11.5	16.4
4.0	22.9	13.8	13.0	18.0
4.5	22.8	14.5	14.0	18.5
5.0	22.0	14.2	14.6	18.5
5.5	20.0	11.5	14.8	18.5
6.0	16.8	8.0	14.8	16.1
6.5	—	—	14.0	14.0
7.0	10.6	—	12.8	10.4
8.0	—	—	10.5	—

TABLE VI

EFFECT OF LAMP CURRENT

(Spectral slit-width = 6.5 Å)

Lamp current (mA)	*Percentage absorption*			
	Mn^{2+} *(5 mg/l)*	*Fe*$^{3+}$ *(10 mg/l)*	*Co*$^{2+}$ *(10 mg/l)*	*Ni*$^{2+}$ *(10 mg/l)*
4	20.4	12.0	—	—
6	20.4	11.8	—	12.7
8	20.2	11.8	15.3	11.9
10	20.2	11.8	15.0	11.0
12	20.0	9.5	14.6	10.5
14	20.0	8.2	14.0	10.1
16	20.0	7.6	13.8	9.5
18	20.0	7.6	13.8	9.5
20	19.6	7.6	13.8	9.5

in Table VI, an increase in lamp current lowered the absorption substantially in the case of iron, the absorption for nickel and cobalt to some extent, whereas that of manganese remained essentially the same.

Effect of slit-width

Slit-width considerably affected the absorption for each of the 4 metals as shown in Table VII. The absorption was observed to be highest at a spectral slit-width of 0.65 Å. However, at such a narrow slit-width the total radiation energy reaching the photomultiplier tube was very low and precise measurements of low signals could not be made. A spectral slit-width of 2 Å was found to be most suitable from the point of view of sensitivity as well as precision.

TABLE VII

EFFECT OF SLIT-WIDTH

(Lamp current = 20 mA)

Spectral slit-width (Å)	*Percentage absorption*			
	Mn^{2+} (5 mg/l)	*Fe^{3+} (10 mg/l)*	*Co^{2+} (10 mg/l)*	*Ni^{2+} (10 mg/l)*
0.65	22.2	16.2	15.8	19.8
2.0	21.7	15.0	15.0	16.5
6.5	19.6	8.0	14.0	9.5
20	16.7	6.5	10.6	7.6

TABLE VIII

INTERFERENCE STUDIES

Group I.	Li^+, Na^+, K^+, Rb^+, Cs^+, Cu^{2+}, Ag^+
Group II.	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}
Group III.	$B_4O_7^{2-}$, Al^{3+}, Ce^{4+}
Group IV.	HCO_3^-, SiO_3^{2-}, Ti^{4+}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Pb^{2+}
Group V.	NH_4^+, NO_3^-, HPO_4^{2-}, VO_3^-, $HAsO_4^{2-}$, Sb^{3+}, Be^{3+}
Group VI.	SO_3^{2-}, SO_4^{2-}, Cr^{3+}, SeO_3^{2-}, MoO_4^{2-}, WO_4^{2-}, UO_4^{2-}
Group VII.	F^-, Cl^-, Br^-, I^-, Mn^{2+}
Group VIII.	Fe^{3+}, Co^{2+}, Ni^{2+}

Miscellaneous substances: citrate, tartrate, oxalate, detergent (Dreft), EDTA, hydrochloric acid, nitric acid, sulfuric acid, perchloric acid and acetic acid.

Interference studies

The interference effects of the ions and compounds listed in Table VIII were examined for both oxy–hydrogen and air–acetylene flames. Respective standard solutions contained 5 mg/l each of manganese, iron, cobalt and nickel. The effects of the presence of fifty-fold excess of various interfering ions were studied. The cations were added as nitrates or chlorides or in some cases as sulfates. The effect of acids was examined by adding 5 ml of the appropriate concentrated acid followed by dilution to 100 ml. None of the ions or compounds listed interfered when the air–acetylene flame was used and only slight interference was observed with a few ions when the oxy–hydrogen flame was employed. Titanium, vanadium and zirconium slightly suppressed the absorption for manganese. These interferences can be eliminated by complexing the ions with fluoride. Silicate and titanium(IV) suppressed the absorption for iron by about 50% and 20% respectively. Interference due to silicate can be removed by the addition of EDTA. The presence of about 5% sulfuric acid suppressed the absorption by about 5% in all the 4 cases. This was due probably to the higher viscosity of the sulfuric acid solution compared to the aqueous standard solution with the consequent decrease in the aspiration rate of the acid solution. Such an interference will only arise if the sample is dissolved in strong sulfuric acid solution and can be easily overcome by preparing comparable standard solutions in sulfuric acid.

Most of the cations when present in excess of 2000 mg/l caused some interference. The interference effect seems similar to that observed and discussed by CHAKRABARTI *et al.*[9] in the case of lead.

RECOMMENDED PROCEDURES

Sampling

All samples must be in a solution form which can be aspirated into a flame.

Air sampling

Any standard method for sampling particulates can be used. However, the sample must be brought into a solution. A procedure similar to the wet ashing method for lead, copper and zinc[10] can be employed for dissolving the sample in 5 or 10 ml of 1 *M* hydrochloric acid or nitric acid. The particulates are collected on an ashless filter paper (Schleicher and Schüll fast flow filter paper is recommended). The filter paper containing the sample is carefully ashed in a porcelain crucible at 600° and the residue is then dissolved in hydrochloric acid. Because iron is generally present in the filter papers, a blank must be carried out and the appropriate correction made in the determination of iron. The procedure for the determination of the metals is described below.

Water samples

Manganese, iron, cobalt and nickel can be directly determined in the water samples containing manganese in the range of 0.02 to 1.2 mg/l and iron, cobalt or nickel in the range of 0.2 to 4 mg/l.

Reagents

Prepare stock solutions of manganese, iron, cobalt or nickel containing 1 g/l of the metal by dissolving 1 g of reagent-grade metal in minimum volumes of nitric acid and diluting to a liter with distilled water.

Equipment

The equipment required is the same as that described under EXPERIMENTAL. The spectrophotometer is fitted with an oxy-hydrogen total consumption burner and a quartz T-piece adapter as described in Fig. 1.

Analytical procedure

Switch on the instrument and allow it to warm up for 10 min. Adjust the instrument setting to the optimum wavelength for the element to be determined as given in Table III. Lower the burner about 6 inches below the T-piece adapter, light the burner, adjust the proper flow rates for oxygen and hydrogen by means of a flow meter, turn on the air-jets, raise the burner gradually until the flame extends past the orifices of the side arms of the T-piece adapter and is deflected upwards by the airjets. Aspirate the metal solution of suitable strength and adjust the position of the burner until maximum absorption is obtained. Aspirate distilled water and adjust the instrument for zero absorption.

Calibration curves

Dilute appropriate volumes of stock solution to obtain 0.02 mg/l to 2 mg/l of metal in 100-ml volumetric flasks. Aspirate the solutions, determine the percentage absorption, convert percentage absorption into absorbance and plot absorbance against concentration for each metal (Fig. 2). Because flame position and the position of the adapter are very critical, new calibration curves should be prepared for each set of experiments.

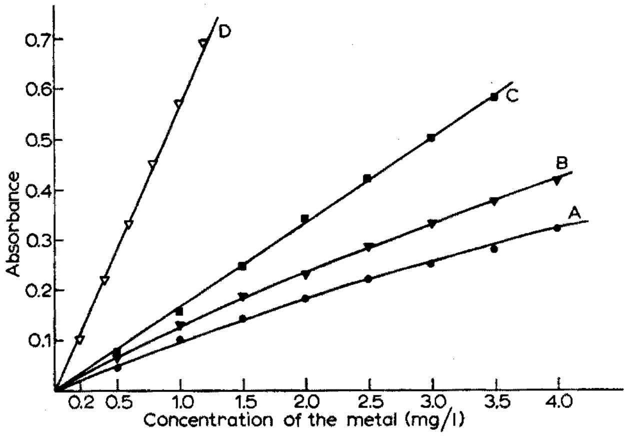


Fig. 2. Calibration curves (with T-piece adapter). (●) Fe; (▼) Co; (■) Ni; (▽) Mn.

Determination of manganese, iron, cobalt and nickel

If the sample is solid, it must be brought into solution form by a suitable procedure depending upon the sample itself. If sulfuric acid is used for dissolving the sample, an equal concentration of sulfuric acid should also be present in the standard solution. Very little interference was observed and if any of the interfering ions as listed under *Interference studies* is suspected or known to be present in the sample, an appropriate procedure to eliminate the interference should be used (described under the *Interference studies*). Solutions of the sample are aspirated into the flame and the percentage absorption is noted. After correction for the blank the results are converted into absorbance and the concentration of the metal is determined from its calibration curve (Fig. 2).

This investigation was supported by the U.S. Public Health Service Research Grant No. AP 00128, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control.

SUMMARY

Flames of 4 different kinds and of various compositions were studied for their suitability for atomic absorption spectroscopy for the determination of manganese, iron, cobalt and nickel. The effects of various other factors such as lamp current, slit-width and position of the burner were also investigated. Interference effects of a large number of ions and compounds were studied. Very few ions were found to interfere and means of eliminating the interferences noted are described. As a result of the investigation, sensitive and selective procedures for the determination of manganese, iron, cobalt and nickel are reported. Sensitivities are Mn, 0.01 mg/l; Fe, 0.05 mg/l; Co, 0.03 mg/l and Ni, 0.02 mg/l for 1% absorption.

RÉSUMÉ

On a examiné des flammes de quatre espèces, et de diverses compositions pour le dosage du manganèse, du fer, du cobalt et du nickel par spectroscopie par absorption atomique. On examine également l'influence d'autres facteurs tels que courant de la lampe, largeur de la fente et position du brûleur. Très peu d'ions peuvent gêner; on décrit les moyens d'éliminer ces interférences. Sensibilité: Mn 0.01 mg/l, Fe 0.05 mg/l, Co 0.03 mg/l et Ni 0.02 mg/l pour une absorption de 1%.

ZUSAMMENFASSUNG

Flammen unterschiedlicher Art und verschiedener Zusammensetzung wurden untersucht und auf ihre Eignung für die Flammenabsorptionsspektroskopie zur Bestimmung von Mangan, Eisen, Kobalt und Nickel geprüft. Sowohl die Einflüsse zahlreicher Faktoren, wie z.B. der Lampenstrom, die Spaltbreite und die Position des Brenners, als auch Störungen einer grösseren Anzahl von Ionen und Verbindungen wurden ermittelt. Methoden zur Beseitigung der Störungen einiger Ionen werden beschrieben. Die Empfindlichkeiten betragen bei 1% Absorption 0.01 mg Mn/l, 0.05 mg Fe/l, 0.03 mg Co/l und 0.02 mg Ni/l.

REFERENCES

1 G. L. McPherson, J. W. Price and P. H. Scaife, *Nature*, 199 (1963) 371.
2 C. B. Belcher and K. Kinson, *Anal. Chim. Acta*, 30 (1964) 483.
3 K. Kinson and C. B. Belcher, *Anal. Chim. Acta*, 30 (1964) 64.
4 D. J. David, *Perkin-Elmer Atomic Absorption Newsletter No. 9*, December 1962.
5 G. K. Billing and J. A. S. Adams, *Perkin-Elmer Atomic Absorption Newsletter No. 23*, August 1964.
6 J. B. Willis, in D. Glick, *Methods of Biochemical Analysis*, Vol. XI, Interscience, New York, 1963.
7 J. W. Robinson, *Anal. Chim. Acta*, 27 (1962) 465.
8 T. V. Ramakrishna, J. W. Robinson and P. W. West, *Anal. Chim. Acta*, 37 (1967) 20.
9 C. L. Chakrabarti, J. W. Robinson and P. W. West, *Anal. Chim. Acta*, 34 (1966) 269.
10 M. B. Jacobs, *Chemical Analysis of Air Pollutants*, Interscience, New York, 1960, p. 98.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF MIXTURES OF *n*-HEXYL SALICYLATE AND SALICYLIC ACID IN PROPYLENE GLYCOL

M. D. BITRON AND Y. SUZIN
Department of Physical Chemistry, Israel Institute for Biological Research, Ness-Ziona (Israel)

(Received November 4th, 1966)

Many studies in industrial hygiene and air pollution involve the sampling of vapors and aerosols with the aid of solvents. It is often advantageous to employ the vapors or aerosols of a "model" compound—generally a stable, non-irritating liquid of rather low volatility, which can be determined easily and accurately in the collecting solvent. For a model absorbing sufficiently in the ultraviolet, UV-spectrophotometry is the most convenient method of analysis, provided that the solvent is transparent at the selected wavelength, does not interact with the solute, and is suitable for collecting samples from the gas phase. If the model is employed under experimental conditions which may cause some decomposition, it becomes necessary to extend the analytical method so that, in the sample, both the model and its decomposition products can be estimated quantitatively.

n-Hexyl salicylate (HS) was chosen as model in the present studies. Since the solvents usually employed in UV-spectrophotometry were found to be too volatile for the sampling of HS from the gas phase, the feasibility of using propylene glycol (PG) was examined. It proved to comply with the requirements and was selected as solvent after its viscosity was found to constitute only a minor inconvenience.

Under the conditions employed in these studies, water was collected by the hygroscopic PG[1-3] and the possibility existed that part of the HS might become hydrolyzed in the gas phase. Therefore, the analytical method had to include the determination of both HS and salicylic acid (SA) at various water contents of the PG solution. Adoption of direct absorbance measurements in the ultraviolet at two wavelengths, as reported for acetylsalicylic acid containing small amounts of SA[4], was precluded because of the similarity of the UV-spectra of SA and its alkyl esters[5,6]. However, a marked bathochromic shift of the secondary band of HS and a slight hypsochromic shift of that of SA may be obtained by suitable addition of potassium hydroxide; this permits, in principle, the separate determination of the two compounds by two absorbance measurements. This phenomenon is due to the ionization of only the phenol group of the ester and the carboxyl group of the acid, with the hydroxyl group of the latter remaining unaffected at the appropriate alkali concentrations[5,7]. For reasons of reproducibility, the final method consisted of measuring the absorbance at 305 nm and 335 nm, the measurements at the greater wavelength being carried out after addition of aqueous potassium hydroxide to the solution. Since *n*-hexanol, the other product of the hydrolysis of HS, is practically transparent at both wavelengths, its presence does not affect the measurements.

The method permitted the determination of the two compounds at concentrations of 0–35 μg per ml with an overall error of a few tenths of a μg per ml.

EXPERIMENTAL

Materials

HS was synthesized from analytical-grade SA and *n*-hexanol (S. COHEN AND Y. ASHANI) and was purified by one additional vacuum distillation (about 0.01 mm Hg at 40°). Further distillations had no effect upon its UV-absorption which also remained unchanged when the compound was kept at room temperature and exposed to light for more than 6 months.

Pure PG was obtained from technical PG by vacuum distillation (about 1 mm Hg at 45°); it was stored at room temperature in 20-l glass bottles. For convenient handling under conditions preventing deterioration, the bottles were equipped with a ground-joint syphoning device, and dry nitrogen was introduced up to an absolute pressure of 1.1 atm. Before use, in order to ensure uniform quality, the following tests were carried out routinely on each 20-l batch.

(*1*) Acidify after 20-fold dilution with distilled water, by addition of 2 ml of 0.1 *N* hydrochloric acid to 100 ml of solution and titrate with 0.01 *N* potassium hydroxide using neutral red as indicator. This procedure permitted the presence of CO_2 to be disregarded.

(*2*) Determine the water content by the Karl Fischer technique[8,9].

(*3*) Measure the absorbance, both in the presence and absence of aqueous potassium hydroxide, at 335 nm and 305 nm, respectively, of: (a) PG against distilled water as blank, and (b) solutions of known concentrations of HS and SA in the PG tested against the corresponding blanks.

On the basis of these tests the following average quality data and maximum deviations were established:

(*1*) The acidity was less than $2 \cdot 10^{-7}$ mol KOH for each ml of PG.

(*2*) The water content was below 0.1%.

(*3*) The absorbance of PG and of the 4 different solutions, each at the wavelengths specified, did not deviate from the corresponding calibration curves by more than the experimental errors involved in the calibrations. The PG was practically transparent with deviations not exceeding an absorbance of ±0.010.

Measurement of UV spectra

The absorption spectra of solutions of HS and SA in PG were determined with the aid of the Zeiss Spectrophotometer Model PMQ II in the range 250–350 nm, both with and without potassium hydroxide, at various concentrations of water*. Corresponding solutions which contained all the components except HS and SA, served as blanks. Concentrations of 40 μg HS/ml and 25 μg SA/ml in PG gave a peak absorbance of about 0.900 in the UV range examined. The solutions were obtained by 5-fold dilution of stock solutions prepared by weighing. All pipettes, measuring flasks, and burettes were recalibrated so that the overall maximum deviation from the nominal concentration of each final solution was below 3% for HS and SA, below 3.5% for PG and water, and below 4.5% for potassium hydroxide (these values also include

---

* Unless specified otherwise, all water concentrations are given in volume percent at 22°±2°.

the deviations due to the rise in temperature when PG is diluted with water[10] or aqueous alkali). The amount of aqueous potassium hydroxide added to the PG solutions—1 ml of 0.16 *N* KOH to 9 ml of PG solution—served to neutralize dissolved carbon dioxide as well as the negligible acidity of the PG and to produce a fixed excess concentration which sufficed to cause the reproducible shift of the peak absorption by HS. The concentration of hydroxide was sufficiently low to ensure negligible ionization of the hydroxyl group of SA[7] as well as the absence of harmful effects upon the dissolved ester[5]; deviations even up to 10% from its nominal value had no significant influence upon the results. The absorptions of HS and SA became constant only several minutes after addition of the potassium hydroxide and, therefore, in the alkaline solutions, the spectrophotometric measurements were carried out 15–30 min after making alkaline. On the other hand, PG solutions to which only water had been added gave constant absorptions almost immediately after preparation.

Determination of calibration curves

The absorbances of solutions of both HS and SA in PG were determined as a function of the concentration for various water contents, in the presence of potassium hydroxide at 335 nm and in its absence at 305 nm. The series of concentrations used for calibration were obtained by one-step dilutions, 2–25-fold, of stock solutions prepared by weighing. At both wavelengths, the HS concentrations required for sufficiently accurate measurements of absorbance were in the range of about 5–45 μg/ml; those of SA about 5–35 μg/ml at 305 nm and 100–1200 μg/ml at 335 nm.

Unless specified otherwise, each calibration curve was drawn from at least 30 points; the corresponding concentrations were obtained by dilution of at least 5 different stock solutions.

Estimation of SA and HS in mixtures

The concentrations of SA and HS in a sample, C_x and C_y respectively, were determined in aliquots by:

(*a*) estimating the water content;

(*b*) measuring absorbance in 1-cm silica cells at 305 nm using appropriately humidified PG as blank; value obtained—A_1.

(*c*) adding 0.16 *N* potassium hydroxide, in the ratio of 1 ml per 9-ml aliquot and measuring absorbance in 1-cm silica cells at 335 nm employing the corresponding blank; value obtained—A_2.

The following 2 equations are then assumed to be valid (Beer's law for both compounds without interaction):

$$a_1^x C_x + a_1^y C_y = A_1 \tag{1}$$

$$a_2^x C_x + a_2^y C_y = A_2/0.9 \tag{2}$$

where a_1^x and a_1^y are the absorptivities (absorbance/light path in cm·concentration in mg/ml) at 305 nm of SA and HS respectively, for the water content determined in the first aliquot; a_2^x and a_2^y are the corresponding values at 335 nm, for a water content 10% higher than that determined in the first aliquot.

From eqns. (1) and (2), one obtains the final expressions for the individual concentrations in the mixture:

$$C_x = \frac{A_1 - \beta A_2/0.9}{a_1^x(1 - \beta \times \gamma)} \tag{3}$$

$$C_y = \frac{A_2/0.9 - \gamma A_1}{a_2^y(1 - \beta \times \gamma)} \tag{4}$$

in which

$$\beta = \frac{a_1^y}{a_2^y}; \quad \gamma = \frac{a_2^x}{a_1^x} \tag{5}$$

For less accurate work, eqns. (3) and (4) may be simplified by taking $a_2^x = \gamma = 0$; moreover, one may assume the absorbances to be independent of water content. When these approximations are adopted, the procedure is rendered simpler, and a considerable part of the calibration curves can be dispensed with.

In order to compare the overall errors involved in employing the present method with and without the suggested approximations, C_x and C_y were estimated spectrophotometrically in a series of known mixtures at 3 different water contents, *viz.* 5%, 15%, and 25%. The latter water concentrations, being intermediate between those at which the absorptivities had been determined experimentally in this study (see Table I), were intentionally chosen so as to ascertain that errors of interpolation would be included. As it was desirable to know the true concentrations more accurately than for the determination of the calibration curves, the various mixtures were prepared by weighing expedient amounts (0–35 μg/ml) from two concentrated stock solutions—one of HS and one of SA—into measuring flasks and adding the appropriately humidified PG up to the mark. One aliquot served for the spectrophotometric measurement at 305 nm and another, after addition of hydroxide, for that at 335 nm. The two concentrated stock solutions, each containing about 800 μg/ml, were also prepared by weighing so that the overall maximum deviations from the nominal concentrations of all the final mixtures were below 1.5% for HS and SA and below 2.5% for water and potassium hydroxide.

TABLE I

ABSORPTIVITIES AT DIFFERENT WATER CONTENTS

(a_1^x, absorptivity of SA in PG at 305 nm (without KOH); a_1^y, absorptivity of HS in PG at 305 nm (without KOH); a_2^x, absorptivity of SA in PG at 335 nm (with KOH); a_2^y, absorptivity of HS in PG at 335 nm (with KOH))

% H_2O[a]	a_1^x	a_1^y	a_2^x	a_2^y	$\beta = a_1^y/a_2^y$	$\gamma = a_2^x/a_1^x$	$\beta \times \gamma$
0:10	29.3	19.8	0.780	20.5	0.965	0.0265	0.026
10:20	28.0	19.4[b]	0.770	21.3	0.910	0.0275	0.025
20:30	26.9	18.9	0.735[b]	22.0[b]	0.860	0.0275	0.024
30:40	25.8	18.3[b]	0.725	22.1	0.830	0.0280	0.023
40:50	24.8	18.3	—	—	—	—	—
Average values	27.0	18.9	0.750	21.5	0.890	0.0275	0.025

[a] In this column, the values on the left correspond to solutions without KOH, those on the right to solutions with KOH.

[b] Determined on the basis of 20 experimental points.

RESULTS

The absorption spectra of HS and SA in PG, with and without alkali are shown in Figs. 1 and 2. The water contents in the solutions without KOH were 0% in Fig. 1 and 30% in Fig. 2; the corresponding values for the solutions with KOH were 10% and 40%. In all the Figures, broken lines indicate that the spectra are less reliable, having been obtained by averaging rather widely varying values. Therefore, these ranges could not be used for sufficiently accurate calibration and analysis.

In the concentration ranges of interest, close agreement with Beer's law was obtained at all water contents. In order to illustrate the deviations of the experimental

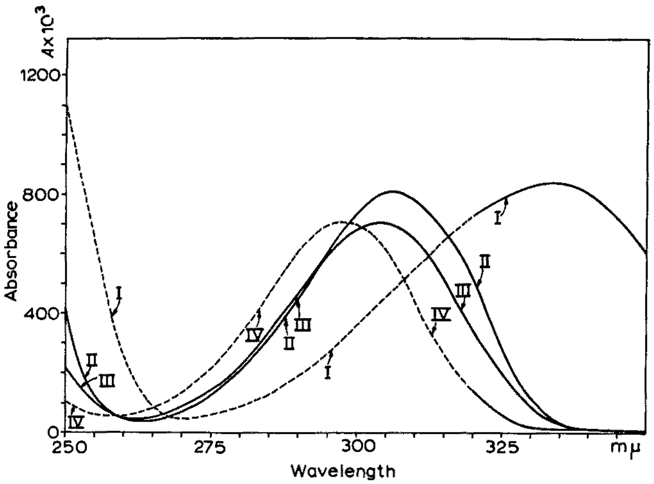


Fig. 1. Absorption spectra of HS and SA in PG at low water content. (I) 40 μg/ml HS with KOH and with 10% H_2O. (II) 40 μg/ml HS without KOH and without H_2O. (III) 25 μg/ml SA without KOH and without H_2O. (IV) 25 μg/ml SA with KOH and with 10% H_2O.

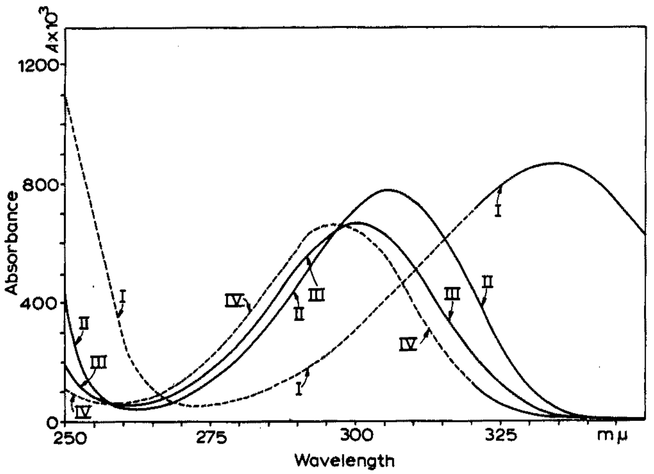


Fig. 2. Absorption spectra of HS and SA in PG at high water content. (I) 40 μg/ml HS with KOH and with 40% H_2O. (II) 40 μg/ml HS without KOH and with 30% H_2O. (III) 25 μg/ml SA without KOH and with 30% H_2O. (IV) 25 μg/ml SA with KOH and with 40% H_2O.

values from the smoothed calibration lines, 4 typical calibration curves are presented in Fig. 3, which include all the measured points.

Table I summarizes all the values obtained for the 4 absorptivities at different concentrations of water; the corresponding computed ratios of β, γ, and $\beta \times \gamma$ are also included. The data presented in the bottom row were calculated by averaging the values in each respective column.

The results of the comparison experiments are summarized in Table II. The

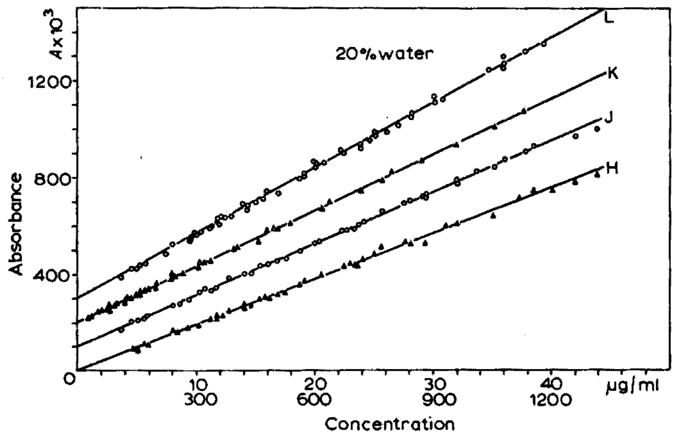


Fig. 3. Typical calibration diagrams. (H) HS without KOH, (J) HS with KOH, (K) SA with KOH, (L) SA without KOH. Lower scale on abscissa for line K. Upper scale on abscissa for lines H, J, L. Lines J, K, L have been shifted in the direction of the ordinate by 0.1, 0.2, 0.3 absorbance units respectively, in order to avoid partial overlap.

TABLE II

STATISTICAL DATA OF COMPARISON EXPERIMENTS

($\bar{D}$, mean deviation of spectrophotometric values from nominal concentrations (µg/ml); *SD*, standard error of the deviations (µg/ml); *SDM*, standard error of the mean (µg/ml); $(D-\bar{D})_{max}$, maximum deviation from the mean (µg/ml); *N*, number of measurements)

	SA				*HS*				%H_2O
	I	*II*	*III*	*IV*	*I*	*II*	*III*	*IV*	
$\bar{D}$	−0.6	−0.9	0.9	0.6	0.0	0.6	−0.3	0.3	5
SD	0.3	0.4	0.4	0.2	0.3	0.5	0.4	0.6	
SDM	<0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.1	
$(D-\bar{D})_{max}$	0.7	1.0	0.7	0.5	1.0	1.1	1.0	1.1	
N	29	29	29	29	29	29	29	29	
$\bar{D}$	−0.3	−0.7	−0.1	−0.5	0.1	0.6	0.4	1.1	15
SD	0.2	0.4	0.3	0.2	0.2	0.4	0.4	0.3	
SDM	0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.1	
$(D-\bar{D})_{max}$	0.4	0.7	0.5	0.3	0.6	0.9	1.1	0.5	
N	14	14	14	14	14	14	14	14	
$\bar{D}$	−0.2	−0.6	−1.1	−1.3	0.0	0.6	0.4	1.1	25
SD	0.2	0.3	0.2	0.6	0.2	0.3	0.6	0.2	
SDM	<0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	
$(D-\bar{D})_{max}$	0.3	0.7	0.5	2.2	0.5	0.5	1.1	0.5	
N	15	15	15	15	15	15	15	15	

two sets of columns I, II, III, and IV correspond to the different approximations adopted for the evaluation of C_x and C_y respectively: columns I, no approximation; columns II, assuming $a_2^x = \gamma = 0$; columns III, assuming constant absorptivities (the average values in the bottom row of Table I) at all the water contents indicated in the last column; columns IV, assuming constant absorptivities and, in addition, $a_2^x = \gamma = 0$.

