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. 31, No. 5, p. 405–500, November 1964

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. (U.S.A.)

or to

Dr. A. M. G. MACDONALD, Department of Chemistry, The University, Edgbaston, Birmingham 15 (Great Britain)

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Tables and legends for figures should be typed on a **separate** page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in **thin pencil.** The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

Standard symbols should be used in line drawings. The following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◘ ⊖ ▣ ▪ □ + ×

All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places. The abbreviations of journals should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition. A summary of 50 to 200 words should be included. Authors of papers in French or German are encouraged to supply also a translation of the summary in English.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints 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 six issues to the volume, approx. 600 pages per volume, two volumes per year.
Subscription prices (post free): $ 17.50 or £ 6.6.0 or Dfl. 63.— per volume; $ 35.— or £ 12.12.0 or Dfl. 126.— per year. 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

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 31, No. 5, November 1964

THE HEAT STABILITIES OF TRIVALENT METAL 8-QUINOLINOL CHELATES IN INERT ATMOSPHERES

The thermal stabilities of Al, Ga, In, Cr and Fe oxinates have been studied by thermogravimetry, differential thermal analysis, thermomanometric analysis and by a sealed tube extraction technique. The order of decreasing heat stability for the anhydrous chelates is Al> Cr∼Ga>In>Fe. The compounds decompose with the evolution of hydrogen and the formation of large amounts of carbonaceous residue. The Al, Cr, Ga, and In oxinates can be melted without major decomposition when heated rapidly.

R. G. Charles,

Anal. Chim. Acta, 31 (1964) 405–412.

DETERMINATION OF COBALT IN STEELS BY THERMAL NEUTRON ACTIVATION

(in French)

A method for the determination of cobalt in 18/8 steels, based on formation of ^{60m}Co is proposed. Most of the iron is extracted, then cobalt is extracted as its α-nitroso-β-naphthol complex into toluene. The losses are determined exactly. A determination is complete within 2 h with a precision of $\pm 9\%$; the limit of sensitivity is 2 μg of cobalt. The results obtained (average 350 p.p.m.) are compared with results obtained spectrophotometrically (average 368 p.p.m.).

D. Monnier, W. Haerdi et A. Rouèche,

Anal. Chim. Acta, 31 (1964) 413–418.

THERMAL ANALYSIS OF SOME METAL N-BENZOYL-N-PHENYLHYDROXYLAMINE CHELATES

The preparation and thermal analysis of the metal chelates of N-benzoyl-N-phenylhydroxylamine (BPHA) with Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II) is discussed. The differential thermal analysis apparatus is described in detail. DTA and TGA curves of BPHA and the chelates from 25 to 700° in oxygen and in nitrogen are presented.

R. A. Meyer, J. F. Hazel and W. M. McNabb,

Anal. Chim, Acta, 31 (1964) 419–425.

A RAPID DIRECT AMPEROMETRIC METHOD FOR THE DETERMINATION OF CALCIUM AND MAGNESIUM IN WATERS, CEMENTS AND SOILS

(in French)

An amperometric method for the successive titration of calcium and magnesium with EGTA and EDTA respectively is proposed. The method is direct and rapid. Calcium and magnesium can be determined in waters (41.5 mg/l and 4.6 mg/l with a precision of ±1.15% and ±6.70%), in cements (66.7% CaO and 1.70% MgO with a precision of ±2% and ±8%), and in soils (16.5% $CaCO_3$ and 1.8% $MgCO_3$ with a precision of ±2.6% and ±5.5%). The results obtained are compared with those obtained by gravimetric or titrimetric methods.

A. Rouèche et D. Monnier,

Anal. Chim. Acta, 31 (1964) 426–433.

THE DETERMINATION OF BROMINE IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

A neutron activation method for the determination of bromine in rocks and minerals is described. After removal of iodine, bromine is separated by oxidation with potassium permanganate and extraction with carbon tetrachloride. Bromine is then precipitated as silver bromide; yields are from 60 to 84%. The method has a sensitivity of 0.001 p.p.m. of bromine and is free from interfering reactions. The values obtained for G-1 and W-1, 0.484 and 0.496 p.p.m. of bromine respectively, are lower than the average values for granites and basalts previously reported.

R. H. Filby,

Anal. Chim. Acta, 31 (1964) 434–440.

NMR ANALYSIS OF α-METHYL BRANCHED ORGANIC ACIDS

A method for analyzing α-methyl branched organic acids has been developed using NMR spectroscopy. The composition is determined in terms of α,α-dimethyl, α-methyl-α-alkyl and α-methyl structures. Peak assignments were made on the basis of model compound studies. This technique has been successfully used in analyzing Koch acid synthesis mixtures.

W. L. Senn, Jr. and L. A. Pine,

Anal. Chim. Acta, 31 (1964) 441–446.

RADIOCHEMICAL SEPARATION OF ZIRCONIUM FROM NIOBIUM WITH SALICYLHYDROXAMIC ACID

Salicylhydroxamic acid was employed for the rapid radiochemical separation of zirconium from niobium. Neutron-deficient isotopes of the 2 elements formed in the spallation of niobium with 340-MeV protons were used as tracers.

The method was employed in the study of short-lived zirconium and niobium activities using scintillation γ-spectrometry. The procedure is complete in about 7 min, and gives a chemical yield of the order of 50–60% and a decontamination factor of at least $5 \cdot 10^4$.

S. M. Qaim,

Anal. Chim. Acta, 31 (1964) 447–451.

DIRECT, RAPID TITRATION OF 8-QUINOLINOL

APPLICATION OF CONSTANT-CURRENT POTENTIOMETRY

The major problems in the direct bromination titration of the important analytical reagent 8-quinolinol have been slow reaction rate and difficulty of end-point detection. A reaction-rate study showed that perchloric acid as the titration medium gives a sufficiently high reaction rate for direct titration. End-points are simply and conveniently detected using constant-current potentiometry. Metal ions do not interfere. Excellent agreement between titration by the proposed method and the conventional indirect iodometric method was observed.

C. O. Huber, J. B. Doe and H. E. Stapelfeldt,
Anal. Chim. Acta, 31 (1964) 452–456.

COMPLEXING EFFECTS IN THE SOLVENT EXTRACTION OF THALLIUM(I) 2-MERCAPTOBENZOTHIAZOLE

Studies of the extraction of thallium(I) from aqueous solution in the absence and presence of aqueous complexing agents into chloroform containing 2-mercaptobenzothiazole are described. Fluoride, chloride, bromide, iodide, thiocyanate, cyanide, and sulfate were employed as aqueous complexing agents. A number of the participating species were identified and association constants are estimated.

G. K. Schweitzer and J. D. Matthews,
Anal. Chim. Acta, 31 (1964) 457–461.

SUGAR SEPARATIONS ON ION-EXCHANGE RESINS IN MIXTURE WITH CELITE

The chromatographic separation of sugars in ethanol–water solutions by means of anion-exchange resins can be improved markedly by using extremely fine resin particles. To avoid an excessively high pressure drop in the column when crushed resin particles are employed the resin can be used in mixture with Celite. Working at elevated temperature results in improved separations and a considerable saving of time.

B. Arwidi and O. Samuelson,
Anal. Chim. Acta, 31 (1964) 462–466.

ANION-EXCHANGE SEPARATION OF URANIUM FROM THE LANTHANIDES

The anion-exchange behavior of uranium and the lanthanides in acetic acid–organic solvent mixtures is described. The distribution coefficients of the elements in 13 organic solvents containing acetic acid as the complexing agent were measured, and methods for the quantitative separation of uranium from the rare-earth elements are proposed.

J. Hazan and J. Korkisch,
Anal. Chim. Acta, 31 (1964) 467–471.

S-BENZYLTHIOURONIUM SALTS OF SOME CARBOXYLIC ACIDS, SULFONIC ACIDS, AND PHENOLS

116 S-Benzylthiouronium salts have been prepared and were, if possible, checked by titration with perchloric acid in glacial acetic acid on a semi-micro scale. Out of these, 110 are salts of carboxylic acids, 2 of sulfonic acids, and 4 of nitrophenols. The melting points determined according to a standard procedure are given.

A. JART, A. J. BIGLER AND V. BITSCH,
Anal. Chim. Acta, 31 (1964) 472–479.

A SIMPLIFIED METHOD FOR THE MICROBIOLOGICAL DETERMINATION OF MYO-INOSITOL

(in French)

A simplified microbiological assay for inositol involving the use of *Schizosaccharomyces pombe* Linder is described. The results are very reproducible and the method is simple to operate.

V. N. PARANJAPYE, J. DESHUSSES ET TH. POSTERNAK,
Anal. Chim. Acta, 31 (1964) 480–483.

EFFECTS OF SAMPLE CELL POSITION AND DIMENSIONS ON THE FLUORESCENCE INTENSITY–CONCENTRATION CURVE FOR "PERPENDICULAR-TYPE" FLUORIMETERS

(Short Communication)

W. E. OHNESORGE,
Anal. Chim. Acta, 31 (1964) 484–487.

SYNTHESIS AND SPECTRAL CHARACTERISTICS OF 4,4′-DIMETHOXYTHIOBENZOPHENONE

(Short Communication)

H. B. WILLIAMS, F. M. HILBURN AND K. YARBROUGH,
Anal. Chim. Acta, 31 (1964) 488–490.

THE DIRECT POLAROGRAPHIC DETERMINATION OF URANIUM(VI) IN NITRIC ACID MEDIA

(Short Communication)

J. MASHALL AND J. KENDLER,
Anal. Chim. Acta, 31 (1964) 490–493.

THE SPECTROGRAPHIC DETERMINATION OF STRONTIUM AND BARIUM IN OXYGEN AND CARBON DIOXIDE ATMOSPHERES

(Short Communication)

F. WILSON AND R. CHESTER,
Anal. Chim. Acta, 31 (1964) 493–497.

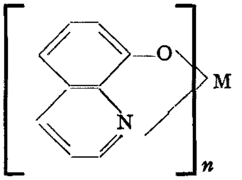
THE HEAT STABILITIES OF TRIVALENT METAL 8-QUINOLINOL CHELATES IN INERT ATMOSPHERES

ROBERT G. CHARLES

Westinghouse Research Laboratories, Pittsburgh 35, Pa. (U.S.A.)

(Received March 13th, 1964)

Previous communications[1-3] from this laboratory have described the thermal characteristics of a number of divalent metal 8-quinolinolates (oxinates, formula Ia). It was of interest to extend these investigations to the corresponding trivalent metal oxinates (Ib). Results obtained for the Al, Ga, In, Cr and Fe chelates are reported below. Although the heat stabilities of all of these compounds have been studied by other workers[4,5], previous investigations have (except for the work of WENDLANDT[5]) been carried out with the samples exposed to air of normal humidity at atmospheric pressure. Under these conditions oxidation and/or hydrolysis, rather than pyrolysis, can determine the temperature at which the compound decomposes. Trivalent rare earth oxinates have been previously studied in the absence of air[6], but these materials do not correspond to structure I. They are best represented as polymeric mixed ligand complexes containing bonded acetate ions[6].



Ia, $n = 2$

Ib, $n = 3$

EXPERIMENTAL

Compound preparation

The methods used in the syntheses of the oxinates were based on conventional analytical procedures[7]. It was necessary, however, to make some modifications in order to obtain larger quantities of product conveniently.

Chromium oxinate. To a solution of 1.5 g of $Cr(NO_3)_3 \cdot 9H_2O$ in 500 ml of water, concentrated ammonia solution was added dropwise until a precipitate persisted. The precipitate was redissolved by the addition of the minimum quantity of 1 : 10 aqueous sulfuric acid. The solution was heated to 70° and the following were added in order, with stirring: 200 ml of 4% oxine in glacial acetic acid, 200 ml of 2 M aqueous sodium hydroxide and 200 ml of 4 M aqueous ammonium acetate. A precipitate gradually formed upon stirring for 2 h at 90°. The mixture was cooled and the precipitate filtered off and washed with hot water. The solid was air-dried at room temperature. Yield 2.0 g.

Aluminum, gallium, indium and iron oxinates. Oxine (7.5 g) was dissolved in 200 ml of methanol. To this was added 0.0167 moles of hydrated aluminum chloride, gallium nitrate, indium nitrate or iron(III) chloride in 500 ml of water, followed by a solution of 13.6 g of sodium acetate trihydrate in 100 ml of water. The mixture was heated briefly nearly to boiling and cooled to room temperature, and the solid filtered off on a sintered glass filter. The product was washed thoroughly with hot water and then allowed to dry in the open air at room temperature for about a week. Yields were essentially quantitative.

Thermogravimetric analysis

The thermobalance has been previously described[8]. Runs were carried out in shallow open platinum crucibles heated at 2°/min in a stream of argon (50 ml/min) at atmospheric pressure. Fifty-mg samples were used to obtain the curves of Fig. 1 and 500-mg samples for those of Fig. 2. Weight–temperature curves were plotted automatically with a Mosely X-Y recorder. Temperature was sensed with a chromel–alumel thermocouple in close proximity to the sample container.

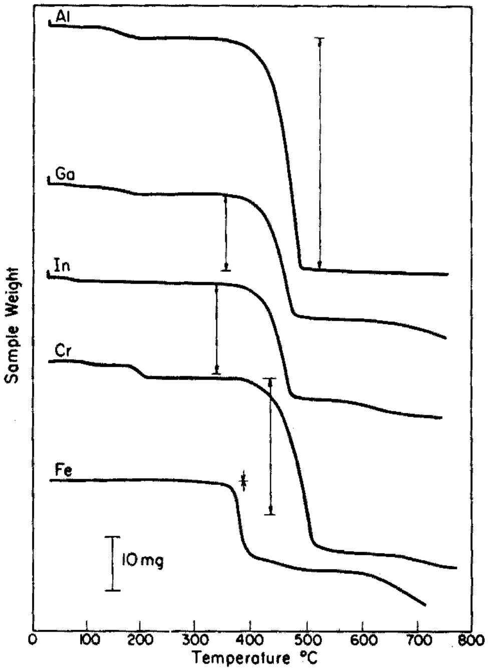


Fig. 1. Thermogravimetric curves for metal oxinates heated in argon (50-mg samples). Arrows show amount of volatilized undecomposed oxinate.

Differential thermal analysis (DTA) and thermomanometric analysis (TMA)

The DTA apparatus was a closed glass and quartz system which has been described in detail elsewhere[3]. Samples (400 mg) of the air-dried oxinates were heated under argon at an initial pressure of 550 mm Hg. The heating rate was 12°/min (above 100°). For the present work, a sensitive Bourdon gauge was incorporated into the system to monitor simultaneously changes in gas pressure resulting from the formation of pyrolysis products during the run. Since products of intermediate volatility tend to condense on the cooler parts of the apparatus, observed pressure rises are due principally to those products which are gaseous, or which have high vapor pressures at room temperature. Total pressure rise during a run was of the order of 100 mm Hg. The TMA curves of Fig. 4 are given in terms of number of moles of gaseous products, calculated on the assumption that the perfect gas laws are obeyed. A small correction was applied to account for the pressure rise resulting from the thermal expansion of the argon in the DTA sample tube.

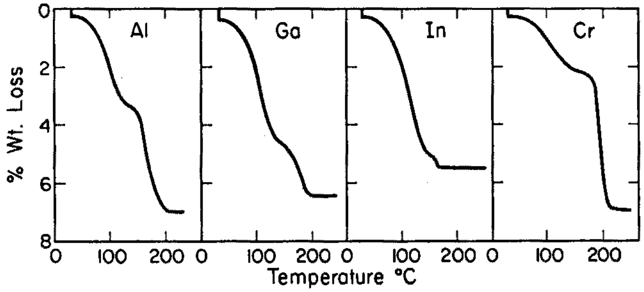


Fig. 2. Thermogravimetric curves for dehydration of metal oxinates in argon.

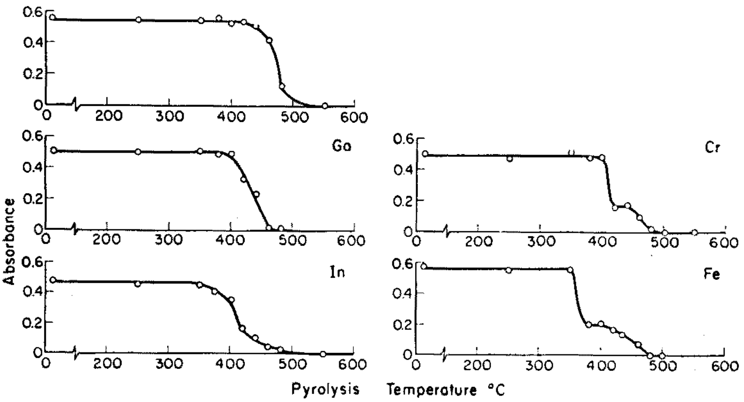


Fig. 3. Variation of absorbance with pyrolysis temperature for metal oxinates heated 4 h at the temperatures indicated (solutions in 0.1 M HCl).

The design of the DTA apparatus was such that evaporation of unchanged oxinate during a run was negligible.

Sealed tube experiments

These experiments were carried out in essentially the manner previously described[2], utilizing oxinates which had been dried at 150° in a vacuum oven. The trivalent metal oxinates did not dissolve as readily in acid as the divalent metal oxinates previously studied[2]. It was necessary to warm the tube contents with 1 M hydrochloric acid for prolonged periods to effect solution. Quantitative dilution was then made to a final hydrochloric acid concentration of 0.1 M. Conditions necessary to dissolve the undecomposed anhydrous chelates were used as a guide in extracting the decomposed residues.

RESULTS AND DISCUSSION

Thermogravimetric studies

The TGA curves of Fig. 1 show two regions of weight loss below 200° (except for the anhydrous iron oxinate). This is shown more clearly in the expanded curves of Fig. 2*. We attribute the weight losses below about 125° to the loss of most of the water of hydration and the weight losses in the region 125° to 200° to the volatilization of oxine formed by the hydrolysis reaction (1)**. Similar hydrolysis has been shown to occur for the alkaline earth oxinates[1]. The results listed for water in Table I have been corrected for the water consumed in reaction (1).

$$(C_9H_6NO)_3\,M \cdot x\,H_2O \rightarrow (C_9H_6NO)_2\,MOH \cdot (x-1)\,H_2O + HC_9H_6NO \qquad (1)$$

TABLE I

COMPOSITIONS AND MELTING POINTS OF OXINATES

	% *Metal*		% H_2O		*M.P.*[b]
	Calculated	*Found*	*Calculated*	*Found*[a]	(°)
$(C_9H_6NO)_3\,Al \cdot H_2O$	5.65	5.68	3.77	3.8	411
$(C_9H_6NO)_3\,Ga \cdot 1.5\,H_2O$	13.40	13.27	5.11	4.8	403
$(C_9H_6NO)_3\,In \cdot 1.5\,H_2O$	19.99	19.96	4.71	5.1	376
$(C_9H_6NO)_3\,Cr \cdot H_2O$	10.35	10.12	3.59	2.7	411
$(C_9H_6NO)_3\,Fe$	11.44	11.42	0	0.0	390

[a] Weight loss from thermogravimetric measurements, corrected for hydrolysis as discussed in text.
[b] Melting points of anhydrous chelates as determined by differential thermal analysis. Average values of 4 determinations each (standard deviation ± 3°).

Weight losses above 200° must be due to volatilization of products resulting from pyrolysis of the anhydrous oxinates, or to evaporation of the unchanged oxinates themselves. From the metal content of the nonvolatile residues remaining at the conclusions of the runs the amount of unchanged oxinate which evaporated could be calculated, on the assumption that the oxinate is the only volatile metal-containing species. The results are indicated by arrows in Fig. 1. Weight losses for iron oxinate are due entirely to decomposition. For the other oxinates, however, volatilization of unchanged chelate constitutes a large fraction of the weight loss above 200°. The TGA curves therefore give little information concerning the relative tendencies of the anhydrous oxinates to undergo pyrolysis.

---

* The initial vertical portions of some of the curves of Figs. 1 and 2 represent loss of water during the initial flushing period with argon at room temperature.

** The possibility cannot be ruled out that some portion of the weight loss in region 125 to 200° is due to loss of occluded oxine.

The TGA curves (Fig. 1) obtained here differ substantially from previously published curves obtained in undried air[4], due principally to the oxidative and hydrolytic reactions possible under the latter conditions.