For the estimation of the errors involved in the preparation of the solutions, it was necessary to know the density changes associated with the heat developed during the dilution of PG with water or aqueous KOH. The maximum rise in temperature encountered was about 10°. Since only scant data[2,11,12] are available on the densities of PG–H_2O binary mixtures at various temperatures, more detailed measurements were carried out. The results, with an overall error of about 0.0005 g/ml are presented in Fig. 4 (density *vs.* temperature), in which curves S, T, U, V, and W refer to water contents of 0, 10, 20, 30, and 40 weight percent respectively.

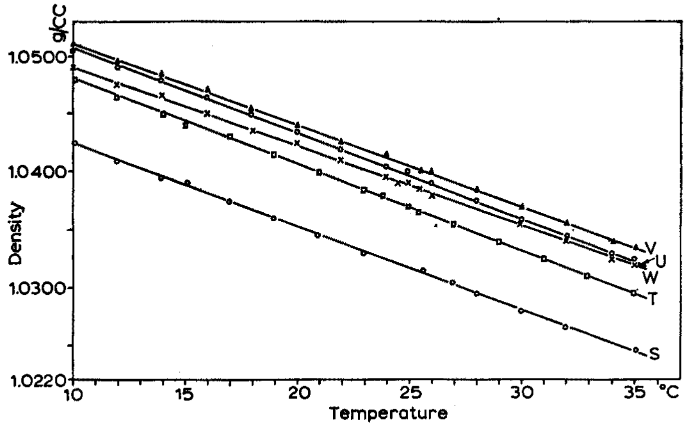


Fig. 4. Densities of PG–H_2O mixtures. (S) PG without water, (T) PG with 10% water, (U) PG with 20% water, (V) PG with 30% water, (W) PG with 40% water. All water concentrations are in percent by weight.

DISCUSSION

Figures 1 and 2 show that, for HS without potassium hydroxide, the position of the absorption peak at about 305 nm is unaffected by the water concentration. On the other hand, the position of the absorption maximum for SA without hydroxide depends slightly on the water content; an increase of water concentration from 0% to 30% results in a hypsochromic shift from about 305 nm to about 300 nm. As expected, addition of hydroxide causes the maxima of HS and SA to shift markedly in opposite directions; independent of water contents, the peak of HS is shifted to about 335 nm and that of SA to about 295 nm. The heights of the two maxima in the presence of potassium hydroxide, their relative position, and the particularly low absorption by SA at the peak of HS, led to an attempt to use these 2 wavelengths for the estimation of C_x and C_y in mixtures; in that case, one aliquot (with hydroxide) from the mixture to be estimated would have sufficed for the spectrophotometric measurements at both wavelengths, and $\beta \times \gamma$ in eqns. (3) and (4) would have become negligible (< 0.01). However, since the results obtained with hydroxide below about 320 nm were not reproducible with sufficient accuracy, this procedure had to be abandoned.

Table I demonstrates that the dependence of the absorptivities upon water content is rather slight, but notably non-linear. In the extreme case of a_1^x, the values at the different water concentrations in the range studied (0–40% water), do not deviate from the average by more than ±9%; for a_1^y, a_2^x, a_2^y the corresponding deviations are less than ±5%. Without hydroxide at 305 nm, both the absorptivities of HS and SA decrease with rising water content. The absorptivity of SA with hydroxide at 335 nm shows the same trend whereas that of HS with hydroxide at 335 nm increases with rising water concentration. Because of the inverse dependence of a_1^y and a_2^y upon water content, β which does not contain a_1^x depends upon water concentration much more markedly than γ which contains a_1^x.

The statistical analysis of the results of the comparison experiments (Table II) was greatly simplified by the finding that, for practical purposes, the individual deviations D are independent of both C_x and C_y at all water concentrations. Table II demonstrates the absence of any significant difference in accuracy between the spectrophotometric determinations of C_x and those of C_y, the only exception being the lack of bias ($\bar{D} \approx 0$) for the case of HS in column I; nor does the Table show any significant difference in accuracy at the 3 water contents examined. As expected, the results obtained without approximations (columns I) are the most accurate and precise, the reverse being true for the results of columns IV; however, even the latter are still sufficient for many practical applications in which an accuracy of about 1 μg/ml is considered satisfactory for the pertinent concentration range.

The instability of the spectrophotometric readings, observed in the case of solutions with hydroxide during the first few minutes after preparation, cannot be attributed to the density changes following the heating and subsequent gradual cooling after dilution with water and/or aqueous potassium hydroxide. Otherwise, a similar phenomenon would have been found in measuring the absorbances of solutions after adding water alone. It is thus to be concluded that the hydroxide is responsible for the observed initial instability and that some reaction of hydroxide with either HS, SA, PG, or impurities in the solution persists at a notable rate for a short while after its addition. The study of the reaction kinetics involved is beyond the scope of this research.

Because of the non-linear dependence of the absorptivities upon water content, an important part of the overall error obtained in the comparison experiments may be due to faulty interpolation. Therefore, it may be worthwhile for higher accuracy, to determine in more detail absorptivity *vs.* water concentration instead of relying upon interpolation between a few discrete values, such as those presented in Table I for the 4 absorptivities. Because of the close agreement with Beer's law as well as the accuracy of the nominal concentrations, it appears probable that the continuous curves of absorptivity *vs.* water content can be obtained directly by a change in calibration procedure, without markedly increasing the number of experimental determinations carried out. This change would involve the measurement of absorbances in a series of PG solutions containing known concentrations of HS or SA, with or without hydroxide, at continuously varying water contents, and the computation of the individual absorptivity values by dividing the measured absorbances by the corresponding nominal concentrations. For a given desired accuracy, the number of individual calibration determinations can be appreciably reduced by adopting, for the preparation of the PG solutions, the more accurate procedure described for the preparation of the mixtures in the comparison experiments.

The authors wish to express their gratitude to D. HALM, E. FISHER and E. MANISTERSKY for the technical assistance rendered.

SUMMARY

Propylene glycol (PG) is proposed as solvent for the collection and analysis of samples of vapors and aerosols, and *n*-hexyl salicylate is suggested as "model" compound for these systems. A UV-spectrophotometric method is described for simultaneous determination of *n*-hexyl salicylate and salicylic acid in pure and aqueous PG solutions, at concentrations of 0–35 μg/ml. The method is based on water content determinations and on absorbance measurements at 305 nm and, after addition of aqueous potassium hydroxide, at 335 nm. Simplifying approximations are proposed for less accurate work, the errors involved are evaluated, and possible improvements are suggested.

RÉSUMÉ

Le propylèneglycol (PG) est proposé comme solvant pour recueillir et analyser des échantillons de vapeurs et d'aérosols; le *n*-hexylsalicylate est proposé comme modèle. On utilise une méthode spectrophotométrique UV pour le dosage simultané du *n*-hexylsalicylate et de l'acide salicylique dans des solutions pures et aqueuses de propylèneglycol, à la concentration de 0–35 μg/ml. Ce procédé est basé sur la détermination de la teneur en eau et sur les mesures d'absorption à 305 nm et après addition d'hydroxyde de potassium à 335 nm.

ZUSAMMENFASSUNG

Eine UV-spektralphotometrische Methode wird beschrieben für die gleichzeitige Bestimmung von 0.35 μg/ml *n*-Hexylsalicilat und Salycilsäure in reinen und wässrigen Lösungen aus Propylenglykol, die als Lösungsmittel für Dämpfe und Aerosole dienen. Die Methode beruht auf der Bestimmung des Wassergehaltes und auf Absorptionsmessungen bei 305 nm bzw. 335 nm nach Zugabe von wässrigem Kaliumhydroxid. Für weniger genaue Arbeiten werden Vereinfachungen vorgeschlagen, die damit verbundenen Fehler abgeschätzt und mögliche Verbesserungen angegeben.

REFERENCES

1 BEILSTEIN, Vol. I, 3rd Supplement, Springer Verlag, Berlin, 1958, p. 2142.
2 W. S. JONES AND W. S. TAMPLIN, in G. O. CURME, JR. AND F. JOHNSTONE, *Glycols*, Reinhold, New York, 1953.
3 J. RAE, *Pharm. J.*, 155 (1945) 151.
4 R. B. TINKER AND A. J. McBAY, *J. Am. Pharm. Ass.*, 43 (1954) 315.

5 L. PEKKARINEN AND E. TOMMILA, *Acta Chem. Scand.*, 13 (1959) 1019.
6 E. R. GARRETT, *J. Am. Chem. Soc.*, 79 (1957) 5206.
7 L. DOUB AND J. M. VANDENBELT, *J. Am. Chem. Soc.*, 71 (1949) 2414.
8 E. EBERIUS, *Wasserbestimmung mit Karl-Fischer-Lösung*, Verlag Chemie G.M.B.H., Weinheim, 1958.
9 J. MITCHELL, JR. AND D. M. SMITH, *Aquametry*, Interscience, London, 1948.
10 K. AMAYA AND R. FUJISHIRO, *Bull. Chem. Soc. Japan*, 30 (1957) 940.
11 Y. KATO, *J. Pharm. Soc. Japan*, 78 (1958) 565.
12 G. MACBETH AND R. THOMPSON, *Anal. Chem.*, 23 (1951) 618.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PHOTOMETRIC TITRATION OF TITANIUM(III) WITH IRON(III)

W. E. VAN DER LINDEN AND G. DEN BOEF
Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)

(Received December 21st, 1966)

In addition to gravimetric, spectrophotometric, polarographic and spectrographic methods, many titrimetric methods for the determination of titanium have been published. Most of these are based on the prereduction of titanium(IV) to titanium(III) followed by titration with an oxidizing agent using visual or potentiometric end-point indication[1]. Direct titrations of titanium(IV) with a reducing agent such as chromium(II) or vanadium(II) have been proposed[2,3], but only recently have found new applications with amperometric end-point indication[4,5]. With the visual titrations, good results can be obtained if the amount of titanium is not too small, but the selectivity of these determinations is poor. In general, potentiometric titrations give better selectivity, but the equilibrium adjustment of the reaction and the electrode response must be reasonably rapid. Down to concentrations of 10^{-3}–10^{-4} *M*, this condition seems to be fulfilled, but at lower concentrations, kinetic difficulties arise[6].

Photometric titrations are often free from the limitations of the potentiometric method, particularly when the system is self-indicating; in that case the titration curves are composed of straight lines, more or less curved near the end-point. In principle, photometric detection of the equivalence point is suitable in the visible region for the titration of the colourless titanium(IV) to the violet titanium(III) or the reverse. However, the molar absorptivity, even at the maximum of the absorption curve, is so small that without additional provisions only large amounts of titanium can be determined. As the purpose of the present work was to determine small amounts of titanium in the presence of large amounts of other metals, it was necessary to add a reagent which forms an intensely coloured compound with titanium in one of its oxidation states.

As described in a previous paper[7], acetylacetone forms a coloured complex with titanium(III). The advantage of acetylacetone in the medium used is that the metal ions which generally accompany titanium(III) either do not form complexes with acetylacetone or form complexes with a low molar absorptivity at the wavelength of maximum absorbance of the titanium(III) complex.

To avoid oxidation and hydrolysis of titanium(III), it is preferable to work with 1 *M* acidic solutions; to obtain a sufficient colour, the acetylacetone concentration must be 0.1–0.5 *M*. Titanium(III) is then mainly converted to $\text{Ti(acetylacetone)}^{2+}$, but small amounts of Ti^{3+} and $\text{Ti(acetylacetone)}_2^{+}$ may also be present. This complex composition depends on the pH and the total ligand concentration (actually on the free ligand concentration, but the difference is insignificant since a large excess is used). Provided that the solution and titrant have approximately the same acidity and that the titrant is sufficiently concentrated for dilution during the titration to be less than *ca.* 10%, both the pH and ligand concentration vary so little that the relative distribution of the various complexes, and thus the effective molar absorptivity of the titanium(III) present, remains constant. Thus the titration curves are composed of straight lines after the usual correction of the absorbance readings for dilution.

Photometric titration curves for the direct reductimetric titration of titanium(IV) with vanadium(II) showed such irregularities near the end-point that, especially at small concentrations, the equivalence point could not be determined accurately. Other disadvantages of this procedure were the instability of the vanadium(II) solution and the interference of traces of oxygen in the cell. Accordingly, an indirect method was examined.

Titanium(IV) was reduced with a small excess of chromium(II) or vanadium(II) and then titrated with an iron(III) solution. No irregularities in the titration curves were observed and the instability of the reductant was far less important. Oxygen present was converted to water by the excess of reductant and did not interfere.

As equilibrium was established rather slowly at room temperature, all titrations were carried out at 50°; all reactions were then sufficiently fast for continuous titration with the exception of the reaction

$$\mathrm{V(III)} + \mathrm{Fe(III)} \rightleftharpoons \mathrm{V(IV)} + \mathrm{Fe(II)}$$

This was particularly noticeable as the vanadium(III) concentration decreased. For a determination of titanium, this slow reaction was not important because it comes after the oxidation of titanium(III) to (IV).

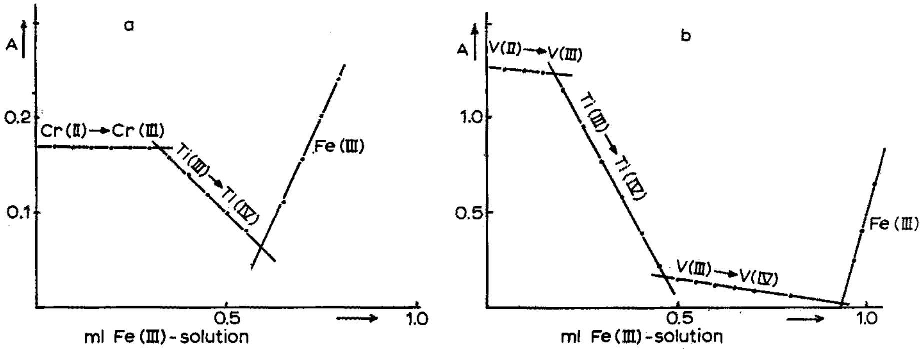


Fig. 1. Photometric titration of (a) 0.142 mg of titanium with 10^{-2} *M* iron(III) solution after prereduction with chromium(II); (b) 1.42 mg of titanium with 10^{-1} *M* iron(III) solution after prereduction with vanadium(II) ($\lambda = 490$ nm; temp. = 50°; Zeiss PMQ II).

Figures 1a and 1b show the photometric titration curves at 490 nm of titanium after reduction to the tervalent state with chromium(II) and vanadium(II) respectively. The shapes of the titration curves can be explained by the fact that only titanium(III) and iron(III) form strongly absorbing complexes with acetylacetone at the wavelength used.

EXPERIMENTAL

Reagents

All the reagent solutions were prepared with 0.5 *M* sulphuric acid.

Titanium(IV) solution, 10^{-2} M. 3.54 g of potassium titanium oxalate was dissolved and heated with concentrated sulphuric acid and the solution was evaporated to almost complete dryness. The percentage of titanium in the oxalate (AnalaR) was determined by reducing the titanium with a cadmium reductor and titrating the solution with iron(III), using thiocyanate as indicator. The iron(III) solution was standardized by reduction to iron(II) and titration with permanganate.

All chemicals used were of p.a. quality.

Apparatus

Zeiss spectrophotometer PMQ II. A prism spectrophotometer, deflection type with photomultiplier.

Zeiss ELKOphotometer II. A filter photometer, substitution principle without amplification.

Procedures

For Zeiss PMQ II. Use the titration assembly supplied with the apparatus, which is provided with a 12-ml titration cell of 20-mm optical path length.

Place 5 ml of an approximately 0.5 *M* sulphuric acid solution containing 60–500 µg of titanium in the titration cell. Add 1 ml of acidic 1 *M* acetylacetone solution and pass nitrogen over the solution for 10 min. Add an excess of acidic 10^{-2} *M* vanadium(II) or chromium(II) solution and place the cell in the cell holder which is thermostatted at 50°. Titrate under nitrogen from a 1-ml burette (Metrohm piston-type) with an acidic iron(III) solution of suitable concentration. Measure the absorbance at 490 nm. For each straight line at least 3 absorbance readings are necessary. The end-point is found graphically from the difference of the 2 points of intersection.

For Zeiss ELKO II. Use the same titration cell as in the case of the PMQ II, and the same procedure, except for the amounts of titanium which can be as low as 5 µg/ml in this case. The filter S 49E is used.

Notes

(*a*) Volume corrections for dilution are necessary.

(*b*) The strength of the iron(III) solution should be such that 0.3–0.4 ml of the reagent is needed for the oxidation of titanium.

(*c*) Stirring was done magnetically; it was not necessary to stop stirring when the absorbances were read.

(*d*) 20-mm cells with two small holes were used. With these cells it was easy to prevent the penetration of air.

(*e*) A temperature change of 1° corresponds to an absorbance change of 1–2%. It is necessary therefore to thermostat well.

RESULTS

The results for the different procedures in the presence of various other metals are summarized in Tables I, II and III. The standard deviation in the absence of other metals calculated from 8 titrations was 0.9% for the determination of 356 μg of titanium. A systematic error of −2.8% was observed when the iron(III) solution was not deoxygenated. After deoxygenation of the titrant the systematic error was −0.3%; the last traces of oxygen were difficult to remove. This could introduce an appreciable systematic error when very dilute iron(III) solutions were used as titrant; for such solutions, it was necessary to standardize against a known amount of titanium.

TABLE I

PHOTOMETRIC TITRATIONS WITH IRON(III) AFTER PREREDUCTION WITH VANADIUM(II)

(Zeiss PMQ II; λ=490 nm; temp.=50°; total volume *ca.* 10 ml; 0.356 mg Ti was taken in each experiment)

No. of exp.	*Ti found (mg)*	*Rel. error (%)*	*Other metals present*	*Amount added (mg)*	*No. of exp.*	*Ti found (mg)*	*Rel. error (%)*	*Other metals present*	*Amount added (mg)*
1	0.357	+0.3	Fe(II)	15	15	0.353	−0.9	Mn(II)	160
2	0.356	0	Fe(II)	15	16	0.356	0	Mn(II)	160
3	0.360	+1.1	Fe(II)	125	17	0.359	+0.9	Al(III)	80
4	0.354	−0.6	Fe(II)	125	18	0.353	−0.9	Al(III)	80
5	0.356	0	Cr(III)	10	19	0.346[a]	−2.6	Fe(III)	80
6	0.355	−0.3	Cr(III)	10	20	0.356[a]	0	Fe(III)	80
7	0.350	−1.5	Cr(III)	40	21	0.352	−1.1	V(IV)	0.5
8	0.352	−1.1	Cr(III)	40	22	0.356	0	V(IV)	1
9	0.359	+0.9	Ni(II)	20	23	0.366[b]	+2.6	V(IV)	1.5
10	0.352	−1.1	Ni(II)	20	24	0.357[b]	+0.3	V(IV)	15
11	0.356	0	Co(II)	10	25	0.357[b]	+0.3	V(IV)	30
12	0.355	−0.3	Co(II)	10	26	0.352[b]	−1.1	V(IV)	30
13	0.352	−1.1	Co(II)	100	27	0.370[b]	+3.6	V(IV) Fe(III)	30 80
14	0.349	−2.0	Co(II)	100					

[a] Prereduction with slightly amalgamated cadmium reductor. [b] Prereduction with tin reductor.

TABLE II

PHOTOMETRIC TITRATIONS WITH IRON(III) AFTER PREREDUCTION WITH VANADIUM(II)

(Zeiss ELKO II; filter S 49E; temp.=50°; total volume *ca.* 10 ml)

No. of exp.	*Ti present (mg)*	*Ti found (mg)*	*Rel. error (%)*	*Other metals present*	*Amount added (mg)*
1	0.142	0.141	−0.7	Fe(II)	165
2	0.142	0.138	−2.8	Fe(II)	165
3	0.142	0.140	−1.4	Fe(II)	165
4	0.142	0.138	−2.8	Co(II)	60
5	0.142	0.141	−0.7	Co(II)	60
6	0.142	0.139	−2.1	Cr(III)	15
7	0.142	0.143	+0.7	Cr(III)	15
8	0.142	0.138	−2.8	Ni(II)	225
9	0.142	0.143	+0.7	Ni(II)	225
10	0.142	0.140	−1.4	Fe(II) Ni(II) Cr(III) Co(II)	80 20 10 10
11	0.142	0.141	−0.7	As exp.	10
12	0.0356	0.0357	+0.3	Al(III)	120
13	0.0356	0.0347	−2.5	Al(III)	120

TABLE III

PHOTOMETRIC TITRATIONS WITH IRON(III) AFTER PREREDUCTION WITH CHROMIUM(II)

(Temp. = 50°; total volume *ca.* 10 ml)

No. of exp.	*Ti present (mg)*	*Ti found (mg)*	*Rel. error (%)*	*Other metals present*	*Amount added (mg)*
Zeiss PMQ II; 490 nm					
1	0.356	0.348	−2.0	V(IV)	0.4
2	0.356	0.351	−1.2	V(IV)	0.4
3	0.356	0.357	+0.3	V(IV)	1.5
4	0.356	0.349	−1.9	V(IV)	1.5
5	0.356	0.353	−0.6	Fe(II)	80
6	0.356	0.355	−0.3	Fe(II) Ni(II) Co(II) Cr(III)	80 20 10 10
7	0.356	0.355	−0.3	As in 6	
ELKO II; filter S 49E					
8	0.0356	0.0359	+0.9	Fe(II)	150
9	0.0356	0.0365	+2.5	Fe(II)	150
10	0.0356	0.0364	+2.2	Ni(II)	150
11	0.0356	0.0364	+2.2	Ni(II)	150
12	0.0356	0.0353	−0.9	Mn(II)	150
13	0.0356	0.0357	+0.3	Mn(II)	150
14	0.0356	0.0362	+1.7	Mn(II)	150
15	0.0356	0.0349	−1.9	Co(II)	15
16	0.0356	0.0353	−0.9	Co(II)	15
17	0.0356	0.0340	−4.5	Cr(III)	15
18	0.0356	0.0347	−2.5	Cr(III)	15
19	0.0356	0.0349	−1.9	Fe(II) Ni(II) Co(II) Cr(III)	75 75 5 5
20	0.0356	0.0347	−2.5	As in 19	
21	0.0356	0.0352	−1.1	Solution 1 *M* in NaCl	
22	0.0356	0.0354	−0.6		
23[a]	0.0356	0.0352	−1.1	Nb(IV)	0.2
24[a]	0.0356	0.0356	0	Nb(IV)	0.2

[a] The solution was evaporated with sulphuric acid and filtered.

Iron, chromium, nickel, vanadium, cobalt, manganese and aluminium did not interfere. In the presence of large amounts of nickel, chromium and especially cobalt, the initial absorbance was large and the relative absorbance change during the titration was small, so that the accuracy decreased.

Iron and vanadium accompanying titanium(IV) are usually present as iron(III) and vanadium(IV) or (V). This can cause difficulties if the amount of titanium is small, for a very large excess of reductant must be added to reduce these elements. Prereduction to iron(II) and vanadium(III) or (II) with slightly amalgamated cadmium or with tin proved satisfactory (see Table I: exp. 19–27). Titanium was also reduced to some extent but this did not cause difficulties. When large amounts of vanadium were present, prereduction with a tin reductor was better, because vanadium was then mainly reduced to vanadium(III); with cadmium, vanadium was mostly reduced to vanadium(II), so that an equivalent amount of titrant was consumed before titanium(III) was oxidized. Copper ions interfered, because they were reduced to finely divided copper on addition of the prereductant; copper was therefore removed by prereduction with an amalgamated reductor, the copper being taken up by the mercury.

Molybdenum, niobium and tungsten interfered. Molybdenum could be separated by electrolysis with a mercury cathode, the titanium remaining in solution. Small amounts of niobium could be separated by evaporation to dryness with concentrated sulphuric acid and filtration of the insoluble niobium(V) oxide. Tungsten usually will remain undissolved during the decomposition of the sample. Nitrate and perchlorate ions have to be removed by evaporation with sulphuric acid.

In the presence of *ca.* 35 μg of titanium, the total change of the absorbance on titration is only 0.02. Nevertheless, an accurate titration was possible with the aid of the ELKO II. This permitted the determination of titanium in the presence of 4000-fold amounts of iron, nickel, aluminium and manganese. A 400-fold amount of cobalt or chromium did not interfere; larger amounts could not be used because of the strong absorbance.

SUMMARY

An oxidimetric titration of titanium(III) with iron(III) with a photometric end-point is proposed. Acetylacetone was used to obtain an intensely coloured titanium(III) complex; titanium(III) was formed by prereduction with chromium(II) or vanadium(II). Amounts of titanium down to 35 μg were determined with fairly good accuracy and precision. Few common elements interfere.

RÉSUMÉ

On propose un titrage oxydimétrique du titane(III) par le fer(III) avec point final photométrique. L'acétylacétone permet d'obtenir un complexe de titane(III) intensément coloré. Le titane(III) est formé par préréduction à l'aide de chrome(II) ou de vanadium(II). On peut doser ainsi avec précision et une bonne exactitude des quantités de titane descendant jusqu'à 35 μg. Peu d'éléments courants gênent.

ZUSAMMENFASSUNG

Es wird die oxidimetrische Titration des Titan(III) mit Eisen(III) vorgeschlagen. Die Endpunktsanzeige erfolgt photometrisch über den intensiv gefärbten Titan(III)-Komplex mit Acetylaceton. Titan(III) wurde durch Reduktion mit Chrom(II) oder Vanadin(II) gebildet. Titanmengen bis hinab zu 35 μg wurden mit guter Genauigkeit und Richtigkeit bestimmt. Nur wenige der üblichen Elemente stören.

REFERENCES

1 A. Claassen, *Handbuch der Analytischen Chemie*, Vol IVb, Springer-Verlag, Berlin, 1950.
2 H. Brintzinger and W. Schieferdecker, *Z. Anal. Chem.*, 76 (1929) 277.
3 J. J. Lingane, *Anal. Chem.*, 20 (1949) 797.
4 S. A. Galla, *Zh. Analit. Khim.*, 18 (1963) 924.
5 P. K. Agasyan and E. R. Nikolaeva, *Zh. Analit. Khim.*, 19 (1964) 1219.
6 Z. Slovák, *Z. Anal. Chem.*, 220 (1966) 179.
7 W. E. van der Linden and G. den Boef, *Anal. Chim. Acta*, 37 (1967) 179.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATION GALLIUM–FER EN PRESENCE D'EDTA

GIOVANNI LANFRANCO
Centro Ricerche Metallurgiche, Torino (Italie)

(Reçu le 23 décembre, 1966)

Beaucoup de méthodes ont été proposées pour la séparation du gallium du fer. Quelques-unes se fondent sur la précipitation du fer(III), d'autres sur la précipitation du gallium ou sur son extraction par des solvants, après réduction du fer à l'état ferreux.

Quelques-unes de ces méthodes ne sont pas tout à fait satisfaisantes, d'autres sont longues. Ces méthodes sont décrites en détail en réf. 1. Récemment les échangeurs d'ions, soit de cations[2] soit d'anions[3,4], ont offert des nouveaux moyens pour la séparation fer–gallium.

Dans une étude de la séparation fer–gallium radioactifs, on a remarqué que le gallium peut être séparé du fer très simplement par précipitation de ce dernier par la soude en présence d'EDTA.

La méthode, décrite ici, a été étudiée au moyen de gallium et de fer radioactifs et rend possible la séparation de macro- et de microquantités de gallium du fer.

Le gallium, qui reste dans la phase aqueuse après la précipitation du fer, peut être dosé, après extraction par le tributylphosphate (TBP) et extraction successive par l'eau du gallium de la phase organique, par précipitation par le cupferron[5] et calcination, ou, dans le cas de microquantité, par colorimétrie par la rhodamine B[6].

PARTIE EXPÉRIMENTALE

Séparation gallium–fer

On ajoute à la solution (15–20 ml) faiblement chlorhydrique, qui contient du gallium et du fer, une solution d'EDTA à 1%, à peu près 20% en excès de la quantité nécessaire pour complexer tout le fer et le gallium. On chauffe au bain-marie et on ajoute goutte à goutte, en agitant, une solution de soude 2 *N* jusqu'à pH 12.5 (contrôlé avec des papiers indicateurs Lyphan, intervalle de pH 10.5–13). On laisse reposer à chaud, on centrifuge et on sépare le liquide. On lave 2 fois le précipité avec des portions de 5 ml de solution 0.2% d'EDTA amené à pH 12.5 par de la soude 2 *N*. On ajoute les eaux de lavage à la solution contenant le gallium.

Dosage du gallium. Neutraliser la solution aqueuse qui contient le gallium par de l'acide chlorhydrique. Ajuster l'acidité (acide chlorhydrique) à 3 *N*. Extraire le gallium de la solution (environ 60 ml) par 3 portions de 10 ml de TBP. Réunir les 3 fractions organiques et faire repasser le gallium extrait dans la phase aqueuse par 4 portions de 10 ml d'eau (les phases aqueuses et organiques ont des densités proches et il est donc nécessaire de centrifuger, avant de les séparer). Réunir les phases aqueuses et les laver avec 4 portions de 10 ml de toluène pour enlever la petite quantité de TBP encore présente.

Si le gallium est présent en macroquantités il est précipité par le cupferron, en milieu acide sulfurique 2 *N*. On pèse l'oxyde de gallium après calcination à 900°.

Les microquantités de gallium sont dosées par colorimétrie par la rhodamine B. S'il y a plus de 10 μg de gallium, on effectue la colorimétrie d'une partie aliquote de la solution; si la solution contient moins de 10 μg de gallium on effectue la colorimétrie sur toute la solution après concentration à 10 ml.

Contrôle de la méthode

La séparation gallium–fer a été contrôlée au moyen de gallium et de fer radioactifs; on a aussi contrôlé au moyen de gallium radioactif l'extraction par le TBP, l'extraction successive du métal de la phase organique par l'eau, le lavage avec le toluène, la précipitation par le cupferron. On a suivi le procédé décrit précédemment.

Préparation du gallium et du fer radioactifs. Le gallium et le fer radioactifs ont été produits par irradiation dans un flux de neutrons thermiques du réacteur nucléaire RA1 (SORIN—Saluggia).

Après l'irradiation on dissout l'échantillon de gallium et celui de fer dans l'acide chlorhydrique 6 *N*. La solution de gallium est amenée à 100 ml en fiole jaugée (1 ml = 0.0021 mg de gallium); après élimination des impuretés radioactives la solution de fer est amenée à 50 ml en fiole jaugée. Dans le Tableau I sont rapportées les données de décroissance caractéristiques des radioisotopes du fer et du gallium formés par irradiation par des neutrons thermiques.

Exécution des mesures. On a mesuré la radioactivité-γ de ^{72}Ga sous le pic photoélectrique qui correspond à l'énergie de 0.835 MeV et celle de ^{59}Fe sous les pics qui correspondent aux énergies de 1.10 et 1.29 MeV.

On a effectué les mesures avec un détecteur constitué par un scintillateur de

TABLEAU I

DONNÉES DE DÉCROISSANCE CARACTÉRISTIQUES DES RADIOISOTOPES OBTENUS PAR IRRADIATION DU FER ET DU GALLIUM PAR DES NEUTRONS THERMIQUES

Radioisotope	*Réaction de formation*	*Période*	*Type de désintégration (MeV)*			*Rayons-γ (MeV)*	
^{55}Fe	^{54}Fe(n,γ)^{55}Fe	2.7 a	E.C.[a]	(100%)		Rayons X 0.0059	
^{59}Fe	^{58}Fe(n,γ)^{59}Fe	45 j	—	0.27 0.46	(46%) (53%)	1.10 1.29	(56%) (44%)
					D'autres moins intenses		
^{70}Ga	^{69}Ga(n,γ)^{70}Ga	21.1 m	—	1.65 Autres	(99.5%) (0.5%)	0.17 1.04	(0.2%) (0.5%)
^{72}Ga	^{71}Ga(n,γ)^{72}Ga	14.1 h	—	0.67 0.96	(41%) (35%)	0.63 0.835 2.20 2.51	(19%) (88%) (29%) (17%)
					D'autres moins intenses		

[a] E.C. Capture d'électrons.

INa(Tl) de 2 × 2″ couplé à un photomultiplicateur RCA 6342 A. Le détecteur est placé dans une chambre blindée en plomb. Les impulsions, en provenance du détecteur sont envoyées par le moyen d'un préamplificateur TMC type DS 13 à un analyseur à 400 canaux TMC type 401*.

Les échantillons à mesurer sont placés dans des récipients en pyrex se trouvant sur un support de plexiglas placé sur le détecteur.

La radioactivité des échantillons liquides est comparée à celle d'un étalon de gallium ou de fer radioactif, mesuré dans les mêmes conditions. On mesure les échantillons solides (oxyde de gallium) dans les mêmes creusets où ils sont calcinés (on emploie des creusets identiques): l'oxyde de gallium calciné est malaxé avec quelques gouttes d'alcool au moyen d'un agitateur en verre et on l'étend uniformément sur le fond du creuset; on lave l'agitateur avec un peu d'alcool et on sèche sous une lampe à rayons infrarouges.

Contrôle de la séparation fer–gallium

Expériences avec le gallium radioactif. On a exécuté 3 séries d'essais (4 essais dans chaque série) sur des solutions contenant du gallium et du fer auxquelles on avait ajouté du gallium radioactif.

On a mesuré la radioactivité de la solution qui reste après la précipitation du fer, à laquelle on a ajouté les eaux de lavage, et la radioactivité du précipité d'hydroxyde ferrique, après sa dissolution dans l'acide chlorhydrique. La composition des solutions et les résultats des essais sont rapportés dans le Tableau II.

Expériences avec le fer radioactif. On a effectué 4 essais sur 4 solutions différentes, 2 contenant 12 mg de fer et 12.8 mg de gallium et 2 contenant 12 mg de fer et 0.0128 mg de gallium.

TABLEAU II

RÉSULTATS DES ESSAIS DE SÉPARATION FER–GALLIUM: ESSAIS AVEC DU GALLIUM RADIOACTIF

Quantité de gallium et de fer en solution (mg)	*Essai no.*	*Gallium présent en solution après précipitation du fer (%)*	*Gallium entraîné par l'hydroxyde ferrique (%)*
Gallium 12.8	I		0.27
Fer 11.37	II	>99.5	0.15
	III		0.08
	IV		0.11
Gallium 0.132	V		0.10
Fer 11.37	VI	>99.5	0.12
	VII		0.09
	VIII		0.08
Gallium 0.014	IX		0.30
Fer 11.37	X	>99.5	0.15
	XI		0.22
	XII		0.26

---

* Dans des expériences antérieures on a mesuré la radioactivité-β avec un compteur de Geiger pour liquides ou la radioactivité-γ avec un détecteur à scintillation de INa(Tl) et un analyseur d'impulsion à un canal. Les résultats obtenus dans ces expériences concordent avec ceux rapportés ici.

Après la précipitation du fer on n'a plus décelé du fer dans les solutions. Pratiquement tout le fer est précipité.

Contrôle de l'extraction de gallium par le TBP

L'extraction du gallium de solutions 3 *N* en acide chlorhydrique par le TBP a été proposée par BENNET ET IRVINE[7]; puisque le travail de ces auteurs a été inaccessible pour nous, on a contrôlé la méthode avant de l'appliquer à ce cas spécifique. On a effectué 4 essais en double avec des solutions contenant du gallium radioactif. Les premiers essais ont été effectués avec 2 solutions 3 *N* en acide chlorhydrique (10 ml), qui contenaient l'une 12.8 mg et l'autre 0.014 mg de gallium; les essais successifs ont été effectués avec les solutions, qui provenaient des essais III, IV, IX et X de Tableau II, amenées à 3 *N* en acide chlorhydrique.

On rapporte dans le Tableau III la moyenne des résultats de chaque essai en double.

TABLEAU III

ESSAIS D'EXTRACTION DU GALLIUM DE SOLUTIONS EN ACIDE CHLORHYDRIQUE 3 *N* PAR LE TBP ET DES PHASES ORGANIQUES PAR L'EAU

Essai no.	*Quantité de gallium en solution (mg)*	*Volume de la solution (ml)*	*Extraction par le TBP. Gallium resté dans la phase aqueuse*[a] *(%)*		*Extraction par l'eau de la phase organique. Gallium resté dans la phase organique*[a] (%)		
			1re Extraction	*2me Extraction*	*1re Extraction*	*2me Extraction*	*3me Extraction*
XIII	12.8	10	2	<0.1	94	3	<0.3
XIV	0.014	10	2	<0.1	85	3	<0.3
XV	12.8 des essais III–IV	60	3	<0.4	94	4	<0.4
XVI	0.014 des essais IX–X	60	3	<0.4	84	4	<0.4

[a] Moyenne des essais en double.

Détermination du gallium

Macroquantités de gallium. La précipitation du gallium par le cupferron de solutions en milieu acide sulfurique 2 *N* n'est pas directement applicable aux solutions qui proviennent de la séparation du gallium–fer puisque on obtient des résultats trop élevés. Des essais conduits avec du gallium radioactif ont démontrés que les dosages gravimétriques donnent lieu à des erreurs de 10–20% en excès. Si on dissout le précipité calciné dans l'acide chlorhydrique et on répète la précipitation du gallium par le cupferron, les résultats des analyses gravimétriques concordent avec ceux des mesures de radioactivité, mais dans la dissolution on perd 5–10% de gallium. Pour éviter cet inconvénient on a eu recours à l'extraction du gallium par le TBP. Le gallium est ramené dans la phase aqueuse et celle-ci est lavée avec du toluène pour enlever complètement le TBP qui y est dissout ou dispersé et qui gêne dans la précipitation par le cupferron (en ajoutant du cupferron des petites gouttes huileuses se forment qui adhèrent au précipité pendant la filtration); les résultats de l'analyse gravimétrique donnent lieu en ce cas à des erreurs par excès grossières. Dans cette opération on ne perd pratiquement pas de gallium.

Les résultats de quelques essais de séparation du fer (11.37 mg)–gallium et de la détermination de ce dernier par le cupferron effectués avec du gallium radioactif, sont rapportés dans le Tableau IV.

TABLEAU IV

ESSAIS DE SÉPARATION FER–GALLIUM ET DE DOSAGE DU GALLIUM PAR LE CUPFERRON (FER EN SOLUTION mg 11.37)

Essais no.	*Gallium en solution (mg)*	*Gallium trouvé*		
		Dosages gravimétriques		*Mesures de radioactivité*[b] *(%)*
		(mg)	*(%)*	
S[a]	12.8	12.8	100	100
I	12.8	12.7	99.2	100.8
II	12.8	12.8	100	99.5
III	12.8	12.6	98.4	99.3
IV	12.8	12.9	100.8	99.3

[a] Etalon préparé d'une solution de gallium par précipitation par le cupferron.
[b] Radioactivité de S = 100.

Microquantités de gallium. Il faut, en ce cas aussi, éliminer complètement de la phase aqueuse toute trace de TBP, qui donne lieu à des résultats trop élevés. On dose le gallium par colorimétrie par la rhodamine B, le complexe coloré est extrait de la solution chlorhydrique par un mélange benzène–acétone. S'il y a moins de 10 μg de gallium on concentre la phase aqueuse à 10 ml environ. S'il y a des quantités supérieures on amène à volume et on effectue l'analyse sur une partie aliquote de la solution.

On a contrôlé la méthode avec des solutions contenant 12.8 μg (2 essais) et 64 μg (4 essais) de gallium en présence de 11.37 mg de fer. Dans le premier cas on a dosé 12.4 et 12.5 μg de gallium, dans le second des quantités variables de 61 à 65 μg de gallium.

RÉSUMÉ

Le gallium présent soit en micro- soit en macroquantités peut être séparé du fer par précipitation de celui-ci par la soude en présence d'EDTA. Pratiquement tout le gallium reste en solution. Le gallium, après séparation du fer, est extrait par le tributylphosphate en milieu acide chlorhydrique 3 *N*, et puis extrait encore une fois avec de l'eau. Finalement le gallium est précipité par le cupferron et on pèse, après calcination, l'oxyde de gallium, ou, si le gallium est présent en microquantité, on effectue la colorimétrie par la rhodamine B.

La méthode a été contrôlée au moyen de gallium et de fer radioactifs.

SUMMARY

Macro- or microquantities of gallium can be separated from iron by precipitating the latter with sodium hydroxide in the presence of EDTA. Nearly all the gallium remains in solution. After the separation of iron, gallium is extracted with tributylphosphate from 3 *N* hydrochloric acid medium, and then re-extracted into water. Gallium is finally determined by precipitation with cupferron and ignition to the oxide, or for trace amounts of gallium, by colorimetric determination with rhodamine B. The method was checked with radioactive gallium and iron.

ZUSAMMENFASSUNG

Makro- oder Mikromengen von Gallium können von Eisen durch Eisenfällung mittels Natriumhydroxyd in Anwesenheit von EDTA getrennt werden. Dabei verbleibt praktisch das gesamte Gallium in der Lösung. Nach der Eisentrennung wird das Gallium mittels Tributylphosphat von 3 *N* Salzsäurelösung getrennt, um dann in Wasser herextrahiert zu werden. Das Gallium wird dann mit Cupferron gefällt und nach den Glühen als Oxyd gewogen, oder, falls nur Galliumspuren vorhanden sind, mittels Rhodamin B kolorimetriert. Die Methode wurde mittels radioaktivem Gallium und Eisen geprüft.

BIBLIOGRAPHIE

1 *Handbuch der analytischen Chemie. Partie III. Vol. III a/III B*, 2e Edn., Springer Verlag, Berlin, 1956, p. 36.
2 R. Klement et H. Sandmann, *Z. Anal. Chem.*, 145 (1955) 325.
3 E. Blasius et M. Negwer, *Z. Anal. Chem.*, 143 (1954) 257.
4 J. Korkisch et F. Hecht, *Mikrochim. Acta*, (1956) 1230.
5 I. M. Kolthoff et P. J. Elving (Editeurs), *Treatise on Analytical Chemistry*, Part II, Vol 11, Interscience, New York, 1962, p. 34.
6 H. Onishi et E. B. Sandell, *Anal. Chim. Acta*, 13 (1959) 159.
7 W. Bennet et J. W. Irvine, *Mass. Inst. Technol. Res. Lab. Nucl. Sci., Progr. Rept.*, Feb. 1953 (de G. H. Morrison et H. Freiser, *Solvent Extraction in Analytical Chemistry*, J. Wiley, New York, 1957).

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

L'EXTRACTION DES LANTHANIDES ET DES ACTINIDES PAR LES OXYDES D'ALKYLPHOSPHINE

TOME II. L'EXTRACTION DE L'ACIDE NITRIQUE PAR LES OXYDES DE TRI-*n*-HEXYLPHOSPHINE, DE TRI-CYCLOHEXYLPHOSPHINE ET DE TRI-*n*-OCTYLPHOSPHINE*

J. GOFFART** ET G. DUYCKAERTS
Laboratoire de Chimie Analytique et Nucléaire, 2. rue A. Stévart, Liège (Belgique)

(Reçu le 3 janvier, 1967)

Dans une première publication[1], nous avons montré la nécessité de déterminer le partage de l'acide nitrique entre une phase aqueuse et une phase organique d'oxyde d'alkylphosphine avant toute mesure de distribution des nitrates métalliques. C'est pourquoi, après avoir étudié le partage de cet acide en présence d'oxyde de tri-*n*-butylphosphine (TBPO), nous avons étendu nos travaux à 3 autres oxydes d'alkylphosphine à savoir: l'oxyde de tri-*n*-hexylphosphine (THPO), l'oxyde de tri-cyclohexylphosphine (TcHPO) et l'oxyde de tri-*n*-octylphosphine (TOPO).

PARTIE EXPÉRIMENTALE

Réactifs

Les oxydes de tri-*n*-hexylphosphine et de tri-*n*-octylphosphine ont été synthétisés et purifiés suivant les mêmes méthodes que celles utilisées pour la préparation et la purification de l'oxyde de tri-*n*-butylphosphine[1].

Par contre, il est impossible de synthétiser l'oxyde de tri-cyclohexylphosphine par la même technique: en effet, la réaction de l'oxychlorure de phosphore (1 mole) sur le bromure de cyclohexylmagnésium (3 moles) fournit principalement, après hydrolyse, de l'acide cyclohexylphosphinique, $(C_6H_{11})_2POOH$. Nous avons alors choisi de faire réagir le trichlorure de phosphore (1 mole) sur le bromure de cyclohexylmagnésium (3 moles); nous avons obtenu la tri-cyclohexylphosphine, $(C_6H_{11})_3P$, que nous avons oxydée par le permanganate de potassium afin d'obtenir[2] l'oxyde de tri-cyclohexylphosphine $(C_6H_{11})_3PO$. Ce dernier produit est dissous dans le benzène, filtré, lavé et recristallisé dans l'acétone.

La pureté des composés organophosphorés préparés a été vérifiée par les mêmes méthodes que celles décrites dans une autre publication[1] (Tableau I).

La fraction de distillation du *n*-octane passant de 125 à 126° a été employée comme diluant dans nos expériences de distribution.

Mode opératoire

Deux séries d'expériences ont été menées: la première a trait à la distribution

---

* Ce travail a été effectué dans le cadre du contrat Euratom 003-61-2 TPUB.
** Chercheur Agréé à l'Institut Interuniversitaire des Sciences Nucléaires.

TABLEAU I

PURETÉ DES OXYDES D'ALKYLPHOSPHINE

Substance	% $P_{\text{théor.}}$	% $P_{\text{exp.}}$	*% Pureté obtenu par titrage à $HClO_4$*	*P.F. exp. (°)*	*P.F. litt. (°)*
THPO	10.24	10.2	99	33–34	32–33[3]
TcHPO	10.45	10.5	96	155	154–156[2]
TOPO	8.01	8.0	99	53	50–52[4] 50–53[5] 51–51.5[6] 52–53[7] 54–55[8]

de l'acide nitrique et du réactif basique entre l'eau et le benzène, comme décrit précédemment[1].

Dans la deuxième série d'expériences, les conditions expérimentales ont été modifiées: en effet, lors des essais préliminaires sur l'extraction des métaux par les oxydes d'alkylphosphine, il nous était apparu que l'interprétation des phénomènes d'extraction était simplifiée lorsque les mesures de partage étaient conduites en présence d'une phase aqueuse de force ionique constante; c'est la raison pour laquelle nous avons déterminé la distribution de l'acide nitrique entre une phase aqueuse de concentration constante 10^{-2} N en HNO_3 et 2 M en $NaNO_3$ et une phase organique de concentration variable en TOPO dans un diluant inerte.

Le choix de la composition de la phase aqueuse résulte de plusieurs facteurs: tout d'abord, nous devons avoir une concentration en acide nitrique suffisante pour maintenir les métaux en solution, mais la quantité qui passe en phase organique doit rester faible devant la concentration en oxyde d'alkylphosphine afin de ne pas trop modifier l'activité du composé organophosphoré non complexé; une concentration 10^{-2} N en acide nitrique répond à ces conditions.

Cependant, d'un autre côté, les essais préliminaires ont indiqué que, pour cette concentration en acide nitrique, on obtient, pour les actinides et les lanthanides trivalents, des coefficients de distribution trop faibles pour être aisément mesurables avec précision; c'est la raison pour laquelle il est indispensable d'ajouter à la phase aqueuse un agent relargant, par exemple, un nitrate qui ne s'extrait pas en phase organique. Le nitrate sodique 2 M joue ce double rôle de stimuler l'extraction des nitrates métalliques en phase organique et de maintenir en phase aqueuse une force ionique pratiquement constante.

Les équilibrations, les dosages et les conventions d'écriture ont été décrits dans la publication précédente[1].

RÉSULTATS

Nous avons tout d'abord déterminé la distribution du réactif et de l'acide nitrique entre l'eau et une solution benzénique soit de THPO (Tableau II), soit de TcHPO (Tableau III), soit de TOPO (Tableau IV).

Nos mesures de partage de l'acide nitrique entre la phase aqueuse de composi-

TABLEAU II

DISTRIBUTION DE HNO_3 ENTRE LE THPO EN SOLUTION DANS LE BENZÈNE ET L'EAU

$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(THPO)$ (M)	$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(THPO)$ (M)
0.174	0.023	0.096	0.634	0.078	0.100
0.181	0.023	0.100	0.634	0.078	0.100
0.359	0.055	0.100	0.723	0.079	0.096
0.530	0.069	0.096	0.752	0.085	0.100
0.532	0.072	0.100	0.905	0.086	0.096

TABLEAU III

DISTRIBUTION DE HNO_3 ENTRE LE TcHPO 0.100 M EN SOLUTION DANS LE BENZÈNE ET L'EAU

$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(TcHPO)$ (M)	$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(TcHPO)$ (M)
0.124	0.006	0.098	0.506	0.048	0.099
0.140	0.009	0.098	0.587	0.054	0.099
0.230	0.016	0.098	0.687	0.065	0.099
0.320	0.028	0.0985	0.801	0.070	0.099
0.400	0.034	0.0985			

TABLEAU IV

PARTAGE DE HNO_3 ENTRE LE TOPO EN SOLUTION DANS LE BENZÈNE ET L'EAU

$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(TOPO)$ (M)	$C_a(HNO_3)$ (M)	$C_o(HNO_3)$ (M)	$C_o(TOPO)$ (M)
0.093	0.008	0.100	0.360	0.051	0.100
0.133	0.017	0.108	0.520	0.071	0.108
0.184	0.025	0.100	0.626	0.076	0.100
0.255	0.041	0.108	0.714	0.086	0.108
0.265	0.036	0.100	0.905	0.0945	0.108
0.340	0.056	0.108	0.905	0.0985	0.108
0.340	0.056	0.108	0.93	0.0865	0.100
0.347	0.050	0.100	1.26	0.093	0.100

tion constante (HNO_3 10^{-2} N et $NaNO_3$ 2 M) et la phase organique constituée de TOPO dans le *n*-octane sont représentées dans le Tableau V. Le choix de ce diluant résulte des travaux de Baes[9] qui a établi les coefficients d'activité du TOPO dans cet hydrocarbure.

Nous avons ensuite entrepris de répéter les mêmes mesures en remplaçant le *n*-octane par du benzène (Tableau VI).

DISCUSSION ET INTERPRÉTATION DES RÉSULTATS

En l'absence d'acide nitrique, il faut noter que le coefficient de distribution $D_{org/aq}$ entre l'eau et le benzène des oxydes d'alkylphosphine étudiés dans cette publication est nettement supérieur à celui du TBPO. Alors que, pour une concentration 0.100 M en oxyde de tri-*n*-butylphosphine dans le benzène, nous avions

TABLEAU V

DISTRIBUTION DE L'ACIDE NITRIQUE 10^{-2} N ENTRE LE TOPO EN SOLUTION DANS LE *n*-OCTANE ET LE $NaNO_3$ 2 M

C_o^1 (TOPO) (M)	C_o (HNO_3) (M)	C_a (HNO_3) (M)	a_{TOPO} (M) Réf. (DPA)[9]	K_1''
0.00125	$2.3 \cdot 10^{-4}$	$9.75 \cdot 10^{-3}$	$1.02 \cdot 10^{-3}$	23.5
0.00250	$4.4 \cdot 10^{-4}$	$9.60 \cdot 10^{-3}$	$2.06 \cdot 10^{-3}$	22.3
0.00375	$6.5 \cdot 10^{-4}$	$9.4 \cdot 10^{-3}$	$3.10 \cdot 10^{-3}$	22.3
0.00500	$8.5 \cdot 10^{-4}$	$9.2 \cdot 10^{-3}$	$4.15 \cdot 10^{-3}$	22.2
	$8.6 \cdot 10^{-4}$	$9.2 \cdot 10^{-3}$	$4.14 \cdot 10^{-3}$	22.5
0.00625	$1.05 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$	$5.20 \cdot 10^{-3}$	22.5
0.00750	$1.1 \cdot 10^{-3}$	$8.8 \cdot 10^{-3}$	$6.18 \cdot 10^{-3}$	20.2
	$1.2 \cdot 10^{-3}$	$8.8 \cdot 10^{-3}$	$6.08 \cdot 10^{-3}$	22.4
0.0125	$1.75 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$	20.9
	$1.8 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$	21.5
	$1.8 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	$1.02 \cdot 10^{-2}$	21.5
0.0250	$3.05 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$1.93 \cdot 10^{-2}$	22.6
0.0375	$4.05 \cdot 10^{-3}$	$6.0 \cdot 10^{-3}$	$2.77 \cdot 10^{-2}$	24.4
0.0500	$4.65 \cdot 10^{-3}$	$5.3 \cdot 10^{-3}$	$3.56 \cdot 10^{-2}$	24.6
0.0625	$5.55 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	$4.21 \cdot 10^{-2}$	
0.0750	$6.6 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$4.82 \cdot 10^{-2}$	
			Moyenne 22.4 ± 1.2 $(M)^{-1}$	

TABLEAU VI

DISTRIBUTION DE L'ACIDE NITRIQUE 10^{-2} N ENTRE LE TOPO EN SOLUTION DANS LE BENZÈNE ET LE $NaNO_3$ 2 M

C_o^1 (TOPO) (M)	C_o (HNO_3) (M)	C_a (HNO_3) (M)	K_1''
0.00232	$3.0 \cdot 10^{-4}$	$9.7 \cdot 10^{-3}$	15.3
0.00465	$5.5 \cdot 10^{-4}$	$9.4 \cdot 10^{-3}$	14.3
0.00697	$8.0 \cdot 10^{-4}$	$9.2 \cdot 10^{-3}$	14.1
0.00900	$1.1 \cdot 10^{-3}$	$9.1 \cdot 10^{-3}$	15.3
0.00929	$1.0 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$	13.4
0.0180	$1.95 \cdot 10^{-3}$	$8.1 \cdot 10^{-3}$	15.1
0.0196	$2.00 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	14.4
0.0270	$2.85 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$	16.4
0.0279	$3.0 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	17.0
0.0360	$3.4 \cdot 10^{-3}$	$6.6 \cdot 10^{-3}$	15.6
0.0720	$5.5 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$	17.5
0.108	$6.3 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	
0.108	$6.2 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	
		Moyenne 15.3 ± 1.2 $(M)^{-1}$	

trouvé $D_{TBPO} = 11.5$ à 25°, nous avons établi, dans des conditions expérimentales identiques, les valeurs suivantes:

$$D_{THPO} = 1.0 \cdot 10^2; \quad D_{TcHPO} = 0.5 \cdot 10^2; \quad D_{TOPO} > 10^5.$$

Comme il fallait s'y attendre, l'allongement des chaînes hydrocarbonées réduit la perte de réactif en phase aqueuse. De plus, le coefficient de distribution des oxydes d'alkylphosphine croît avec l'augmentation de la concentration en acide nitrique;

dans ces conditions, nous pourrons, en première approximation, négliger la quantité de THPO et de TOPO qui passe dans la phase aqueuse lors des mesures de distribution de HNO_3.

Distribution de l'acide nitrique à force ionique variable

Si nous comparons les courbes de distribution de l'acide nitrique entre l'eau et une solution benzénique de THPO, de TcHPO ou de TOPO et celles obtenues avec le TBPO[1], il apparaît que les phénomènes d'extraction de l'acide sont identiques, c'est-à-dire que nous avons la réaction établie pour le TBPO, à savoir:

$$(H^+)_a + (NO_3^-)_a + (Alk_3PO)_o \rightleftharpoons (Alk_3PO \cdot HNO_3)_o \tag{1}$$

en négligeant l'influence de l'hydratation de l'oxyde d'alkylphosphine.

Si nous admettons que le rapport des coefficients d'activité des substances présentes en phase organique est constant, nous pouvons écrire

$$K_1' = \frac{[Alk_3PO \cdot HNO_3]_o}{a_{HNO_3}\,[Alk_3PO]_o} \tag{2}$$

En utilisant les valeurs de DAVIS ET DE BRUIN[10] pour l'activité de l'acide nitrique, nous avons calculé, pour les différents oxydes d'alkylphosphine, une constante apparente de stabilité K_1'; les valeurs trouvées à 25° valent 17.2 ± 1.0 $(M)^{-2}$ pour le $THPO \cdot HNO_3$, 7.0 ± 0.8 $(M)^{-2}$ pour le $TcHPO \cdot HNO_3$ et 15.2 ± 1.1 $(M)^{-2}$ pour le $TOPO \cdot HNO_3$.

La constante K_1' trouvée pour le complexe $TBPO \cdot HNO_3$ étant de 17.5 ± 1.3 $(M)^{-2}$, nous pouvons conclure que l'allongement des chaînes hydrocarbonées liées au groupement PO provoque une légère diminution du caractère basique. BLAKE *et al.*[3] ont montré, au contraire, pour d'autres composés organophosphorés neutres, que l'allongement des chaînes latérales s'accompagne d'une augmentation de la basicité du PO; ils ajoutent, cependant, que cette influence n'est plus sensible au-delà de 4 carbones.

La valeur comparativement plus faible de la constante apparente de stabilité pour le complexe $TcHPO \cdot HNO_3$ est probablement due à l'intervention de facteurs stériques dont l'importance est déjà apparue lors de la synthèse de ce composé organophosphoré.