Sealed tube experiments

By heating the anhydrous oxinates (vacuum-dried) in sealed tubes, evaporation of unchanged chelate can be prevented. The occurrence of pyrolysis can be detected by dissolving the contents of a tube, which has been heated to a specified temperature, in aqueous acid and comparing the optical absorbance with that of a solution prepared from undecomposed oxinate[2]. The absorbance values at 252 mμ are plotted in Fig. 3 as a function of pyrolysis temperature. Decomposition is accompanied by a drop in absorbance. From the positions of the descending portions of the curves along the temperature axis the relative heat stabilities are found to be $\text{Al} > \text{Cr} \sim \text{Ga} > \text{In} > \text{Fe}$. By way of comparison with the divalent oxinates, previously studied[2] by the same procedure, the aluminum chelate is somewhat less stable than the cadmium oxinate while iron oxinate is slightly more stable than lead oxinate. The curves (Fig. 3) for chromium oxinate and iron oxinate do not fall smoothly to zero absorbance but display an intermediate plateau. This behavior probably indicates the formation of oxine as a decomposition product, as has been observed for the corresponding divalent lead and copper chelates[2].

Differential thermal analysis and thermomanometric studies

DTA and TMA curves for the trivalent hydrated oxinates are given in Fig. 4.

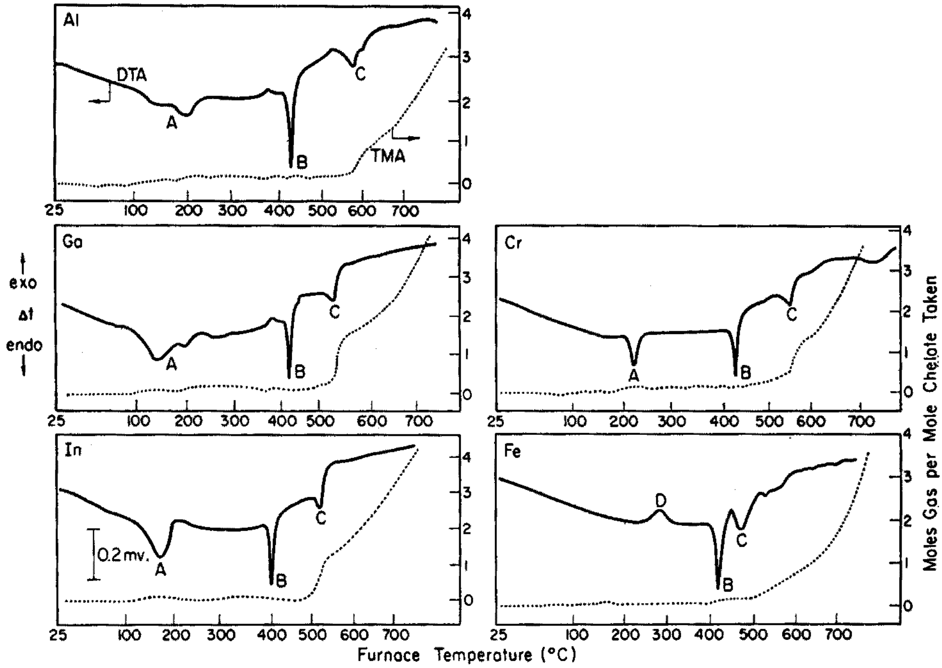


Fig. 4. Differential thermal analysis and thermomanometric analysis curves for trivalent metal 8-quinolinolates heated in argon.

Endotherms occurring below 250° (marked A) are due to dehydration and the volatilization of oxine formed through hydrolysis. The evolution of water and oxine is not indicated clearly on the corresponding TMA curves since both substances condense on the cool portions of the apparatus, outside the furnace, and do not make large contributions to the gas pressure of the system. The endotherms B are due to melting of the anhydrous oxinates as shown by visual observation. Except for iron oxinate, melting occurs without significant decomposition. This was shown by separate DTA runs in which heating was terminated just beyond the endotherms B. Upon cooling, exotherms having very nearly the same area as B were observed for each of the chelates except iron oxinate. The iron chelate undergoes partial decomposition at the melting point as shown by the absence of a definite exotherm on cooling. Corrected[3] melting points for the oxinates are listed in Table I. In contrast to the divalent metal oxinates[3], the melting points of the trivalent metal chelates are rather insensitive to the natuie of the metal. Similarities have also been noted among the vapor pressures of the trivalent metal oxinates[8]. Both lines of evidence suggest that intermolecular forces in trivalent metal oxinates are not much affected by changes in the metal.

WENDLANDT[5] has published DTA curves for aluminum and iron oxinates. He found endotherms at 415° and 390°, respectively, which are very close to the values listed in Table I. The endotherm for aluminum oxinate, however, was thought to be due to vaporization. The present direct visual observation leaves little doubt that the heat uptake is actually due to melting.

Endotherms (Fig. 4) occurring at C correspond to pyrolysis. The endotherms C are accompanied by the formation of volatile decomposition products as shown by rather abrupt rises in the TMA curves. Decomposition occurs at substantially higher temperatures at the rapid heating rates used for the DTA runs as compared with the curves of Fig. 3. The order of decreasing heat stability as determined fiom the position of C (Fig. 4) is, however, essentially the same as that found from Fig. 3, *viz.* Al > Cr > Ga > In > Fe.

An exotherm, D, occurs in the DTA curve for iron oxinate. This peak may represent a solid state phase transition or the crystallization of an initially amorphous material, as has been observed for some of the divalent metal oxinates[3].

Nature of the pyrolysis products

The gaseous decomposition products produced at 500° in sealed tubes were analyzed by means of a mass spectrometer. The results are listed in Table II. The principal

TABLE II

GASEOUS DECOMPOSITION PRODUCTS FROM TRIVALENT METAL OXINATES AT 500° (4 h)

	Product (mole % of total gas produced)			
	H_2	CH_4	CO	CO_2
Al	89	5	3	2
Ga	97	1	1	1
In	95	3	2	1
Cr	94	2	2	2
Fe	93	2	4	1

product is hydrogen. Hydrogen is also the major product for the divalent metal oxinates[2] and for the rare earth oxinates[6]. The production of hydrogen is thought to be the result of intermolecular condensation reactions which do not necessarily involve disruption of the metal-containing rings[1,2].

Relatively large amounts of dark-colored carbonaceous residues remain from the pyrolysis of the oxinates (Table III). Elemental analysis showed the presence of C, H, N, metal and O (by difference). X-Ray powder patterns of the Al, Ga and Cr residues showed no crystalline components but the In and Fe oxinate residues were found to contain In_2O_3 and FeO respectively. The iron oxinate residue was found to be noticeably attracted to a magnet and hence may contain Fe_3O_4 and/or Fe metal as well.

TABLE III

PYROLYSIS RESIDUES (4 h AT 500°)

Oxinate	*Wt. residue/wt. sample*[a]	*Elemental composition*				*X-ray diffraction results*
		% C	*% H*	*% N*	*% Metal*	
Al	0.61	[b]	[b]	[b]	9.7	Amorphous
Ga	0.88	60.9	2.84	7.7	15.8	Amorphous
In	0.93	[b]	[b]	[b]	22.5	In_2O_3
Cr	0.79	55.7	2.81	7.6	13.7	Amorphous
Fe	0.68	61.6	2.63	7.5	16.7	FeO

[a] Ratio corrected for sublimed oxinate by subtracting the quantity of volatilized unchanged oxinate from the sample weight taken.

[b] Not determined.

In addition to the gaseous products (Table II) and nonvolatile residues (Table III), products of intermediate volatility are probably also formed. These were not specifically investigated but the curves of Fig. 3 suggest that oxine is produced, at least by chromium oxinate and iron oxinate.

The writer is grateful to Miss ANTOINETTE PERROTTO for help in the experimental portion of this work and to Mr. W. M. HICKAM for the mass spectrometer results.

SUMMARY

The thermal stabilities of Al, Ga, In, Cr and Fe oxinates have been studied by thermogravimetry, differential thermal analysis, thermomanometric analysis and by a sealed tube extraction technique. The order of decreasing heat stability for the anhydrous chelates is $Al > Cr \sim Ga > In > Fe$. The compounds decompose with the evolution of hydrogen and the formation of large amounts of carbonaceous residue. The Al, Cr, Ga, and In oxinates can be melted without major decomposition when heated rapidly.

RÉSUMÉ

L'auteur a examiné les stabilités thermiques des oxinates d'aluminium, de gallium, d'indium, de chrome et de fer, par thermogravimétrie, analyse thermique différentielle, analyse thermomanométrique et extraction en tube scellé. L'ordre de stabilité thermique décroissante pour les chélates anhydres est le suivant: $Al > Cr \sim Ga > In > Fe$. Les composés se décomposent avec dégagement d'hydrogène et formation de résidus charbonneux.

ZUSAMMENFASSUNG

Die thermischen Stabilitäten von Al, Ga, In, Cr und Fe-Oxinaten wurden thermogravimetrisch, mit der Differentialthermoanalyse, der thermomanometrischen Analyse und mittels einer besonderen Technik in einer geschlossenen Röhre untersucht. Die Wärmestabilität der wasserfreien Chelate fällt in folgender Reihenfolge Al > Cr ∼ Ga > In > Fe. Die Verbindungen zersetzen sich unter Wasserstoffentwicklung und unter Bildung grösserer Anteile von carbonathaltigem Rückstand. Die Al-, Cr-, Ga- und In-Oxinate können, wenn man sie schnell erhitzt, ohne wesentliche Zersetzung geschmolzen werden.

REFERENCES

[1] R. G. CHARLES, *J. Inorg. & Nucl. Chem.*, 20 (1961) 211.
[2] R. G. CHARLES, A. PERROTTO AND M. A. DOLAN, *J. Inorg. & Nucl. Chem.*, 25 (1963) 45.
[3] R. G. CHARLES, *Anal. Chim. Acta*, 27 (1962) 474.
[4] C. DUVAL, *Inorganic Thermogravimetric Analysis*, 2nd Ed., Elsevier, New York, 1963. See also the 1st edition (1953) which contains a large number of TGA curves not published in the 2nd edition.
[5] W. W. WENDLANDT AND G. R. HORTON, *Anal. Chem.*, 34 (1962) 1098.
[6] R. G. CHARLES AND A. PERROTTO, *Anal. Chim. Acta*, 30 (1964) 131.
[7] R. G. W. HOLLINGSHEAD, *Oxine and its Derivatives*, Vols. I and II, Butterworths, London, 1954.
[8] R. G. CHARLES AND A. LANGER, *J. Phys. Chem.*, 63 (1959) 603.

DOSAGE DU COBALT DANS LES ACIERS 18/8 BASE SUR LA FORMATION DU ^{60m}Co PAR ACTIVATION AUX NEUTRONS THERMIQUES

D. MONNIER, W. HAERDI ET A. ROUÈCHE

Laboratoires de Chimie Minérale et Analytique, Université de Genève, Genève (Suisse)

(Reçu le 5 mars, 1964)

Le dosage de traces de cobalt basé sur la formation de ^{60}Co n'est sensible que si l'on soumet l'échantillon à un flux élevé pendant un temps d'irradiation suffisamment long, car la période de cet isotope dépasse 5 ans. L'emploi de ^{60m}Co, de 10.5 min de période, dont la section efficace est de 16 barns et l'énergie-γ de 0.059 MeV, se prête particulièrement bien au dosage lorsqu'on dispose d'un flux de neutrons maximum de 10^9 n.cm^{-2} sec^{-1}. L'emploi du cobalt-60m a déjà été préconisé par divers auteurs dont WESTERMARCK ET FINEMAN[1], mais la technique utilisée n'est pas décrite en détail et les limites de sensibilité n'ont pas été déterminées avec précision. Nous l'avons aussi utilisé pour le dosage du cobalt dans des mélanges synthétiques[2]. Nous nous proposons d'appliquer cette méthode à l'acier 18/8. L'expérience et le calcul montrent qu'en irradiant pendant 15 min un alliage ferreux, l'activité du ^{59}Fe qui se forme à partir du ^{58}Fe est négligeable (de l'ordre de 10^{-7} μC) car la section efficace de formation est petite (0.022 barns) et la période relativement longue (45 jours). Quant au ^{55}Fe, résultat de la réaction ^{54}Fe(n, γ)^{55}Fe avec une période de 2.94 ans, son activité est encore beaucoup plus faible. Par contre un certain nombre d'isotopes à courte période se forment lors de l'irradiation et présentent une activité gênante. Dans le Tableau I nous donnons la liste des diverses caractéristiques correspondant à l'irradiation de 5 mg d'acier 18/8 pendant 15 min dans un flux de 10^9 n.cm^{-2} sec^{-1} (conditions les plus favorables du réacteur de l'Institut de Physique de notre Université).

Pour ces calculs nous avons utilisé la formule donnée par MONNIER, HAERDI ET VOGEL[2]. Les ε sont tirés de FRIEDLANDER ET KENNEDY[3].

Le dosage est basé sur la mesure, au spectromètre-γ, de l'intensité des rayons-γ (0.059 MeV) du ^{60m}Co formé. Dans ces conditions seuls gênent les isotopes radioactifs qui se forment en quantité suffisante et dont le spectre interfère avec celui du cobalt-60m. C'est le cas particulièrement du ^{56}Mn et dans une moindre proportion du ^{101}Mo, du ^{65}Ni, du ^{51}Cr et du ^{52}V.

Etant donné la très courte période du ^{60m}Co, on doit avoir recours à des séparations radiochimiques très rapides permettant de diminuer suffisamment les activités gênantes. Les pertes en cobalt peuvent aller jusqu'à 50 et même 60% (puisqu'elles sont exactement déterminées), s'il en résulte une diminution sensible de temps nécessaire à cette opération.

La plupart des méthodes de séparation sont inutilisables car elles sont trop longues. L'extraction par contre est rapide, elle permet en une seule opération de quelques minutes, de séparer le cobalt au moyen du toluène, comme complexe Co-α-nitroso-β-naphtol, avec un rendement de 70–80% et sans dispositifs spéciaux[2]. La détermination des pertes se fait au moyen d'un traceur. On ajoute, après ou avant l'irradiation, à l'échantillon à analyser, un peu de cobalt-60, de masse négligeable, et dont on a établi préalablement le spectre-γ. L'activité de ce radioisotope est donc exactement connue par la hauteur h_1 d'un de ses pics, par exemple celui correspondant à une énergie de 1.33 MeV. Ce traceur ne gêne pas la mesure de l'activité du ^{60m}Co s'il n'est pas en trop grande quantité, car les rayons-γ de ces deux isotopes ont des énergies très différentes.

TABLEAU I

RADIOISOTOPES LES PLUS IMPORTANTS FORMÉS LORS DE L'IRRADIATION DE 5 mg D'ACIER 18/8 AU FLUX DE 10^9 n/cm² sec PENDANT 15 min

Eléments (M)	*μg/5 mg (P)*	*Isotopes de formation*	*Section efficace, ε (barns)*	*Réaction nucléaire*	*Radio-isotopes formés*	*Energie gamma (MeV)*	*Période (T)*	*Activité γ totale, μC(A_t)*
Fe (55.85)	3600	^{58}Fe ^{54}Fe	0.0022 0.128	(n, γ) (n, γ)	^{59}Fe ^{55}Fe	1.10–1.29 (β)	45 j 2.94a	$3 \cdot 10^{-7}$ —
Cr (52.01)	900	^{50}Cr	0.69	(n, γ)	^{51}Cr	0.323	27.8 j	$5 \cdot 10^{-5}$
Ni (58.69)	400	^{64}Ni ^{62}Ni ^{58}Ni	0.0292 0.549 0.0061	(n, γ) (n, γ) (n, p)	^{65}Ni ^{63}Ni ^{58}Co	0.37–1.12 1.49 (β)	2.56 h 125 a 71 j	$2 \cdot 10^{-4}$ — $7 \cdot 10^{-8}$
Mn (54.93)	< 100	^{55}Mn	13.4	(n, γ)	^{56}Mn	0.85–1.81 2.12	2.58 h	$< 2.73 \cdot 10^{-3}$
Mo (95.95)	< 100	^{98}Mo ^{100}Mo	0.031 0.019	(n, γ) (n, γ)	^{99}Mo ^{101}Mo	0.04–0.78 0.19–0.96	6.7 h 15 min	$< 1.5 \cdot 10^{-}$ $< 2 \cdot 10^{-4}$
Si (28.06)	25	^{30}Si	0.0034	(n, γ)	^{31}Si	1.26	2.62 h	$3.5 \cdot 10^{-6}$
Co (58.94)	2.3	^{59}Co ^{59}Co	37 17	(n, γ) (n, γ)	^{60}Co ^{60m}Co	1.13–1.33 0.059	5.27 a 10.5 min	Négligeable $\sim 10^{-2}$
V (50.95)	3.6	^{51}V	4.489	(n, γ)	^{52}V	1.43	3.76 min	$\sim 1.4 \cdot 10^{-2}$

La marche générale d'une telle analyse peut être résumée ainsi: on irradie simultanément un étalon de teneur connue en cobalt (50 μg par exemple) et l'échantillon à analyser renfermant environ 70 μg de cobalt. Après une irradiation de 10 à 15 min environ, on enregistre le spectre-γ de l'étalon et on mesure la hauteur h du photopic du ^{60m}Co à 0.059 MeV, en tenant compte du temps de désintégration t'.

$$A_0 = A_{t'}/e^{-0.693t'/T}$$

où

A_0 = activité calculée au temps $t' = 0$ à la sortie de la pile

$A_{t'}$ = activité mesurée au temps t' après la fin de l'irradiation

T = période du radioisotope (10.7 min)

t' = temps de désintégration.

Pour la détermination des pertes on ajoute à l'échantillon, après l'irradiation, un peu de ^{60}Co dont on détermine le spectre-γ, puis on effectue la séparation du cobalt qui exige environ 15 min.

PARTIE EXPÉRIMENTALE

Solutions utilisées

Tampon acétique pH 6. 16 g d'acétate de sodium, 16 g de citrate de sodium et 6 g de KF sont dissous dans un ballon de 100 ml au moyen d'eau bidistillée. On porte la solution au pH 6 par addition d'acide acétique glacial.

Solution d'α-nitroso-β-naphtol à 0.5% dans l'acide acétique glacial.

Solution de cobalt-60: 1000 cpm/ml.

Solution de cobalt inactif: 2 mg/ml.

Solutions de séparation: toluène, éther, eau bidistillée.

Produits p.a. Merck.

Mode opératoire

Les conditions d'irradiation, l'appareillage, les mesures du temps et de l'activité, et la technique pour la préparation des échantillons ont été décrits[2]. Les rondelles de papier filtre étant dans ce cas imbibées de 10 μl de solution étalon renfermant 50 μg de cobalt et les échantillons solides d'acier 18/8 étant introduits dans de petits sachets en polyéthylène, soit fixés dans le porte-échantillon. La mesure des activités se fait de la façon suivante: le témoin irradié est introduit dans une capsule cylindrique de verre (20 mm de haut et 25 mm de diamètre) contenant 5 ml d'eau bidistillée et cette dernière est placée sur le cristal surmontant le photomultiplicateur.

L'échantillon irradié (100–200 mg d'acier) est placé dans un bécher contenant 3 ml d'eau régale et 2 ml d'une solution de ^{60}Co (environ 2000 cpm). On chauffe pour accélérer la mise en solution tout en évitant une évaporation à sec au cours de laquelle il pourrait se former des oxydes très peu solubles. La solution est reprise par 8–10 ml d'eau bidistillée et transvasée quantitativement dans une ampoule à décanter contenant 15 ml d'éther. On agite et la plus grande partie du fer est extraite. On recueille la phase aqueuse, qui renferme le cobalt, dans une seconde ampoule à décanter dans laquelle on ajoute 10 ml d'un tampon acétique pour complexer le fer n'ayant pas été extrait et 5 ml d'une solution d'α-nitroso-β-naphtol à 0.5%. Après environ 1 min, temps nécessaire à la formation du complexe, on extrait ce dernier par 5 ml de toluène. On sépare les phases. La phase aqueuse renferme le manganèse, le fer (non extrait précédemment) et le vanadium, alors que la phase organique renferme le cobalt. On effectue un lavage de cette dernière au moyen de 5 ml d'un tampon acétique, puis on enregistre le spectre-γ de celle-ci. On observe 3 pics caractéristiques, celui du ^{60m}Co à 0.059 MeV et les 2 pics du ^{60}Co (ajouté comme traceur de pertes avant la séparation) à 1.17 et 1.33 MeV. On mesure la hauteur h_2 de ce dernier. La différence entre h_1 (mesurée avant la séparation) et h_2 permet de calculer les pertes.

La hauteur h_x du spectre du ^{60m}Co de l'échantillon ramené au temps $t' = 0$, multi-

TABLEAU

ACTIVITÉ MESURÉE SUR LE SPECTRE DU ^{60m}Co

Echantillons acier 18/8 (mg)	*Irradiation*		*Activité ^{60m}Co*		
	Temps (min)	*Flux (n/cm² sec)*	*cpm mesurés au temps t'*	*t' en min*	*cpm calculés au temps t' = 0*
98.8	8	$5 \cdot 10^9$	412	29	2690
190.7	10	$5 \cdot 10^9$	874	28	5363
211.8	8	$5 \cdot 10^9$	1655	20	6041
102.7	8	$5 \cdot 10^9$	678	23.5	3112
116.0	15	$5 \cdot 10^9$	1389	21	5048
184.0	8	$5 \cdot 10^9$	594	25	3002

pliée par le coefficient de perte h_2/h_1 est comparée à la hauteur du pic 0.059 MeV de l'échantillon dont la quantité en cobalt est connue. Il est alors facile de calculer la teneur en cobalt de l'échantillon à analyser.