Distribution à force ionique constante

Qu'il s'agisse de l'extraction de l'acide nitrique par une solution de TOPO soit dans le *n*-octane, soit dans le benzène, à partir d'une solution aqueuse de force ionique constante (HNO_3 10^{-2} N + $NaNO_3$ 2 M), l'équilibre de distribution de l'acide correspondant à la réaction (1) peut être représenté par l'équation suivante:

$$K_1 = \frac{[TOPO \cdot HNO_3]_o \gamma_2}{a_{HNO_3}\,[TOPO]_o \gamma_1} \tag{3}$$

où γ_1 et γ_2 sont respectivement les coefficients d'activité molaire du TOPO et du $TOPO \cdot HNO_3$ dans la phase organique.

Comme, dans nos conditions expérimentales, le coefficient d'activité de l'acide nitrique peut être considéré comme constant et comme nous connaissons a_{TOPO}, l'activité du TOPO libre dans le *n*-octane déterminée par BAES[9], l'équation (3) peut se mettre sous la forme

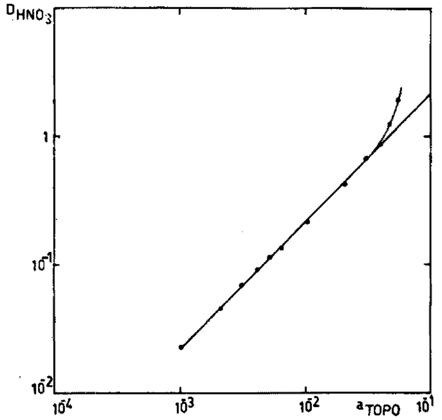
$$K_1{}^* = \frac{[\mathrm{TOPO \cdot HNO_3}]_o \gamma_2}{C_a\,(\mathrm{HNO_3})\, a_{\mathrm{TOPO}}} = \frac{D_{\mathrm{HNO_3}} \gamma_2}{a_{\mathrm{TOPO}}} \tag{4}$$

Dans la Fig. 1, nous avons porté log $D_{\mathrm{HNO_3}}$ en fonction de log a_{TOPO}; nous obtenons une droite de pente unitaire jusqu'à une activité correspondant à une concentration $5 \cdot 10^{-2}\,M$ en TOPO; on peut alors considérer γ_2 comme constant et (4) devient

$$K_1'' = \frac{D_{\mathrm{HNO_3}}}{a_{\mathrm{TOPO}}} \tag{5}$$

La valeur de K_1'' pour le TOPO·HNO$_3$ dans le *n*-octane est de 22.4 ± 1.2 $(M)^{-1}$.

Pour les concentrations supérieures à $5 \cdot 10^{-2}\,M$ en TOPO, on note, sur la Fig. 1, un écart important entre la droite théorique et la courbe expérimentale bien que la concentration en TOPO libre soit de près de 90% de la quantité initiale. Cette déviation que ne peut corriger l'emploi des coefficients d'activité du TOPO doit probablement trouver son explication dans une modification des coefficients d'activité des autres constituants de la phase organique ou dans la formation, aux concentrations plus élevées en TOPO de plusieurs hydrates.



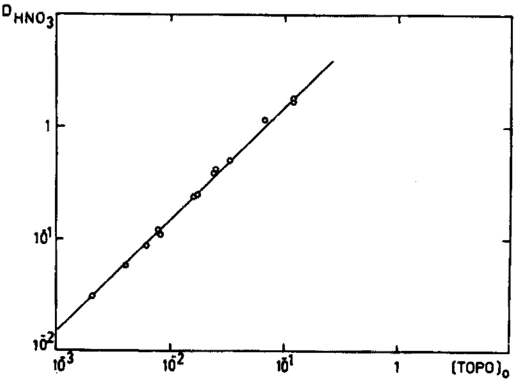


Fig. 1. Distribution de l'acide nitrique entre le TOPO en solution dans le *n*-octane et une phase aqueuse 2 *M* en NaNO$_3$. $C_a{}^i(\mathrm{HNO_3}) = 10^{-2}\,N$.

Fig. 2. Distribution de l'acide nitrique entre le TOPO en solution dans le benzène et une phase aqueuse 2 *M* en NaNO$_3$. $C_a{}^i(\mathrm{HNO_3}) = 10^{-2}\,N$.

Dans le cas des solutions de TOPO dans le benzène, nous ignorons les coefficients d'activité de l'oxyde de tri-*n*-octylphosphine dans la phase organique, aussi sommes-nous amenés à porter en graphique log $D_{\mathrm{HNO_3}}$ en fonction de log $[\mathrm{TOPO}]_o$ (Fig. 2). On peut constater que l'on obtient une droite de pente unitaire jusqu'à une concentration proche de 0.1 *M* sans correction d'activité[11]. Ce fait nous permet de conclure que les solutions de TOPO dans le benzène s'écartent moins rapidement de l'idéalité que les solutions de ce réactif dans les hydrocarbures saturés à chaînes droites. Cette conclusion rejoint celle tirée par ALCOCK *et al.*[12] à propos des solutions de phosphate de tri-*n*-butyle.

La constante K_1'' donnée par l'équation suivante

$$K_1'' = \frac{D_{HNO_3}}{[TOPO]_o} \tag{7}$$

vaut $15.3 \pm 1.2 (M)^{-1}$.

Nous tenons à remercier EURATOM et spécialement le Dr. J. Kooi ainsi que l'Institut Interuniversitaire des Sciences Nucléaires pour les subsides accordés à notre laboratoire. Nous remercions également Mr. F. Gilnay pour son aide technique.

RÉSUMÉ

La distribution de l'acide nitrique entre une phase aqueuse et une phase benzénique de THPO, de TcHPO et de TOPO a été déterminée à 25°. Les constantes apparentes de stabilité K_1' valent respectivement 17.2 ± 1.0 $(M)^{-2}$ pour le THPO·HNO$_3$, 7.0 ± 0.8 $(M)^{-2}$ pour le TcHPO·HNO$_3$ et 15.2 ± 1.1 $(M)^{-2}$ pour le TOPO·HNO$_3$. La stoechiométrie de ce dernier complexe a été confirmée dans le *n*-octane à force ionique constante dans la phase aqueuse.

SUMMARY

The distribution of nitric acid between an aqueous phase and a solution of THPO, TcHPO and TOPO in benzene was measured at 25°. The apparent stability constants K_1' were found to be 17.2 ± 1.0 $(M)^{-2}$ for THPO·HNO$_3$, 7.0 ± 0.8 $(M)^{-2}$ for TcHPO·HNO$_3$ and 15.2 ± 1.1 $(M)^{-2}$ for TOPO·HNO$_3$. The stoichiometry of the last complex was confirmed in *n*-octane solution at constant ionic strength in the aqueous phase.

ZUSAMMENFASSUNG

Die Verteilung von HNO$_3$ zwischen einer wässrigen Phase und einer Lösung von THPO, TcHPO und TOPO in Benzol werde bei 25° untersucht.

Die scheinbaren Stabilitätskonstanten der Komplexen THPO·HNO$_3$ (K_1': 17.2 ± 1.0 $(M)^{-2}$), TcHPO·HNO$_3$ (K_1': 7.0 ± 0.8 $(M)^{-2}$) und TOPO·HNO$_3$ ($K_1' = 15.2 \pm 1.1$ $(M)^{-2}$) wurden bestimmt. Die Stöchiometrie des letzteren Komplexes in *n*-Oktan wurde für eine wässrige Phase konstanter Ionenstärke bestätigt.

BIBLIOGRAPHIE

1 J. Goffart et G. Duyckaerts, *Anal. Chim. Acta*, 36 (1966) 499.
2 K. Issleib et A. Brack, *Z. Anorg. Allgem. Chem.*, 227 (1954) 260.
3 C. A. Blake, K. B. Brown et C. F. Coleman, *U.S. At. Energy Comm. Report ORNL-1964*, 1965.
4 B. Martin, D. W. Ockenden et J. K. Foreman, *J. Inorg. & Nucl. Chem.*, 21 (1961) 96.
5 E. Cerrai et C. Testa, *J. Chromatog.*, 9 (1962) 216.
6 A. H. A. Heyn et Y. D. Soman, *J. Inorg. & Nucl. Chem.*, 26 (1964) 287.
7 E. Cerrai et C. Testa, *Energia Nucl. (Milan)*, 8 (1961) 510.
8 J. J. Richard, K. E. Burke, J. W. O'Laughlin et C. V. Banks, *J. Am. Chem. Soc.*, 83 (1961) 1722.

9 C. F. BAES, *J. Phys. Chem.*, 66 (1962) 1929.
10 W. DAVIS ET H. J. DE BRUIN, *J. Inorg. & Nucl. Chem.*, 26 (1964) 1069.
11 R. A. ZINGARO ET J. C. WHITE, *J. Inorg. & Nucl. Chem.*, 12 (1960) 315.
12 K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY ET H. A. C. MAC KAY, *Trans. Faraday Soc.*, 52 (1956) 39.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DOSAGE DE L'AZOTE DANS LE VANADIUM PAR FUSION REDUCTRICE SOUS VIDE

G. BAUDIN, J. DESREUMAUX ET R. FONTAINE
Département de Chimie, Centre d'Etudes Nucléaires de Fontenay-aux-Roses, Commissariat à l'Energie Atomique (France)

(Reçu le 2 janvier, 1967)

Les propriétés mécaniques du vanadium semblent dépendre notablement de la teneur en gaz contenu dans ce métal.

Le problème initialement posé consistait à suivre l'évolution de la teneur en gaz (oxygène, azote, hydrogène) au cours des cycles de purification de ce métal; par suite, le nombre d'échantillons traités était important. D'autre part, la reproductibilité recherchée était de l'ordre de 5% et l'analyse rapide: la méthode de dosage par fusion réductrice sous vide, répondant à ces caractéristiques a été choisie.

Nous nous proposons de déterminer les meilleures conditions d'utilisation de cette méthode; nous rechercherons d'abord les conditions optimales d'extraction de l'azote, puis nous vérifierons par comparaison avec une autre méthode qu'elles conduisent à des résultats exacts.

Le présent travail a été effectué à l'aide d'un appareil de dosage de gaz opérant par fusion réductrice sous vide, commercialisé par la firme Balzers (Exhalographe E.A. 1). La nécessité d'extraire l'azote à une température supérieure à 1900° (*cf.* p. 541), exclue l'utilisation du dispositif de renouvellement automatique du bain de fusion commercialisé par Balzers, sous sa forme actuelle. Par suite nous définirons dans cette étude les conditions de travail pour l'analyse successive de plusieurs échantillons avec le même bain.

Généralités

En se référant aux travaux de SLOMAN, HARVEY ET KUBASCHEVSKI[1] relatifs au dosage de l'oxygène, de l'azote et de l'hydrogène dans le vanadium, il apparaît que ces déterminations ne présentent pas de difficultés majeures en opérant par fusion sous vide. Ces auteurs travaillent avec le fer comme bain de fusion et préconisent une température de 1560°. L'extraction est rapide (de l'ordre de 5 min). Toutefois, ils attirent l'attention sur le fait que, la volatilité du vanadium étant appréciable, il faut limiter sa concentration dans le bain à 20% en poids. La carburation excessive d'un bain de fer[2] après quelques heures d'utilisation, et l'augmentation de la viscosité qui en résulte, lui font préférer souvent un bain de platine.

C'est ainsi que KAMIN, O'LAUGHLIN ET BANKS[3] utilisent un bain de platine pour la détermination de l'oxygène dans le vanadium. Il faut toutefois noter que, dans ce travail, ces derniers auteurs opèrent par extraction sous gaz inerte (hélium) et non par extraction sous vide. Ils parviennent à établir que, dans ces conditions, l'extraction de l'oxygène est totale à condition que le rapport de la masse de platine au bain à la masse de vanadium soit supérieur à 2.

Pour le dosage de l'azote dans le vanadium, EVERETT[3] opère par fusion sous vide en bain de platine à 1900°. Avec une masse de platine de 3.5 g et des échantillons de 50 mg, il peut analyser successivement jusqu'à 12 échantillons (c'est-à-dire que les rapports Pt/V varient de 70 à 6). La limite de détection est alors de 1 p.p.m. Dans le présent travail nous choisirons un bain de platine.

PARTIE EXPÉRIMENTALE

Appareillage

Le processus de dosage avec "l'Exhalographe" comporte 3 phases: (*a*) Fusion de l'échantillon dans le bain, (*b*) extraction et transfert des composés gazeux, (*c*) analyse des gaz extraits.

On réalise la fusion sous vide du métal en introduisant l'échantillon par l'intermédiaire d'un sas dans un bain métallique fondu contenu dans un creuset de graphite. L'oxygène est extrait sous forme d'oxyde de carbone, l'azote et l'hydrogène à l'état d'éléments.

Le transfert des gaz extraits est assuré, d'abord par une pompe à diffusion d'huile à grande vitesse de pompage, puis par une pompe collectrice mécanique qui comprime les gaz extraits dans un volume connu. Un dispositif électrique permet d'enregistrer automatiquement la quantité totale de gaz extraits en fonction du temps d'extraction.

L'analyse se fait en plusieurs temps. Tout d'abord, une jauge à conductibilité thermique permet, après étalonnage, de déterminer la quantité d'hydrogène présente dans le mélange. Ensuite une cellule mesure par absorption des rayons infrarouges la quantité d'oxyde de carbone. L'azote est obtenu par différence. La reproductibilité des mesures est d'environ 10%.

Premiers essais

Les séries de dosages effectués dans des conditions analogues à celles décrites par EVERETT (fusion réductrice sous vide à 1900° en bain de platine) nous ont donné des résultats présentant entre eux des écarts importants, les valeurs peuvent différer d'un facteur 3; 300 et 1000 p.p.m. pour des échantillons d'un métal réputé homogène.

Notre appareil permettant l'enregistrement direct de la quantité totale de gaz extraits à tout moment nous avons cherché à expliquer les écarts constatés en étudiant la reproductibilité de cette extraction sur une série d'echantillons dans les conditions décrites ci-dessus.

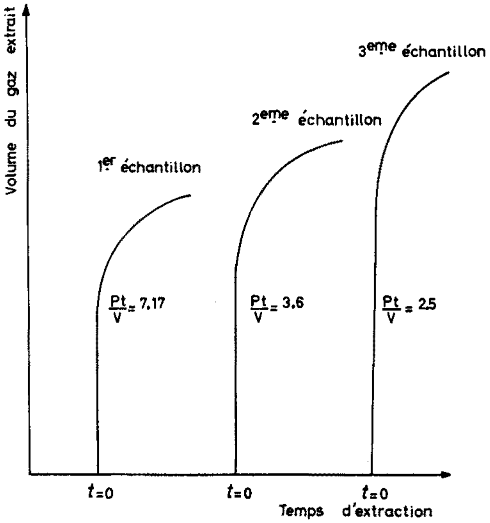
Dans une masse de platine (1.78 g) fondue initialement dans le creuset et maintenue à 1900° on introduit successivement 3 échantillons de 250 mg provenant d'un même lingot.

Les courbes de la Fig. 1 montrent l'évolution de l'extraction pour chacun des 3 échantillons.

Au fur et à mesure que l'on ajoute du vanadium dans le bain de platine initialement mis en jeu, on constate 2 phénomènes distincts: d'une part, la quantité totale de gaz extrait varie, d'autre part, la cinétique de l'extraction évolue.

L'analyse des gaz extraits nous montre que dans les 3 essais, les quantités d'oxygène et d'hydrogène dosés restent sensiblement constantes, seule la quantité d'azote extrait par échantillon augmente avec l'ordre d'introduction.

L'extraction de l'azote n'est certainement pas totale pour l'essai 1 et vraisemblablement pas pour les essais 2 et 3. On peut toutefois envisager une rétention d'azote dans le bain fondu, gaz qui serait libéré (en partie ou en totalité) lors de l'introduction d'un nouvel échantillon auquel on attribuerait l'azote relatif aux échantillons précédents. Au cours de cette manipulation seul le rapport R = masse de platine/masse de vanadium varie:



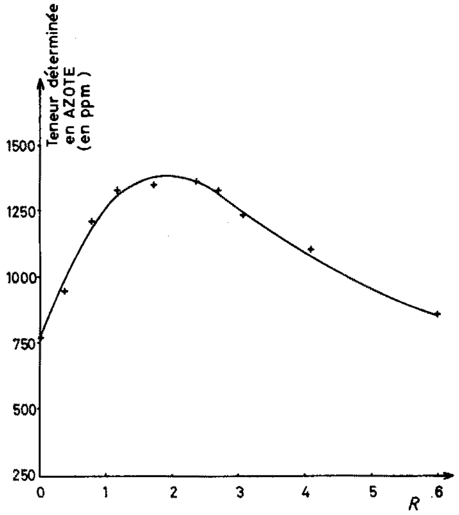


Fig. 1. Variation de la quantité de gaz extraite en fonction du nombre d'échantillons ajoutés dans le bain.

Fig. 2. Variation de la quantité d'azote déterminée en fonction du rapport R = masse de platine/masse de vanadium.

en effet, pour l'essai 1, $R = 7.2$
en effet, pour l'essai 2, $R = 3.6$
en effet, pour l'essai 3, $R = 2.5$

Il apparaît donc que ce rapport R joue un rôle important. De plus, l'augmentation de la quantité de gaz extrait pour une diminution de R va à l'encontre des résultats trouvés pour le dosage des gaz dans d'autres métaux pour lesquels, à partir d'une certaine valeur de R, la quantité de gaz extrait est constante.

Etude de la quantité d'azote déterminée dans le vanadium pour différentes valeurs du rapport R

Pour étudier la variation de la teneur trouvée en azote dans un échantillon de vanadium en fonction du rapport R = masse de platine/masse de vanadium, un certain nombre de précautions doivent être observées.

En particulier, si pour certaines valeurs de R, on a rétention de l'azote par le bain, il faut éviter de l'extraire lors de l'introduction de l'échantillon suivant et de l'attribuer à ce dernier.

On procède donc à des additions alternées de vanadium et de platine. Avant chaque introduction de vanadium, on dégaze soigneusement le four et on effectue un essai à blanc.

On effectue également un dosage des gaz extraits lors de chaque addition de platine. Ceci permet de vérifier que la modification du bain résultant de cette addition n'entraine pas une extraction complémentaire de gaz provenant de l'échantillon de vanadium précédent.

Nous avons adopté les conditions opératoires suivantes:

Température d'extraction: 1900°*

Temps d'extraction: 5 min

Cycle d'opérations: dans un creuset dégazé, introduction initiale du premier échantillon de vanadium (en absence de platine), fournissant la valeur pour $R=0$, puis introductions successives de masses de platine et de vanadium.

Tous les échantillons utilisés pour cette étude ont été refondus 5 fois en vue d'obtenir une bonne homogénéité.

Résultats obtenus. La courbe tracée à l'aide des valeurs obtenues (Fig. 2) présente un maximum. La valeur de R maximale R_m est sensiblement égale à 2. Toutefois, les variations de quantité de gaz extraits sont suffisamment faibles, pour les valeurs de R comprises entre 1.5 et 2.5 pour que, compte tenu de la précision des méthodes de mesure, les valeurs obtenues ne soient pas considérées comme significativement différentes.

En opérant avec des additions de platine telles que le rapport R reste voisin de 2, il est possible de procéder à l'analyse de séries d'échantillons (jusqu'à 20) sans changer le creuset de graphite.

Les résultats obtenus sont alors très reproductibles et on n'enregistre pas d'évolution sensible du bain. Toutefois, après un chauffage de plusieurs heures (entre 4 et 5 h), et surtout après un refroidissement et rechauffage du bain, la cinétique d'extraction diminue notablement ce qui entraine une erreur dans le résultat si les analyses sont effectuées à temps constant.

Etude de l'influence de la température sur l'extraction de l'azote

La courbe de la Fig. 1 correspond à des valeurs obtenues à partir d'expériences réalisées à 1900°. Or, la valeur maximale de la quantité d'azote extraite peut être variable selon la température. Pour étudier l'influence de ce facteur nous avons effectué une nouvelle série d'essais sans modifier les paramètres autres que la température.

Les valeurs de température choisies sont: (*a*) 1800° et (*b*) 1850°.

La valeur de 1900° étant la température maximale admissible pour l'appareil utilisé pour les essais qui précèdent, on pratique une série d'essais similaires sur un autre appareil à 2200° mais en procédant par extraction sous gaz inerte**. Les résultats obtenus permettent de tracer un réseau de courbes (Fig. 3) représentant l'évolution de la quantité d'azote dosée en fonction de R, pour diverses températures. L'élévation de température entraine 3 conséquences:

---

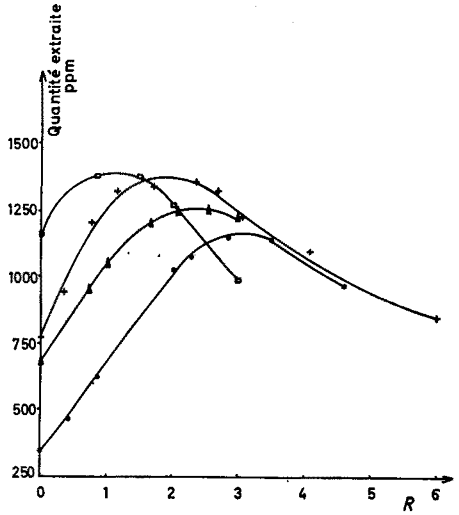
* Mesuré avec un pyromètre optique.

** Essai réalisé avec un appareil du type NITROX 6 commercialisé par la firme LECO.

(*1*) La quantité d'azote extraite est plus importante pour un temps donné,

(*2*) à partir de 1900° une élévation de température n'entraine plus d'augmentation de la quantité de gaz extrait pour la valeur de R_m,

(*3*) les valeurs de R_m diminuent à mesure que la température croît.



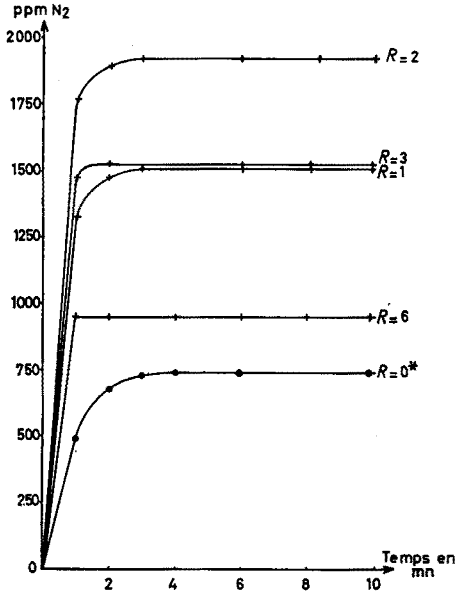


Fig. 3. Variation de la quantité d'azote déterminée en fonction de rapport *R* à diverses températures. (○) 1800°, (▲) 1850°, (+) 1900°, (□) 2200°.

Fig. 4. Cinétique d'extraction de l'azote à 1900° pour diverse valeur de *R*.

On peut donc conclure qu'en opérant à une température d'au moins 1900° en fixant le rapport *R* à une valeur comprise entre 1.5 et 2.5 on obtient les valeurs maximales pour la teneur en azote déterminée par la méthode de fusion sous vide.

D'autre part, dans ces conditions opératoires on obtient une bonne reproductibilité du résultat.

Influence de la durée d'extraction sur la quantité d'azote extraite

Les résultats précédents ont été obtenus avec un temps total d'extraction fixé à 5 min en accord avec les travaux de SLOMAN *et al.*[1].

Il est intéressant de vérifier: (*1*) qu'une extraction prolongée ne conduit pas à une augmentation de la quantité d'azote dosée, ni à un déplacement du maximum R_m.

(*2*) que le temps de 5 min ne peut être diminué pour des raisons de rendement de l'appareillage.

Nous avons effectué cette vérification dans les conditions opératoires suivantes:

Température d'extraction: 1900°.

Rapport *R* croissant suivant les valeurs: 0, 1, 2, 3, 6.

Mesure de la teneur déterminée en azote pour les durées d'extraction de 1, 2, 3, 4, 6 et 10 min.

On a trouvé les résultats groupés dans le Tableau I pour un échantillon homogène (différent de l'échantillon correspondant aux courbes 1 et 2).

TABLEAU I

TENEUR TROUVÉE (AZOTE EN p.p.m. PONDÉRALE)

R	*Durée d'extraction (min)*					
	1	2	3	4	6	10
Creuset neuf	490	680	730	730	730	730
1	1270	1460	1520	1520	1520	1520
2	1770	1890	1920	1920	1920	1920
3	1480	1530	1530	1530	1530	1530
6	960	960	960	960	960	960

Ces valeurs ont permis de tracer un réseau de courbes (Fig. 4). Ces courbes montrent que, en travaillant avec des bains de fusion correspondant aux valeurs de $R = R_{\mathrm{m}}$, en 4 min, la quantité d'azote est maximale. Ce dernier essai légitime les valeurs trouvées pour la teneur en azote dans les essais précédents pour lesquels on avait pris 5 min comme durée d'extraction.

ETUDE DU RÉSULTAT

Comparaison avec une autre méthode de dosage

Il faut encore vérifier que dans ces conditions la totalité de l'azote est extraite. En raison de l'absence d'étalons de teneurs connues avec exactitude, la méthode de vérification choisie n'est que relative puisqu'elle consiste à comparer les résultats de fusion sous vide avec ceux obtenus sur des échantillons de même provenance par la méthode de Kjeldahl. Le principe de cette méthode est totalement différent: par

TABLEAU II

COMPARAISON DE MÉTHODES

Echantillons	*No. de l'essai*	*Teneur en azote (p.p.m.)*	
		Fusion sous vide	*Méthode Kjeldahl*
VK2A	1	220±20[a]	280±30
	2	120±20[b]	
V 244 A	1	590±60	730±70
	2	610±60	650±70
V 221 D	1	810±80	860±20
	2	890±90	1060±100
V 221 B	1	980±100	1030±100
	2	1050±100	1120±110
V 100 B	1	1160±120	1180±120
	2	1090±110	
V 64 E	1	1400±140	1450±150
	2	1350±140	

[a] Voir plus loin le calcul de précision.

[b] Valeur très probablement aberrante qu'aucune explication ne permet d'éliminer.

suite on diminue dans la comparaison les risques d'erreurs systématiques. Le Tableau II montre les résultats obtenus.

Les résultats obtenus par la méthode de Kjeldahl sont en moyenne légèrement supérieurs. Néanmoins, pour un domaine variant de 200 à 1400 p.p.m. on peut admettre, compte tenu de la reproductibilité des 2 méthodes, que les résultats sont en bon accord, et que, en raison du gain de temps que permet la méthode de fusion sous vide, cette dernière peut être avantageusement utilisée pour le dosage de l'azote dans le vanadium.

Reproductibilité des résultats

L'étude effectuée précédemment nous a conduit à adopter les conditions opératoires suivantes:

Rapport Pt/V: $1.7 < \mathrm{Pt/V} < 2.3$.
Température: 1950°.
Temps d'extraction: 5 min.

L'étude de la reproductibilité de la méthode effectuée par exemple sur 13 déterminations successives a donné les résultats suivants: 1340, 1460, 1350, 1330, 1330, 1390, 1510, 1320, 1400, 1350, 1370, 1330, 1350; soit:

une valeur moyenne: $\bar{x} = 1372$ p.p.m.

$$\text{un écart type } \sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}} = \pm 56.55$$

$$\text{écart moyen } \sigma_{\mathrm{m}} = \frac{\sigma}{\sqrt{n}} = 15.75$$

La valeur moyenne vraie* a 95% de chances de se trouver dans les limites $\bar{x} \pm \sigma_{\mathrm{m}} t$ soit 1372 ± 35 p.p.m.

L'erreur relative est donc:

$$100\sigma_{\mathrm{m}} t/x = 2.6\%$$

Cette reproductibilité a été confirmée pour une série de 15 échantillons analysés 2 fois.

Recherche d'une interprétation des résultats

Nous avons vu que, suivant la valeur du rapport *R*, la cinétique de l'extraction et la quantité totale d'azote extraite variaient notablement. Il apparaît donc une corrélation entre la cinétique d'extraction et le résultat de l'analyse. Dans une revue très complète[5] des travaux publiés sur l'analyse de l'azote dans les métaux, GOWARD consacre un chapitre à l'analyse par fusion sous vide. S'appuyant sur les travaux de SLOMAN *et al.*[1] il distingue plusieurs processus possibles pour l'extraction de l'azote:

(*a*) dissociation thermique du nitrure

$$\mathrm{MN_{solide}} \rightarrow \mathrm{M_{liquide}} + \tfrac{1}{2}\,\mathrm{N_2}$$

(*b*) dissociation thermique du nitrure et dissolution du métal dans le bain liquide

$$\mathrm{MN_{solide}} \rightarrow (\mathrm{M})_{\mathrm{Pt}} + \tfrac{1}{2}\,\mathrm{N_2}$$

---

* Au sens "statique" du terme.

(*c*) réaction du nitrure avec le carbone pour donner l'azote et le carbure métallique

$$MN_{\text{solide}} + C_{\text{solide}} \rightarrow MC_{\text{solide}} + \tfrac{1}{2}\, N_2$$

Mais l'auteur mentionne qu'en raison des quantités relativement importantes d'azote que les métaux étudiés (Mo, Si, V, Zr) peuvent dissoudre, il n'est pas réaliste de baser le mécanisme d'extraction de l'azote sur la décomposition des nitrures.

Cette remarque nous laisse entrevoir la possibilité de plusieurs mécanismes différents pour l'extraction de l'azote en fonction de la valeur de *R*.

EL TAYEB ET PARLEE[6] montrent que pour les alliages fer–vanadium la solubilité de l'azote est fonction de la teneur en vanadium. Pour des teneurs en vanadium dépassant une valeur limite on observe alors une précipitation d'un nitrure de vanadium VN.

Si cette hypothèse est vérifiée, on pourrait envisager un phénomène analogue dans le cas du bain de platine–vanadium, qui expliquerait une diminution de la quantité d'azote extraite lorsque les valeurs de *R* sont faibles.

Nous avons entrepris une série d'études micrographiques en vue d'essayer de déterminer, après trempe de différents bains correspondant à des valeurs de *R* croissantes, s'il est possible de préciser la forme sous laquelle l'azote est fixé. Malheureusement la présence de précipité de carbure rend difficile l'exploitation des micrographies. En l'absence de connaissance sur le diagramme Pt/V/N nous ne voyons pas d'explication sur la diminution de la quantité d'azote extraite pour les valeurs élevées de *R*.

Conclusion

L'étude précédente montre que le dosage de l'azote dans le vanadium par fusion sous vide en bain de platine, donne des résultats bien reproductibles à condition d'opérer avec un rapport platine/vanadium voisin de 2. La température d'extraction doit être égale ou supérieure à 1900°. Les résultats obtenus concordent alors avec ceux donnés par la méthode Kjeldahl, ainsi qu'avec quelques premiers essais effectués en fusion oxydante.

Cette étude expérimentale définit les meilleures conditions d'application de la méthode de fusion réductrice sous vide au dosage de l'azote dans le vanadium en bain statique. Nous n'avons pu expliquer les raisons des variations de quantité d'azote extraite en particulier la diminution pour les valeurs élevées de *R* qu'éclaircirait peut-être la connaissance des diagrammes Pt/C/V, Pt/V/N et C/V/N que nous n'avons pas trouvés dans la littérature.

Du point de vue pratique notons que les conditions (valeur du rapport *R*) étant différentes de celles imposées par le dosage de l'oxygène (*R* égal ou supérieur à 5), il paraît impossible de déterminer simultanément l'oxygène et l'azote dans les meilleures conditions pour chacun des éléments.

RÉSUMÉ

L'étude des conditions de dosage de l'azote dans le vanadium par la méthode de fusion réductrice sous vide en bain de platine a montré que: (*1*) la quantité d'azote extraite variait avec le rapport *R* des masses de platine et de vanadium; et (*2*) la

quantité extraite passait par une valeur maximale pour une valeur de R variable avec la température. Opérant avec une valeur de R voisine de 2 et une température d'extraction supérieure à 1900°, les résultats concordent avec les valeurs obtenues par la méthode Kjeldahl, la reproductibilité étant de 2 à 3%.

SUMMARY

A study of the conditions for the determination of nitrogen in vanadium by vacuum fusion in a platinum bath has shown that (*a*) the amount of nitrogen extracted depends on the ratio (R) of the weights of platinum and vanadium, and (*b*) the amount extracted passes through a maximum value for a particular R value depending on the temperature. With R values of *ca.* 2 and extraction temperatures above 1900°, results were in reasonable agreement with those obtained by the Kjeldahl method, the reproducibility being 2–3%.

ZUSAMMENFASSUNG

Eine Untersuchung der Bedingungen für die Bestimmung des Stickstoffs in Vanadin mittels Vakuumschmelzen in Platin zeigte, dass (a) die Menge des extrahierten Stickstoffs von dem Gewichtsverhältnis R zwischen Platin und Vanadin abhängt und (b) die für einen bestimmten R-Wert extrahierte Menge ein Maximum durchläuft, das von der Temperatur abhängt. Bei R-Werten von etwa 2 und Extraktionstemperaturen oberhalb 1900° stimmen die Werte mit denen überein, die mit der Kjeldahl-Methode erhalten wurden. Die Reproduzierbarkeit beträgt 2–3%.

BIBLIOGRAPHIE

1 H. A. SLOMAN, C. A. HARVEY ET O. KUBASCHEVSKI, *J. Inst. Metals*, 80 (1952) 391.
2 W. H. SMITH, *Anal. Chem.*, 27 (1955) 1636.
3 G. J. KAMIN, J. W. O'LAUGHLIN ET C. V. BANKS, *Anal. Chem.*, 35 (1963) 1053.
4 M. R. EVERETT, *Analyst*, 83 (1958) 321.
5 G. W. GOWARD, *Anal. Chem.*, 37 (1965) 117R.
6 N. M. EL TAYEB ET N. PARLEE, *Trans. AIME*, 227 (1963) 929.
7 E. A. GULBRANSEN ET K. F. ANDREW, *J. Electrochem. Soc.*, 97 (1950) 396.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands .

EXTRACTION OF COBALT(II) FROM AQUEOUS THIOCYANATE SOLUTIONS BY TRI-*n*-OCTYLAMINE

HIROTO WATANABE AND KUNIHIKO AKATSUKA
Department of Industrial Chemistry, The Muroran Institute of Technology, Muroran, Hokkaido (Japan)

(Received October 27th, 1966)

Cobalt(II) ions form a pink-colored thiocyanate complex which can be extracted as a blue complex with amines and ammonium salts such as tri-iso-octylamine, tricaprylmethylammonium thiocyanate and tetradecyldimethylbenzylammonium chloride dissolved in various diluents[1-5]. It is generally accepted that the cobalt(II) species thus extracted is the tetrathiocyanate complex of cobalt(II) ion[1,2]. The present investigation was undertaken to obtain further information about the extraction behavior of cobalt(II) by tri-*n*-octylamine dissolved in various diluents. The stoichiometry of the extracted species was also studied by measuring the cobalt(II) to amine loading ratio and the effect of amine concentration on the extractability of cobalt(II) ion.

EXPERIMENTAL

Apparatus

An Iwaki-V-S Shaking Unit was employed to carry out the equilibration. A Hitachi Model-139 Spectrophotometer was used to determine the concentration of cobalt(II) spectrophotometrically.

Reagents

All the reagents used were of analytical grade, and were further purified, if necessary. Tri-*n*-octylamine (from Kao Soap Co., Ltd.) was converted almost quantitatively to the thiocyanate form by equilibrating the amine solution (0.1 or 0.2 *M*) with a 0.25 *N* thiocyanic acid solution. Then, the organic phase was separated and diluted to cover the concentration range studied. The amine concentration was accurately determined by measuring the concentration of thiocyanate in tri-*n*-octylammonium thiocyanate (0.1 and 0.2 *M*) by the Volhard method after back-extraction with a 0.1 *N* sodium hydroxide solution.

Thiocyanic acid was prepared from ammonium thiocyanate by ion exchange using Amberlite IR-120 (H^+ form)[6,7], and a trace of iron(III) in the acid solutions was removed by extraction with small amounts of the amine solutions. A stock solution of cobalt(II) thiocyanate was prepared by treating Amberlite IR-120 in the cobalt(II) form with a thiocyanic acid solution. The solutions described above were prepared daily before use.

Diluents and their dielectric constants in Debye units were as follows: *n*-hexane

(1.9), cyclohexane (2.0), xylene, benzene (2.3), carbon tetrachloride (2.2), chloroform (5.0), *o*-dichlorobenzene (9.9), chlorobenzene (5.9) and nitrobenzene (36.1). The xylene used in the present investigation was a mixture of 3 isomers, and, therefore, the dielectric constant is not given.

Procedure

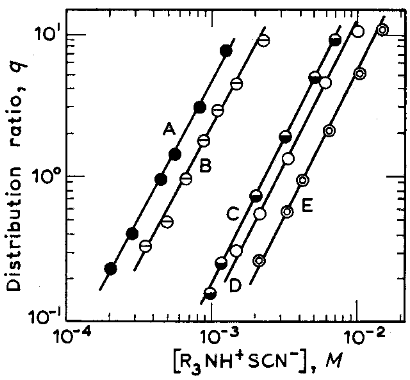
For all operations, 25 ml each of tri-*n*-octylammonium thiocyanate solution and cobalt(II) thicyanate solution were mixed together in 100-ml glass separatory funnels and equilibrated at room temperature. Equilibration between two phases was accomplished very rapidly. A 2-min shaking period at a rate of 120 strokes per min was more than adequate. After standing for 5 min, the aqueous phase was filtered through paper to remove entrained organic phase. The cobalt(II) concentration in an aliquot of the aqueous phase was determined either spectrophotometrically with 4-(2-pyridylazo)resorcinol[8] or compleximetrically with pyrocatechol violet as an indicator. The concentration of thiocyanate ion was determined in another aliquot by the Volhard method. The final acidity of the aqueous solution was either 0.1 or 0.2 *N* in thiocyanic acid. The amount of cobalt(II) in the organic phase was calculated by material balance.

RESULTS

The effect of amine concentration on the distribution ratio of cobalt(II) between both phases was examined at fixed concentrations of cobalt(II) and thiocyanic acid. The distribution ratio is defined as the total concentration of cobalt(II) in the organic phase divided by that in the aqueous phase,

$$q = \Sigma(\mathrm{Co})_o / \Sigma(\mathrm{Co})_w \qquad (1)$$

Figures 1 and 2 summarize the results with various diluents. It can be seen that there



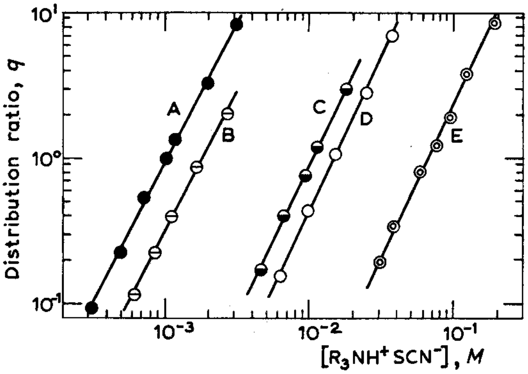


Fig. 1. Extraction of cobalt from 0.1 *N* thiocyanic acid solution by tri-*n*-octylamine. (A) *n*-hexane (thiocyanic acid concn., $9.6 \cdot 10^{-2}$ *N*, total cobalt concn., $1.88 \cdot 10^{-5}$ *M*), (B) cyclohexane ($1.07 \cdot 10^{-1}$, $1.86 \cdot 10^{-5}$), (C) xylene ($1.11 \cdot 10^{-1}$, $1.86 \cdot 10^{-5}$), (D) carbon tetrachloride ($1.03 \cdot 10^{-1}$, $1.81 \cdot 10^{-5}$), (E) benzene ($1.03 \cdot 10^{-1}$, $2.22 \cdot 10^{-5}$).

Fig. 2. Extraction of cobalt from 0.2 *N* thiocyanic acid solution by tri-*n*-octylamine. (A) nitrobenzene (thiocyanic acid concn., $2.34 \cdot 10^{-1}$ *N*, total cobalt concn., $2.00 \cdot 10^{-5}$ *M*), (B) xylene ($2.40 \cdot 10^{-1}$, $1.82 \cdot 10^{-5}$), (C) monochlorobenzene ($2.43 \cdot 10^{-1}$, $2.22 \cdot 10^{-5}$), (D) *o*-dichlorobenzene ($2.33 \cdot 10^{-1}$, $2.22 \cdot 10^{-5}$), (E) chloroform ($2.35 \cdot 10^{-1}$, $6.41 \cdot 10^{-5}$).

is a close relationship between the extractability of the amine and the dielectric constant of the diluent, and that the distribution ratio is a function of the concentration of amine. This tendency agrees with results obtained in a previous study[9] dealing with the extraction of iron(III) from thiocyanate media by tri-*n*-octylamine dissolved in various diluents.

To determine the stoichiometry of the organic cobalt(II) species by the so-called limiting loading method (extraction isotherm)[10], extractions were made by varying the initial aqueous concentration of cobalt(II) at a fixed concentration of the amine ($5 \cdot 10^{-3}$ *M*) dissolved in xylene and nitrobenzene. The results (Figs. 3 and 4) indicate a limiting cobalt(II) to amine mole ratio of 1 to 2.

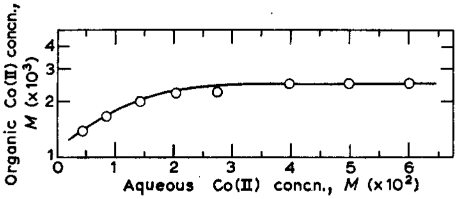


Fig. 3. Cobalt extraction isotherm; $5.1 \cdot 10^{-3}$ *M* tri-*n*-octylamine in xylene, $2.40 \cdot 10^{-1}$ *N* thiocyanic acid in aqueous phase.

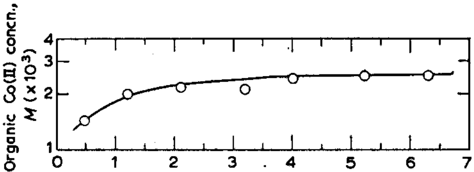


Fig. 4. Cobalt extraction isotherm; $5.0 \cdot 10^{-3}$ *M* tri-*n*-octylamine in nitrobenzene, $2.31 \cdot 10^{-1}$ *N* thiocyanic acid in aqueous phase.

DISCUSSION

The extraction of the excess thiocyanic acid by tri-*n*-octylamine can be assumed to be negligibly small at any strength of acid used in the present study, since the extraction of the excess acid occurs generally only at extremely high concentrations[11,12]. Thus the reaction between the amine in various diluents and thiocyanic acid can be written as:

$$R_3N + H^+ + SCN^- \rightleftharpoons R_3NH^+SCN^- \qquad (2)$$

where R_3N refers to the tri-*n*-octylamine and $R_3NH^+SCN^-$ indicates its ammonium salt form. As is generally the case, the following two different mechanisms may be postulated to explain the extraction behavior of cobalt(II) ion[13].

(*a*) The extraction of a neutral cobalt(II) thiocyanate forming a further complex with tri-*n*-octylammonium thiocyanate in an organic phase.

(*b*) An anion exchange of thiocyanate ion in the organic phase with an anionic cobalt(II) thiocyanate species already formed in the aqueous phase. As far as measurable net results are concerned, these 2 sets of mechanisms are equivalent.

As for extraction mechanism (*a*), the extracted species should be $Co(SCN)_2$*, which then associates various numbers of monomeric tri-*n*-octylammonium thiocyanate ion pairs to form a more complex ion pair,

$$m\ R_3NH^+SCN^- + Co(SCN)_2 \rightleftharpoons (R_3NH^+)_m Co(SCN)_{2+m}^{m-} \qquad (3)$$

The equilibrium constant K_m is given by

---

* Aquo groups have been omitted for simplicity.

$$K_m = [(R_3NH^+)_mCo(SCN)_{2+m}^{m-}]J/[R_3NH^+SCN^-]^m[Co(SCN)_2] = K_m'J \qquad (4)$$

where the quantities in brackets represent the concentration of each species in moles per liter and J symbolizes the corresponding activity coefficient quotient. If the activity coefficient of each species in both phases is kept essentially unchanged throughout the experiments and the predominant cobalt(II) species in the organic phase is $(R_3NH^+)_jCo(SCN)_{2+j}$, where j is a fixed number of m, then the distribution ratio, q, may be expressed in terms of the equilibrium quotient K_j':

$$q = \beta_3K_j'[SCN^-]^m[R_3NH^+SCN^-]^m/(1 + \sum_{n=1}^{N}\beta_n[SCN^-]^n) \qquad (5)$$

where n is the number of ligands associated with cobalt(II) ion in each aqueous species present and β_n denotes their respective cumulative formation constants. Differentiation of the logarithmic form of eqn. (5) with respect to $\log[R_3NH^+SCN^-]$ gives

$$(\partial \log q/\partial \log [R_3NH^+SCN^-])_{SCN^-} = j \text{ or}$$

$$\log q = j \log [R_3NH^+SCN^-] + C \qquad (6)$$

where C is a constant. Equation (6) shows that, if the ligand concentration is kept constant, a linear relationship exists between $\log q$ and $\log[R_3NH^+SCN^-]$ and the slope gives the number of amine molecules combined with cobalt(II) thiocyanate complex in the organic phase. For the extraction mechanism (*b*), a similar relationship is derived between $\log q$ and $\log[R_3NH^+SCN^-]$ and the slope has the same meaning as j. As shown in Figs. 1 and 2, log–log plots of q *vs.* $[R_3NH^+SCN^-]$ for the different diluents at a fixed concentration of the aqueous thiocyanic acid yield straight lines whose slopes are nearly 2. This indicates that the species of cobalt(II) thiocyanate with an amine–cobalt(II) ratio of two is predominant in the organic phase.

In eqn. (6), $[R_3NH^+SCN^-]$ denotes the equilibrium concentration. As the total concentration of cobalt(II) is of the order of $10^{-5}\,M$, and the analytical concentration of the tri-*n*-octylammonium thiocyanate is very large, the latter is assumed to be kept unchanged throughout the extraction of cobalt(II) into the organic phase. The same applies to the equilibrium concentrations of thiocyanate ion. Analytical concentrations of thiocyanate ion in the aqueous phase are 0.1 and 0.2 N, and are large enough compared to the total concentrations of cobalt(II).

Provided that various species are extracted simultaneously in the extraction mechanism (*a*), q is given by

$$q = \sum_{m=1}^{M}[(R_3NH^+)_mCo(SCN)_{2+m}]/[Co^{2+}]\left(1 + \sum_{n=1}^{N}\beta_n[SCN^-]^n\right) \qquad (7)$$

Rearrangement of eqn. (7) in terms of K_m' gives

$$q = \beta_3[SCN^-]^3\left(\sum_{m=1}^{M}K_m'[R_3NH^+SCN^-]^m\right)\Big/\left(1 + \sum_{n=1}^{N}\beta_n[SCN^-]^n\right) \qquad (8)$$

This equation shows that the linear relationship of $\log q$ to $\log[R_3NH^+SCN^-]$ would not be expected if coextraction occurs appreciably. For other cases, for instance, if mechanisms (*a*) and (*b*) occur simultaneously, a similar relationship to eqn. (8) can be derived. The experimental results, however, indicate the presence of linear relationships between log q and log[$R_3NH^+SCN^-$) and the validity of the assumption that only one extractable species predominates in the organic phase. Although the validity of the assumption, *i.e.*, the presence of monomeric species of tri-*n*-octylammonium thiocyanate, was not examined in the present study, this assumption seems to be valid for dilute solution since it has been reported by some workers that the monobasic strong acid salt form of tri-*n*-octylamine is monomeric in dilute solutions[14–17].

The results in Figs. 1 and 2 are confirmed by the presence of the extraction isotherms shown in Figs. 3 and 4. The loading numbers (equivalents of amine per mole of cobalt(II) in organic phase) calculated from the plateau height in Figs. 3 and 4 indicate two equivalents of amine per mole of cobalt(II) in xylene and nitrobenzene and presumably in other diluents. Finally, it is concluded that the blue-colored species extracted with tri-*n*-octylamine dissolved in various diluents is binegatively charged and hence the complete formula is bis(tri-*n*-octylammonium)tetrathiocyanatocobaltate(II).

The effects of diluent on the extractability of cobalt(II) with tri-*n*-octylamine are also shown in Figs. 1 and 2. These figures indicate that the extractability of cobalt(II) is correlated approximately with the dielectric constant of the diluent, with the exception of nitrobenzene (whose extracting power is comparable to that of cyclohexane) and chloroform. Thus, the smaller the value of the dielectric constant, the larger the extractability. No explanation can be given for the effect of chloroform in the present investigation. Pure nitrobenzene has an abnormally larger extracting power for thiocyanic acid compared to other diluents, and this abnormality seems responsible for the irregular order shown in Figs. 1 and 2; when equal volumes of 0.25 N thiocyanic acid solution and pure diluent saturated with water are equilibrated, the acid concentrations in organic phase determined volumetrically are of the order of $5 \cdot 10^{-3}$ N for nitrobenzene and below 10^{-4} N for other diluents. Further, it was shown clearly that no cobalt(II) can be extracted into pure diluents from thiocyanic acid solutions.

A comparison of the present results with other results on extractions of iron(III)[9] showed that in the thiocyanate–amine extraction system, the effects of diluent are exactly identical for iron(III) and cobalt(II).

Special thanks are due to Professor MASAYO MUROZUMI of the Muroran Institute of Technology for his sustained interest and encouragement and for reading and criticizing the manuscript.

SUMMARY

The distribution of cobalt(II) between acidic thiocyanate solutions and tri-*n*-octylamine dissolved in various diluents has been measured for several cobalt(II) loadings and amine concentrations. Diluents investigated included *n*-hexane, cyclohexane, benzene, xylene, carbon tetrachloride, chloroform, chlorobenzene, *o*-dichlorobenzene and nitrobenzene. In all cases, the species extracted is bis(tri-*n*-octylammonium)tetrathiocyanatocobaltate(II). The ability of each diluent to extract cobalt(II) from acidic thiocyanate solutions is approximately correlated with the dielectric constant of the pure diluent, *i.e.*, the smaller the dielectric constant, the larger the distribution ratio, with the exceptions of nitrobenzene and chloroform.

RÉSUMÉ

On a effectué une étude sur l'extraction du cobalt à partir de solutions aqueuses de thiocyanate, au moyen de tri-*n*-octylamine. Divers solvants ont été examinés: n-hexane, cyclohexane, benzène, xylène, tétrachlorure de carbone, chloroforme, chlorobenzène, *o*-dichlorobenzène et nitrobenzène. L'aptitude du solvant à extraire le cobalt dans ces conditions dépend de sa constante diélectrique; plus elle est petite plus le coefficient de partage est grand, à l'exception du nitrobenzène et du chloroforme.

ZUSAMMENFASSUNG

Es wird die Verteilung des Kobalt(II) bestimmt zwischen thiocyansauren Lösungen und Tri-n-octylamin, gelöst in verschiedenen Verdünnungsmitteln, und zwar in Abhängigkeit von der Kobalt(II)- und der Amin-Konzentration. Folgende Verdünnungsmittel wurden untersucht: n-Hexan, Cyclohexan, Benzol, Xylol, Tetrachlorkohlenstoff, Chloroform, Chlorbenzol, *o*-Dichlorbenzol und Nitrobenzol. In allen Fällen wird Bis(tri-n-Octylammonium)tetrathiocyanatokobaltat(II) extrahiert. Die Fähigkeit eines jeden Verdünnungsmittels, Kobalt(II) zu extrahieren, hängt mit Ausnahme von Nitrobenzol und Chloroform näherungsweise mit der Dielektrizitätskonstanten des reinen Verdünnungsmittels zusammen: je kleiner die Dielektrizitätskonstante desto grösser der Verteilungskoeffizient.

REFERENCES

1 A. R. Selmer-Olsen, *Anal. Chim. Acta*, 31 (1964) 33.
2 H. Matsuo, S. Chaki and S. Hara, *Japan Analyst*, 14 (1965) 935.
3 A. M. Wilson and O. K. McFarland, *Anal. Chem.*, 35 (1963) 302.
4 A. W. Ashbrook, *Analyst*, 84 (1959) 177.
5 M. Fujimoto and Y. Nakatsukasa, *Anal. Chim. Acta*, 27 (1962).
6 M. Fujimoto, *Japan Analyst*, 2 (1953) 360.
7 M. Fujimoto, *Bull. Chem. Soc. Japan*, 26 (1953) 353.
8 Y. Shijo and T. Takeuchi, *Japan Analyst*, 13 (1964) 536.
9 H. Watanabe and M. Murozumi, to be published.
10 K. A. Allen, *J. Am. Chem. Soc.*, 80 (1958) 4133.
11 F. Baroncelli, G. Scibona and M. Zifferero, *J. Inorg. & Nucl. Chem.*, 24 (1962) 405.
12 A. S. Wilson and N. A. Wogman, *J. Phys. Chem.*, 66 (1962) 1552.
13 Y. Marcus, *Chem. Rev.*, 63 (1963) 139.
14 L. Newman and P. Klotz, *J. Phys. Chem.*, 65 (1961) 796.
15 J. M. White, P. Kelly and N. C. Li, *J. Inorg. & Nucl. Chem.*, 16 (1961) 337.
16 J. M. P. J. Verstegen, *J. Inorg. & Nucl. Chem.*, 26 (1964) 1085.
17 A. D. Nelson, J. L. Fascing and R. L. McDonald, *J. Inorg. & Nucl. Chem.*, 27 (1965) 439.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POLAROGRAPHIC BEHAVIOR OF URANIUM(VI) IN MALONIC ACID MEDIA

DETERMINATION OF URANIUM IN PLUTONIUM*

C. E. PLOCK AND F. J. MINER
Chemistry–Physics Research and Development, The Dow Chemical Company, Rocky Flats Division, Golden, Colo. (U.S.A.)

(Received December 12th, 1966)

Polarographic methods are widely used for the determination of uranium[1,2]. It is known that uranium forms a malonate complex and from the information available[3], further investigation of this complex appeared to be warranted to determine if the uranium–malonate complex could be used for analytical purposes.

Some malonate complexes have been investigated polarographically. SCHAPP *et al.*[4] studied the iron–malonate complexes. The association constant of the copper–malonate complex was also determined by polarography[5]. While the present study was in progress, LAI AND HSIEH[6] investigated the polarography of the uranium–malonate complex with an electrolyte consisting of sodium perchlorate and 0.1 *M* malonic acid. Their results, obtained in a slightly different medium, do not always agree with the results obtained in our work. The reason for these differences is not always apparent. No attempt is made in this report to indicate where these differences exist or to attempt to explain the reasons for them.

EXPERIMENTAL

Apparatus

All polarograms were obtained using a calibrated Sargent Model XV recording polarograph. For the analysis of solutions of low uranium concentration ($2.0 \cdot 10^{-5}$ to $2.0 \cdot 10^{-4}$ *M*), a Sargent Micro Range Extender was used as an accessory. The electrolysis cell was a two-piece, H-form cell which contained a saturated calomel electrode. The sample compartment was connected to the saturated calomel electrode by means of an agar-saturated potassium chloride bridge. A Sargent constant head dropping mercury electrode assembly was used. None of the polarographic measurements were damped.

Two capillaries were used to obtain all measurements. The first capillary had a value of 1.48 for $m^{2/3}t^{1/6}$ and the second 1.72. Both $m^{2/3}t^{1/6}$ values were obtained in the calibration supporting electrolyte at -0.300 V *vs.* saturated calomel electrode.

A Davis Differential Cathode Ray Polarotrace, Type A-1660 (Southern Analytical Ltd., Camberley, England) was used to test the reversibility of the reduction of the uranium–malonate complex.

---

* Work performed under U. S. Atomic Energy Commission Contract AT(29-1)-1106.

The pH values of the solutions were measured using a Beckman Model 76 Expanded Scale pH meter and a glass electrode. The pH was adjusted with hydrochloric acid or sodium hydroxide.

The spectrophotometric data were obtained with a Cary Recording Spectrophotometer Model 14.

Reagents

Stock solutions of uranyl chloride were prepared from standard sample 950a, U_3O_8 (U. S. National Bureau of Standards).

Disodium malonate stock solutions were prepared from the monohydrate salt (Matheson, Coleman, and Bell) and the stock solutions of sodium hydrogen malonate were prepared by neutralizing malonic acid (Eastman Organic Chemicals) with the proper quantity of sodium hydroxide.

All other reagents were analytical grade and were prepared in the normal manner.

Safety precautions

Extreme care must be exercised in the handling of plutonium because of its toxicity. All work with plutonium metal was performed in a glove box. The solutions containing plutonium were analyzed polarographically in a well-ventilated hood.

BEHAVIOR OF URANIUM(VI) MALONATE

Effect of pH

The effects of changes in acidity on the half-wave potential and on the diffusion current of the uranium–malonate complex were determined in solutions $2.00 \cdot 10^{-3}$ *M* in uranium, 0.5 *M* in disodium malonate, and 0.5 *M* in sodium hydrogen malonate. The lowest value (pH 1.1) in the pH range investigated was selected because the half-wave potential of uranium at this pH is nearly the same as the half-wave potential of uranium without malonate present. Above the highest pH investigated (pH 6.5), uranium begins to precipitate.