RÉSULTATS

Sensibilité et précision

Les résultats sont donnés dans les Tableaux II et III.

TABLEAU III

COMPARAISON DES RÉSULTATS DE LA MÉTHODE D'ACTIVATION AVEC CEUX DU DOSAGE SPECTROPHOTOMÉTRIQUE ET CALCULS D'ERREURS

Méthode d'analyse	*Echantillons prise (mg)*	*% Co*	*Erreurs extrêmes (%)*	*Déviation standard*	*Limite de confiance à 95%*	*Durée d'une analyse*
	98.8	0.0350				
	190.7	0.0370				
	211.8	0.0346		±0.0022	±0.0056	2 h
Activation	102.7	0.0355	8.82	ou	ou	environ
	116.0	0.0310		±6.21%	±15.95%	
	184.0	0.0368				
		Moy = 0.0350				
	11.7	0.0376				
Spectro-	12.0	0.0342		±0.0014	±0.0036	10–12
photométrie	13.8	0.0377	4.98	ou	ou	h
	14.0	0.0364		±3.76%	±9.66%	
	10.8	0.0370				
	15.8	0.0379				
		Moy = 0.0368				

La moyenne de ceux-ci est de l'ordre de 0.0350% de cobalt et la précision de ±8.8%.

Ces résultats ont été comparés à ceux obtenus par la méthode de dosage spectrophotométrique du cobalt mise au point dans nos laboratoires[4]. Les valeurs obtenues sont données dans le Tableau III. La méthode colorimétrique est plus précise (±5%)

L'EMPLACEMENT DU PHOTOPIC DE 0.059 MeV

Pertes lors séparation Co			*Cobalt trouvé*			*Etalon Co*	
	^{60}Co		^{60m}Co			^{60m}Co	
m *ι)*	*cpm* *(h_2)*	*% Pertes en Co*^{a}	*cpm corrigés pour pertes à* $t' = 0$	*p.p.m. Co dans acier 18/8*	*% Co*	*Prise (µg)*	*Activité au temps* $t' = 0$
06	529	41.5	4598	350	0.0350	20	2658
91	745	53.2	11459	370	0.0370	50	11459
20	3143	38.6	9838	346	0.0346	100	9838
21	581	29.3	4402	355	0.0355	20	4402
33	622	15.5	6401	310	0.0310	40	6401
27	263	71.6	10572	368	0.0368	50	10572

$$\% = \frac{(h_1 - h_2) \cdot 100}{h_1}$$

que la méthode par activation aux neutrons, mais demande par contre 10 à 12 h de travail alors que celle que nous avons mise au point s'effectue en 2 h environ.

La limite de sensibilité est de 2 µg de cobalt; en effet dans nos conditions d'irradiation et d'enregistrement des spectres, il est possible de mesurer avec une précision suffisante l'activité d'un photopic correspondant à la moitié de la valeur du bruit de fond à l'endroit de la mesure, soit 20 cpm (B.F. = 40), avec une erreur de 20% environ ce qui correspond à 2 µg de cobalt.

Cependant, étant donné nos conditions de travail, c'est-à-dire le temps nécessaire au transport de l'échantillon irradié de la pile au local de mesure, à la séparation du cobalt (20 min) et à l'enregistrement des spectres, la limite de dosage est de 10 µg de cobalt environ.

Le temps pour une analyse est de 2 h environ soit: 10–15 min pour l'irradiation, 15–20 min pour la séparation du cobalt, 30 min pour l'enregistrement des spectres, et 60 min pour les calculs. Quant au temps *t'*, il est de 20 min environ. Avec un appareil plus perfectionné, ces temps pourront être sensiblement réduits.

Nous tenons à remercier le Fonds National Suisse pour la Science Atomique, grâce auquel il nous a été possible de mener à bien ce travail.

RÉSUMÉ

Une méthode de dosage du cobalt dans les aciers 18/8, basée sur l'emploi du ^{60m}Co, est proposée. Après élimination de la plus grande partie du fer par l'éther chlorhydrique, le cobalt est extrait au moyen du toluène comme complexe Co-α-nitroso-β-naphtol. Les pertes sont exactement déterminées. De cette façon on dose en moins de 2 h, le cobalt contenu dans un acier 18/8, avec une précision de ±9%, la limite de sensibilité étant de 2 µg de cobalt. Les résultats obtenus par cette méthode (moyenne = 350 p.p.m.) ont été comparés aux résultats obtenus par une méthode spectrophotométrique (moyenne = 368 p.p.m.).

SUMMARY

A method for the determination of cobalt in 18/8 steels, based on formation of ^{60m}Co is proposed. Most of the iron is extracted, then cobalt is extracted as its α-nitroso-β-naphthol complex into toluene. The losses are determined exactly. A determination is complete within 2 h with a precision of ±9%; the limit of sensitivity is 2 µg of cobalt. The results obtained (average 350 p.p.m.) are compared with results obtained spectrophotometrically (average 368 p.p.m.).

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Kobalt in 18/8 Stählen vorgeschlagen. Sie beruht auf der Bildung von ^{60m}Co mit der Neutronenaktivierungsanalyse. Nach der Abtrennung des Eisens wird das Kobalt mit Toluol als Komplex des α-Nitroso-β-Naphthols extrahiert. Die Bestimmung lässt sich in 2 Stunden mit einer Genauigkeit von ±9% und einer Empfindlichkeit von 2 µg Co durchführen. Die Ergebnisse werden mit spektralphotometrischen Messungen verglichen.

BIBLIOGRAPHIE

[1] T. Westermarck et Fineman, *2e Conf. Int. de Genève*, C-11, 1958, p. 140.
[2] D. Monnier, W. Haerdi et J. Vogel, *Helv. Chim. Acta*, 44 (1961) 1565.
[3] G. Friedlander et J. W. Kennedy, *Chimie Nucléaire et Radiochimie*, Dunod, Paris, 1960, p. 425 et 436.
[4] D. Monnier, W. Haerdi et J. Vogel, *Helv. Chim. Acta*, 44 (1961) 897.

Anal. Chim. Acta, 31 (1964) 413–418

THERMAL ANALYSIS OF SOME METAL N-BENZOYL-N-PHENYLHYDROXYLAMINE CHELATES

RAYMOND A. MEYER, J. FREDERIC HAZEL AND WALLACE M. McNABB

Chemistry Department, University of Pennsylvania, Philadelphia, Pa. (U.S.A.)

(Received April 10th, 1964)

N-Benzoyl-N-phenylhydroxylamine (BPHA) has received a great deal of attention as a precipitating agent for various metal ions. The reagent was originally synthesized by BAMBERGER[1] in 1919 and was first used as a precipitant for aluminum, iron, copper and titanium by SHOME[2]. SHOME and his coworkers[3-9] have since used BPHA to precipitate beryllium, cobalt, gallium, indium, molybdenum, nickel, thorium, titanium and uranium. Several investigators have studied the precipitation of niobium and tantalum[10-12]. Other metals precipitated have included zirconium[13,14], scandium[15], and tin[16].

Although the BPHA chelates have been widely studied as analytical precipitates, little has been done in the field of thermal analysis. DUVAL[17] has reported the thermogravimetric curves of the copper and iron chelates. Thermogravimetric analysis has also been used on the scandium precipitate[15] and the niobium and tantalum precipitates[10]. No differential thermal analysis has been reported.

The present paper describes the differential thermal analysis and thermogravimetric analysis of BPHA and 9 of its precipitates with common metals. The precipitates studied were those of aluminum, cobalt, copper, iron, nickel, cadmium, chromium, manganese and zinc.

EXPERIMENTAL

Differential thermal analysis apparatus

The DTA apparatus used was conventional in nature and employed atmosphere control by the dynamic gas method of STONE[18].

The sample holder–furnace assembly is shown diagrammatically in Fig. 1. The sample block was machined from a 2-inch diameter × 2-inch high block of Inconel and contained 4 holes, 90° apart, for sample, reference, temperature control thermocouple, and gas exit. The block was supported by 4 1/4-inch diameter Inconel tubes, which also acted as thermocouple protection tubes and gas inlet and exit tubes. Two inches below the block, the tubes passed through a 1-inch thick × 4-inch diameter Transite insulating plate and were fastened with tube fittings to a 1/2-inch thick × 9-inch diameter aluminum base plate.

An Inconel cover piece was bolted to the top of the sample block and the assembly could be made gas tight by use of gaskets when collection of effluent gases was desired. The sample holder assembly entered the furnace from the bottom and was held in place by means of wing nuts on studs which were fastened to the furnace and fitted through holes in the aluminum base plate. The furnace itself was supported by a rack made of aluminum Flexaframe rods.

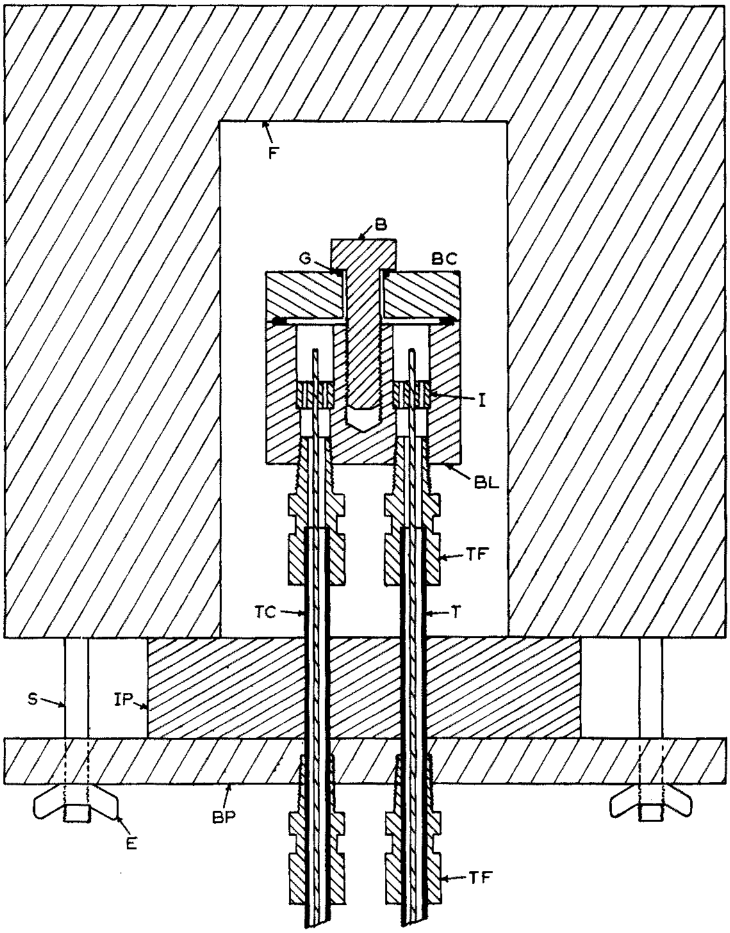


Fig. 1. Differential thermal analysis sample holder–furnace assembly cross-section. F, furnace; B, bolt; G, gasket; BC, Inconel block cover; I, Inconel sample support piece; BL, Inconel block; TF, stainless steel tube fitting; T, Inconel tube; TC, sheathed thermocouple; S, stud; W, wing nut; IP, Transite insulating piece; BP, aluminum base plate.

In operation, the sample and reference were supported by glass-fiber filter mats which were in turn supported by perforated Inconel disks. The mode of thermocouple entry from the bottom was chosen for the ease of packing and cleaning it afforded. The thermocouples themselves were Inconel-sheathed Chromel–Alumel thermocouples, used because of their ruggedness and the protection from contamination given by the sheathing, although their sensitivity and speed of response were not as good as those of bare wire thermocouples.

Temperature was controlled by a West Instrument Company Model JSBG cam program controller utilizing a separate thermocouple. Temperature was recorded by a Leeds and Northrup Speedomax H strip-chart recorder, utilizing the reference half of the differential thermocouple pair. The differential signal was amplified by a Leeds and Northrup 9835-B amplifier and recorded by another Leeds and Northrup Speedomax H strip-chart recorder.

Differential thermal analysis procedure

For DTA runs in nitrogen, a 60–80-mg sample was ground with 500 mg of 180-mesh silicon carbide in a small test tube and transferred to the sample hole of the block. The sample was packed firmly with a small flattened glass rod. For runs in oxygen, 20 mg of sample and 600 mg of SiC were used. An equal volume of SiC alone was used as the reference. All runs were made with a gas flow rate of 10 ml/min through sample and reference and a heating rate of 8°/min.

Temperature calibration of the apparatus was carried out by use of the melting points of benzoic acid, silver nitrate, anthracene, sodium nitrate, and aluminum metal. In each case, the peak minimum was found to agree with the literature value to within 5°, which was the maximum readability of the chart.

Thermogravimetry apparatus

The thermobalance used was an instrument utilizing semiconductor strain gages for weight measurement. Its description may be found elsewhere[19].

Thermogravimetry procedure

Thermogravimetric analysis was carried out with a sample size of 70–100 mg and a heating rate of 5°/min.

Preparation of samples

Eastman 7297 N-phenylbenzohydroxamic acid (BPHA) was used as received.

The precipitates were prepared by adaptations of the procedures described elsewhere in the cases of the aluminum[2], cobalt[4], copper[2], iron[2], and nickel[4] compounds. Similar procedures were used in preparing the cadmium, chromium, manganese, and zinc chelates.

The general procedure consisted of dilution of an aliquot of a standard metal ion solution to about 400 ml in a 600-ml beaker and heating to 50–70°. A 5–10% excess of BPHA in 30 ml of absolute ethanol was added and the pH adjusted to the desired value with 1 *M* sodium acetate or 1 *M* sodium acetate–1 *M* acetic acid solution. After an hour of digestion the precipitate was washed twice with hot 0.1% aqueous BPHA and filtered on a weighed fritted glass filter crucible. The crucible was allowed to air-dry overnight and weighed, then dried for 2h at 110° and weighed again.

Details of individual procedure and yield are summarized in Table I.

The precipitates were analyzed by ignition to the corresponding oxide or, in the cases of cobalt and manganese, converted to the sulfate. Agreements were within 1% of theoretical for $M(C_{13}H_{10}NO_2)_n$ for the compounds of BPHA and M^{n+}. The ignition analyses, together with the yield determinations, showed that the BPHA precipitates formed no stable hydrates.

TABLE I

PREPARATION OF METAL–BPHA CHELATES

Compound	*Metal taken (mg)*	*pH*	*Temperature (°)*	*Yield*			*% Yield*
				Air-dry (mg)	*Oven-dry (mg)*	*Theory (mg)*	
$Al(C_{13}H_{10}NO_2)_3$	23.7	5.5	50–60[a]	582	581	584	99.5
$Cd(C_{13}H_{10}NO_2)_2$	131.5	6.5	60–70	633	629	629	100
$Cr(C_{13}H_{10}NO_2)_3$	47.0	5.0	60–65	376	375	622	60.2
$Co(C_{13}H_{10}NO_2)_2$	73.5[b]	5.0	60–70	601	599	603	99.5
$Cu(C_{13}H_{10}NO_2)_2$	85.0	4.5	60–70	651	648	653	99.2
$Fe(C_{13}H_{10}NO_2)_3$	50.7	4.0	50–60[a]	631	631	630	100.2
$Mn(C_{13}H_{10}NO_2)_2$	73.4[b]	5.0	60–70	633	633	641	98.7
$Ni(C_{13}H_{10}NO_2)_2$	87.6	5.0	60–70	720	719	721	99.7
$Zn(C_{13}H_{10}NO_2)_2$	81.6	7.0	60–70	612	611	611	100

[a] If the temperature became higher than 60°, the precipitate appeared to fuse and stuck to the walls of the beaker.

[b] 10 ml of 1% hydroxylamine hydrochloride solution was added to prevent oxidation of the metal.

RESULTS AND DISCUSSION

The DTA curves of BPHA and the 9 chelates in oxygen and in nitrogen are shown in Figs. 2 and 3. The corresponding TGA curves are shown in Figs. 4 and 5.

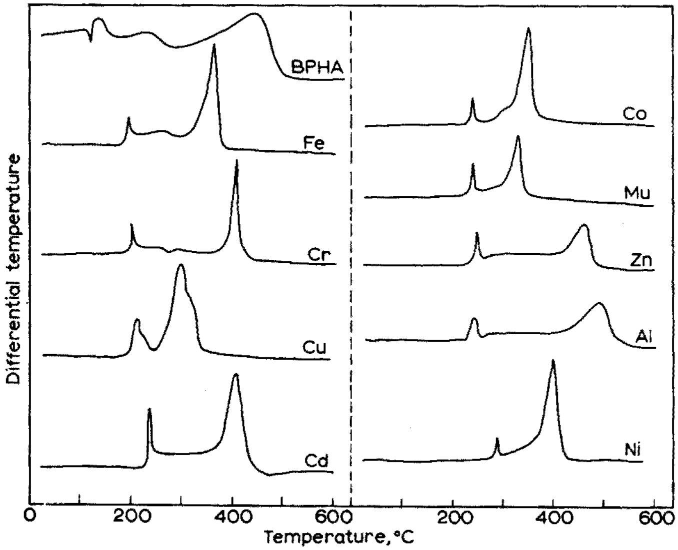


Fig. 2. DTA curves in oxygen.

The curves have a number of similar features. First, all of the chelates show an exothermic decomposition which appears as a peak in DTA and as an abrupt weight loss in TGA. There is no evidence of melting except in the cases of BPHA, which shows a melting endotherm at 120°, and the aluminum chelate, which shows a small endotherm at the beginning of the decomposition peak. In both cases, observation in capillary melting-point tubes indicates that melting occurs with some decomposition.

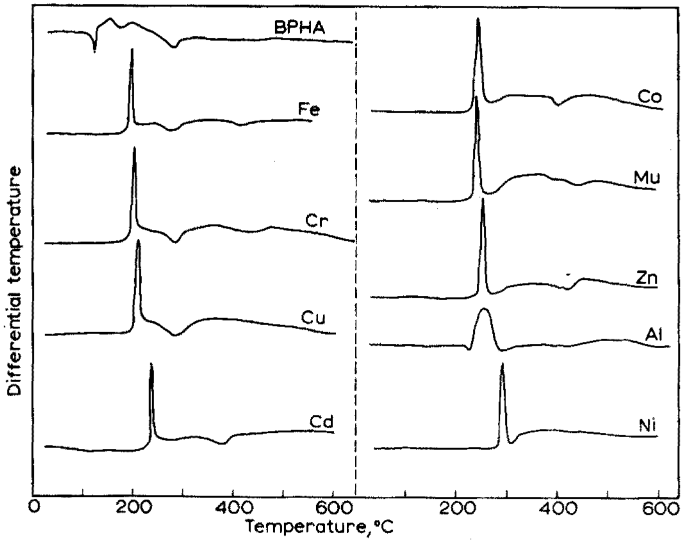


Fig. 3. DTA curves in nitrogen.

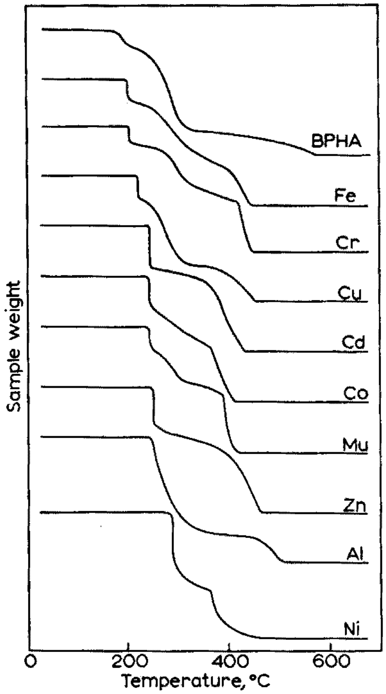


Fig. 4. TGA curves in oxygen.

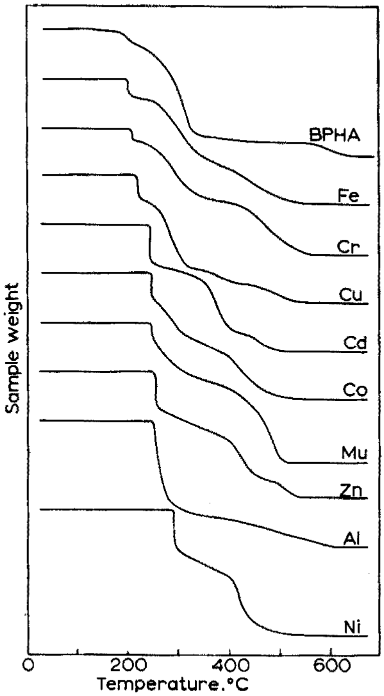


Fig. 5. TGA curves in nitrogen.