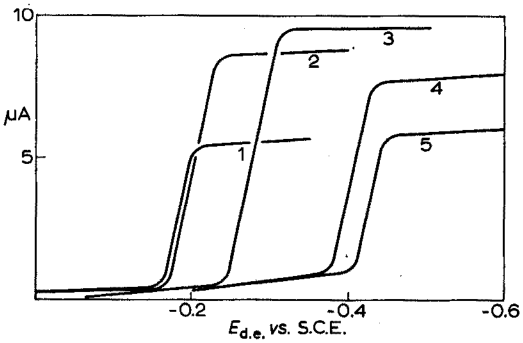


Fig. 1. Typical polarograms. $2.00 \cdot 10^{-3}$ *M* uranium, 0.5 *M* $Na_2C_3H_2O_4$, 0.5 *M* $NaHC_3H_2O_4$. (1) (no malonate present) at pH 2.50, (2) at pH 1.10, (3) at pH 2.50, (4) at pH 4.45, (5) at pH 5.55.

Traces of typical polarograms are shown in Fig. 1. Note the difference between polarograms 1 and 3. The two polarograms were obtained from solutions having the same concentration of uranium and the same pH. The only difference was that solution 1 contained no malonate whereas solution 3 was 1 *M* in malonate. The shift in half-wave potential from -0.18 to -0.29 V *vs.* S.C.E. was caused by the formation of a uranium–malonate complex.

The effect of pH on the formation of the uranium malonate complex is indicated by polarograms 2 and 3. At low pH there is very little complex formation as indicated by the very small shift in the half-wave potential (0.020 V) between polarogram 1, with no malonate, and polarogram 2. This small amount of complexation is due to the very low concentration of free malonate ion at pH 1.10. Based on ionization calculations, the free malonate concentration at pH 1.10 is $3 \cdot 10^{-4}$ *M* while at pH 2.50, this has increased to 0.2 *M*.

The influence of the pH on half-wave potential is also apparent if half-wave potential values are plotted against pH. The plot can be divided into straight-line portions, corresponding to the pH regions 1.0–3.3, 3.3–4.8 and 4.8–6.5. In the pH range 1.0–3.3, the plot is a straight line and the shift of the half-wave potential with change of pH may be represented by the equation:

$$E_{\frac{1}{2}} = -0.104 - 0.081 \text{ pH}$$

In the pH range 3.3–4.8, the plot is again a straight line and the shift of the half-wave potential with change of pH may be represented by the equation:

$$E_{\frac{1}{2}} = -0.250 - 0.037 \text{ pH}$$

In the pH range 4.8–6.5, the slope of the curve is approximately zero which indicates that above 4.8 the half-wave potential is not a function of pH.

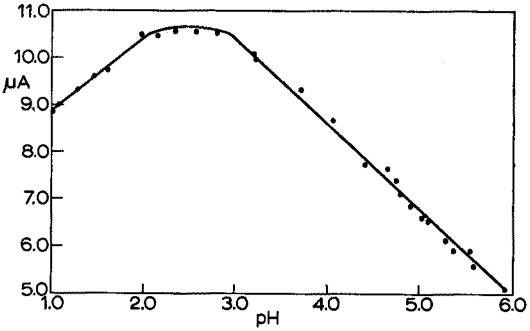


Fig. 2. Variation of diffusion current with pH. $2.00 \cdot 10^{-3}$ *M* uranium, 0.5 *M* $Na_2C_3H_2O_4$, 0.5 *M* $NaHC_3H_2O_4$.

Figure 2 shows the variation of the diffusion current with pH. At pH 2.0–3.0 the diffusion current is constant, but at pH 1.0–2.0 the diffusion current increases with an increase of pH. The increase in diffusion current is interpreted as an increase in the rate of disproportionation of uranium(V)[7].

It has been established by HARRIS AND KOLTHOFF that uranium(VI) is reduced to uranium(V) at the dropping mercury electrode[8], and that uranium(V) will disproportionate, giving uranium(IV) and uranium(VI)[7]. Moreover, the rate of disproportionation increases on addition of a complex-forming ion[7].

The ratio[7] of the concentration of uranium(IV) to the concentration of uranium(V) is shown in Table I. As the free malonate concentration increases with the increase of pH, so does the diffusion current increase, indicating that the rate of disproportionation of uranium(V) has increased. The increase in the rate of disproportionation is also shown by the fact that the ratio of the concentration of uranium(IV) to the concentration of uranium(V) approaches infinity.

TABLE I

EFFECT OF pH ON DIFFUSION CURRENT AND ON THE U(IV)–U(V) CONCENTRATION RATIO
($2.00 \cdot 10^{-3}$ *M* U; 0.5 *M* $Na_2C_3H_2O_4$; 0.5 *M* $NaHC_3H_2O_4$)

pH	i_d (*μA*)	*U(IV)/U(V) concentration*	*pH*	i_d (*μA*)	*U(IV)/U(V) concentration*
1.00	8.80	2.74	2.97	10.38	$\rightarrow\infty$
1.10	8.98	3.31	3.70	9.62	8.41
1.25	9.25	4.58	4.11	8.67	2.41
1.46	9.56	7.47	4.70	7.68	1.05
1.61	9.70	10.0	5.02	6.53	0.40
2.00	10.38	$\rightarrow\infty$	5.36	5.96	0.21
2.43	10.42	$\rightarrow\infty$	5.88	5.14	0.01

Above pH 3.0 the diffusion current decreases with the increase of pH which would indicate that there is a lessening of the complexation of the uranium with the malonate owing to the competition with hydroxyl ions. The ratio of the concentration of uranium(IV) to the concentration of uranium(V) decreases to less than one (Table I) indicating that the uranium(V) becomes stable with respect to disproportionation. It is also in this pH region that the half-wave potential ceases to be a function of pH.

Reversibility

The reversibility of the electrode reaction was judged from the plots of log $i/(i_d - i)$ *versus* $E_{d.e.}$, the temperature coefficient, and a study of the polarograms obtained with the Davis Differential Cathode Ray Polarotrace. The slopes of the plots at pH 4.9 or greater were -0.057 V which is in good agreement with the theoretical value of -0.059 V for a one-electron reduction; and the temperature coefficient of the half-wave potential and the diffusion current were determined to be -0.48 mV per degree and 1.69% per degree, respectively. These values compare well with the theoretical values of ± 2 mV per degree and $< 2\%$ per degree for a reversible electrode reduction. Excellent peaks were obtained in both the forward and reverse sweeps when the Polarotrace was used to polarograph uranium malonate solutions with a pH greater than 4.9, indicating that the reduction is reversible.

The effect of the height of the mercury column on the diffusion current was determined, and $i_d/h^{1/2}$ was found to have a value of 0.720 ± 0.014.

These results indicate that the electrode reduction is one-electron, reversible and diffusion-controlled at pH 4.9 or greater.

The value of the slopes for the plots of log $i/(i_d - i)$ *versus* $E_{d.e.}$ ranged from -0.045 to -0.048 V for a series of polarograms when the pH of the solutions was less than 4.9. An excellent peak was obtained using the forward sweep of the Polarotrace to polarograph a uranium malonate solution. However, no peak was obtained when the reverse sweep was used; only the trace of an irreversible reaction appeared, as described by DAVIS AND SHALGOSKY[9]. The temperature coefficient of the half-wave potential and the diffusion current were found to be −0.20 mV per degree and 2.94% per degree, respectively. The effect of the mercury pressure on the diffusion current was also determined, and the value for $i_d/h^{1/2}$ was calculated as 1.26 ± 0.02. In a further attempt to determine the electrode reduction at pH values less than 4.9, a comparison of the uranium(IV)–uranium(III) reduction was made with the uranium(VI) reduction. The ratio of the diffusion current was 1.62. These data, therefore, indicate the electrode reduction to be diffusion-controlled and one-electron with disproportionation of uranium(V). The disproportionation would explain the intermediate values obtained for the slopes of the log plots of log $i/(i_d - i)$ *versus* $E_{d.e.}$ and also explains the intermediate "*n*" value obtained when the uranium(IV)–uranium(III) reduction was compared with the uranium(VI) reduction.

As shown in Table I, in the pH range 2.0–3.0, the ratio of the concentration of uranium(IV) to the concentration of uranium(V) approaches infinity which indicates that the disproportionation of uranium(V) is nearly instantaneous. Nearly instantaneous disproportionation indicates the electrode reaction is a pseudo-uranium(VI)–uranium(IV) reduction. The reduction of uranium(V) to uranium(IV) involves the breaking of oxygen bonds, which produces an irreversible reaction. The Differential Cathode Ray Polarotrace indicated that the reaction of the uranium(VI) malonate was irreversible at pH 2.0–3.0, and this can be explained by the pseudo-uranium(VI)–uranium(IV) reduction.

Effect of malonate concentration

The effect of the malonate concentration on the half-wave potential and on the ratio of the concentration of uranium(IV) to the concentration of uranium(V) was investigated by varying the concentration of the malonate and keeping the concentration of the uranium constant at $2.0 \cdot 10^{-3}$ *M*. The pH of the solutions was 2.50 ± 0.15. The plot of the logarithm of the malonate concentration *versus* the half-wave potential gave 3 straight lines (Fig. 3). The sections of the plot which correspond to the malonate concentration ranges of $1.0 \cdot 10^{-3}$ to $1.0 \cdot 10^{-2}$ *M* and 0.1 to 1.0 *M* had slopes approximately equal to zero which indicates that the half-wave

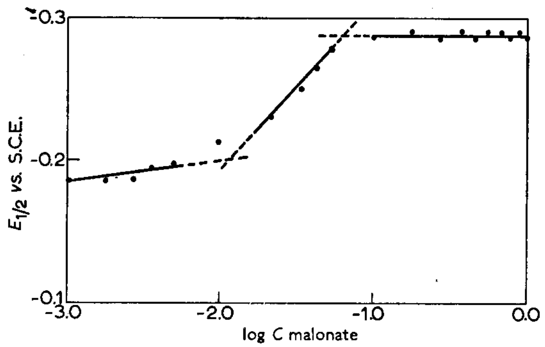


Fig. 3. Variation of half-wave potential with malonate concentration. $2.00 \cdot 10^{-3}$ *M* uranium, pH 2.50 ± 0.15.

potential is independent of the malonate concentration in these concentration ranges. The slope of the plot in the malonate concentration range $1.0 \cdot 10^{-2}$ to 0.1 M indicates that here the half-wave potential is a function of the malonate concentration.

Table II shows the increase of the ratio of the concentration of uranium(IV) to the concentration of uranium(V). As the concentration of the malonate increases, so does the ratio which indicates that the rate of disproportionation of uranium(V) increases with the increase of malonate concentration. KOLTHOFF AND HARRIS also experienced an increase in the rate of disproportionation of uranium(V) when they increased the concentration of oxalic acid[7].

TABLE II

EFFECT OF VARYING MALONATE CONCENTRATION ON THE HALF-WAVE POTENTIAL AND ON U(IV)–U(V) CONCENTRATION RATIO ($2.00 \cdot 10^{-3}$ M U at pH 2.50)

Malonate concentration (M)	$E_{\frac{1}{2}}$	*U(IV)/U(V) concentration*	*Malonate concentration (M)*	$E_{\frac{1}{2}}$	*U(IV)/U(V) concentration*
None	−0.180	0.38	0.1	−0.288	6.15
$1 \cdot 10^{-3}$	−0.187	0.40	0.2	−0.291	$\rightarrow\infty$
$2 \cdot 10^{-3}$	−0.189	0.43	0.3	−0.290	$\rightarrow\infty$
$3 \cdot 10^{-3}$	−0.192	0.45	0.4	−0.293	$\rightarrow\infty$
$4 \cdot 10^{-3}$	−0.196	0.46	0.5	−0.292	$\rightarrow\infty$
$5 \cdot 10^{-3}$	−0.198	0.47	0.6	−0.293	$\rightarrow\infty$
$1 \cdot 10^{-2}$	−0.216	0.58	0.7	−0.293	$\rightarrow\infty$
$2 \cdot 10^{-2}$	−0.229	0.98	0.8	−0.291	$\rightarrow\infty$
$3 \cdot 10^{-2}$	−0.246	1.39	0.9	−0.292	$\rightarrow\infty$
$4 \cdot 10^{-2}$	−0.265	1.99	1.0	−0.290	$\rightarrow\infty$
$5 \cdot 10^{-2}$	−0.278	3.40			

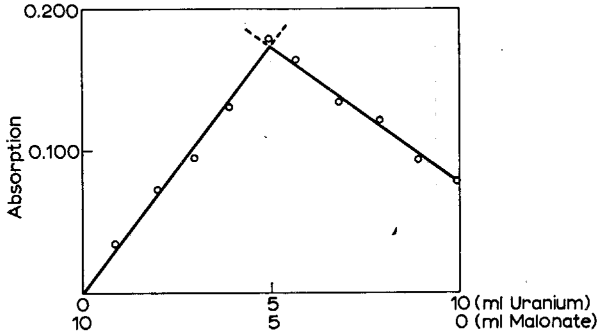


Fig. 4. Variation of absorption with malonate concentration. $2.00 \cdot 10^{-2}$ M uranium, $2.0 \cdot 10^{-2}$ M $Na_2C_3H_2O_4$, pH 2.50±0.15.

When the concentration of the malonate is low, $1.0 \cdot 10^{-2}$ M or less, the ratio of the concentration of uranium(IV) to the concentration of uranium(V) is less than one indicating that the uranium(V) may be regarded as stable with respect to disproportionation. However, at malonate concentrations greater than $1.0 \cdot 10^{-2}$ M, the ratio of the concentration of uranium(IV) to the concentration of uranium(V) increases until the ratio approaches infinity near malonate concentrations of 0.2 M.

Composition of uranium(VI) malonate complex

The composition of uranium(VI) malonate complex was determined by the method of continuous variations[10,11]. Spectrophotometric measurements were made with varying mixtures of $2.0 \cdot 10^{-3}$ *M* solutions of disodium malonate and uranium. The pH of the solutions was adjusted to 2.50. An examination of the spectra indicated that the complex had a peak at 418 nm. The plot of the optical density *versus* the malonate–uranium ratio was found to increase linearly to a mole ratio of 1:1, indicating a 1:1 complex (Fig. 4).

DETERMINATION OF URANIUM IN PLUTONIUM

Procedure for sample preparation

The plutonium metal sample (1 g or less) is weighed directly into a tared 50-ml volumetric flask. The metal is dissolved by adding 5 ml of 6 *M* hydrochloric acid; then 3 ml of nitric acid are added, and the solution is evaporated to dryness on a hot plate. To the still warm crystals, 10 ml of 5 *M* hydroxylamine hydrochloride are cautiously added, followed by 7.5 ml of 6 *M* hydrochloric acid. The solution is warmed on a hot plate for 10 min. The hydroxylamine hydrochloride is added to reduce the plutonium to plutonium(III). After cooling, the solution is made 0.5 *M* in disodium malonate and 0.5 *M* in sodium hydrogen malonate by slowly adding these reagents with continuous swirling of the volumetric flask. The solution is diluted to volume with water. The pH of the solution is 2.5. A portion is transferred to the electrolysis cell where oxygen is removed by bubbling nitrogen through the solution for 10 min.

Calibration procedure

A calibration curve for uranium was prepared by pipetting the proper aliquot of the standard uranium stock solution into a 50-ml volumetric flask. These solutions were analyzed in the same way as discussed above except that the hydroxylamine hydrochloride was omitted. Uranium solutions of 10 different concentrations were prepared, and 4 polarograms were recorded for each concentration.

It can be seen from Table III that the diffusion current is proportional to the

TABLE III

DIFFUSION CURRENT AS A FUNCTION OF THE URANIUM(VI) CONCENTRATION

UO_2^{2+} concn. (C) (M)	*i_d (μA)*	*i_d/C (μA/mM)*	*Rel. Std. Dev.*
$2.00 \cdot 10^{-5}$	0.0826	4.13	1.09
$4.00 \cdot 10^{-5}$	0.164	4.10	1.04
$6.00 \cdot 10^{-5}$	0.246	4.10	0.66
$8.00 \cdot 10^{-5}$	0.329	4.11	0.58
$1.20 \cdot 10^{-4}$	0.490	4.08	0.59
$2.00 \cdot 10^{-4}$	0.811	4.06	1.09
$4.00 \cdot 10^{-4}$	1.63	4.08	0.25
$8.00 \cdot 10^{-4}$	3.32	4.15	0.22
$2.00 \cdot 10^{-3}$	8.31	4.15	0.46
$4.00 \cdot 10^{-3}$	16.8	4.20	0.27

concentration of uranium at pH 2.5 in a 1 *M* malonate solution. The average relative standard deviation of the diffusion current quotient[12], i_d/C, for all concentrations was 1.22%.

Reliability of the method

The reliability of the method was determined by analyzing standard uranium solutions, by investigating the effect of impurities, and by analyzing plutonium solutions containing known amounts of uranium.

Analysis of standard uranium solutions

Ten standard uranium solutions covering the range 11.9–1190.0 µg UO_2^{2+}/ml, were analyzed as described above. The average percent recovery for these 10 solutions was 99.8%, and the relative standard deviation of the percent recovery was ±0.97%.

Investigation of impurities

Impurities that are found in plutonium metal were investigated to determine what effect they might have on the determination of uranium. The results are shown in Table IV. It was found that antimony, chromium, copper, iron, lead, nickel, and titanium interfere. Chromium and nickel interfere if the ratio of the ion to uranium is greater than 2.1 and 5.3, respectively, and copper, iron, lead, and antimony interfere if these ion ratios to uranium are greater than 0.011, 0.11, 0.21, and 0.011, respectively. Titanium was found to interfere when only trace amounts were present.

TABLE IV

INVESTIGATION OF IMPURITIES

Ion added	*Weight ratio ion/U*	*Recovery of UO_2^{2+}(%)*
Ag	0.053	[a]
Al	5.3	[a]
B	0.21	[a]
Ba	0.21	[a]
Ca	0.36	[a]
Cd	0.11	[a]
Cr	8.4	93
	2.1	[a]
Cu	0.53	135
	0.011	[a]
Fe	8.4	68
	0.11	[a]
Ga	1.6	[a]
K	0.26	[a]
Mg	2.1	[a]
Mn	0.32	[a]
Mo	0.42	[a]
Ni	10.5	96
	5.3	[a]
Pb	2.1	84
	0.21	[a]
Sb	0.11	118
	0.011	[a]
Sn	0.095	[a]
Sr	0.084	[a]
Ti	1.1	Ill-defined wave
	0.0053	93
	0.0025	96
Zn	1.1	[a]

[a] Error $< \pm 2\%$.

Each of the above impurities was removed completely by mercury cathode electrolysis except antimony and titanium. The antimony is only partially removed. The ratio of antimony to uranium can be sufficiently lowered, however, to eliminate the antimony interference. A semi-micro electrolysis cell[13] proved convenient for removing the interfering metal impurities. If mercury cathode electrolysis is required, perchloric acid should be used to adjust the pH in place of hydrochloric acid.

Titanium can be separated from uranium by the use of Dowex-1 (200–300 mesh) anion-exchange resin[14,15]. Uranium remains on the column while titanium passes through.

Recovery of uranium in the presence of plutonium

The effect of plutonium on the polarographic determination of uranium in a malonate supporting electrolyte was determined by spiking plutonium solutions with standard uranium solutions. The concentration of the uranium in the plutonium solutions ranged from $2.0 \cdot 10^{-5}$–$2.0 \cdot 10^{-3}$ M and the plutonium solutions contained 8–20 g Pu/l. These solutions were analyzed as given for the sample preparation procedure. The average percent recovery was 98.8% with a recovery ranging from 96.5 to 100.3%.

In the usual methods for dissolving plutonium metal, uranium is not oxidized to uranium(VI), the oxidation state required for polarographic analysis. Nitric acid was investigated to determine if it would effect this oxidation in the presence of plutonium.

TABLE V

RECOVERY OF URANIUM IN THE PRESENCE OF PLUTONIUM USING REDUCED SOLUTIONS OF URANIUM
(Plutonium concentration range: 8 to 20 g/l)

Number of polarograms	*Concn. UO_2^{2+} (µg/ml)*		*Recovery of UO_2^{2+} (%)*
	Present	*Found*	
2	95.2	95.0	99.8
2	190.0	189.0	98.3
2	286.0	280.0	97.9
6	476.0	477.0	100.3

Twelve plutonium solutions were spiked with standard uranium which had been reduced by a Jones reductor, and were polarographed. The concentrations of the uranium in the plutonium solutions ranged from $4.0 \cdot 10^{-4}$ to $2.0 \cdot 10^{-3}$ M (Table V). The average percent recovery was 99.3% with a recovery ranging from 97.9 to 100.3%. The use of nitric acid to oxidize the uranium is incorporated in the procedure given above.

The authors are grateful to G. A. SHEPHERD for his help in obtaining the spectrophotometric data.

SUMMARY

The polarographic behavior of the uranium–malonate complex was investigated over the pH range 1.1–6.5. A reversible, one-electron wave was obtained. Below pH 4.9, the rate of disproportionation is nearly instantaneous and gives rise to a pseudo uranium(VI)–uranium(IV) reduction. Above pH 4.8 the concentration of uranium(V) is stable with respect to disproportionation. The half-wave potential is pH-dependent below pH 4.9, but it is independent of the malonate concentration above 0.1 M. The diffusion current constant is 2.78 for the conditions described. A procedure for the determination of uranium in plutonium was developed for uranium concentrations greater than 225 p.p.m. Of 21 common impurities found in plutonium metal, only Cu, Fe, Pb, Sb and Ti cause significant interference; titanium can be removed by ion exchange, and the other interferences by mercury cathode electrolysis.

RÉSUMÉ

On a étudié le comportement polarographique du malonate d'uranium complexe à des pH variant de 1.1 à 6.5. On obtient une vague réversible à un électron. Le potentiel $E_{\frac{1}{2}}$ varie avec le pH, en dessous de 4.9; mais il est indépendant de la concentration en malonate au-dessus de 0.1 M. Dans les conditions décrites, la constante du courant de diffusion est de 2.78. On propose une méthode de dosage de l'uranium (>225 p.p.m.) dans le plutonium. Parmi 21 impuretés courantes du plutonium métal, seuls Cu, Fe, Pb, Sb et Ti gênent. Le titane peut être éliminé par échangeur d'ions et les autres métaux par électrolyse sur cathode de mercure.

ZUSAMMENFASSUNG

Das polarographische Verhalten des Uranmalonat-Komplexes wurde im pH-Bereich von 1.1–6.5 untersucht. Eine reversible Einelektronen-Stufe wurde erhalten. Unterhalb des pH 4.9 erfolgt die Disproportionierung nahezu sofort und ergibt den Anstieg einer U(VI)–U(IV)-Pseudoreduktion. Oberhalb des pH 4.8 ist die Konzentration des Uran(V) im Bezug auf die Disproportionierung beständig. Das Halbstufenpotential ist unterhalb des pH 4.9 pH-abhängig, jedoch oberhalb einer Malonatkonzentration von 0.1 M pH-unabhängig. Die Diffusionsstrom-Konstante beträgt unter diesen Bedingungen 2.78. Für Urankonzentrationen >225 p.p.m. wurde ein Verfahren für die Bestimmung des Urans in Plutonium entwickelt. Von 21 im Plutoniummetall vorkommenden Verunreinigungen verursachen nur Cu, Fe, Pb, Sb und Ti ernsthafte Störungen. Titan kann durch Ionenaustausch abgetrennt werden; die anderen Störungen durch Elektrolyse an einer Quecksilberkathode.

REFERENCES

1 *Bibliography of Polarographic Literature*, E. H. Sargent and Co., 1956.
2 G. L. Booman and J. E. Rein, in I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Vol. 9, Part II, Interscience, New York, 1962, p. 115.
3 E. J. Breda, L. Meites, T. B. Reddy and P. W. West, *Anal. Chim. Acta*, 14 (1956) 390.
4 W. B. Schapp, H. A. Laitinen and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 76 (1954) 5868.
5 E. Gelles and G. H. Nancollas, *J. Chem. Soc.*, (1956) 4847.
6 T. T. Lai and C. C. Hsieh, *J. Inorg. & Nucl. Chem.*, 26 (1964) 1215.
7 I. M. Kolthoff and W. E. Harris, *J. Am. Chem. Soc.*, 68 (1946) 1175.
8 W. E. Harris and I. M. Kolthoff, *J. Am. Chem. Soc.*, 67 (1945) 1484.
9 H. M. Davis and H. I. Shalgosky, *J. Polarog. Soc.*, 6 (1960) 12.
10 P. Job, *Ann. Chim. (Paris)*, 9 (1928) 113.
11 W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, 63 (1941) 437.
12 I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd Edn., Interscience, New York, 1952, p. 377.
13 T. M. Florence, *Anal. Chim. Acta*, 21 (1959) 418.
14 K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, 58 (1954) 11.
15 K. A. Kraus, F. Nelson and G. E. Moore, *J. Am. Chem. Soc.*, 77 (1955) 3972.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CHARACTERIZATION OF LINEAR POLYURETHANES

J. L. MULDER
Central Research Institute of AKU (Algemene Kunstzijde Unie n.v.) and affiliated Companies, Arnhem (The Netherlands)

(Received December 14th, 1966)

The poly-addition reaction between di- or triisocyanates and compounds with 2 or more hydroxyl groups leads to the formation of polymers with the urethane group, –NHCOO– in the chain:

$$n\ \mathrm{OCN{-}R{-}NCO} + n\ \mathrm{HO{-}R'{-}OH} \rightarrow (\mathrm{{-}OCNH{\cdot}R{\cdot}NHCOO{\cdot}R'{\cdot}O{-}})_n$$

Depending on the type of starting materials and on the ratio in which they are used, more or less branched polymers are formed with a large field of application. When the reacting compounds are both bifunctional, the resulting linear polyurethanes may be used for the production of synthetic fibres, the qualitative analysis of which is described below.

Starting products for this type of polyurethane are on the one hand aliphatic or aromatic diisocyanates, and on the other hand bifunctional hydroxyl compounds. The latter may be classified as:

(*a*) diols, HO–R–OR, in which R may be either linear or branched;

(*b*) polyesters such as diols and aliphatic or aromatic dicarboxylic acids with terminal OH-groups: $\mathrm{HO{\cdot}R{\cdot}O(OC{\cdot}R{\cdot}COO{\cdot}R'{\cdot}O)_nH}$, or polyesters based on ω-hydroxy acids: $\mathrm{HO(RCOO)_nH}$;

(*c*) polyethers with terminal OH-groups: $\mathrm{HO{\cdot}(RO)_nH}$.

Besides the urethane and the ester or ether groups in the polymer chains, other molecular groups may occur. For instance, partly formed polymer with isocyanate end groups may react with small amounts of water, which are almost always present in glycols, polyesters, and polyethers, and this leads to extension of the polymer chains via a urea bridge. Terminal isocyanate groups may then further react with the urea bridge formed, so that branching occurs via biuret groups. Branching may also occur by reaction of free isocyanate groups with the urethane compounds already present to form allophanate bridges. Finally, there is a third possibility of branching, *viz.* the formation of isocyanurate groups by trimerization of polymer chains with terminal isocyanate groups[1].

Linear polyurethanes are only slightly branched, so that in the analysis of the hydrolysis products the products resulting from hydrolysis of the branches hardly interfere. In the present work, no attempts were therefore made to analyze the latter products, the primary purpose being the characterization of polyurethanes of unknown composition according to the main components.

For the identification of polyurethanes it is very important to know which analysis products may be expected. The number of raw materials used in the production of polyurethane fibres is generally limited; a survey is given in Table I. In view of the rapid development of new polyurethanes, and, particularly, new diisocyanates[2], this survey cannot be exhaustive; not listed are the important tetrahydrofurans, polymerization of which leads to polybutylene glycol, and lactones, which can be converted to ω-hydroxyacid polyesters.

TABLE I

RAW MATERIALS FOR PRODUCTION OF POLYURETHANE FIBRES

Diisocyanates	*Hydroxyl compounds*
Aliphatic diisocyanates C_4–C_{12}	Diols C_2–C_{10}
p-Phenylene diisocyanate	Branched diols
Diphenylene 4,4′-diisocyanate	Triols
Toluene-2,4-diisocyanate	Polyethers
Toluene-2,6-diisocyanate	
Carboxylic acids	
Aliphatic di-acids C_4–C_{10}	
o-Phthalic acid	

The literature covering this analytical field is still limited, and in most cases is concerned with the analysis of polyurethanes from 1,6-hexane diisocyanate and 1,4-butanediol. Chemical and I. R. examination of other polyurethanes has been described by CORISH[3] and NMR work on model compounds has been reported by SUMI[4].

Chemical examination

Hydrolysis forms the basis of chemical investigations. Polyurethanes from diisocyanates and diols are thus converted to diamines and glycols:

$$[\text{-OCNH-R-NHCOO-R}'\text{-O}\cdot]_n + 2\,n\text{H}_2\text{O} \rightarrow n\text{H}_2\text{N-R-NH}_2 + n\text{HO-R}'\text{-OH} + 2\,n\text{CO}_2$$

When the polyurethane is based on diisocyanate and polyester, dicarboxylic acid is formed in addition to diamine and diol. When the polyester part consists of a polylactone, an ω-hydroxy acid is formed in additon to diamine. Polyurethanes from diisocyanates and polyethers are decomposed by alkaline hydrolysis under pressure into diamine and polyether.