The major products of the chelate decompositions were found by ultraviolet and infrared spectrophotometry to be benzanilide, metal benzoate, metal oxide, and tars.

The next common feature in the curves is the vaporization of benzanilide from about 250 to 325°, which appears as a small endotherm in DTA and as a relatively gradual weight loss. Above 325°, the curves show the decomposition of metal benzoates and the degradation of tars. In oxygen, these appear as large DTA oxidation exotherms and sharp weight losses. In nitrogen, the weight losses are more gradual and the corresponding DTA endotherms are small and broad.

The relative decomposition temperatures of the chelates were found to be, in order of increasing stability: Fe(III), Cr(III), Cu(II), Al(III), Cd(II) = Mn(II) = Co(II), Zn(II), Ni(II). Attempts to correlate decomposition temperatures with properties of the metal such as ionic radius or atomic weight showed no relationship. The relative decomposition temperatures do agree well with reported decomposition temperatures for other metal chelates[20-23], as shown in Fig. 6. It appears that the relative thermal stabilities of metal chelates are primarily determined by the metal present, although the reason for this is not understood.

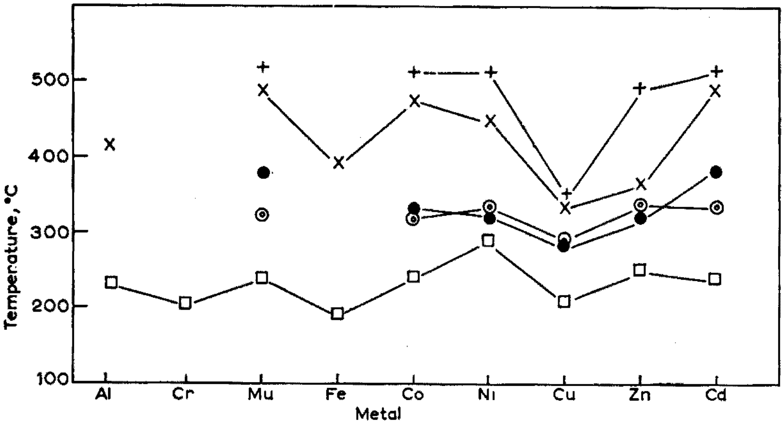


Fig. 6. Thermal decomposition temperatures of various metal chelates. + oxinates, according to CHARLES[20]; × oxinates, according to WENDLANDT AND HORTON[21]; ● picolates, according to THOMAS[22]; ◎ quinaldates, according to THOMAS AND PARIS[23]; ☐ BPHA chelates, from DTA in nitrogen.

One difference between the BPHA chelates and the others cited is the fact that the others decompose endothermically, while the BPHA compounds show exothermic decomposition. This is believed to be caused by the exothermic formation of N_2 in the BPHA chelate decompositions.

The authors would like to express their appreciation to Mr. OLIVER SHANNON for his help in the construction of the apparatus used.

SUMMARY

The preparation and thermal analysis of the metal chelates of N-benzoyl-N-phenylhydroxylamine (BPHA) with Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II) is discussed. The differential thermal analysis apparatus is described in detail. DTA and TGA curves of BPHA and the chelates from 25 to 700° in oxygen and in nitrogen are presented.

RÉSUMÉ

Les auteurs ont effectué une étude sur la préparation et sur l'analyse thermique de chélates métalliques de la N-benzoyl-N-phénylhydroxylamine avec Al(III), Cd(II), Co(II), Cr(III), Cu(II),Fe(III), Mn(II), Ni(II) et Zn(II). Les courbes obtenues par analyse thermique différentielle et les courbes thermogravimétriques sont données pour des températures de 25 à 700°, dans l'oxygène et dans l'azote.

ZUSAMMENFASSUNG

Die Darstellung und thermische Analyse der Metallchelate des N-Benzoyl-N-phenylhydroxylamins (BPHA) mit Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) und Zn(II) wird diskutiert. Es werden Kurven angegeben, wie sie für BPHA und seine Chelate zwischen 25 und 700° in Sauerstoff und Stickstoff mit der Differentialthermoanalyse und der thermogravimetrischen Analyse erhalten wurden. Die Apparatur wird genau beschrieben.

REFERENCES

[1] E. Bamberger, *Ber.*, 52 (1919) 1116.
[2] S. C. Shome, *Analyst*, 75 (1950) 27.
[3] S. K. Sinha and S. C. Shome, *Anal. Chim. Acta*, 21 (1959) 415.
[4] S. K. Sinha and S. C. Shome, *Anal. Chim. Acta*, 21 (1959) 459.
[5] S. K. Sinha and S. C. Shome, *Anal. Chim. Acta*, 24 (1961) 33.
[6] J. Das and S. C. Shome, *Anal. Chim. Acta*, 24 (1961) 37.
[7] J. Das and S. C. Shome, *Anal. Chim. Acta*, 27 (1962) 58.
[8] J. Das and S. C. Shome, *Anal. Chim. Acta*, 27 (1962) 545.
[9] V. R. M. Kaimal and S. C. Shome, *Anal. Chim. Acta*, 27 (1962) 298.
[10] A. K. Majumdar and A. K. Mukherjee, *Anal. Chim. Acta*, 21 (1959) 245.
[11] F. J. Langmyhr and T. Hongslo, *Anal. Chim. Acta*, 22 (1960) 301.
[12] R. W. Moshier and E. Schwarberg, *Anal. Chem.*, 29 (1957) 947.
[13] D. E. Ryan, *Can. J. Chem.*, 38 (1960) 2488.
[14] I. P. Alimarin and T. Yun'-Syan, *Zh. Analit. Khim.*, 14 (1959) 574.
[15] I. P. Alimarin and T. Yung-Schaing, *Talanta*, 8 (1961) 317.
[16] D. E. Ryan and G. D. Lutwick, *Can. J. Chem.*, 31 (1953) 9.
[17] C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, New York, 1953.
[18] R. L. Stone, *J. Am. Ceram. Soc.*, 35 (1952) 76.
[19] R. A. Meyer, *Dissertation*, University of Pennsylvania, Philadelphia, Pa., U.S.A., 1963.
[20] R. G. Charles, *Anal. Chim. Acta*, 27 (1962) 474.
[21] W. W. Wendlandt and G. R. Horton, *Anal. Chem.*, 34 (1962) 1098.
[22] G. Thomas, *Thèse*, Lyon, 27 février 1960.
[23] G. Thomas and R. A. Paris, *Anal. Chim. Acta*, 25 (1961) 159.

DOSAGE AMPEROMETRIQUE RAPIDE ET DIRECTE DE CALCIUM ET DE MAGNESIUM DANS L'EAU, LES CIMENTS ET LE SOL

A. ROUÈCHE ET D. MONNIER

Laboratoires de Chimie Minérale et Analytique,
Université de Genève, Genève (Suisse)

(Reçu le 23 mars, 1964)

La titrimétrie complexométrique à l'EDTA est la plus utilisée pour le dosage du calcium et du magnésium dans l'eau, le point final étant mis en évidence par un indicateur métallique. JANUSZKIEWICZ[1] utilise la murexide pour le calcium et l'ériochrome T pour la somme calcium–magnésium. Les ions gênants sont masqués par le cyanure. On peut aussi extraire les métaux lourds gênants, au pH $= 7$, par une solution chloroformique de diéthyldithiocarbamate[2].

La méthode spectrophotométrique à l'acide chloranilique[3] permet de doser le calcium en présence de 5 fois plus de magnésium. Quant à ce dernier il est déterminé comme pyrophosphate.

Pour le dosage de ces deux éléments dans les ciments et dans les terres on emploie la méthode complexométrique[4,5]; elle nécessite une séparation préalable, au moyen de l'oxalate d'ammonium et on dose le calcium par l'EDTA et le magnésium comme pyrophosphate. On peut aussi doser ce dernier par spectrophotométrie avec le magonsulfonate[6] après avoir éliminé les métaux lourds comme hydroxydes.

Comme on le voit la détermination du calcium et du magnésium dans ces échantillons exige une séparation préalable. On peut parfois l'éviter mais alors le magnésium s'obtient par différence et la méthode n'est précise que si le rapport Mg/Ca est suffisamment grand.

Nous proposons une méthode de dosage directe qui permet de déterminer, en une seule opération, successivement le calcium et le magnésium, pour des rapports Ca/Mg pouvant varier de 1/1000 à 1000.

La principe de la méthode consiste à doser successivement, en milieu alcalin, par titrimétrie ampérométrique, le calcium par l'ion éthylène-glycol-bis-(2-aminoéthyléther)-N,N'-tétracétate (EGTA ou Z^{4-}) et le magnésium par l'ion éthylène-diaminetétracétate (EDTA ou Y^{4-}). Les points équivalents sont déterminés grâce à un circuit ampérométrique. En présence d'un excès de l'un ou l'autre de ces réactifs, le mercure est oxydé selon la réaction:

$$\mathrm{Hg} + \mathrm{Z^{4-}(Y^{4-})} \rightarrow \mathrm{HgZ^{2-}(HgY^{2-})} + 2\,e$$

Il se produit donc un saut de courant aux deux points équivalents qui marquent la fin de chaque titration. Le dispositif ampérométrique est constitué d'une électrode de mercure et d'une électrode de référence (ECS) auxquelles on applique une différence de potentiel E_a de 20 mV environ (Fig. 1). Les bases théoriques concernant cette méthode ont été présentées dans une publication précédente[7].

On peut remplacer l'électrode de référence par une deuxième électrode indicatrice à mercure. Dans le circuit on insère un galvanomètre suffisamment sensible (0.1 μA). On utilise pour la titration deux burettes graduées au 1/100 ml contenant l'une la solution d'EGTA, l'autre celle d'EDTA dont la molarité dépend de la concentration du calcium et du magnésium de l'échantillon. Des courbes de titration typiques sont données dans la Fig. 2.

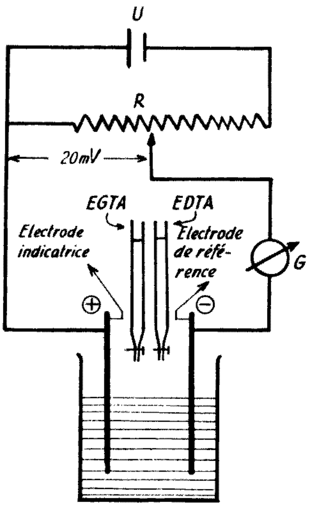


Fig. 1. Dispositif de dosage ampérométrique.

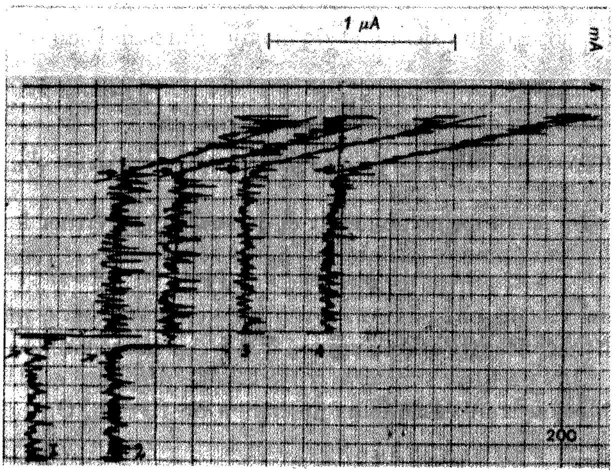


Fig. 2. Courbes de titration. Courbes 1 et 2: dosage simultané de Ca et Mg sur 10 ml d'une solution renfermant $[Ca^{2+}] = 30$ μg/ml (titré par l'EGTA 10^{-2} *M*) et $[Mg^{2+}] = 0.81$ μg/ml (titré par l'EDTA 10^{-3} *M*). Courbes 3 et 4: dosage du magnésium seul sur 30 ml de solution renfermant $[Mg^{2+}] = 0.81$ μg/ml.

PARTIE EXPÉRIMENTALE

Réactifs

Solution tampon d'éthanolamine 10^{-1} *M*.

Solution renfermant 1% de citrate d'ammonium et 1% de tartrate sodico-potassique (cette solution permet de complexer les ions gênants; elle joue aussi le rôle de tampon) (Solution A).

Solution d'EGTA 10^{-2} à 10^{-4} *M*, solution d'EDTA 10^{-2} à 10^{-4} *M*, selon la concentration du calcium et du magnésium dans les échantillons.

(*I*) *Dosage du calcium et du magnésium dans l'eau*

Ces déterminations ont été faites:

(*1*) sur des échantillons de 20 ml d'eau du lac de Genève,

(*2*) sur le résidu d'évaporation de 0.6 l de cette même eau prélevée plusieurs jours après. Dans ce dernier cas, 0.109 g du résidu ont été dissous dans un ballon de 50 ml par 2 gouttes d'HCl concentré. Le volume est complété au trait de jauge par de l'eau bidistillée (Solution B). Le calcium et le magnésium sont dosés sur des parties aliquotes de 2 ml.

Mode opératoire. A la solution à doser (20 ml d'eau ou 2 ml de la Solution B) on ajoute 10 ml du tampon éthanolamine (pH = 10.6), 0.2 ml de la solution A et on porte la solution à 30 ml par addition d'eau bidistillée. On introduit dans le bécher des électrodes auxquelles on applique un potentiel de 20 mV; un agitateur magnétique assure l'homogénéité de la solution. Le calcium est titré au moyen de l'EGTA 10^{-2} *M* jusqu'à ce qu'un saut de courant se manifeste dans le galvanomètre. On arrête immédiatement la titration pour éviter un excès de réactif. On effectue alors le dosage du magnésium avec l'EDTA 10^{-2} *M* jusqu'à l'apparition d'un second saut de courant. La lecture des deux burettes permet de calculer la quantité de calcium et de magnésium de l'échantillon, en tenant compte de la valeur du blanc obtenue comme indiqué ci-dessus mais sans ajouter l'échantillon. La durée du dosage proprement dit est de 4 à 5 min.

Les résultats du dosage du calcium et du magnésium dans l'eau du lac sont donnés dans le Tableau I.

(*II*) *Dosage du calcium et du magnésium dans les ciments*

Composition moyenne: SiO_2 20–24%, Al_2O_3 6–9%, Fe_2O_3 2–4%, CaO 61–66%, MgO 1–3%, SO_3 1–1.5%.

Ce dosage est basé sur le principe décrit ci-dessus. Pour vérifier les résultats nous avons dosé le calcium comme oxalate, et après séparation, le magnésium comme pyrophosphate.

Mode opératoire. On dissout environ 0.100 g de ciment dans 5 ml de HCl 12 *N*, et 2 gouttes d'HNO_3 concentré et on évapore à sec. Après insolubilisation de la silice par 4 ml de HCl 12 *N* on filtre sur verre fritté G3. Le précipité est lavé par 5 ml de HCl 6 *N* et la solution transvasée dans un ballon de 100 ml. On porte au trait de jauge par l'eau bidistillée.

A 0.2 ml de cette solution, on ajoute 10 ml du tampon éthanolamine et 0.2 ml de la solution A (citrate–tartrate). On complète à 30 ml par de l'eau bidistillée, titre le calcium par une solution d'EGTA 10^{-3} *M* et le magnésium par une solution d'EDTA 10^{-3} *M*. On effectue un blanc comme dans le dosage du ciment. Les résultats

TABLEAU I

RÉSULTATS DU DOSAGE DU CALCIUM ET DU MAGNÉSIUM DANS L'EAU DU LAC

	Echantillons[a] *Prise*	*Quantités trouvées*[b, c] *(mg/l)*		*Ecarts extrêmes (%)*		*Déviation standard*		*Limite de confiance à 95%*		*Concentration des complexons (M)*	
		Ca^{2+}	*Mg^{2+}*	*Ca^{2+}*	*Mg^{2+}*	*Ca^{2+}*	*Mg^{2+}*	*Ca^{2+}*	*Mg^{2+}*	*EGTA*	*EDTA*
1	20 ml d'eau du lac	41.9, 41.5 40.9, 41.9 41.3 Moy. = 41.5	4.86, 4.35 4.76, 4.25 4.86 Moy. = 4.62	1.15	6.66	±0.36 ou ±0.90%	±0.27 ou ±5.90%	±2.50	±16.34	10^{-2}	10^{-2}
2	2 ml Solution B	39.9, 39.1, 39.5 39.0, 39.6 Moy. = 39.4	5.50, 5.50 5.30, 5.60 5.10 Moy. = 5.40[d]	1.01	4.76	±0.37 ou ±0.95%	±0.20 ou ±3.70%	±2.63	±10.24	10^{-2}	10^{-2}

[a] Les échantillons 1 et 2 ont été prélevés dans le lac, au même endroit mais à des époques différentes.
[b] Chaque valeur donnée dans les colonnes 2 et 3 correspond à une analyse complète sur le même échantillon.
[c] Résultats moyens donnés par le Service des Eaux du Canton de Genève: Ca^{2+} = 45 à 48 mg/l; Mg^{2+} = 5.5 à 6 mg/l.
[d] Résultat du dosage du Mg^{2+} par activation aux neutrons sur l'échantillon 2: Mg^{2+} = 5.2 mg/l.

TABLEAU

DOSAGE DU CALCIUM ET DU

Echantillons no.	*Prises*	*Quantités trouvées*				*Erreurs extrêmes (%)*	
		Ca^{2+}(µg)	*Mg^{2+}(µg)*	*CaO(%)*	*MgO(%)*	*Ca^{2+}*	*Mg^{2+}*
1	0.2 ml solution contenant 0.1196 g de ciment dans 100 ml	118 114 115 113 114 Moy = 115	2.5, 2.7 2.5, 2.6 2.4 Moy = 2.54	66.70	1.72	2.16	5.88
1	0.1 ml solution contenant 0.105 g de ciment dans 100 ml	97.0, 94.9 95.1 94.0 94.2 Moy = 95.1	2.5, 2.4 2.2, 2.5 2.1 Moy = 2.34	64.7	1.77	1.57	8.70
1	0.1 ml solution contenant 0.1379 g de ciment dans 100 ml	132.5 132.0 130.0 132.5 Moy = 132	3.4, 3.4 3.2 3.5 Moy = 3.37	66.8	1.85	0.73	4.48
2	0.1 ml solution contenant 0.1023 g de ciment dans 100 ml	90.9, 90.9 92.0, 93.3 91.0 94.5 Moy = 92.1	2.1, 2.2 2.4, 2.5 2,3 2.4 Moy = 2.3	63.00	1.82	1.94	8.70
2	0.1 ml solution contenant 0.1049 g de ciment dans 100 ml	100.7, 99.3 99.6 98.0 97.7 97.7 Moy = 98.8	2.5, 2.4 2.3, 2.3 2.4 2.5 Moy = 2.4	67.00	1.90	1.51	4.17
2	0.1 ml solution contenant 0.094 g de ciment dans 100 ml	88.0, 88.1 86.0 88.2 88.3 Moy = 87.7	2.4, 2.4 2.2, 2.25 2.3 Moy = 2.30	65.00	1.86	1.32	4.35

sont donnés dans le Tableau II. La durée de cette double détermination est de moins de 2 h (mise en solution et séparation comprises). La titration elle-même dure quelques minutes.

Remarque: Etant donné la grande quantité de CaO renfermée dans les ciments, la précision de la méthode pour ce composé est sensiblement moins bonne que celle obtenue par les méthodes classiques.

(*III*) *Dosage du calcium et du magnésium dans le sol*

Nous avons dosé ces deux élements dans quelques échantillons de terre prélevés au voisinage de l'Ecole de Chimie de Genève. Pour comparer les résultats obtenus par cette méthode, nous avons dosé parallèlement le calcium et le magnésium par

II

MAGNÉSIUM DANS LES CIMENTS

Déviation standard		*Limite de confiance à 95%*		*Concentration des complexons (M)*		*Quantités trouvées par méthode gravimétrique*	
Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	*EGTA*	*EDTA*	*CaO(%)*	*MgO(%)*
±1.93 ou ±1.68%	±0.134 ou ±5.27%	±4.65%	±14.60%	10^{-3}	10^{-3}	65.34	1.82
±1.00 ou ±1.06%	±0.188 ou ±8.04%	±2.94%	±22.27%	10^{-3}	10^{-4}	65.34	1.82
±1.23 ou ±0.93%	±0.121 ou ±3.62%	±2.88%	±11.58%	10^{-3}	10^{-4}	65.34	1.82
±1.63 ou ±1.77%	±0.149 ou ±6.42%	±4.60%	±16.69%	10^{-3}	10^{-3}	65.20	1.86
±1.42 ou ±1.44%	±0.100 ou ±4.17%	±3.74%	±10.84%	10^{-3}	10^{-4}	65.20	1.86
±0.978 ou ±1.12%	±0.090 ou ±3.91%	±3.10%	±10.85%	10^{-3}	10^{-4}	65.20	1.86

une méthode gravimétrique, le calcium étant séparé comme CaC_2O_4 puis dosé par le $KMnO_4$ $N/10$, et le magnésium séparé comme PO_4MgNH_4 est dosé comme $Mg_2P_2O_7$.

Mode opératoire. On traite environ 1.0 g de terre séchée par 10 ml HCl 3.6%, à chaud pendant 30 min. On filtre le résidu sur verre fritté G3, lave au moyen d'une solution HCl 3.6% (10 ml), transvase la solution obtenue dans un ballon de 50 ml et on complète au trait de jauge par l'eau bidistillée.

Pour le dosage on prélève 0.1 ml de cette solution, ajoute 10 ml de tampon éthanolamine $10^{-1}\,M$ (pH = 10.5), 0.2 ml de la solution A (citrate–tartrate) et complète au volume de 30 ml par de l'eau bidistillée.

On titre le calcium par une solution d'EGTA $10^{-3}\,M$ puis le magnésium par une solution d'EDTA $10^{-3}\,M$, le dispositif ampérométrique étant le même que ci-dessus.

TABLEAU

DOSAGE DU CALCIUM ET DU MAGNÉSIUM

Echantillons Prises	*Résultats*				*Erreurs extrêmes (%)*	
	Ca^{2+}(µg)	*$CaCO_3$*	*Mg^{2+}(µg)*	*$MgCO_3$*	*Ca^{2+}*	*Mg^{2+}*
(1) 0.1 ml solution contenant 1.005 g de terre dans 50 ml solution	130		10.6			
	133		10.2			
	131		10.6			
	129	16.50%	9.7	1.80%	2.64	5.37
	136		10.8			
	131.8		10.4			
(2) 0.1 ml solution contenant 1.0816 g de terre dans 50 ml solution	151		11.6			
	149		11.2			
	144		10.6			
	151	17.72%	11.0	1.78%	2.37	4.50
	146		10.6			
	148.2		11.0			
(3) 0.1 ml solution contenant 1.0086 g de terre dans 50 ml de solution	146		9.4			
	144		9.5			
	143		8.6			
	142	17.85%	8.5	1.55%	1.39	5.55
	144		9.5			
	143.8		9.1			

On effectue un blanc comme dans le dosage du ciment.

Les résultats sont donnés dans le Tableau III.

La durée d'une double détermination est de moins de 2 h, mise en solution et séparation comprises. Le dosage proprement dit s'effectue en 3 à 4 min.

Nous remercions le Fonds National Suisse grâce auquel ce travail a pu être mené à bien.

RÉSUMÉ

Une méthode de dosage ampérométrique du calcium et du magnésium dans l'eau, les ciments et le sol, est proposée; elle consiste à doser successivement le calcium par EGTA et le magnésium par EDTA. La méthode est directe, rapide et permet de doser le calcium et le magnésium respectivement: dans l'eau (41.5 mg/l et 4.6 mg/l) avec une précision de ±1.15% et ±6.70%; dans les ciments (66.7% CaO et 1.70% MgO) avec une précision de ±2% et ±8%; dans le sol (16.5% $CaCO_3$ et 1.80% $MgCO_3$) avec une précision de ±2.6% et ±5.5%.

Les résultats obtenus par cette méthode sont comparés aux résultats obtenus par une méthode gravimétrique ou volumétrique.

SUMMARY

An amperometric method for the successive titration of calcium and magnesium with EGTA and EDTA respectively is proposed. The method is direct and rapid. Calcium and magnesium can be determined in waters (41.5 mg/l and 4.6 mg/l with a precision of ±1.15% and ±6.70%), in cements (66.7% CaO and 1.70% MgO with a precision of ±2% and ±8%), and in soils (16.5% $CaCO_3$ and 1.8% $MgCO_3$ with a precision of ±2.6% and ±5.5%). The results obtained are compared with those obtained by gravimetric or titrimetric methods.

ZUSAMMENFASSUNG

Es wird eine amperometrische Methode für die aufeinander folgende Titration von Calcium und Magnesium mit EGTA bzw. EDTA vorgeschlagen. Calcium und Magnesium können ohne besondere Vorbereitungen und in kurzer Zeit in Wasser, Zement und Erdproben bestimmt werden.

III

DANS DES ÉCHANTILLONS DE TERRE

Déviation standard		*Limite de confiance à 95%*		*Concentrations des complexons (M)*		*Résultats trouvés par méthode gravimétrique (%)*			
Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	*EGTA*	*EDTA*	Ca^{2+}	$CaCo_3$	Mg^{2+}	$MgCO_3$
±2.79 ou ±2.12%	±0.30 ou ±2.92%	±5.87%	±14.87%	10^{-2}	10^{-3}				
±3.42 ou ±2.31%	±0.425 ou ±3.86%	±6.40%	±10.69%	10^{-2}	10^{-3}	7.14	17.84		
±1.60 ou ±1.11%	±0.448 ou ±4.92%	±3.07%	±13.63%	10^{-2}	10^{-3}	7.06	17.64	0.406	1.41

Die Ergebnisse werden mit denen, die mit gravimetrischen oder massanalytischen Methoden erhalten wurden, verglichen. Die Genauigkeit beträgt bei grösseren Calciumgehalten *ca.* 2%, bei kleineren Magnesiumgehalten 6–8%.

BIBLIOGRAPHIE

[1] T. Januszkiewicz, *Chem. Abstr.*, 57 (1962) 14895c.
[2] G. Solomin, *Chem. Abstr.*, 57 (1962) 9596h.
[3] M. le Peintre, *Compt. Rend.*, 231 (1950) 968.
[4] G. Schwarzenbach et T. W. Biedermann, *Helv. Chim. Acta*, 29 (1946) 811.
[5] F. Hahn, *Anal. Chim. Acta*, 4 (1950) 583.
[6] J. Abbey, *Anal. Chim. Acta*, 27 (1962) 233.
[7] D. Monnier et A. Rouèche, *Helv. Chim. Acta*, 47 (1964) 103; A. Rouèche, *Thèse*, no. 1370, Université de Genève.

THE DETERMINATION OF BROMINE IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

R. H. FILBY*

Mineralogical–Geological Museum,
University of Oslo,
Oslo (Norway)

(Received March 7th, 1964)

Recent neutron activation determinations of iodine in meteorites[1] suggest that previous abundance data for iodine in meteorites (and probably rocks) are too high by factors of from 5 to 30. A similar situation may also apply to bromine abundance data because a satisfactory method for the determination of sub-microgram amounts of bromine in rocks has not been described. Chemical methods for bromine may suffer seriously from contamination by reagents and thus extreme care must be taken with samples of very low bromine contents. In addition, the chemical complexity of silicate rocks often means that involved dissolution and separation procedures must be adopted, resulting in a high probability of error. The most recent and reliable determinations of bromine in rocks have been made by BEHNE[2] who determined bromine (plus iodine) titrimetrically; the method had a sensitivity of 1 μg and thus was not suitable for rocks containing less than 1 p.p.m. of bromine. Moreover, the bromine values included iodine, which may introduce a significant error in certain cases. An accurate, sensitive and contamination-free method for the determination of sub-microgram amounts of bromine in rocks would enable the geochemistry of bromine to be more accurately established.

Neutron activation analysis is very sensitive for many elements and should be suitable for sub-microgram amounts of bromine, as the thermal neutron cross-sections of the two stable isotopes, ^{79}Br and ^{81}Br are 2.9/8.5 barns(^{80m}Br/^{80}Br) and 2.6 barns respectively. Bromine has been previously determined by neutron activation in zinc sulphide[3], in biological materials[4] and in high purity silicon[5].

The method described in this paper was developed for the accurate determination of bromine in silicate rocks and minerals and has been used to determine the bromine contents of the standard rocks, granite G-1 and diabase W-1.

Data for the thermal neutron-capture reactions of the bromine isotopes are shown in Table I. The ^{81}Br (n,γ)^{82}Br reaction was used for the determination of bromine as ^{82}Br has a very convenient half-life. The method is equally suitable, however, for the determination of bromine using ^{79}Br(n,γ)^{80m}Br (see *Sources of error* section).

Irradiation of the samples was carried out in the JEEP reactor, Institute for Atomic Energy, Kjeller, Norway for 1 week at a flux of $2.5 \cdot 10^{12}$ n/cm^2/sec.

---

* Present address: Department of Chemistry, Universidad de El Salvador, San Salvador, El Salvador.

Ammonium bromide was used as a standard and experiments with more than 10 mg of ammonium bromide showed that slight self-absorption of neutrons occurred. Standards were thus prepared by evaporation to dryness of 0.05 ml of a solution containing 0.5 mg of bromine per ml (as ammonium bromide). It was noticed after irradiation of ammonium bromide that some free bromine was produced as a result of radiation damage. Therefore the standards were dissolved and hydrazine sulphate was added to reduce bromine to bromide. The possibility of loss of bromine during irradiation and dissolution was investigated but found to be insignificant.

TABLE I

THERMAL NEUTRON-CAPTURE REACTIONS OF THE BROMINE ISOTOPES

Stable isotope	*Abundance (%)*	*Cross-section (barns)*	*(n,γ) reaction product*	*Mode of decay*	*Half-life*	*Gamma-energies (MeV)*
^{79}Br	50.6	2.9	^{80m}Br	IT,γ	4.6 h	0.04
^{79}Br	50.6	8.5	^{80}Br	β^-,γ	18 min	0.62
^{81}Br	49.4	2.6	^{82}Br	β^-,γ	35.9 h	0.55, 0.77, 1.04, 1.32, 1.90

The decomposition procedure for silicate rocks had to be chosen with care because of the ease of oxidation of bromide to bromine and its subsequent loss by volatilization. Most rock-forming silicate minerals are decomposed by fusion with sodium hydroxide, and this procedure was adopted. For samples containing sulphides which are not decomposed by sodium hydroxide, a mixture of sodium carbonate and potassium nitrate was used.

The procedure adopted for the separation of bromine was based on the selective oxidation of iodide to iodine by sodium nitrite and bromide to bromine by potassium permanganate. Bromine was extracted by carbon tetrachloride, stripped from the organic layer and determined as silver bromide. The separation of iodine was necessary because in normal silicate rocks significant ^{131}I, ^{133}I and ^{135}I are formed by thermal neutron fission of ^{235}U. Chemical yields for bromine ranged from 60 to 84%.

Bromine-82 was measured *ca.* 30 h after irradiation (to allow ^{80m}Br to decay). To obtain maximum sensitivity, the total γ-activity (>0.3 MeV) was measured with a scintillation counter and single-channel pulse-height analyzer. As a check on the results the counts within the 0.55 MeV ^{82}Br photopeak were also measured. Gamma spectra were recorded and ^{82}Br half-life measurements were made to check the radiochemical purity.

EXPERIMENTAL

Apparatus and reagents

A single-channel pulse-height analyzer with scintillation counter equipped with 2 × 2″ NaI(Tl) well-type crystal was used. Standard bromine solution (0.5 mg of bromine per ml) was prepared from AnalaR (B.D.H.) ammonium bromide. The bromine content was established by gravimetric determination as silver bromide.

Bromine carrier solution (5.0 mg of bromine per ml) was prepared from AnalaR ammonium bromide. Iodine hold-back carrier solution (1 mg of iodine per ml) was prepared from potassium iodide.

Preparation and irradiation

Weigh accurately 500 mg of the sample on to a 5-cm square of aluminium foil (washed with water followed by acetone), and carefully wrap the foil around the sample to form an envelope; wrap this in another piece of foil. For the standard, weigh out 0.05 ml of the standard bromine solution on to a 5-cm square of aluminium foil and evaporate to dryness under an infrared lamp. Fold the foil once and then wrap in another piece of foil. Prepare several standards and pack them together with the samples in an aluminium irradiation can. Irradiate in a thermal neutron flux of $2.5 \cdot 10^{12}$ n/cm^2/sec for 1 week. After irradiation allow the samples to stand for 1 day, unless ^{80m}Br is to be measured, in which case the chemical separations should begin as soon as possible after irradiation.

Treatment of samples

Unwrap the foil envelopes and quantitatively transfer the sample to a 40-ml nickel crucible. Add 5 g of sodium hydroxide pellets and 75 mg of potassium bromide to the crucible, cover, and heat to 700° for 10 min. Remove the crucible from the heat, cool, and then place it in a 250-ml beaker. Add 10 ml of iodine hold-back carrier solution and 50 ml of water. Cover the beaker and digest on a steam bath until the cake has dissolved. Remove the crucible and lid from the beaker and wash with a little water. Neutralize the solution with 5 *M* sulphuric acid and add 10 ml in excess.

Cool the solution, transfer it to a 250-ml separating funnel and wash the beaker with water. Add 50 ml of carbon tetrachloride, a few drops of 0.5 *M* sodium nitrite solution and shake to extract the liberated iodine. Add more sodium nitrite and repeat the procedure until no more iodine is liberated on addition of sodium nitrite. Discard the iodine extract and wash the aqueous solution with 20 ml of carbon tetrachloride. Discard the organic layer, and add 30 ml of carbon tetrachloride and 0.1 *M* potassium permanganate solution until the pink color just persists in the aqueous phase. Shake for 1 min to extract the bromine and wash with 30 ml of carbon tetrachloride. Combine the organic extracts and filter through a dry filter paper into a 100-ml separating funnel. Add 30 ml of water and 1 ml of a 1% solution of hydrazine sulphate. Shake until both layers are colourless and discard the organic layer. Transfer the solution to a 100-ml beaker, add 1 ml of concentrated nitric acid and 1 ml of a 1% solution of iron(III) nitrate (prepared by dissolving iron(III) hydroxide in dilute nitric acid). Neutralize the solution with 50% ammonium hydroxide solution and add 2 ml in excess. Heat on a steam bath for 10 min and then filter the solution. Wash the iron(III) hydroxide with 1% ammonium hydroxide solution and discard the precipitate. Make the solution just acid with 5 *M* nitric acid and slowly add a slight excess of a 5% solution of silver nitrate. Heat on the steam bath for 30 min and then filter through a sintered glass crucible. Wash the precipitate with 1% nitric acid solution followed by water, and dry at 130° for 2 h. Cool the crucible in a desiccator and then weigh accurately as much as possible of the silver bromide into a glass counting vial. Determine the chemical yield from the weight of silver bromide.

Treatment of standards

Carefully unwrap the outer foil and discard. Unfold the foil containing the bromine standard and transfer it to a 100-ml beaker. Add 25 ml of water, 1 ml of 1% hydrazine sulphate solution and 5 ml of bromine-carrier solution. Cover the beaker, place on the steam bath for 10 min and then cool. Transfer the solution to a 1000-ml volumetric flask and wash the beaker repeatedly with water. Make up to volume with water. Pipet 2 ml of the standard solution into a glass counting vial.

Measurement of radioactivity

With the scintillation counter–pulse-height analyzer assembly, record the γ-spectra, between 0 and 2 MeV, of the silver bromide precipitates and standards. To determine the ^{82}Br activity of samples and standards, set the analyzer discriminator to record all counts with γ-energies greater than 0.3 MeV. Count the samples and standards and record at least 10,000 counts for each measurement. Re-set the analyzer window to record counts with energies between 0.45 and 0.65 MeV (0.55 MeV ^{82}Br photopeak) and re-count samples and standards (at least 10,000 counts). Apply corrections for decay of ^{82}Br during counting, if necessary. For each sample measure the ^{82}Br activity through at least 4 half-lives as a further check on radiochemical purity. Calculate the bromine content of the sample from the expression:

$$\text{per cent bromine in the sample} = \frac{R_{\text{AgBr}} \cdot m_s \cdot 10^4}{R_s \cdot m \cdot c}$$

where R_{AgBr} = count rate of sample silver bromide,
c = chemical yield of bromine (%),
m_s = mass of bromine in standard aliquot counted (g),
m = mass of sample (g),
R_s = count rate of standard aliquot.

RESULTS AND DISCUSSION

A synthetic standard containing 50 p.p.m. of bromine (as ammonium bromide in an aluminium oxide matrix) was analyzed by the neutron activation method. The results (Table II) show that there is very good agreement between the neutron activation values and the known bromine content. The standard rocks G-1 and W-1 were analyzed for bromine and the results are also shown in Table II. No previous determinations of bromine in these two rocks have been reported and it is thus impossible to assess the accuracy of the neutron activation values.

The bromine values for G-1 and W-1 are lower than the average bromine contents of granites and basalts, 1.3 p.p.m. and 3.6 p.p.m. of bromine respectively[2]. There is thus an indication that the previous abundance figures for bromine are too high, as has been shown to be the case for iodine[1]. More determinations of bromine in rocks need to be made before this can be substantiated.

Sources of error

The results may be in error if bromine isotopes are produced by conflicting reactions, for example, (n,p) or (n,α) reactions with fast neutrons. Possible interfering

TABLE II

VALUES FOR BROMINE IN G-1, W-1 AND A SYNTHETIC STANDARD

Sample	*Neutron activation value (p.p.m.)*		*Standard deviation*	*Half-life of ^{82}Br*
	0.55 MeV	*>0.3 MeV*	*(>0.3 MeV)*	*(>0.3 MeV)*[a]
G-1	0.452	0.432		
	0.492	0.438		
	0.505	0.512		
	0.550	0.538		
Mean	0.500	0.484	0.043	35.8 h
W-1	0.437	0.435		
	0.476	0.457		
	0.555	0.532		
	0.604	0.559		
Mean	0.518	0.496	0.051	36.0 h
50 p.p.m. standard	50.9			
	51.0			
	51.7			
	53.2			
Mean	51.7	—	—	35.9 h

[a] Half-life of ^{82}Br is 35.9 h.

(n,p) reactions are: ^{80}Kr(n,p)$^{80m/80}$Br; ^{82}Kr(n,p)^{82}Br; ^{83}Kr(n,p)^{83}Br; ^{84}Kr(n,p)^{84}Br. These reactions will not constitute any interference because krypton is undetectable in normal silicate rocks and minerals. Of more importance are interfering reactions with rubidium isotopes: ^{85}Rb(n,α)^{82}Br; ^{87}Rb(n,α)^{84}Br. Interference from 32-min ^{84}Br may be ignored because it will have decayed under the conditions of the method. The ^{85}Rb(n,α)^{82}Br reaction may be significant, as rubidium is normally much more abundant than bromine in silicate rocks (G-1, 220 p.p.m. of rubidium; W-1, 22 p.p.m. of rubidium[6]). The cross-sections of (n,α) reactions with reactor spectrum neutrons are generally small, but as the fast neutron flux was not known, the effect was investigated experimentally. A sample of 21.3 mg of rubidium chloride (Johnson-Matthey "Specpure") and a bromine standard were irradiated for 1 week in a flux of $2.5 \cdot 10^{12}$ n/cm^2/sec. After irradiation the rubidium chloride was dissolved in 50 ml of water and 1 ml of 1% hydrazine sulphate solution; 10 ml of bromine-carrier solution were added and bromine was separated as described under EXPERIMENTAL. The ^{82}Br activity was due to ^{82}Br from the ^{85}Rb(n,α)^{82}Br reaction plus ^{82}Br from the (n,γ) reaction with ^{81}Br of the normal bromine impurity in the rubidium chloride. ^{80m}Br will only be produced by the ^{79}Br(n,γ)^{80m}Br on the bromine impurity. Thus for the rubidium chloride, the ^{82}Br/^{80m}Br activity ratio relative to that of the bromine standard gives a measure of the interference from ^{85}Rb. The activities of the 0.04-MeV ^{80m}Br and 0.55-MeV ^{82}Br peaks were measured and the ^{82}Br from the ^{85}Rb (n,α)^{82}Br reaction was calculated from the expression

$$^{82}\mathrm{Br}_{\mathrm{Rb}} = {}^{82}\mathrm{Br}_{\mathrm{total}} - {}^{80m}\mathrm{Br}_{\mathrm{Rb}} \left(\frac{^{82}\mathrm{Br}}{^{80m}\mathrm{Br}}\right)_{\mathrm{standard}}$$

where

$^{82}\mathrm{Br}_{\mathrm{Rb}}$ = ^{82}Br produced by ^{85}Rb(n,α)^{82}Br in rubidium chloride, and

$^{80m}\mathrm{Br}_{\mathrm{Rb}}$ = ^{80m}Br produced by ^{79}Br(n,γ)^{80m}Br in rubidium chloride.

From the experimental data shown in Table III, it was calculated that the spurious bromine contents of G-1 and W-1 from the rubidium content were $2 \cdot 10^{-5}$ p.p.m. and $2 \cdot 10^{-6}$ p.p.m. of bromine respectively. Interference from rubidium was thus negligible.