The method described by HASLAM *et al.*[5,6] with 50% hydrochloric acid was found to give incomplete hydrolysis, despite long reaction times (60 h), and side-reactions also occurred; in the case of polyurethane from aliphatic diisocyanate and 1,4-butanediol, the diol was found to be partly converted to tetrahydrofuran and 1,4-dichlorobutane.

Hydrolysis of a similar type of polyurethane with 60% sulphuric acid as described by WINTERSCHEIDT[7] proved to be quantitative after short reaction times (2 h), but also involved the occurrence of side-reactions. As in the hydrolysis with hydrochloric acid, ring closure of the 1,4-butanediol occurred. In addition, a dark-brown hydrolyzate was always obtained from polyurethanes based on aromatic diisocyanates.

The alkaline hydrolysis with 30% sodium hydroxide in a sealed glass tube at 160°, also described by WINTERSCHEIDT, proceeded without formation of by-products. However, the hydrolyzate contained relatively large amounts of silicate, which were very troublesome in further analysis (see also CORISH[3]).

Hydrolysis with water under pressure[8] was only applicable to polyurethanes from aliphatic diisocyanates and polyvalent alcohols. It proved impossible to decompose completely aromatic polyurethanes in this manner. Carbamic acid derivatives are formed as by-products, as evidenced by SCHRÖDER[9,10], though their formation can be prevented by carrying out the hydrolysis in the presence of barium or magnesium oxide. Identification of the hydrolysis products from this type of polyurethane can then be effected by paper chromatography or by colour reactions. The diamine is quantitatively determined by titration[9-11]. Isolation and identification of the

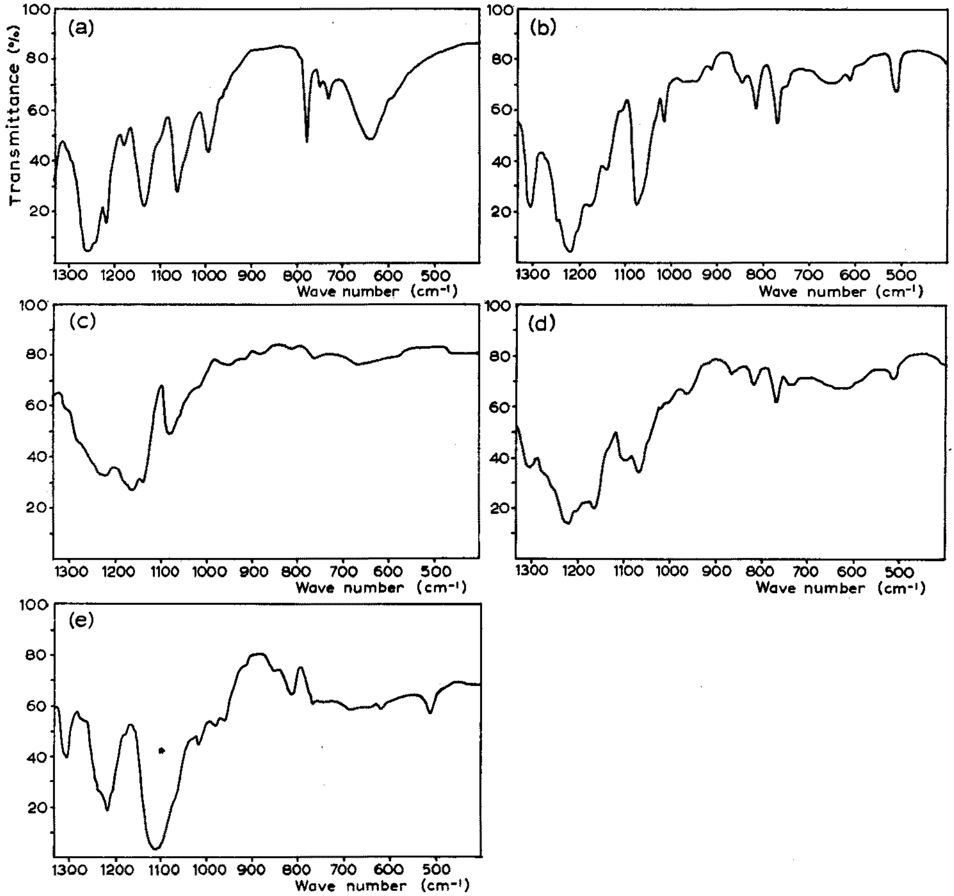


Fig. 1 a–e. Axes: transmittance % *versus* wave number (cm^{-1}). (a) Aliphatic polyurethane based on 1,6-hexane diisocyanate and 1,4-butanediol. (b) Aromatic polyurethane based on 4,4′-diphenylmethane diisocyanate and adipic acid/glycol polyester. (c) Aromatic polyurethane based on 2,4-toluene diisocyanate and adipic acid/glycol-1,2-propanediol polyester. (d) Aromatic polyurethane based on 4,4′-diphenylmethane diisocyanate and polycaprolactone. (e) Aromatic polyurethane based on 4,4′-diphenylmethane diisocyanate and polybutylene glycol.

hydrolysis products from other types of polyurethane by wet chemical means have not been described.

Infrared examination

In the I.R. spectra of polyurethanes the absorption bands at 3330 cm^{-1} (NH), 1730 cm^{-1} (C=O), about 1530 cm^{-1} (CN), and at 1260 or 1220 cm^{-1} (CO) are characteristic for the urethane grouping. For aliphatic polyurethanes the CO-band is at 1260 cm^{-1}, and for aromatic polyurethanes at 1220 cm^{-1} (Fig. 1).

Aromatic polyurethanes are also characterized by the aromatic bands at 1600 and 1420 cm^{-1}, while the range between 670 and 900 cm^{-1} may provide information on the substitution pattern of the aromatic ring in the diisocyanate used, if the ratio of aromatic to aliphatic is favourable. When the aromatic part is only a small part of the molecule, identification in this range is difficult and often impossible.

Polyurethanes from diisocyanates and polyesters or polylactones are characterized by bands at about 1170 and 1070 cm^{-1}, and polyurethanes from diisocyanates and polyethers by a very heavy band at about 1120 cm^{-1} (C–O–C).

CORISH[3] described the I.R. identification of a number of polyurethanes based on different diisocyanates and polyesters from dicarboxylic acids and polyglycols, and stated that the frequencies of the crystallinity bands in the spectrum in the range 700–750 cm^{-1} are characteristic for the acid present in the polyester. On the basis of the substitution pattern of the aromatic ring, the COC–ether band at about 1120 cm^{-1}, and the above-mentioned crystallinity bands, it would be possible to identify polyurethanes. Though the described method is essentially correct, CORISH was only concerned with a limited number of polyurethanes of known composition. Therefore, the method does not seem to be generally applicable, as in the I.R. identification of a polymer it is not possible to distinguish with certainty all components in the spectrum. Thus, it is considered that the polymer spectrum can only serve to characterize the type of polymer, and a good insight into the polymer composition can only be obtained by systematic examination of the hydrolysis products.

The purpose of the work described here therefore was:

(*a*) to determine the type of polymer from the presence of aliphatic or aromatic ester or ether in the I.R. spectrum of a polymer film, made from a formic acid or dimethylformamide solution;

(*b*) after hydrolysis, identical for all types of polyurethane, to follow a separation scheme which is dependent upon the type of polymer, and to identify the isolated compounds by means of I.R. analysis, TLC or GLC.

EXPERIMENTAL

Hydrolysis

In view of the unfavourable experiences with acid hydrolysis, hydrolysis was carried out in alkaline medium. Initial tests were made with 30% sodium hydroxide in glass apparatus but the hydrolyzate appeared to be strongly contaminated by silicates. Therefore, the glass apparatus was replaced by one of stainless steel coated with nickel, and to shorten reaction times, the hydrolysis was carried out at elevated temperature and pressure; the conditions were, therefore, rather similar to those used by CORISH[3]. The apparatus used was a Parr bomb of 18 ml capacity, provided with a

Teflon gasket. This bomb could be used for the hydrolysis of about 0.5 g of polymer. It appeared that the initial alkali concentration could be drastically reduced from 30% to 2%. At this concentration both aliphatic and aromatic polyurethanes could be completely decomposed. Hydrolysis with water alone was found to be complete for aliphatic polyurethanes only.

The reaction time depended on the alkali concentration. For decomposition of 0.5 g of polymer with 2% sodium hydroxide, a hydrolysis time of 6 h was found to be amply sufficient.

In the final procedure 0.3–0.5 g of polymer was weighed into the Parr bomb, and 15 ml of 2% sodium hydroxide solution added. After the bomb had been sealed and heated at 180–200° for 6 h, it was cooled to room temperature and cautiously opened. The contents were rinsed with water into a beaker. A clear or weakly turbid hydrolyzate indicated the presence of aliphatic diamines. If aromatic diamines were present, a distinct precipitate was observed. For fibre-forming polyurethanes, no account need be taken of the presence of substituted urea derivatives, which would also precipitate on hydrolysis. In all cases investigated the hydrolyzate, after extraction of the diamines with diethyl ether, was all but clear.

The extent to which branched polymers can be hydrolyzed as described, needs further investigation. It was found, however, that a few polyurethane rubbers, the degree of branching of which could be expected to be much higher than that of polyurethane fibres, could be completely decomposed.

ISOLATION AND IDENTIFICATION OF HYDROLYSIS PRODUCTS

Aliphatic polyurethanes

The only compounds to be expected in the hydrolyzate are aliphatic diamine and polyvalent alcohols. Aliphatic polyurethanes on other bases have so far not been applied.

A clear solution indicates the presence of lower diamines, *e.g.* hexamethylenediamine.

In the presence of higher aliphatic diamines the solution is more or less turbid. Because of the fair solubility of aliphatic diamines in water, it is not possible to extract them quantitatively with ether, so that another procedure must be followed. The hydrolyzate in this case is neutralized with 4 *N* hydrochloric acid, so that the diamines are converted to the acid salts, and a clear solution is obtained, also in the presence of higher diamines. The hydrolyzate can also be diluted with an equal volume of *p*-dioxane, which also leads to a clear solution.

This solution is passed through a cation-exchanger Dowex 50-X12, 20–50 mesh, in the H^+-form in a column of 25 cm high and 1.5 cm diameter, after which 100 ml of water is used for elution. The eluate contains the alcohols present, while the diamine is retained by the resin. The eluate is evaporated at 40° to dryness in a rotary vacuum evaporator; the isolated alcohols are then identified by means of I.R. analysis, TLC, or GLC. If more than one diol is present in the hydrolyzate, the I.R. spectrum offers too little information. Recourse can then be had to chromatographic techniques. It was found that in the presence of 1,4-butanediol no ring closure occurred during hydrolysis and subsequent separation, and no losses occurred in the presence of lower diols.

The diamine on the column can be eluted with 100 ml of 4 *N* hydrochloric acid; here again, the eluate is evaporated to dryness at 40°. The evaporation residue contains, apart from the acid salt of the diamine, sodium chloride, which, however, does not interfere with the identification of the diamine by I.R. spectroscopy or TLC.

Aromatic polyurethanes

In the hydrolyzate of polyurethanes based on aromatic diisocyanates a precipitate of aromatic diamine is present. In this case, extraction with ether of the aromatic amine was not attempted, because not all aromatic diamines can be quantitatively extracted with ether; moreover, if a polyether is present, the extract would always contain relatively large amounts of polyether, which would interfere with the identification of the diamine. The solubility of aromatic diamines in aqueous systems is not negligible, so that quantitative removal by filtration is also impossible, and other methods must be used.

The following types of polyurethane can be distinguished.

(*a*) *Aromatic diisocyanate/polyether.* The hydrolyzate is diluted with an equal volume of methanol, which leads to a clear or practically clear solution. This is passed through a column of Dowex 50-X12 in the H^+-form, after which the column is rinsed with 100 ml of a mixture of equal volumes of methanol and water. The eluate contains the polyether, which, after evaporation as indicated earlier, can be identified by means of I.R. spectroscopy. If the I.R. spectrum provides too little information, a better insight into the composition of the polyether can be obtained by refluxing the isolated substance with potassium iodide and phosphoric acid, as described by OBRUBA *et al.*[12,13], and subjecting the reaction products to I.R. analysis. In this manner, lower-molecular-weight polyethers, *e.g.* polyethylene glycols, are converted to ethene and alkyl iodide, whereas only the less volatile diiodoalkane is formed from higher-molecular-weight polyethers, such as polybutylene glycol. In both cases the reaction was found to be complete; no polyether could be detected at all. The aromatic diamine present on the column is strongly bound to the cation exchanger and is only slowly eluted by large quantities of 4 *N* hydrochloric acid. It is therefore recommended to elute with 100 ml of a mixture of equal volumes of methanol and concentrated hydrochloric acid. The resulting acid salt of the diamine can be identified by I.R. analysis after evaporation.

(*b*) *Aromatic diisocyanate/polyester.* The hydrolyzate contains aromatic diamine, salt of dicarboxylic acid, and polyvalent alcohols.

In this case, again, the hydrolyzate is diluted with an equal volume of methanol to obtain a clear solution. For the separation of the components, a combination of anion and cation exchangers is required. The dicarboxylic acid is isolated by passing the solution over the anion exchanger Dowex 2-X4, OH^-, in a column of 15 mm in diam, and 25 cm long. After elution with a mixture of equal volumes of methanol and water, the dicarboxylic acid is retained by the resin, whereas the eluate contains the other components. By elution with a mixture of equal volumes of methanol and 50% (v/v) hydrochloric acid in water, the acid is removed from the column, and after evaporation of the solution, can be identified by I.R. analysis or by TLC.

The first eluate, containing aromatic diamine and polyvalent alcohols, is passed through a column of cation-exchange resin and the column is rinsed with methanol/water 1:1. After evaporation of the effluent, the polyvalent alcohols are identified by I.R. analysis, TLC or GLC. After removal of the diamine from the column, as described under (*a*), it is identified by I.R. analysis or TLC.

In this type of polyurethane several dicarboxylic acids and diols can be expected in the hydrolyzate, and the I.R. analysis may give insufficient information. Therefore, the application of chromatographic techniques is recommended.

(*c*) *Aromatic diisocyanate/polylactone.* The hydrolyzate contains, apart from the aromatic diamine, salts of ω-hydroxy acids. Only one representative of this type of polyurethane was available for examination. The hydrolyzate is again diluted with an equal volume of methanol to a clear solution, after which it is passed through an anion exchanger. The hydroxy acid is retained by the resin, whereas the diamine appears in the effluent. The column is rinsed with 100 ml of a mixture of equal volumes of methanol and water, the combined effluents are neutralized with 4 *N* hydrochloric acid, and the diamine is then identified as indicated above. The hydroxy acid is removed from the column with 100 ml of a mixture of equal volumes of methanol and hydrochloric acid. After evaporation of the eluate, it was found from the I.R. spectrum, that the residue did not consist of ω-hydroxy acid, but of polylactone. It can therefore be assumed that, in spite of the low temperature during the evaporation, the fairly strong acid medium causes polymerization. The same phenomenon could be observed with ω-caprolactone which under the conditions described was converted to polycaprolactone.

In this case the hydroxy acid can be isolated by heating the evaporation residue on the steambath with 15 ml of 1 *N* sodium hydroxide solution for 1 h, then making slightly acid, and shaking with diethylether. After evaporation of the ether at room temperature the hydroxy acid can be identified by I.R. analysis or TLC.

The difference between polyurethanes based on polyester and polylactone is not shown directly by I.R. spectroscopy. In both cases this will be interpreted as polyester. It is therefore recommended that part of the hydrolyzate should be tested for the presence of polyvalent alcohols by successive treatment with basic and acid ion exchangers. If polyester is present, the hydrolyzate contains polyvalent alcohols, which are absent in the case of polylactone.

TLC OF DIAMINES, POLYVALENT ALCOHOLS, AND DICARBOXYLIC ACIDS

Diamines

For the identification of diamines, various systems were tested for suitability. It was found impossible to develop aliphatic and aromatic diamines with the same eluant. A good separation of aliphatic diamines can be obtained on cellulose powder (Macheray & Nagel 300 G) in a layer of 0.2 mm, with an eluant consisting of 13 volumes of *n*-butanol, 5 volumes of water, and 2 volumes of acetic acid. After evaporation of the adhering liquid, the chromatogram is sprayed with a solution of 300 mg of ninhydrin in a mixture of 100 ml of *n*-butanol and 3 ml of acetic acid. After heating the plate at 110° for 5 min, the diamines are visible as purple spots on a white background.

Aromatic diamines in this system move with the liquid front, and are not separated. No attempts were made to develop a suitable mobile phase for aromatic diamines on cellulose as an adsorbent.

On Kieselgel-G-HR (Macheray & Nagel) both aliphatic and aromatic diamines may be well separated, though different eluants must be used. For aliphatic diamines, a mixture of 5 volumes of 17% ammonia, 10 volumes of chloroform, and 11 volumes of methanol can be used. In this system the aromatic diamines have high R_F values and are practically not separated. A good separation of aromatic diamines can be obtained by using a mixture of 12 volumes of chloroform and 1 volume of methanol. In this system the aliphatic diamines remain on the starting line. Aromatic diamines are coloured differently with ninhydrin, so that, in addition to the R_F value, the colour, too, may be an indication of the presence of a certain amine. A survey of the R_F values obtained under different conditions is given in Table II.

TABLE II

R_F VALUES OF ALIPHATIC AND AROMATIC DIAMINES

	Adsorbent		
	Cellulose	*Kieselgel G-HR*	
Eluant	*BuOH 13 vol.* *H_2O 5* *Hac 2*	*Amm. 17% 5 vol.* *$CHCl_3$ 10* *MeOH 11*	*$CHCl_3$ 12 vol.* *MeOH 1*
Diamine			
C_3	0.26		
C_5	0.47		
C_6	0.52	0.10	
C_7	0.58	0.20	
C_8	0.64	0.33	
C_9	0.68	0.48	
C_{10}	0.75	0.69	
4,4'-Diphenylmethane			0.43 (red)
2,4-Toluene			0.27 (yellow)
2,6-Toluene			0.37 (yellow)
1,5-Naphthalene			0.53 (brown)
4,4',4''-Triphenylmethane			0.29 (red)

Polyvalent alcohols

In the general literature[14-16] and in literature surveys[17-20] little is said on the separation of polyvalent alcohols. This may be due to the lack of generally applicable detection agents. The sensitivity of recommended reagents, such as silver nitrate, lead tetraacetate, and potassium periodate, is relatively low, and, in addition, dependent upon the number of C-atoms. KUČERA[21] describes the separation of a number of glycols, which can be detected by means of iodine vapour. In the present work, a strong oxidizing agent, *e.g.* alkaline permanganate or acid dichromate, was found to be satisfactory. A solution of 10 g of potassium dichromate in 80 ml of water, to which 20 ml of concentrated sulphuric acid was added, was used. After spraying of the chromatogram the plate is heated at 110° for 5 min, after which the alcohols show as light blue spots on a yellow background. Diols, di- and triglycols, glycol ethers, and polyalcohols can all be detected with this reagent; in all cases the limit of detectability is 0.5–2 μg.

For the separation of polyvalent alcohols and similar compounds various adsorbents and eluants can be used.

Linear and branched polyvalent alcohols up to 6 C-atoms can be separated by a somewhat modified method for polyglycol derivatives described by BÜRGER[22], a mixture of equal weights of Kieselgel G and Kieselguhr G in a 0.2-mm layer being used as the adsorbent. Elution is effected with the butanone phase of a 1:1 mixture of butanone and water, shaken vigorously for 1 min. If the R_F values are close together, a system may be chosen with aluminium oxide G and 3% (w/w) of boric acid as adsorbent, and a mixture of 12 volumes of chloroform and 1 volume of methanol as mobile phase. Two other possibilities are: (*a*) Kieselgel G and a mixture of 9 volumes of diethylether and 1 volume of methanol as eluant, and (*b*) aluminium oxide G and a mixture of 14 volumes of diethylether and 1 volume of methanol as mobile phase.

For a number of polyvalent alcohols up to 6 C-atoms, the R_F values obtained under the conditions described are listed in Table III.

TABLE III

R_F VALUES OF POLYVALENT ALCOHOLS

	Adsorbent			
	Kieselgel G Kieselguhr G 1 + 1	*Aluminium oxide G + 3% boric acid*	*Kieselgel G*	*Aluminium oxide G*
Eluant	*Water-saturated butanone*	*$CHCl_3$ 12 vol. MeOH 1 vol.*	*Ether 9 vol. MeOH 1 vol.*	*Ether 14 vol. EtOH 1 vol.*
Alcohol				
Glycol	0.49	0.30	0.54	0.30
Glycerol	0.27	0.05	0.26	0.09
Diethylene glycol	0.43	0.46	0.44	0.28
Triethylene glycol	0.33	0.55	0.32	0.27
1,3-Propanediol	0.56	0.76	0.61	0.39
1,2-Propanediol	0.60	0.48	0.66	0.48
1,4-Butanediol	0.62	0.58	0.67	0.51
2,3-Butanediol	0.70	0.65	0.73	0.65
1,5-Pentanediol	0.67	0.61	0.70	0.68

As linear and branched polyvalent alcohols with C_6 to C_{10} were of little importance to us, little work was done on their separation. It appeared, however, that separations are possible on aluminium oxide G with a mixture of 10 volumes of benzene and 1 volume of diethylether as eluant.

Polyvalent alcohols can also be quantitatively determined by gas–liquid chromatography. For this purpose a Beckman gas chromatograph was used under the following conditions:

stationary phase : Versamid 900 on Gaspack F (60–80 mesh);
column : aluminium, 2 m long, 5 mm diameter;
carrier gas : hydrogen at 60 ml/min;
column temperature: 170°
detection : katharometer.

Further details of this method will be published at a later date.

Dicarboxylic acids

Dicarboxylic acids can be separated by the method of KNAPPE AND PETERI[23], with which very good results were obtained. The stationary phase is Kieselguhr G impregnated with polyethylene glycol M 4000 at a weight ratio of 10:3, and the eluant is a mixture of di-isopropylether, formic acid, and water at a volume ratio of 90 : 7 : 3. The detection is effected with a 0.04% solution of bromocresol purple in 50% methanol, adjusted with sodium hydroxide solution to pH 10. The dicarboxylic acids are visible as yellow spots on a blue background. The method of Knappe and Rohdewald[24] was also found to be satisfactory; in this the acids are separated on polyamide powder (Woelm) with a mobile phase consisting of a mixture of di-isopropylether, petroleum ether, carbon tetrachloride, formic acid, and water, at a volume ratio of 50 : 25 : 25 : 8 : 1. The R_F values obtained with these methods are given in Table IV; the values between brackets are those given by Knappe and Peteri, and Knappe and Rohdewald, respectively.

TABLE IV

R_F VALUES OF DICARBOXYLIC ACIDS

	Adsorbent	
	Kieselguhr G *Polyethylene glycol* *10 + 3*	*Polyamide* *(Woelm)*
Eluant	*Di-isoprop. ether 90 vol.* *Formic acid 7 vol.* *Water 3 vol.*	*Di-isoprop. ether 50 vol.* *Petr. ether 25 vol.* *CCl_4 25 vol.* *Formic acid 8 vol.* *Water 1 vol.*
Dicarboxylic acid		
Oxalic acid	0.19 (0.19)	0.13 (0.10)
Maleic acid	0.29 (0.27)	0.27 (0.27)
Succinic acid	0.39 (0.34)	0.31 (0.40)
Glutaric acid	0.53 (0.44)	0.44 (0.50)
Adipic acid	0.62 (0.51)	0.49 (0.57)
Pimelic acid	0.74 (0.62)	0.62 (0.72)
Suberic acid	0.85 (0.75)	0.65 (0.84)
Azelaic acid	0.92 (0.85)	0.75 (0.95)
Sebacic acid	0.96	0.82 (0.98)
ω-Hydroxycaproic acid	0.62	
o-Phthalic acid	0.84	0.33 (0.39)
Isophthalic acid	0.78	0.54 (0.71)
Terephthalic acid	0	0.62 (0.81)

SUMMARY

Methods are described for the qualitative analysis of linear polyurethanes of unknown composition. Based on the type of polymer, determined from the I.R.-spectrum of a polymer film, the products obtained on alkaline hydrolysis under pressure in a Parr bomb are separated by means of ion-exchangers, the course of the analysis being dependent on the type of polymer to be examined. Identification of the isolated hydrolysis products is accomplished by I.R. analysis or thin-layer chromatography.

RÉSUMÉ

On décrit des méthodes pour l'analyse qualitative de polyuréthanes linéaires de composition inconnue. On procède à une hydrolyse alcaline sous pression dans une bombe de Parr; les produits obtenus et isolés sont identifiés par analyse infra-rouge ou par chromatographie sur couche mince.

ZUSAMMENFASSUNG

Es wird eine Methode zur qualitativen Analyse linearer Polyurethane unbekannter Zusammensetzung beschrieben. Sie stützt sich auf den Polymertyp, der mittels des IR-Spektrums eines Polymerfilms bestimmt wird. Produkte, die durch alkalische Hydrolyse unter Druck erhalten werden, werden mit Ionenaustauschern getrennt. Der Verlauf der Analyse ist vom Polymertype, der geprüft werden soll, abhängig. Die Identifizierung der isolierten Hydrolyseprodukte geschieht mit der IR-Analyse oder der Dünnschichtchromatographie.

REFERENCES

1 E. Müller, *Kautschuk Gummi*, 18 (1965) 67.
2 V. V. Korshak and S. V. Vinogladova, *Polyesters*, Pergamon Press, 1965.
3 P. J. Corish, *Anal. Chem.*, 31 (1959) 1298.
4 M. Sumi, *Makromol. Chem.*, 78 (1964) 146.
5 J. Haslam and M. Clasper, *Analyst*, 76 (1951) 33.
6 J. Haslam and H. A. Willis, *Identification and Analysis of Plastics*, Iliffe Books Ltd., London, 1965.
7 H. Winterscheidt, *Seifen-Oele-Fette-Wachse*, 15 (1954) 404.
8 H. Rinke, *Germ. Pat. 951 268 Cl. 12q Gr. 101.*
9 E. Schröder, *Plaste Kautschuk*, 9 (1962) 121.
10 E. Schröder, *Plaste Kautschuk*, 9 (1962) 186.
11 H. Zahn and H. Wolf, *Melliand Textilber.*, 32 (1951) 317.
12 K. Obruba, *Mikrochim. Acta*, (1961) 801.
13 K. Obruba, E. Kucerova and M. Jurecek, *Mikrochim. Acta*, (1964) 44.
14 E. Stahl, *Dünnschichtchromatographie*, Springer Verlag, 1962.
15 K. Randerath, *Dünnschichtchromatographie*, Verlag Chemie, 1962.
16 J. M. Bobitt, *Thin-layer Chromatography*, Reinhold Publ. Corp., 1963.
17 J. P. Garel, *Bull. Soc. Chim. France*, 5 (1965) 1563.
18 G. Demole, *J. Chromatog.*, 6 (1961) 2.
19 E. Heftman, *Anal. Chem.*, 36 (1964) 14R.
20 A. A. Akhrem and A. J. Kuznetsova, *Russ. Chem. Rev. (English Transl.)*, 32 (1963) 366.
21 J. Kučera, *Collection Czech. Chem. Commun.*, 28 (1963) 1341.
22 K. Bürger, *Z. Anal. Chem.*, 196 (1963) 259.
23 E. Knappe and D. Peteri, *Z. Anal. Chem.*, 190 (1962) 380.
24 E. Knappe and I. Rohdewald, *Z. Anal. Chem.*, 210 (1965) 183.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

Determination of alkanes in technical fatty alcohols

Technical fatty alcohols which are used as raw materials for specific types of detergents are prepared by reduction of fatty acids or by oxidation of hydrocarbons. Since these fatty alcohols contain alkanes as a by-product[1], a rapid and reliable method has been developed to determine the alkane content via absorption in the near infrared. After isolation of the alkanes by adsorption chromatography, the spectrum of the alkane fraction is measured between 2200 and 3050 nm. In this spectrum the alkanes are characterized by absorption maxima caused by the $=CH_2$ and the $-CH_3$ groups. The alkane content can then be calculated by measuring the extinction belonging to the absorption maxima and by comparing them with those of a standard alkane.

Chromatographic separation

In addition to the main product, a technical fatty alcohol may contain fatty acids, fatty esters and alkanes. The alkanes can be separated from the other components by adsorption chromatography over alumina in carbon tetrachloride. The fatty alcohol, the fatty acid and the fatty ester are adsorbed, while the alkane is collected in the effluent.

Alumina (Merck, No. 1097) is a suitable adsorbent. Its adsorption capacity for fatty alcohol, fatty acid and fatty ester after activation is given in Table I. This Table shows that from a sample of, for example, 4 g of technical fatty alcohol, which as a commercial product in most cases contains less than 20% contamination, the alkane can be separated quantitatively with carbon tetrachloride.