TABLE III

FORMATION OF ^{82}Br BY CONFLICTING ^{85}Rb(n,α)^{82}Br REACTION

Sample	^{80m}Br *activity (counts/min)*	^{82}Br *activity (counts/min)*	$^{82}Br/^{80m}Br$	*Calculated* ^{82}Br *from* $^{81}Br(n,\gamma)^{82}Br$	*Impurity bromine content (p.p.m.)*	*Spurious bromine content (p.p.m.)*
Rubidium chloride	131	209	1.728	160	0.18	0.076
Bromine standard	1642	2010	1.224	—	—	—

The interfering secondary reaction,

$$^{80}\text{Se}(n,\gamma)^{81}\text{Se} \xrightarrow{\beta^-} {}^{82}\text{Br}(n,\gamma)^{82}\text{Br}$$

will only be significant for selenium matrix materials and can be ignored for geological samples (except selenide minerals).

Bromine isotopes may be produced by thermal neutron fission of ^{235}U, although yields are low. For the mass-80 and mass-82 chains the yields are 0.06 and 0.28% respectively[7]. ^{80}Br and ^{82}Br are shielded by stable ^{80}Se and ^{82}Se so that the proportion of ^{80}Br and ^{82}Br in the mass-80 and mass-82 fission products is very low (0.01%

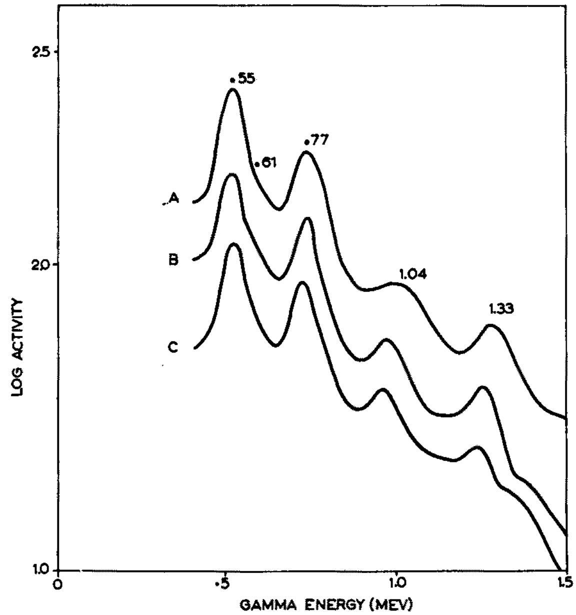


Fig. 1. γ-Ray spectra of ^{82}Br. (A) G-1 silver bromide. (B) W-1 silver bromide. (C) Standard bromine.

for ^{80}Br and 0.06% for ^{82}Br)[8]. Interference from fission with samples of high uranium content will be insignificant.

The γ-spectra of the silver bromide isolated from G-1 and W-1, and the spectrum for the standard are shown in Fig. 1. It can be seen that radiochemically the precipitates were essentially identical with the standard. Further confirmation that only ^{82}Br was measured was provided by the ^{82}Br half-life data shown in Table II.

Sensitivity and precision

For a 1-week irradiation in a flux of $2.5 \cdot 10^{12}$ n/cm^2/sec, it was found that $5 \cdot 10^{-7}$ g of bromine gave an integral count-rate of 270,000 counts/min, 30 h after irradiation. Assuming a minimum count-rate of 3 times the background, the sensitivity was calculated to be $1 \cdot 10^{-9}$ g of bromine, *i.e.* 0.001 p.p.m. of bromine for a 1-g sample. This sensitivity is much superior to that attained by most chemical methods.

The precision of the method may be seen from the data for replicate determinations of bromine in G-1 and W-1. The standard deviations given in Table II were calculated from the determinations, not the counting data.

SUMMARY

A neutron activation method for the determination of bromine in rocks and minerals is described. After removal of iodine, bromine is separated by oxidation with potassium permanganate and extraction with carbon tetrachloride. Bromine is then precipitated as silver bromide; yields are from 60 to 84%. The method has a sensitivity of 0.001 p.p.m. of bromine and is free from interfering reactions. The values obtained for G-1 and W-1, 0.484 and 0.496 p.p.m. of bromine respectively, are lower than the average values for granites and basalts previously reported.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est décrite pour le dosage du brome dans des roches et des mineraux. Après élimination de l'iode, le brome est séparé par oxydation au moyen de permanganate de potassium et par extraction dans le tétrachlorure de carbone. Le brome est ensuite précipité sous forme de bromure d'argent (rendement 60 à 84%). Cette méthode présente une sensibilité de 0.001 p.p.m. de brome; elle n'est pas perturbée par d'autres réactions.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Brom in Gesteinen und Mineralien mit der Neutronenaktivierungsanalyse beschrieben. Nach Entfernung des Jods wird das Brom durch Oxydation mit Kaliumpermanganat und Extraktion mit Tetrachlorkohlenstoff abgetrennt und als Silberbromid ausgefällt. Die Ausbeute beträgt 60–84%. Die Empfindlichkeit der Methode beträgt 0.001 p.p.m. Brom und ist frei von störenden Reaktionen.

REFERENCES

[1] G. G. Goles and E. Anders, *Geochim. Cosmochim. Acta*, 26 (1962) 723.
[2] W. Behne, *Geochim. Cosmochim. Acta*, 3 (1953) 186.
[3] J. F. Cosgrove, R. P. Bastian and G. H. Morrison, *Anal. Chem.*, 30 (1958) 1873.
[4] H. J. M. Bowen, *Biochem. J.*, 73 (1959) 381.
[5] T. Nozaki, T. Kawashima, H. Baba and H. Araki, *Bull. Chem. Soc. Japan*, 33 (1960) 1428.
[6] M. Fleischer and R. E. Stevens, *Geochim. Cosmochim. Acta*, 26 (1962) 525.
[7] C. D. Coryell and N. Sugarman, Eds., *Radiochemical Studies: The Fission Products*, McGraw-Hill, New York, 1951.
[8] T. J. Kennett and H. G. Thode, *Phys. Rev.*, 103 (1956) 323.

NMR ANALYSIS OF α-METHYL BRANCHED ORGANIC ACIDS

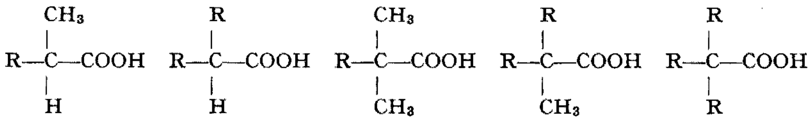
WILLIAM L. SENN, JR. AND LLOYD A. PINE

Esso Research Laboratories, Humble Oil and Refining Company, Baton Rouge, La. (U.S.A.)

(Received March 3rd, 1964)

During a study of KOCH's[1] carboxylic acid synthesis, it became necessary to develop a quick, simple method of analyzing for the different types of isomers produced. In this synthesis, an olefin is reacted with carbon monoxide in the presence of a strong acid catalyst to produce a catalyst–olefin–carbon monoxide complex. Subsequent hydrolysis of this complex produces a carboxylic acid.

As a result of this carbonium ion mechanism, the product contains all of the structures shown below. (R = alkyl group larger than methyl.)



$R{-}\underset{H}{\overset{CH_3}{C}}{-}COOH \quad R{-}\underset{H}{\overset{R}{C}}{-}COOH \quad R{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COOH \quad R{-}\underset{CH_3}{\overset{R}{C}}{-}COOH \quad R{-}\underset{R}{\overset{R}{C}}{-}COOH$

In order to determine the effect of reaction conditions on the relative amounts of these isomers in the product, the following technique of analysis by NMR was developed.

EXPERIMENTAL

Apparatus

Spectra were obtained at a frequency of 60 megacycles per sec using a Varian A-60 NMR spectrometer. Spectral calibration was checked using an SIE Model M-2 R-C Oscillator in conjunction with a Hewlett-Packard 5243L electronic counter. The spectra were calibrated for tetramethylsilane equal to zero p.p.m. The temperature of the probe was regulated with a V-6040 A-60 temperature controller.

Solutions

The organic acids used in deriving the correlations were: I = α,α-dimethylpropanoic acid, II = α,α-dimethylbutanoic acid, III = α,α-dimethylpentanoic acid, IV = α-methylheptanoic acid, V = α-methyl-α-ethylhexanoic acid. These acids were normally run undiluted. Tetramethylsilane was added as an internal standard. When necessary, dilutions were made with deutero-chloroform.

Peak assignments

The general chemical shift assignments for aliphatic organic acids have been given by CHAMBERLAIN[2]. In particular, it is shown that methyl groups in the α-position absorb at 2.0 to 2.2 p.p.m. (from tetramethylsilane), while those in the β-position absorb at 1.2 p.p.m. and those at the γ- or higher position at *ca.* 1 p.p.m. These chemical shifts result primarily from the electronegativity and the magnetic anisotropy of the carboxyl group. CAVANAUGH AND DAILEY[3] found that these 2 factors did not fully explain chemical shift variations in α-substituted compounds. They found it necessary to attribute a chemical shift to the presence of the carbon–carbon bond which replaced the carbon–hydrogen bond present in the normal case. In addition, the size of this shift is dependent on the substituent attached to the α-carbon. Hence the exact resonance position of α-methyl substituents should reflect the types of branching occurring at the α-carbon.

A study was made to correlate types of α-methyl structures in organic acids with chemical shift data. In this study, a selected series of organic acids was run and the

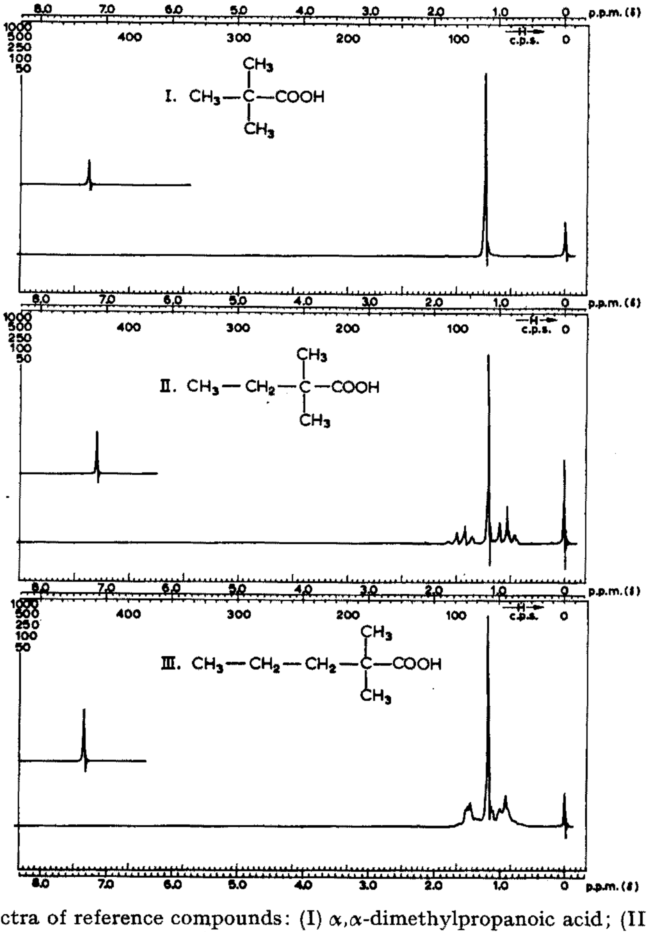
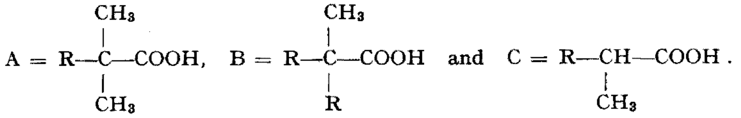


Fig. 1. NMR spectra of reference compounds: (I) α,α-dimethylpropanoic acid; (II) α,α-dimethylbutanoic acid; (III) α,α-dimethylpentanoic acid.

NMR spectra were analyzed. This series was selected to represent the structures:



$$A = R-\overset{CH_3}{\underset{CH_3}{C}}-COOH,\quad B = R-\overset{CH_3}{\underset{R}{C}}-COOH\quad \text{and}\quad C = R-\underset{CH_3}{CH}-COOH\,.$$

Three class A type compounds were studied. The spectra of these compounds are shown in Fig. 1. Compound I presents a very simple spectrum consisting of two lines, the methyl resonance occurring at 1.23 p.p.m. (74 c/s). If one of the methyl groups is replaced by an ethyl group, compound II, the methyl resonance shifts to 1.18 p.p.m. (71 c/s). Increasing the length of the alkyl chain beyond this has little or no effect on the methyl resonance position, as illustrated by a chemical shift of 1.18 p.p.m. (71 c/s) for compound III. Since there is no hydrogen on the α-carbon atom, and hence no spin–spin coupling possible, all of these methyl resonances occur as singlets.

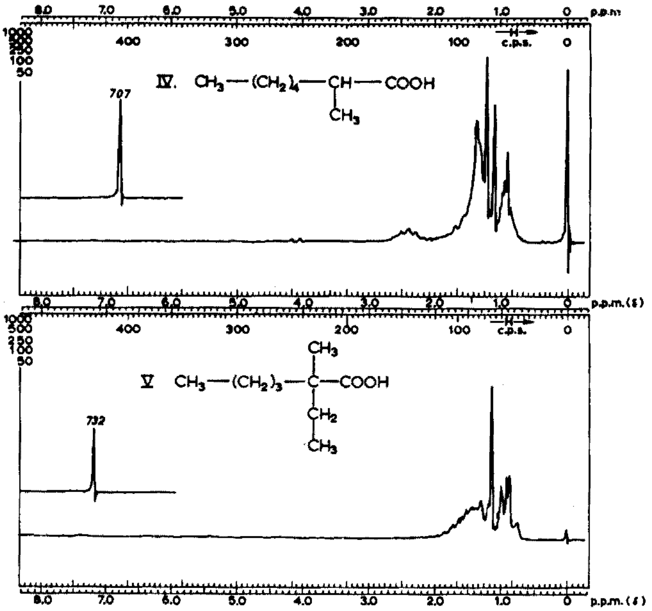


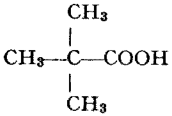
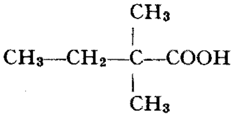
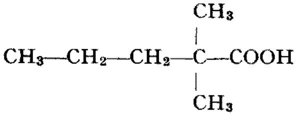
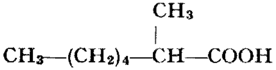
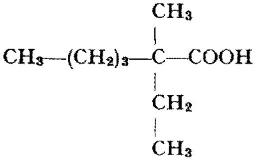
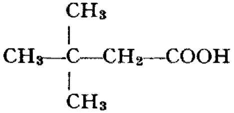
Fig. 2. NMR spectra of reference compounds: (IV) α-methylheptanoic acid; (V) α-methyl-α-ethylhexanoic acid.

The spectra of the reference compounds illustrating classes B and C are shown in Fig. 2. For compound IV, spin–spin coupling between the methyl protons and the proton located on the α-carbon occurs, splitting the methyl resonance into a doublet at 1.10 and 1.22 p.p.m. The coupling constant for this doublet is 7 c/s. For the α-methyl-α-alkyl case, compound V, the methyl protons resonate at 1.13 (68 c/s) p.p.m. The peak is again a singlet.

A chart summarizing these results is shown in Table I.

TABLE I

α-METHYL RESONANCE FREQUENCIES

	1.050	1.067	1.083	1.100	1.117	1.133	1.150	1.167	1.183	1.200	1.217	1.233	(p.p.m.)
Acid structure	63	64	65	66	67	68	69	70	71	72	73	74	(c/s)
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-COOH$												▨	
 $CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-COOH$									▨				
 $CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-COOH$									▨				
 $CH_3-(CH_2)_4-\overset{CH_3}{CH}-COOH$				▨	←		J = 7 c/s			→	▨		
 $CH_3-(CH_2)_3-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-COOH$						▨							
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-COOH$		▨											

DISCUSSION

On the basis of these peak assignments the following correlations were established.

Compound type	*Chemical shift of α-CH_3*
α,α-dimethyl	1.18
α-methyl-α-alkyl	1.13
α-methyl	1.10, 1.22 (J = 7 c/s)

Although these different chemical shifts are not large, they can be resolved in 60 mC operation. This is illustrated in Fig. 3 where NMR spectra of 3 synthetic blends, expanded in the α-methyl region, are shown. In most cases the 3 different acid types are distinguishable, although not necessarily determinable. This is illustrated by a comparison of theoretical composition with that obtained by integrating the NMR spectra as shown in Table II. As might be expected, the component having the

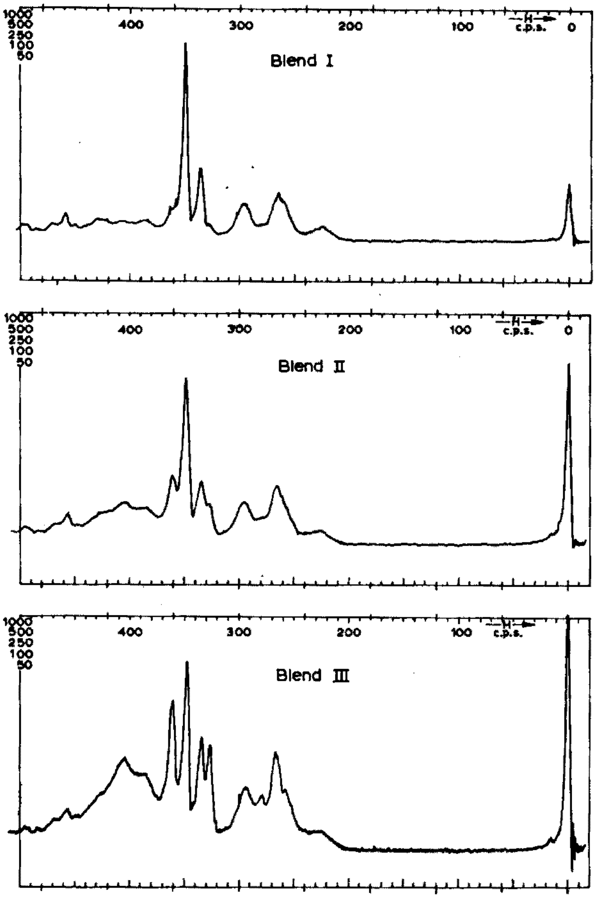


Fig. 3. NMR spectra of synthetic blends.

TABLE II

ANALYSIS OF SYNTHETIC BLENDS

Component	*Mole per cent*					
	Blend I		*Blend II*		*Blend III*	
	Theoretical	*Calculated*	*Theoretical*	*Calculated*	*Theoretical*	*Calculated*
α-Methylheptanoic acid	9.4	19.4	37.5	43.2	58.7	57.5
α,α-Dimethylbutanoic acid	47.4	41.1	36.0	32.1	18.6	19.4
α-Methyl-α-ethylhexanoic acid	43.2	39.5	26.5	24.7	22.7	23.1

largest effect on this analysis is the α-methyl acid, since it contributes only 3 hydrogens per molecule to this region and their absorption occurs as a doublet. Hence, NMR spectra may be used in obtaining quantitative data when this species is either absent or present in appreciable concentrations.

The correlations have been used in analyzing acid mixtures over the C_5 to C_{13} range.

In addition to the α-methyl acids produced by the carbonium ion mechanism occurring in the KOCH synthesis, α,α-dialkyl acids may also be produced. These acids have no peaks peculiar to their structure. However, their presence can be detected by determining total hydrogen on the sample and making a hydrogen balance based on the determinable structures. This calculation assumes that the molecular weight of the acids is known.

This technique has proved to be extremely useful in screening synthesis mixtures and securing quantitative data on those products of interest.

The authors wish to thank the Esso Research Laboratories, Humble Oil & Refining Co., for permission to publish this material.

SUMMARY

A method for analyzing α-methyl branched organic acids has been developed using NMR spectroscopy. The composition is determined in terms of α,α-dimethyl, α-methyl-α-alkyl and α-methyl structures. Peak assignments were made on the basis of model compound studies. This technique has been successfully used in analyzing KOCH acid synthesis mixtures.

RÉSUMÉ

Une méthode par spectroscopie (avec spectromètre Varian A-60 NMR) a été mise au point pour l'analyse d'acides organiques α-méthylés. Cette technique a été appliquée avec succès à l'analyse de mélanges d'acides (synthèse de KOCH).

ZUSAMMENFASSUNG

Es wurde eine kernresonanzspektroskopische Methode für die Analyse organischer Säuren mit einer Methylgruppe in α-Stellung entwickelt. Die Maximumsbestimmungen wurden an Hand von Untersuchungen an Modellverbindungen durchgeführt. Diese Technik wurde erfolgreich bei der Analyse von Mischungen nach der KOCHschen Säure-Synthese benutzt.

REFERENCES

[1] H. KOCH, *Brennstoff-Chem.*, 36 (1955) 321.
[2] N. F. CHAMBERLAIN, *Anal. Chem.*, 31 (1959) 56.
[3] J. R. CAVANAUGH AND B. P. DAILEY, *J. Chem. Phys.*, 34 (1961) 1099.

RADIOCHEMICAL SEPARATION OF ZIRCONIUM FROM NIOBIUM WITH SALICYLHYDROXAMIC ACID

SYED MUHAMMAD QAIM*

Department of Inorganic and Physical Chemistry,
University of Liverpool, Liverpool (Great Britain)

(Received March 20th, 1964)

Zirconium and niobium show a marked analogy in chemical behaviour, and their separation in a high state of purity presents some difficulty. Various procedures for their radiochemical separations from other fission products have been reviewed[1] in 2 recent monographs but very few methods have been suggested for rapid separation of the 2 elements from each other. The radioisotopes of these elements which have been commonly employed in tracer studies are 65-d ^{95}Zr and 35-d ^{95}Nb, both of which are formed in the fission of ^{235}U. As the half-lives of these isotopes are long, a separation time of the order of a few hours does not matter. However, if some short-lived isotopes were to be used, a more rapid procedure would be required.

During a radiochemical study of the short-lived neutron-deficient isotopes of niobium produced by (p, pxn) reactions in the spallation of niobium with 340 MeV protons, it was desired to separate the daughter zirconium activities from the parent niobium, quantitatively and rapidly. Zirconium activities in the carrier-free state are notorious for their adsorption on foreign matter and glass-ware, thereby resulting in serious losses. In order to avoid this, and conveniently to apply corrections for the chemical yield, addition of a few milligrams of inert carrier was found to be essential. Solvent extraction procedures using TTA[2-5] and tri-*n*-butylphosphine oxide[6] (supplied by K and K Labs., Inc., New York) were tried. They are rapid and provide good decontaminations but the removal of the activities was found to be non-quantitative. Precipitation[1] as $BaZrF_6$ and co-precipitation[1] with LaF_3 are quick but the subsequent purification using mandelic acid is rather slow. Moreover, about 0.5% of the niobium activity was always found to accompany the separated zirconium even after the purification step. Ion-exchange procedures have been recommended for carrier-free separations[1], but the presence of milligram amounts of carrier would make the process time-consuming.

Salicylhydroxamic acid has been reported[7] as a specific reagent for the separation of zirconium from niobium and tantalum but the method has not been studied at tracer level. This reagent was employed in the present radiochemical separation and gave a high degree of decontamination. Zirconium was precipitated from a solution

---

* Permanent address: Atomic Energy Commission, Pakistan.

2 M in sulphuric acid and 1 M in hydrogen peroxide containing niobium activities. The precipitate was digested in fuming nitric acid, precipitated as hydroxide, taken up in an acid solution and reprecipitated with the reagent. It was finally calcined at 600° to obtain ZrO_2, in which form it was counted.

EXPERIMENTAL

Radioactive tracers

Samples (100 mg) of spectroscopically pure niobium metal powder (supplied by Johnson and Matthey Ltd.) were irradiated with 340 MeV protons for periods of 10–30 min in the internal beam of the Liverpool University Synchrocyclotron at 1 μA. When very active sources were needed, about 2-g samples of niobium were bombarded for 40 min. After irradiation the target material was chemically processed.

(*a*) *Recovery of niobium tracers.* These were obtained by extracting with di-isopropyl ketone[8] from 10 M hydrochloric acid and back-extracting with an equal volume of a solution 2 M in sulphuric acid and 1 M in hydrogen peroxide. This solution, obtained about 50 min after the end of the irradiation, was used in experiments for assaying radiochemical purity. The activities[9] present were very minute quantities of 10-d ^{92}Nb, long-lived ^{91}Nb, 72-d ^{91m}Nb and major amounts of 15-h ^{90}Nb, 2-h ^{89}Nb and 42-min ^{89m}Nb. In addition a new 21-min activity due to ^{88}Nb, whose existence has been reported elsewhere[10], was present. In experiments for the determination of the decontamination factor, however, the irradiated targets were cooled for about 24 h and then niobium was separated. In this case the short-lived activities due to ^{88}Nb, ^{89}Nb and ^{89m}Nb were not present.

(*b*) *Recovery of zirconium tracers.* Zirconium was extracted as the TTA complex in xylene from a solution 6 M in nitric acid and 1 M in hydrogen peroxide and stripped back in an equal volume of 4 M hydrofluoric acid. It was then precipitated as $BaZrF_6$ and dissolved in a mixture of nitric acid and boric acid. Barium was removed as its sulphate and zirconium was precipitated as hydroxide which was then dissolved in 2 M sulphuric acid. This solution was used in experiments for the determination of chemical yield. The separation of zirconium tracers was usually carried out 24 h after the end of the irradiation. Only 79-h ^{89}Zr, 85-d ^{88}Zr and 17-h ^{86}Zr were present[9].

Reagents and solutions

Zirconium carrier. A solution of $ZrO(NO_3)_2 \cdot 2H_2O$ (B.D.H.) was prepared in water containing a few drops of nitric acid (Zr = 10 mg/ml).

Niobium carrier. Freshly precipitated Nb_2O_5 was dissolved in 0.5 M oxalic acid solution (Nb = 10 mg/ml).

Salicylhydroxamic acid (L. Light and Co. Ltd.). A 2% solution of the reagent was prepared in hot water immediately before use.

All the other chemicals used were reagent grade.

Procedure

Allow the niobium activities held in a solution 2 M in sulphuric acid and 1 M in hydrogen peroxide to decay for about 10 min and then add 0.5 ml of the zirconium carrier solution and warm to about 50°. Add 2.5 ml of the salicylhydroxamic acid solution and centrifuge. Collect the precipitate and wash twice with 5-ml portions of a 1% hydrogen peroxide solution. Take it up in 5 ml of fuming nitric acid and transfer the solution to a 50-ml conical flask. Add 0.5 g of potassium bromate and 1 ml of niobium carrier solution, boil the mixture for a few sec, centrifuge and discard the precipitated niobium oxide. Neutralize the supernate with aqueous ammonia, centrifuge and collect the $Zr(OH)_4$ precipitate. Dissolve it in about 10 ml of the 2 *M* sulphuric acid–1 *M* hydrogen peroxide solution and warm to about 50°. Add 3 ml of the salicylhydroxamic acid solution, centrifuge and collect the precipitate. Wash it once with 5 ml of 1% hydrogen peroxide solution and once with 5 ml of a 1% ammonium nitrate solution. Dissolve it in about 0.5 ml of acetone and mount on a platinum planchet. Heat under an infrared lamp to remove acetone and then transfer to a furnace maintained at 600° for about 1 min. Count the sample in the γ-scintillation counter or as desired. The final composition of mounted material is ZrO_2.

The procedure is rapid and if everything is pre-arranged, it should be complete in about 7 min.

RESULTS AND DISCUSSION

Radiochemical purity

Immediately after separation the zirconium samples were counted in a 3″ × 3″ NaI(Tl) scintillator and the γ-spectra analysed using a 50-channel analyser. In addition to the annihilation peak at 0.51 MeV, γ-peaks at 0.59 and 0.90 MeV and a weak one at 1.5 MeV energies were observed. The peaks at 0.59 and 1.5 MeV disappeared after about an hour and were due to 4.5-min ^{89m}Zr. There was some decay of the annihilation peak also during this period due to the same isotope. When this isotope had decayed out, the 2 peaks at 0.51 and 0.9 MeV decayed with the characteristic 80-h half-life of ^{89}Zr. A very weak peak at 0.4 MeV also became apparent after about 2 weeks. This was due to 85-d ^{88}Zr and was masked in the spectra taken not long after separation. These zirconium isotopes were formed in the decay of parent niobium activities.

None of the γ-peaks associated with the isotopes of niobium was observed in any significant proportion and hence it is inferred that the separation provided good radiochemical purity.

Decontamination factor

This was determined using comparatively longer-lived niobium activities. The zirconium decay products of all these isotopes are stable and so the separated zirconium samples should not show any activity. In different experiments, the activities in the solution gave about 10^6 counts per minute but the zirconium samples separated by this method from this solution gave no more than 20 counts per minute. Thus a decontamination factor of at least $5 \cdot 10^4$ was obtained.

Chemical yield

This was determined employing zirconium tracers. Inactive niobium was held in the 2 *M* sulphuric acid–1 *M* hydrogen peroxide solution and a known amount of the zirconium tracer was added. In the samples finally obtained usually 50–60% of the added zirconium activity was recovered.

Applications and advantages

The method is rapid, and hence has been found useful when short-lived zirconium activities, such as 4.5-min ^{89m}Zr, must be separated from parent niobium in a high state of purity. It also has the advantage of providing solid sources suitable for counting. Solvent extraction procedures require a long time to obtain solid sources and ^{89m}Zr decays out during that period.

The method was applied to the determination of the half-life of short-lived ^{88}Nb by the so-called "milking technique", which implies a number of successive separations of the daughter activities at regular intervals of time. The zirconium activities were separated successively from very active parent niobium at regular intervals of 15 min and the separated samples were left for about 30 days so that ^{89}Zr and ^{89m}Zr had decayed out. The γ-spectra of the separated samples were then analysed. Only one prominent peak at 0.4 MeV due to 85-d ^{88}Zr was observed. The area under this peak was determined in each case, corrected for the chemical yield and for the period of decay after the separation, and was plotted against time of milking. Results of two experiments are shown in Fig. 1. The slope of the line gives the half-life of the parent niobium; the mean of these 2 determinations gives a value of 21.5 min for the half-life of ^{88}Nb.

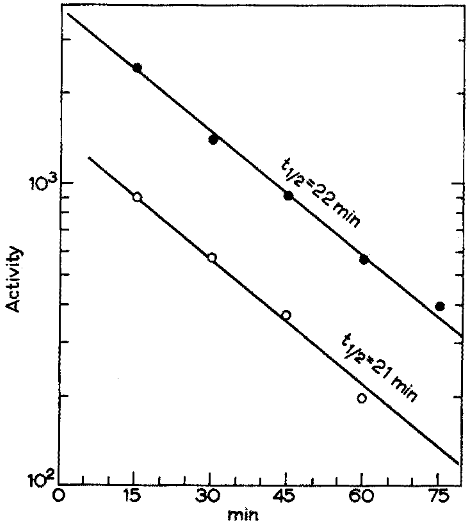


Fig. 1. Yields of ^{88}Zr (area under the 0.4 MeV γ-peak) separated from niobium at 15-min intervals.

When the niobium samples were counted on Geiger Counters through aluminium absorbers thick enough to absorb 3.15 MeV positrons, a short component with a half-life of about 21 min assigned[10] to ^{88}Nb was noted. Results obtained by the 2 methods are thus in agreement.

It has been reported elsewhere[10] that the value for the half-life of ^{88}Nb obtained by similar milking experiments using TTA extraction of zirconium activities is 26 min, which although within the limits of error is longer than the value of 21 min obtained by direct counting. From the present work it is clear that some systematic error of a chemical nature was involved in the TTA extractions; probably the extraction of carrier zirconium by TTA is not quantitative when a short contact period is applied. This makes the half-life appear rather longer.

The correct value of the half-life of ^{88}Nb obtained by the use of salicylhydroxamic acid shows indirectly that zirconium is completely precipitated instantaneously and that exchange between the radioactive and inert forms is 100%. Subsequent purification steps, however, result in some losses and the final chemical yield is 50–60%.

The author is grateful to Dr. F. D. S. BUTEMENT for providing facilities and for helpful discussions, to the crew of the Liverpool University Synchrocyclotron for their help in irradiations, to the Pakistan Atomic Energy Commission for granting leave of absence and to the British Government for the award of a fellowship under the auspices of the Colombo Plan.

SUMMARY

Salicylhydroxamic acid was employed for the rapid radiochemical separation of zirconium from niobium. Neutron-deficient isotopes of the 2 elements formed in the spallation of niobium with 340-MeV protons were used as tracers.

The method was employed in the study of short-lived zirconium and niobium activities using scintillation γ-spectrometry. The procedure is complete in about 7 min, and gives a chemical yield of the order of 50–60% and a decontamination factor of at least $5 \cdot 10^4$.

RÉSUMÉ

L'auteur propose l'emploi de l'acide salicylhydroxamique pour la séparation radiochimique rapide du zirconium d'avec le niobium. Cette méthode a été appliquée à l'étude des activités du zirconium et du niobium de courtes périodes, en utilisant la spectrométrie-γ à scintillations. Ce procédé est rapide (7 min) et donne un rendement chimique de l'ordre de 50–60%, avec un facteur de décontamination d'au moins $5 \cdot 10^4$.

ZUSAMMENFASSUNG

Zur schnellen radiochemischen Trennung des Zirkoniums vom Niob wurde Salicylhydroxamsäure verwendet. Die methode wurde bei der Untersuchung von kurzlebigen Zirkonium- und Niob-Aktivitäten mit der γ-Spektrometrie benutzt. Das Verfahren benötigt etwa 7 Minuten bei einer chemischen Ausbeute von etwa 50–60% und einem Dekontaminationsfaktor von wenigstens $5 \cdot 10^4$.

REFERENCES

[1] E. P. STEINBERG, *The Radiochemistry of Zirconium and Hafnium*, U.S. Atomic Energy Commission, National Academy of Sciences, Nuclear Science Series, report no. 3011, 1960; *The Radiochemistry of Niobium and Tantalum*, U.S. Atomic Energy Commission, Nat. Acad. Sci., Nucl. Sci. Ser., report no. 3039, 1961.
[2] F. L. MOORE, *Anal. Chem.*, 28 (1956) 997.
[3] C. J. HARDY AND D. SCARGILL, *J. Inorg. & Nucl. Chem.*, 9 (1959) 322.
[4] H. L. SCHERFF AND G. HERRMANN, *J. Inorg. & Nucl. Chem.*, 11 (1959) 247.
[5] W. J. MAECK, S. F. MARSH AND J. E. REIN, *Anal. Chem.*, 35 (1963) 292.
[6] H. UMEZAWA AND R. HARA, *Anal. Chim. Acta*, 23 (1960) 267.
[7] A. K. MAJUMDAR AND A. K. MUKHERJI, *Anal. Chim. Acta*, 22 (1960) 25.
[8] H. G. HICKS AND R. S. GILBERT, *Anal. Chem.*, 26 (1954) 1205.
[9] *Nuclear Data Sheets*, U.S. Atomic Energy Commission, National Academy of Sciences, National Research Council, 1963; D. STROMINGER, J. M. HOLLANDER AND G. T. SEABORG, *Rev. Mod. Phys.*, 30 (1958) 585.
[10] F. D. S. BUTEMENT AND S. M. QAIM, *J. Inorg. & Nucl. Chem.*, in press.

DIRECT, RAPID TITRATION OF 8-QUINOLINOL

APPLICATION OF CONSTANT-CURRENT POTENTIOMETRY

C. O. HUBER, J. B. DOE AND H. E. STAPELFELDT

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisc. (U.S.A.)

(Received February 8th, 1964)

The importance of 8-quinolinol (*i.e.*, 8-hydroxyquinoline, oxine) as an analytical reagent is due to its ability to form a variety of metal quinolinates which are insoluble at specific pH levels. Early applications of 8-quinolinol for analytical purposes centered around the gravimetric determination of isolated metal 8-hydroxyquinolinates. The usual volumetric method involves indirect bromination titration. A known excess of bromate is added to a 2 *M* hydrochloric acid solution containing the 8-quinolinol and bromide; after standing a few min, iodide is added and the solution is back-titrated with standard thiosulfate. Direct titration methods are usually slow and are limited by the lack of a good end-point indicator[1]. The use of methyl red can result in a premature end-point owing to destruction of the indicator by local excesses of bromine. BELCHER[2] considers α-naphthoflavone the best visual indicator for direct bromination of 8-quinolinol.

Methods employing amperometric[3], "dead-stop" type[4], photometric[3] and potentiometric[5] end-point detection have been proposed. Constant-current potentiometry has previously been applied to the non-aqueous bromination titration of phenols[6], but not to the direct titration of 8-quinolinol with bromate. Since it is based on potential differences between electrodes which are deliberately polarized with constant currents at the μA level, rapid and unmistakable response to excess bromine in solution is observed. Contrary to amperometric techniques, controlled convection is unnecessary. The apparatus required is extremely simple. This end-point detection technique is applied here.

The bromination of 8-quinolinol proceeds slowly under normal conditions. It was, therefore, considered highly desirable to increase the reaction rate by means other than increasing the temperature in order to minimize losses of bromine through evaporation and to provide for distinctive end-point indication. The development of a considerably faster titration reaction is described.

EXPERIMENTAL

Materials

All chemicals were reagent grade and were used without further purification.

Apparatus

The constant-current potentiometry apparatus used was similar to that described in an excellent exposition of this method by REILLEY, COOKE AND FURMAN[7]. The

2 electrodes were identical and consisted of 0.5 mm diameter platinum wire fused into soft glass tubing, leaving about 3 cm exposed. The constant currents were supplied by a 45 V dry cell battery and 9 or 22 megohm resistors in series. Potential differences between the 2 electrodes were followed on a commercial pH meter using the 1400 mV scale. The titration vessel was a 150-ml beaker. Ordinary volumetric burets were used. Titration and rate study solutions were stirred with a magnetic stirrer.

Preliminary studies

Measured volumes of 8-quinolinol stock solution were titrated with standard bromate stock solution in the presence of bromide. The potential difference between the platinum electrodes was measured, noting that the temporary local excess of bromine caused a momentary drop in the potential measured. Before the equivalence point, the potential difference recovered to approximately 1.0 V (see Fig. 1) with the disappearance of the local bromine excess. In the vicinity of the equivalence point dropwise addition of titrant were made. On reaching the equivalence point, excess of free bromine caused bromine reduction at the electrode which served as the cathode, resulting in a sharp and permanent potential drop of approximately 300 mV per 0.10 ml (Fig. 1). The proposed titration method was compared to the conventional method involving addition of excess standard bromate followed by back-titration with thiosulfate. The thiosulfate solutions used were first standardized against the standard bromate solution in presence of iodide to a starch end-point. The thiosulfate solution thus standardized was used for the back-titration in the conventional indirect titration method.

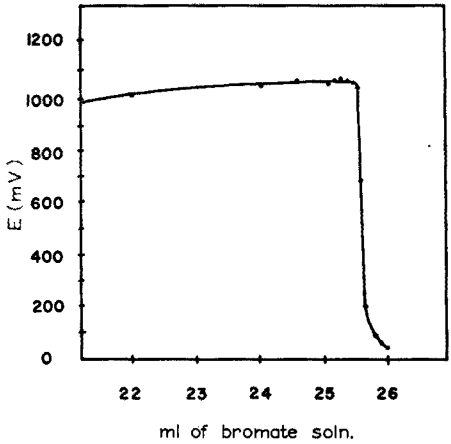


Fig. 1. Constant-current potentiometric titration curve for titration of 0.03 M 8-quinolinol with 0.02 M bromate.

Reaction rates were studied by adding constant increments of bromate solution to known excesses of acidic 8-quinolinol solution in presence of bromide and measuring the time to the disappearance of bromine from solution. The removal of bromine was followed using the constant-current titration apparatus described above. A

20.00-ml volume of 0.02 M bromate standard solution was added to a solution containing 25.00 ml of standard 0.03 M 8-quinolinol and 1 g of sodium bromide at 25°. The total solution volume was 100 ml and the effects of acid, acid concentration, salt concentration and aluminum ion concentration on the reaction time were observed. The reaction time was taken as the time required for the potential difference between the electrodes, which is less than 100 mV in the presence of bromine (Fig. 1), to return to 700 mV, indicating completion of the bromine reaction.

Titration procedure

Add the 8-quinolinol or 8-hydroxyquinolinate to 50 ml of 2 M perchloric acid in a 150-ml beaker which serves as the titration cell. Add 1–2 g of sodium bromide, immerse the electrodes and titrate with stirring using standard sodium bromate. Near the end-point, add the titrant dropwise. The end-point is the first drop which causes a decrease in potential which is stable for at least 20 sec.

RESULTS AND DISCUSSION

Reaction times for the various solution media are given in Table I. The reaction rate is considerably increased when perchloric acid is used instead of hydrochloric acid. The mechanism can be assumed to be the usual aromatic halogen substitution mechanism involving a bromine–aromatic nucleus intermediate followed by formation of product with release of a proton and bromide ion[8]. Presumably, perchlorate ions decrease the activation energy for ionization of the bromine–8-quinolinol active intermediate.