TABLE I

ADSORPTION CAPACITY OF A 100-g ACTIVATED (17 h AT 550°) ALUMINA COLUMN (DIAM. 21 mm)

Compound adsorbed	*Concentration in CCl_4 (g/l)*	*Capacity (g)*
Decanol	250	7.4
Octadecanol	250	14.0
Coconut fatty acid	90	9.4
Tallow fatty acid	90	11.3
Coconut fatty ester[a]	90	2.9
Tallow fatty ester[a]	90	3.3

[a] The ester of the fatty alcohol and the corresponding fatty acid.

A column of inner diameter 21 mm, is packed in the usual way with a slurry of 100 g of activated alumina in carbon tetrachloride. *Ca.* 4 g of the technical fatty alcohol is weighed into a glass beaker (an accuracy of 10 mg is sufficient). The technical fatty alcohol may not contain more than 0.8 g of ester. This amount can be estimated from the saponification value of the sample.

After the technical alcohol has been dissolved in *ca.* 15 ml of carbon tetrachloride, the solution is brought quantitatively onto the alumina column. Subsequently, the column is eluted with carbon tetrachloride at a rate of 1–2 ml/min, the eluate being collected in measuring flasks in three 50-ml fractions. The second 50-ml fraction contains the alkanes. The third fraction serves to check the completeness of the elution. A blank determination is carried out in the same way.

Spectrophotometric determination

In a carbon tetrachloride solution the components of the technical fatty alcohol give characteristic absorption maxima in the near infrared. The spectrum of the alkane fraction obtained after chromatographic separation may show absorption maxima only at 2355 and 2315 nm. The absence of other absorption maxima is a criterion of the completeness of the separation.

The spectrophotometric determination is standardized with standard solutions of alkane in carbon tetrachloride. For the analysis of coconut fatty alcohol and tallow fatty alcohol, dodecane and octadecane respectively are used as standard alkanes. The spectra of these standard alkanes are also recorded and their extinctions are measured at 2355 and 2315 nm.

A 10-cm cylindrical quartz cuvette is filled with the alkane fraction. The absorption spectrum between 2200 and 3050 nm is recorded, using a Beckman DK2-spectrophotometer. For a spectrophotometric blank a 10-cm quartz cuvette is filled with the second fraction of the blank determination.

An amount of standard alkane (dodecane or octadecane) approximately equal to the expected amount of alkane in the sample is weighed into a measuring flask and dissolved in 50 ml of carbon tetrachloride. A 10-cm quartz cuvette is filled with this standard alkane solution, after which the spectrum between 2200 and 3050 nm is measured against a blank of the carbon tetrachloride used.

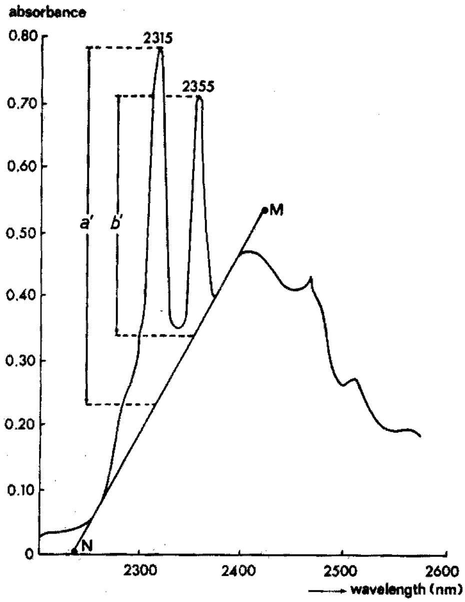


Fig. 1. Calculation of alkane content from spectra measured. 2.5 g of octadecane/l CCl$_4$; 10-cm cell.

Calculation

The baseline (NM in Fig. 1) is drawn in the spectrum of the alkane fraction and that of the standard alkane solution. The extinctions at 2315 and 2355 nm (a and b of the alkane fraction and a' and b' of the standard alkane solution) are measured.

If the volumes of the alkane fraction and the standard alkane solution are equal, the alkane content of the sample can be expressed as follows:

$$\%\ \text{alkane} = 100\,\frac{W'\,(a+b)}{W\,(a'+b')}$$

where $a+b$ = sum of the extinctions of the $=CH_2$ and the $-CH_3$ groups in the alkane fraction; $a'+b'$ = sum of the extinctions of the $=CH_2$ and the $-CH_3$ groups in the standard alkane solution; W = weight of sample (g); W' = weight of standard alkane (g).

Results and conclusions

A number of mixtures (*ca.* 4 g) consisting of varying amounts of dodecane, coconut fatty alcohol, coconut fatty acid and coconut fatty ester, as well as mixtures consisting of octadecane, tallow fatty alcohol, tallow fatty acid and tallow fatty ester were analysed by the method described above. The recoveries of the added amounts of alkanes are given in Table II.

TABLE II

RECOVERY OF DODECANE OR OCTADECANE ADDED TO MIXTURES OF COCONUT OR TALLOW FATTY ALCOHOL, ACID AND ESTER RESPECTIVELY

Content[a] *(%)*			*Alkane recovery (%)*
Alkane	*Fatty acid*	*Fatty ester*	
1–15			98.3–101.6
1–13	*ca.* 20		97.6–101.4
2–12	*ca.* 18	*ca.* 23	97.1–100.0

[a] Fatty alcohol up to 100%.

The results show that in technical fatty alcohols which contain less than *ca.* 20% of fatty ester, the alkane content can be determined with a relative accuracy of *ca.* 2%. The advantage of this method is that from the spectrum of the alkane fraction, it can be concluded whether the preceding chromatographic separation was complete.

Unilever Research Laboratory,
Vlaardingen (The Netherlands)

G. W. VAN GALEN
H. DRONKERS
P. W. HENDRIKSE

1 K. M. K. MUTTZALL, *Thesis*, Delft, 1966.

(Received December 7th, 1966)

Chloridtitration nach Mohr ohne Korrekturen

Die Mohr-Titration ist 110 Jahre alt und gilt immer noch als ein Standard-Verfahren, vor allem in der Wasseranalyse, weil sie einfach und rasch zu durchaus brauchbaren Werten führt. Ideal aber ist das Verfahren durchaus nicht, denn es müssen von dem bis zum Farbumschlag zugesetzten Reagensvolumen bestimmte Beträge abgezogen werden, die sowohl vom Volumen der titrierten Lösung wie auch vom Reagensverbrauch abhängen können, und, was besonders peinlich ist, über die Grösse der erforderlichen Korrekturen sind verschiedene, gleich erfahrene und zuverlässige Forscher durchaus verschiedener Meinung. Der Grund hierfür ist, dass der Umschlag von gelb nach braunrot schwer erkannt wird, und zwar um so schwerer, je kräftiger gelb die titrierte Lösung ist; bei hoher Konzentration an Kaliumchromat muss also ziemlich viel Silberchromat ausfallen, damit eine Farbänderung beachtet werden kann; also wird übertitriert. Bei geringer Chromatkonzentration, also ganz schwach gelber Lösung, genügt zwar eine sehr geringe Silberchromatmenge, um den Farbton erkennbar zu ändern, aber die Ausfällung des Silberchromats beginnt darin erst bei einer Ag^+-Konzentration die merklich über 10^{-5} (Aequivalenz-Konzentration einer Chlorsilberfällung) liegt; also wird auch hier übertitriert. Im allgemeinen haben nun die verschiedenen Forscher durch Versuchen in reinem Wasser die Chromatkonzentration ermittelt, bei der jeder individuell die Farbänderung bei einem möglichst kleinen Silberzusatz *erkennen* konnte. Für diese Konzentration und unter normierten Titrationsbedingungen gelten dann die "Verbesserungszahlen" mit bemerkenswerter Konstanz, sobald der betreffende Forscher oder sein Laboratoriumspersonal sich auf gerade diese Bedingungen eingearbeitet haben; daher die Zufriedenheit. Für andere Beobachter aber gelten die Bedingungen nicht; daher die Meinungsverschiedenheiten.

Ausser der eben erörterten "subjektiv günstigsten" Chromatkonzentration gibt es aber eine "objektiv richtige". Sie ist dadurch definiert, dass im Aequivalenzpunkt, also bei $C_{Ag^+} = 10^{-5}$, die Lösung zugleich an Ag_2CrO_4 gesättigt sein soll[1]. Sie wäre sogar noch etwas höher anzusetzen, denn im AeP. soll ja bereits soviel Silberchromat ausgefallen sein, dass die Umfärbung erkannt wird. Setzt man aber der Probelösung diese Chromatmenge, nämlich 0.6–0.7 ml gesättigtes Kaliumchromat je 100 ml zu, dann wird die Gelbfärbung so stark, dass die Mehrzahl der Beobachter recht merklich übertitrieren muss, um eine Farbänderung wahrzunehmen. *Die "theoretisch richtige" ist eine "physiologisch recht ungünstige" Chromatkonzentration.* Dem Übelstand kann wie folgt abgeholfen werden.

(*1*) Man gebe einen Kontrastfarbstoff zu; Indigokarmin hat sich gut bewährt. Wieviel zugegeben wird ist individuell bedingt. Jeder Beobachter muss feststellen, wann er in einer chloridfreien Chromatlösung der theoretischen Konzentration den Umschlag auf den kleinsten Silberzusatz hin erkennen kann.

(*2*) Man erzeuge in der zu titrierenden Lösung eine kräftig reflektierende weisse Trübung; dann erscheint die Lösung trotz des hohen Chromatgehaltes nur ganz schwach zitronengelb, weil das Licht an der Oberfläche reflektiert wird, und der Umschlag erfolgt mit einem Tropfen Silberlösung (0.1 oder sogar 0.0282 $N = 1$ mg Cl^-/ml) scharf nach rosa (leichte Permanganat-Farbe). Die gleiche Erscheinung wurde schon vor 12 Jahren bei der Titration von Kaliumtetraphenylborat mit Silber beobachtet (massanalytische Kaliumbestimmung), die der Mohr-Titration völlig analog ist[2]. Damals konnte man an einen spezifischen Effekt des Niederschlages, Silbertetraphenylborat, oder des Lösungsmittels, 50%iges Aceton glauben; jetzt muss man nach einem den beiden Fällen gemeinsamen Faktor suchen und der ist eben die reflektierende Trübung in der Lösung, damals die Reflektion an den feinen Asbestfasern des benutzten Tauchfilters und nun am Calciumcarbonat, das beim Neutralisieren synthetischer "Wässer" nach der folgenden Arbeitsvorschrift entsteht.

Die Titration carbonat-(oder/und phosphat-)haltiger Wässer

Von den Anionen, die in der Mohr-Titration stören, weil sie ebenfalls Silber fällen, sind praktisch Carbonat, Phosphat und Hydroxyd von Bedeutung; sie können in einfachster Weise entfernt werden.

Man gebe Calciumnitrat zu, am einfachsten eine Prise festes Salz, Phenolphthalein und nun verdünnte Natronlauge bis zur Rötung; darauf sehr verdünnte Salpetersäure in kleinen Tropfen bis eben zur Entfärbung; das pH der Lösung liegt dann immer zwischen 6.7 und 7.0.

Prüfung. Zehntelnormale Lösungen von Natriumchlorid und Silbernitrat wurden genauest verglichen und dann zur Herstellung "synthetischer Wässer" und verdünnterer Reagentien (1 ml = 1 mg Cl^-) verwendet; die Analysenwerte waren ohne jede Korrektur innerhalb der unvermeidlichen Schwankungen von ± 1 Tropfen genau.

Angel Urraza 718–303, México, D.F. F. L. HAHN

1 H. W. VAN URK, *Z. Anal. Chem.*, 67 (1925/26) 281.
2 F. L. HAHN, *Z. Anal. Chem.*, 145 (1955) 97.

(Eingegangen den 29. November, 1966)

Anal. Chim. Acta, 38 (1967) 578–579

Emploi de plusieurs méthodes en analyse par activation pour fer et cobalt

La CETAMA (Commission d'établissement des méthodes d'analyse du Commissariat français à l'Energie atomique) a patronné un programme de comparaison de méthodes et d'étalons en analyse par activation. Dans le cadre de ce programme, l'Atome Industriel a utilisé différentes méthodes pour analyser la même solution (inconnue) distribuée par la CETAMA. Nous examinerons brièvement les méthodes utilisées pour le fer et le cobalt.

Fer

La réaction a été dans tous les cas $^{58}Fe(n,\gamma)^{59}Fe$ (46 jours). Les méthodes de mesure ont été les suivantes

(1.1) Spectrométrie γ sur le photopic de 1.10 MeV en non destructif,
(1.2) Spectrométrie γ sur le photopic de 1.29 MeV en non destructif,
(1.3) Spectrométrie γ sur le photopic de 1.10 MeV après séparation,
(1.4) Spectrométrie γ sur le photopic de 1.29 MeV après séparation.

L'activation a été effectuée sur 250 μl de solution desséchée, en tube de quartz, pendant 56 heures à $1.3 \cdot 10^{13}$ neutrons thermiques par centimètre carré et par seconde dans le réacteur à eau légère Mélusine. Les mesures ont été faites après un temps de 4 semaines. Le témoin de comparaison était du Fe en solution chlorhydrique à 1.00 mg/ml. La séparation était effectuée sur un mélange Fe, Co, Zn, Cr de la manière suivante: colonne échangeuse d'ions Dowex 1-X10 (100–200), ∅8, h 120 (mm). Fixation: HCl 9 *N*–HF 1 *N* 10 ml. Elutions: HCl 9 *N*–HF 1 *N* 9 vol pour Cr, HCl 4 *N*–HF 1 *N* 12 vol pour Co, HCl 0.4 *N*–HF 1 *N* 9 vol pour Fe.

Les résultats obtenus sont les suivants:

Méthode	1.1	1.2	1.3	1.4
Résultats obtenus (mg/ml)	0.96_2	1.04_4	1.08_5	1.09_3

Dans la mesure où l'on peut appliquer un traitement statistique à aussi peu de résultats, la moyenne M est 1.046, l'écart-type estimé s est de $M \pm t\, s/\sqrt{4}$ soit 0.99–1.11 pour l'intervalle de confiance à 95%.

La solution inconnue a été révélée par la suite comme étant dosée à 1.10 ± 1% (σ) mg/ml.

Cobalt

Les méthodes utilisées ont été les suivantes:

(2.1) Réaction ^{59}Co(n,γ)^{60m}Co (10.5 min). Spectrométrie γ sur le photopic de 0.059 MeV en non destructif.

(2.2) Réaction ^{59}Co(n,γ)^{60}Co (5.3 ans). Spectrométrie γ sur le photopic de 1.17 MeV en non destructif.

(2.3) ^{60}Co, photopic de 1.33 MeV en non destructif.

(2.4) ^{60}Co, photopic de 1.17 MeV après séparation.

(2.5) ^{60}Co, photopic de 1.33 MeV après séparation.

(2.6) Dilution par un facteur 5, même méthode que 2.4.

(2.7) Dilution par un facteur 5, même méthode que 2.5.

Pour (2.1), l'activation a été effectuée sur 1 ml de solution en tube de quartz pendant 10 min à un flux thermique de $4 \cdot 10^{12}$ (tube pneumatique du réacteur Mélusine). Pour (2.2) à (2.7), 20 μl ont été irradiés dans les mêmes conditions que le fer.

Le témoin de comparaison était du Co en solution nitrique à 1.00 mg/ml. La séparation a été celle du fer.

Les résultats obtenus sont les suivants:

Méthode	2.1	2.2	2.3	2.4	2.5	2.6	2.7
Résultats obtenus (mg/ml)	0.52_5	0.52_6	0.52_4	0.54_9	0.56	0.52_3	0.52_4

La moyenne des résultats est 0.533, l'écart-type estimé de 0.006_2 (soit 1.2%). L'intervalle de confiance à 95% est de 0.527–0.539.

La solution inconnue a été révélée par la suite comme étant dosée à 0.54 ± 1% (σ) mg/ml.

Nous tenons à remercier Mademoiselle J. DURAND de notre Laboratoire et la CETAMA en la personne de Monsieur E. JUNOD.

Atome Industriel, BP 269, 38-Grenoble (France) CHARLES BONDY

(Reçu le 29 décembre, 1966)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEW

D. SEYFERTH AND R. B. KING, *Annual Surveys of Organometallic Chemistry*, Elsevier Publishing Company, Amsterdam.
Vol. I covering the year 1964, xii+330 pp., 1965, price Dfl. 55.—.
Vol. II covering the year 1965, xv+424 pp., 1966, price Dfl. 55.—.

These are the first two volumes of an annual series each volume covering the literature of the previous year. For rapid publication, the second volume has been produced by an offset process. The contents are divided between "main" and transition group compounds. The surveys are fairly complete though the authors do not claim that they are exhaustive. Their claim that only "significant" work has been included is, however, a debatable point; it is difficult to believe that all 182 references to organo-tin compounds in 1965 are significant. Most usefully, the coverage includes silicon and boron compounds.

A glance at the list of highlights which the authors have compiled leaves one in no doubt about the worthwhile nature of their task. These splendid volumes will be invaluable to anyone working in the field and future issues will be eagerly awaited. So great is the amount of work covered by these volumes that non-specialists may find the surveys somewhat daunting. Most individuals will find the price too high, which is a pity since the potential sales must be considerable.

E. J. FORBES (Birmingham)

Anal. Chim. Acta, 38 (1967) 581

ERRATA

J. F. K. HUBER AND J. A. R. J. HULSMAN, A study of liquid chromatography in columns. The time of separation, *Anal. Chim. Acta*, 38 (1967) 305.
p. 306, the term d_s which appears in the 4th and 6th equations should read d_p; the d_s occurring in the 9th and 24th text lines should likewise read d_p.
p. 308, last line before heading "Results", for small read large.
p. 309, 4th line from bottom of page, σ_{tr}^2 should read $\Delta\sigma_{tr}$.
p. 311, line 10 and p. 312, line 1, H–$\langle v \rangle$ should read $H/\langle v \rangle$.

Anal. Chim. Acta, 38 (1967) 581

ANALYTICA CHIMICA ACTA, VOL. 38 (1967)

AUTHOR INDEX

ANALYTICA CHIMICA ACTA, VOL. 38 (1967)

SUBJECT INDEX

HROMATOGRAPHIC REVIEWS

CHROMATOGRAPHIC REVIEWS

PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS

Edited by Michael Lederer

For each of the past 8 years the publication of the volumes of CHROMATOGRAPHIC REVIEWS has been widely welcomed and eagerly awaited. Because only one volume appeared each year, however, some authors have been inconvenienced by the unduly long delay between submission and publication. In order to eliminate this difficulty it has been decided that, beginning with Volume 9, CHROMATOGRAPHIC REVIEWS will be published as a journal.

Each issue of the new journal (the title will remain unchanged) will contain about 100 pages and two or three issues will appear each year depending upon the amount of material available. Publication delay will thus be reduced to a minimum.

Suggestions for reviews, or submitted manuscripts, will be welcomed by the editor, Dr. M. Lederer, Laboratorio di Cromatografia del C.N.R., Istituto di Chimica Generale ed Inorganica, Piazzale delle Scienze 5, Rome, Italy.

Contents of Volume 9, No. 1

Subscription Information

6½ × 9½″. Two issues per volume. Subscription price £3.10.0, US\$10.00, Dfl. 35.00 per volume plus postage. Special subscription price to subscribers to the Journal of Chromatography: £3.0.0, US\$8.50, Dfl. 30.00 per volume plus postage.

Subscription orders should be sent to your usual supplier or to ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands.

Details of CHROMATOGRAPHIC REVIEWS volumes already published:

VOL. 1 (1959), out of print.

VOL. 2 (1960), out of print.

VOL. 3 (1961): 6½ × 9½″, viii + 187 pages, 32 tables, 71 illus., 986 lit. refs., 80s., US$14.00, Dfl. 37.50.

VOL. 4 (1962): 6½ × 9½″, viii + 184 pages, 39 tables, 41 illus., 80s., US$14.00, Dfl. 37.50.

VOL. 5 (1963): 6½ × 9½″, ix + 244 pages, 51 tables, 35 illus. 80s., US$14.00, Dfl. 37.50.

VOL. 6 (1964): 6½ × 9½″, viii + 220 pages, 32 tables, 100 illus 80s., US$14.00, Dfl. 37.50.

VOL. 7 (1965): 6½ × 9½″, viii + 202 pages, 27 tables, 39 illus. 80s., US$14.00, Dfl. 37.50.

VOL 8 (1966): 6½ × 9½″, viii + 298 pages, 48 tables, 76 illus. £5.10.0, US$18.00, Dfl. 50.00.

VOL. 3: 1. Multiple zones and spots in chromatography. 2. Starch electrophoresis (II): Starch column electrophoresis. 3. Starch electrophoresis (III): Starch gel electrophoresis. 4. Continuous electrophoresis and two-dimensional electrochromatography. 5. Supplementary data for the paper-chromatographic separation and identification of phenol derivatives and related compounds of biochemical interest, using a 'reference system'. 6. Chromatography of lipids on silicic acid. 7. Inorganic paper chromatography. A progress report. 8. A comprehensive bibliography of recent separations of inorganic ions by electromigration in paper. Subject index (666 entries).

VOL. 4: 1. Quantitative radio paper chromatography. 2. Gas chromatography of radioactive substances—techniques and applications. 3. Recent progress in thin-layer chromatography. 4. Studies of chromatographic media: (I) The use of conventional paper chromatography with particular reference to the separation of mixtures of amino acids; (II) The use of strong cation-exchange papers for the separation of mixtures of amino acids. 5. The separation and identification of oligosaccharides. 6. Chromatography of porphyrins and metalloporphyrins. 7. Paper chromatography of higher fatty acids. Subject index (708 entries).

VOL. 5: 1. Protein mobilities and ion binding constants evaluated by zone electrophoresis. 2. Furnishing a laboratory for paper chromatography and thin-layer chromatography. 3. Paper chromatography and chemical structure: Parts I-VIII. 4. A comprehensive bibliography of separations of organic substances by countercurrent distribution. 5. Paper chromatography of oestrogens. 6. Gas chromatography in inorganic chemistry. Subject index (932 entries).

VOL. 6: 1. Commercial equipment for gas chromatography. 2. Centrifugal chromatography. 3. Chromatography of free nucleotides. 4. Paper chromatography of iodoamino acids and related compounds. 5. Chromatographic techniques for pesticide residue analysis. 6. Liquid ion exchangers: separations on inert supports impregnated with liquid ion exchangers. 7. Polymeric coordination compounds. The synthesis and applications of selective ion exchangers and polymeric chelate compounds. 8. Application of paper ionophoresis and electrochromatography to the study of metal complexes in solution. Subject index.

VOL. 7: 1. Principles of gradient elution. 2. Application of chromatographic and electrophoretic methods to the study of the Szilard-Chalmers effect. 3. Paper chromatography of chloroplast pigments. 4. Mapping plant lipids by paper chromatography. 5. Paper chromatography of antibiotics. 6. Thin-layer chromatography of steroids. Index.

VOL. 8: 1. Flow of gases in porous media. 2. Pyrolysis gas chromatography. 3. Trace analysis by means of gas chromatography. 4. Quantitative lipid analysis by combined thin-layer and gas-liquid chromatographic systems. 5. The chromatography of triglycerides. 6. Separation techniques for denaturation and degradation products of collagen and other fibrous proteins. 7. Chromatographic separations on paper impregnated with inorganic ion exchangers. 8. Chromatography in the study of coordination compounds in solution. Index.

ELSEVIER PUBLISHING COMPANY
P.O. BOX 211 - AMSTERDAM - THE NETHERLANDS

Some related titles:

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged
by F. FEIGL, *Rio de Janeiro, Brazil*
in collaboration with Dr. Vinzenz Anger, *Vienna, Austria.*
Translated by Ralph E. Oesper, Ohio, U.S.A.
6 × 9″, xxiii + 772 pages, 19 tables, 2000 lit. refs., 1966
£8.10.0, US$30.00 and Dfl. 85.00

AGAR GEL ELECTROPHORESIS

by R. J. WIEME, *Ghent, Belgium*
6 × 9″, xiii + 425 pages, 25 tables, 116 illus., 820 lit. refs., 1965
£6.0.0., US$21.00 and Dfl. 57.50

CROSS ELECTROPHORESIS

Its Principle and Applications
by S. NAKAMURA, *Yamaguchi University, Japan*
7¼ × 10¼″, ix + 194 pages, 177 illus., 21 tables, 400 lit. refs., 1966
£5.0.0., US$17.00 and Dfl. 47.50.

STEROID CHROMATOGRAPHY

by R. NEHER, *Basel, Switzerland*
5½ × 8½″, xiii + 389 pages, 78 tables, 31 illus., 1964
80s., US$13.50 and Dfl. 37.50

TECHNIQUES IN PROTEIN CHEMISTRY

Second, revised and expanded edition
by J. LEGGETT BAILEY, *London, England*
6 × 9″, xiv + 406 pages, 54 tables, 120 illus. 1966
£5.10.0., US$20.00 and Dfl. 55.00

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Proceedings of the second International Symposium organized by the Chromatography Group of The Czechoslovak Chemical Society at Liblice, 10-12 June, 1964.
Edited by K. MACEK *and* I. M. HAIS
7 × 10″, 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965
£5.0.0., US$17.00 and Dfl. 47.50

ZONE ELECTROPHORESIS IN BLOCKS AND COLUMNS

by H. BLOEMENDAL, *Amsterdam, The Netherlands*
5 × 7½″, viii + 219 pages, 13 tables, 75 illus., 450 lit. refs., 1963
60s., US$11.00 and Dfl. 30.00

✓ PAPER ELECTROPHORESIS

A Review of Methods and Results
by L. P. RIBEIRO, E. MITIDIERI *and* O. R. AFFONSO, *Rio de Janeiro, Brazil*
6 × 9″, xii + 463 pages, 42 tables, 130 illus., 3226 lit. refs., 1961
£5.10.0., US$19.00 and Dfl. 52.50

ELSEVIER PUBLISHING COMPANY

P.O. BOX 211 - AMSTERDAM - THE NETHERLANDS

VOL. **38** NO. 4 ANALYTICA CHIMICA ACTA AUGUST 1967

CONTENTS

Short communications

PRINTED IN THE NETHERLANDS

INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. CARSWELL

ix + 279 pages, 23 tables, 69 illus., 1967, Dfl. 32.50, 65s., $11.00

Contents: 1. The development of nuclear chemistry. 2. Fundamental particles and nuclear structure. 3. Nuclear reactions and radioactivity. 4. Properties of nuclear radiations. 5. The detection and measurement of nuclear radiation. 6. Nuclear instrumentation. 7. Radiation chemistry. 8. Isotope measurement and separation methods. 9. Charged particle accelerators, neutron sources, production and properties of the actinide elements. 10. Uses of isotopes. 11. Experimental nuclear chemistry (including 16 selected experiments). Index.

STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. HAYMAN

ix + 256 pages, 14 illus., 1967, Dfl. 47.50, 95s., $17.00

Contents: Preface. Nomenclature. 1. An introductory survey. 2. Some simple partition functions. 3. The microcanonical assembly. 4. The second law of thermodynamics. 5. The canonical assembly. 6. The third law of thermodynamics. 7. Dilute gases. 8. The grand canonical assembly. 9. Fermi-Dirac, Bose-Einstein and imperfect gases. 10. The partition function method applied to Fermi-Dirac, Bose-Einstein and photon gases. 11. Classical statistical thermodynamics. 12. The relationship between classical and quantum statistics.
Appendices: 1. The probability integral. 2. Stirling's formula for ln $n!$. 3. The method of variation of constants. 4. The dynamic equilibrium of a microcanonical assembly. 5. The adiabatic principle. 6. Liouville's theorem. Index.

THE STRUCTURE OF INORGANIC RADICALS

An Application of Electron Spin Resonance to the Study of Molecular Structure

by P. W. ATKINS and M. C. R. SYMONS

x + 280 pages, 57 tables, 74 illus., 357 lit. refs., 1967, Dfl. 60.00, £6.0.0, $21.75

Contents: 1. Introduction. 2. An introduction to electron spin resonance. 3. Formation and trapping of radicals. 4. Trapped and solvated electrons. 5. Atoms and monatomic ions. 6. Diatomic radicals. 7. Triatomic radicals. 8. Tetra-atomic radicals. 9. Penta-atomic radicals. 10. Summary and conclusions.
Appendices: 1. The language of group theory. 2. The spin Hamiltonian. 3. Calculation of g-values. 4. Determination of spin-density distribution and bond angles. 5. Analysis of electron spin resonance spectra. Index of data. Subject index.

FUNDAMENTALS OF METAL DEPOSITION

by E. RAUB and K. MÜLLER

viii + 265 pages, 10 tables, 138 illus., 245 lit. refs., 1967, Dfl. 60.00, £6.5.0, $21.50

Contents: 1. Chemical and electrochemical principles. 2. Electrode processes. 3. The cathodic discharge of ions. 4. The structure of electrolytic metal deposits. 5. Physical and chemical properties of electrolytic metal deposits. 6. Distribution of electrolytic metal deposits on the cathode. Index.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

453 E