TABLE I

REACTION TIMES FOR VARIOUS REACTION MEDIA

Reaction medium	*Reaction time (sec)*
2 M HCl	375
4 M HCl	172
4 M HCl + 1.0 g $AlCl_3$	92
4 M HCl + 3.0 g $AlCl_3$	94
4 M HCl + 3.0 g $AlCl_3$ + 15 g NaCl	106
1 M $HClO_4$	26
2 M $HClO_4$	21
4 M $HClO_4$	124[a]
2 M $HClO_4$ + 1 g $Al(ClO_4)_3$	17

[a] 4 M $HClO_4$ oxidizes bromide.

The reaction rate increases somewhat with increasing acid concentration. With 4 M perchloric acid, however, visible amounts of bromine appeared in the solution indicating that the oxidizing potential of this concentration of perchloric acid is sufficient to oxidize bromide. Accordingly, 2 M perchloric acid was chosen as the titration medium.

Table I shows that in both hydrochloric and perchloric acid solutions, a moderate increase in reaction rate resulted when the aluminum salt was added. This rate increase was not significant for titration purposes in perchloric acid. When sodium chloride was added to the hydrochloric acid reaction media the reaction rate decreased. This may indicate an inhibiting effect by chloride ion.

Analytical results presented in Table II show good precision for the constant-current potentiometric direct titration and good agreement with the conventional indirect titration method at several concentration levels. The amounts of 8-quinolinol titrated correspond to the analysis of 0.6–14 mg of aluminum via the precipitation of aluminum 8-hydroxyquinolinate. When 0.15 M 8-quinolinol was titrated, the product precipitated near the end-point. This precipitation, however, did not affect the accuracy or convenience of the constant-current potentiometric end-point. Titration could easily be performed in less than 10 min.

TABLE II

COMPARISON OF TITRATION PROCEDURES

Titration	*Titrant volume (ml)*	
	Conventional method	*Constant-current potentiometric method*
10.00 ml 0.15 M oxine with 0.10 M $NaBrO_3$	Mean, 10.43 St. dev. (5)[b], 0.01	Mean, 10.43[a] St. dev. (6), 0.02
10.00 ml 0.03 M oxine with 0.02 M $NaBrO_3$	Mean, 10.42 St. dev. (5), 0.02	Mean, 10.43[a] St. dev. (7), 0.02
10.00 ml 0.006 M oxine with 0.004 M $NaBrO_3$	Mean 10.44 St. dev. (7), 0.05	Mean 10.46[c] St. dev. (7), 0.05

[a] 5 μA constant current.

[b] Numbers in parentheses indicate number of titrations performed.

[c] 2 μA constant current.

TABLE III

CONSTANT-CURRENT POTENTIOMETRIC TITRATION RESULTS IN PRESENCE OF METAL IONS

Sample	*Titrant volume (ml)*	*Standard deviation (4 titrations) (ml)*
25.00 ml 0.03 M oxine in 2 M $HClO_4$ with 20 mg each of Al, Cd, Fe, Mg, Zn	26.12	0.03
25.00 ml 0.03 M oxine in 2 M $HClO_4$	26.15	0.04

The presence of metal ions with more negative reduction potentials than bromine, would not be expected to interfere with the end-point detection. Table III shows that quantitative results are obtained in the presence of several such metals. Accordingly, none of the metals commonly precipitated with 8-quinolinol would interfere. The presence of metal ions which are reduced at the cathode at only slightly more negative potentials than bromine, such as iron(III), decreases the titration potential difference observed before the end-point, but does not impair the distinctiveness of the end-point indication.

The authors gratefully acknowledge the help of Mr. HARVEY HONG who assembled some of the equipment and collected some preliminary data.

SUMMARY

The major problems in the direct bromination titration of the important analytical reagent 8-quinolinol have been slow reaction rate and difficulty of end-point detection. A reaction-rate study showed that perchloric acid as the titration medium gives a sufficiently high reaction rate for direct titration. End-points are simply and conveniently detected using constant-current potentiometry. Metal ions do not interfere. Excellent agreement between titration by the proposed method and the conventional indirect iodometric method was observed.

RÉSUMÉ

Le problème majeur du titrage direct de l'hydroxy-8-quinoléine par bromuration est dû à une vitesse de réaction trop lente et à la difficulté de déceler le point final. Cependant les auteurs ont montré que l'utilisation de l'acide perchlorique comme milieu permet d'obtenir une vitesse de réaction suffisamment grande pour pouvoir effectuer un titrage direct. Le point final est décelé par potentiométrie à courant constant. Les ions métalliques ne gênent pas.

ZUSAMMENFASSUNG

Die Hauptprobleme bei der direkten Bromierung des wichtigen analytischen Reagenzes 8-Hydroxychinolin mittels Titration sind die langsame Reaktionsgeschwindigkeit und Schwierigkeiten bei der Endpunktsanzeige. Eine Untersuchung der Reaktionsgeschwindigkeit zeigte, dass Perchlorsäure als Titrationsmedium eine befriedigend hohe Reaktionsgeschwindigkeit für die direkte Titration ergibt. Die Endpunkte werden einfach und befriedigend potentiometrisch (constant-current potentiometry) angezeigt. Metallionen stören nicht. Es wurde eine ausgezeichnete Übereinstimmung zwischen der Titration mit der vorgeschlagenen Methode und der konventionellen indirekten jodometrischen Methode beobachtet.

REFERENCES

[1] H. F. WALTON, *Principles and Methods of Chemical Analysis*, Prentice-Hall, 1952, p. 341.
[2] R. BELCHER, *Anal. Chim. Acta*, 3 (1949) 578.
[3] R. M. POWERS, R. A. DAY, JR. AND N. F. FURMAN, *Anal. Chem.*, 23 (1958) 254.
[4] G. F. SMITH AND R. L. MAY, *J. Am. Ceram. Soc.*, 22 (1939) 31.
[5] J. A. ATANSIU AND A. J. VELCULESCU, *Z. Anal. Chem.*, 97 (1934) 97.
[6] C. O. HUBER AND J. M. GILBERT, *Anal. Chem.*, 34 (1962) 247.
[7] C. N. REILLEY, W. D. COOKE AND N. H. FURMAN, *Anal. Chem.*, 23 (1951) 1223.
[8] E. S. GOULD, *Mechanism and Structure in Organic Chemistry*, 2nd Ed., Henry Holt and Company, New York, 1959, p. 442.

COMPLEXING EFFECTS IN THE SOLVENT EXTRACTION OF THALLIUM(I) 2-MERCAPTOBENZOTHIAZOLE

GEORGE K. SCHWEITZER AND JAMES D. MATTHEWS

Department of Chemistry, University of Tennessee, Knoxville, Tenn. (U.S.A.)

(Received March 4th, 1964)

Thallium(I) extractions

In the past several years, a variety of organic chelating reagents has been utilized for the extraction of thallium(I) from aqueous solution into an immiscible organic solvent[1]. Detailed equilibrium studies have been carried out on 14 of these reagents, equilibrium constants being calculated and species identification made[2]. The purpose of this study was to investigate the effects of aqueous complexing agents upon the extraction of thallium(I) with one of the most efficient extracting reagents, namely, 2-mercaptobenzothiazole. It was hoped that the data would allow identification of the predominant aqueous complexes and the calculation of their association constants.

Theoretical considerations

In the extraction of thallium(I) from an aqueous phase containing a complexing agent X in a concentration [X] into an organic phase containing mercaptobenzothiazole (MBT or HR) in a concentration $[\mathrm{HR}]_\mathrm{o}$, the most likely extracting organic species can be represented as $\mathrm{TlR(HR)}_\mathrm{a}$ and the most likely aqueous species as $\mathrm{TlR}_\mathrm{r}\mathrm{X}_\mathrm{x}$. These assumptions seem reasonable when one observes similar systems, considers the low concentration of HR in the aqueous phase, and realizes that the association constant of TlOH is about unity[3].

When experiments are conducted to ascertain the organic/aqueous distribution coefficient of the total thallium D, it is generally desirable to determine D as a function of 3 variables: the pH, $[\mathrm{HR}]_\mathrm{o}$, and [X]. The data are then plotted as curves of log D against each of the variables (expressed as pH, log $[\mathrm{HR}]_\mathrm{o}$, or log [X]), the other 2 variables having been held constant. These curves often show regions of constant slope and regions of changing slope, the constant-slope regions generally representing conditions under which a single species predominates in each phase.

The value D in a constant-slope region of a curve may be approximated by the following relationship: $D = [\mathrm{TlR(HR)}_\mathrm{a}]_\mathrm{o}/[\mathrm{TlR}_\mathrm{r}\mathrm{X}_\mathrm{x}]$, where the subscript "o" indicates the organic phase and the unsubscripted brackets signify the aqueous phase. Charges have been omitted for simplicity. By the substitution of a appropriate association constants and partition constants, the following results:

$$D = K_\mathrm{a}P_\mathrm{a}[\mathrm{HR}]_\mathrm{o}^{1-\mathrm{r}+\mathrm{a}}/K_\mathrm{r}^{1-\mathrm{r}}P_\mathrm{r}^{1-\mathrm{r}+\mathrm{a}}C_\mathrm{rx}[\mathrm{H}]^{1-\mathrm{r}}[\mathrm{X}]^\mathrm{x}$$

where K_a is the association constant of $TlR(HR)_a$, P_a is the partition constant of $TlR(HR)_a$, K_r is the acid association constant of HR (MBT in this case), P_r is the partition constant of HR, and C_{rx} is the association constant of TlR_rX_x. It will be noted that the slope of a log D-against-pH plot at constant $[HR]_o$ and [X] will be $1-r$, the slope of a log D-against-log $[HR]_o$ plot at constant [H] and [X] will be $1-r+a$, and the slope of a log D-against-log [X] plot at constant $[HR]_o$ and [H] will be $-x$. These relationships allow decisions as to possible predominating species on the constant-slope portions of the experimental curves and calculations of constants.

Regions of the experimental curves with changing slopes usually reflect that several species are involved in one of the phases, that is, that a species transformation is occurring. Such regions can often be represented by the sum of several terms of the type given above, r or a or x differing in the successive terms. By proper slope analysis and curve fitting, the terms needed to write the complete equation for a total system can be ascertained and usually many of the constants (K_a, P_a, C_{rx}) can be estimated. A more detailed treatment of the theory was presented in a previous paper[4].

EXPERIMENTAL PROCEDURES

Thallium-204 in nitric acid, as obtained from Oak Ridge National Laboratory, was converted to the perchlorate by successive evaporations with perchloric acid. From the product a stock solution was prepared. All chemicals used were reagent-grade. All water and chloroform were purified by double-distillation. Using 30-ml glass bottles, 10-ml portions of the aqueous phase were stirred to equilibrium (for at least 1 h) with 10-ml portions of the chloroform phase at 30.0 ± 0.5°. In all cases, the original thallium concentration in the aqueous phase was 10^{-6} M and the ionic strength was made up to 0.1 with sodium perchlorate if necessary. Anions were introduced as the sodium salts. Adjustments of pH were made with perchloric acid and sodium hydroxide solutions, and pH measurements were conducted with a Beckman Model 76 Meter equipped with Beckman fiber junction and glass electrodes. The instrument was calibrated frequently with Coleman buffers at pH values of 2.00, 4.00, 7.00, 9.00, and 11.00. After a given system had reached equilibrium, a 200-µl pipet was used to sample each phase. The samples were placed onto planchets, dried, and counted with a Tracerlab Beta Scintillation Counter.

RESULTS

In Table I are presented extraction data for 21 systems in which log D was determined as a function of pH or $[HR]_o$ or [X] with the other 2 variables being held constant. These data were plotted and regions of constant slope were identified. The slope values are generally accurate within ± 0.2 slope units.

Non-complexed systems

Data on 2-mercaptobenzothiazole as an extractant for thallium from a perchlorate medium are given in systems 1–8. The curves in systems 1–5 and 8 rise with a slope of 1.0, then plateau to a slope of 0.0, indicating a $1-r$ value of 1.0 at low pH values and of 0.0 at high pH values. This would correspond with an aqueous species Tl^+ and an organic species $TlR(HR)_a$ at low pH and an aqueous species TlR and an organic species $TlR(HR)_a$ at high pH. The curve in system 6 shows a slope of 2.0 indicating $1-r+a$ equal to 2 or the organic species $TlR \cdot HR$ in the region of pH 7.0. Likewise, in the region

TABLE I

EXTRACTION RESULTS

System number — Experimental parameters[a] *— Data*

1. 0.1 M MBT: pH(log D), 5.9(−0.35), 6.3(−0.26), 6.9(0.11), 7.4(0.52), 8.0(0.90), 8.4(0.90), 8.8(0.90); slopes 1.0 and 0.0
2. 0.03 M MBT: pH(log D), 6.3(−0.98), 6.6(−0.66), 7.1(−0.14), 7.4(0.26), 8.0(0.56), 9.1(0.78); slope 1.0
3. 0.01 M MBT: pH(log D), 6.0(−1.46), 6.5(−1.20), 7.3(−0.38), 7.8(−0.13), 8.1(0.26), 8.5(0.43), 8.6(0.43), 10.1(0.40); slopes 1.0 and 0.0
4. 0.003 M MBT: pH(log D), 6.2(−2.03), 6.6(−1.62), 7.1(−1.54), 9.2(−0.24), 9.4(−0.30), 9.3(−0.30), 10.5(−0.20); slopes 1.0 and 0.0
5. 0.001 M MBT: pH(log D), 6.3(−2.74), 6.9(−2.57), 7.6(−1.74), 7.7(−1.66), 10.3(−0.70), 10.4(−0.67), 10.7(−0.60); slopes 1.0 and 0.0

6. Variable MBT at pH 7.0: log $[HR]_o$(log D), −3.0(−2.30), −2.5(−1.26), −2.0(−0.66), −1.5(−0.33), −1.0(0.20); slope 2.0
7. Variable MBT at pH 9.0: log $[HR]_o$(log D), −3.0(−0.66), −2.5(−0.25), −2.5(0.43), −1.5 (0.78), −1.0(0.90); slope 1.0
8. 0.01 M MBT with 1.0 M perchlorate: pH(log D), 5.8(−1.52), 6.9(−0.83), 7.4(−0.35), 7.9(0.04), 8.5(0.28), 8.8(0.26), 10.1(0.26), 10.8(0.18), 10.9(0.12); slopes 1.0 and 0.0
9. 0.01 M MBT with variable iodide at pH 7.0: log [X](log D), −0.7(−1.10), −0.5(−1.46), −0.3(−1.60), 0.0(−1.82); slope 1.0
10. 0.01 M MBT with variable iodide at pH 9.0: log [X] (log D), −0.7(0.18), −0.5(0.00), −0.3 (−0.69), 0.0(−1.10); slope 2.0

11. 0.01 M MBT with variable thiocyanate at pH 7.0: log [X](log D), −0.7 (−0.75), −0.5 (−0.96), −0.3(−1.15), 0.0(−1.42); slope 1.0
12. 0.01 M MBT with variable thiocyanate at pH 9.0: log[X](log D), −0.7(0.04), −0.5(−0.11), −0.3(−0.19), 0.0(−0.46); slope 0.8
13. 0.01 M MBT with variable bromide at pH 7.0: log [X](log D), −0.7(−1.05), −0.5(−1.21), −0.3(−1.40), 0.0(−1.74); slope 1.0
14. 0.01 M MBT with variable bromide at pH 9.0: log[X](log D), −0.7(0.10), −0.5(−0.01), −0.3(−0.17), 0.0(−0.55); slope 1.0
15. 0.01 M MBT with variable chloride at pH 7.0: log[X](log D), −0.7(−0.77), −0.5(−0.94), −0.3(−1.13), 0.0(−1.39); slope 1.0

16. 0.01 M MBT with variable chloride at pH 9.0: log [X](log D), −0.7(0.15), −0.5(0.08), −0.3 (−0.04), 0.0(−0.13); slope 0.4
17. 0.01 M MBT with variable fluoride at pH 7.0: log [X](log D), −0.7(−0.82), −0.5(−1.00), 0.0(−1.18); slope 0.7
18. 0.01 M MBT with variable fluoride at pH 9.0: log [X](log D), −0.7(0.10), −0.5(0.02), 0.0 (−0.10); slope 0.3
19. 0.01 M MBT with 1.0 M cyanide: pH (log D), 7.2(−0.66), 7.7(−0.30), 8.5 (0.09), 9.0(0.11)
20. 0.01 M MBT with 0.3 M sulfate: pH(log D), 7.0(−0.87), 8.8(0.72)
21. 0.01 M MBT with 1.0 M sulfate: pH(log D), 6.8(−0.07), 9.0(0.08)

[a] All systems were made up of MBT in chloroform equilibrated with an aqueous solution 10^{-6} M in radiolabelled thallium perchlorate and 0.1 M in sodium perchlorate. Anions were added to the aqueous phases as the sodium salts in systems 8–21.

of pH 9.0, system 7 points to an organic species TlR · HR, since 1−r+a equals 1. The data of systems 1–8 may thus be represented by writing $D = ([Tl] + [TlR])/[TlR \cdot HR]_o$ or $1/D = [Tl]/[TlR \cdot HR]_o + [TlR]/[TlR \cdot HR]_o$ or $1/D = K_r P_r^2 [H]/K_1 P_1 [HR]_o^2 + P_r C_{10}/K_1 P_1 [HR]_o$. Knowing log K_r to be 7.8 and log P_r to be 2.2[2], curve fitting yields a log K_1P_1 equal to 7.9 and a log C_{10} of 2.4. The influence of increased ionic strength is shown in systems 3 and 8, the result being negligible on the rising portion of the curve and effecting a lowering of the plateau on the zero-sloped portion of the curve.

Complexed systems

Systems 9 and 10 indicate the complexing effect of the iodide ion at pH values of 7.0 and 9.0. Slopes of 1.0 and 2.0 were respectively observed indicating aqueous complexes of TlI and $TlRI_2^{2-}$ as the predominating species. Expressions for the iodide systems might be written as follows: $1/D = ([TlI] + [TlRI_2])/[TlR \cdot HR]_o = K_rP_r^2C_{01}[H][X]/K_1P_1[HR]_o^2 + P_rC_{12}[X]^2/K_1P_1[HR]_o$. Utilizing this relationship, log C_{01} has an estimated value of 0.4 and log C_{12} of 5.0.

Systems 11 and 12 indicate the complexing effect on the thiocyanate ion at pH values of 7.0 and 9.0. The indications from slope values are that the aqueous species are TlSCN and $TlRSCN^-$. Writing equations similar to that in the previous paragraph, log C_{01} equals 0.2 and log C_{11} equals 4.3. Similar results are obtained with bromide (systems 13 and 14) with log C_{01} equalling 0.2 and log C_{11} 4.3. In the chloride systems (15 and 16), at a pH of 7.0, the indicated aqueous species is TlCl, and log C_{01} calculates to be 0.2. At a pH of 9.0, 3 aqueous terms corresponding to species TlCl, TlR, and TlRCl, must be introduced into the expression for D in order to describe adequately the system. Log C_{11} turns out to be 4.1. The fluoride systems (17 and 18) behave very similarly to the chloride ones, log C_{01} being 0.3 and log C_{11} being 4.0. The complexing capabilities of cyanide and sulfate were both very weak (systems 19–21), allowing no species identification nor association constant estimation.

The values of C_{01} for the first complex of thallium with iodide, thiocyanate, bromide, chloride, and fluoride obtained in this study agree quite well with other determinations. For the iodide NILSSON[5] reports a log C_{01} of 0.7, for the thiocyanate he gives a log C_{01} of 0.2, for the bromide a log C_{01} value of 0.3, and for the chloride a log C_{01} of 0.0; for the fluoride, BELL AND GEORGE[3] report a log C_{01} value of 0.0. Other investigators report values very close to these[6]. The lack of complexing in the case of cyanide is in agreement with previous results[5], but a log C_{01} value foi sulfate of about 1.4 is generally recognized[6], which seems to disagree with the effect reported herein.

SUMMARY

Studies of the extraction of thallium(I) from aqueous solution in the absence and presence of aqueous complexing agents into chloroform containing 2-mercaptobenzothiazole are described. Fluoride, chloride, bromide, iodide, thiocyanate, cyanide, and sulfate were employed as aqueous complexing agents. A number of the participating species were identified and association constants are estimated.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du thallium(I) dans le chloroforme renfermant du 2-mercaptobenzothiazole, en présence ou en l'absence d'agents complexants aqueux (fluorure, chlorure, bromure, iodure, thiocyanate, cyanure et sulfate).

ZUSAMMENFASSUNG

Es wurde die Extraktion des Thallium(I) aus wässriger Lösung in Ab- und Anwesenheit von Komplexbildnern mit 2-Mercaptobenzthiazol in Chloroform untersucht. Als Komplexbildner wurden Fluorid, Chlorid, Bromid, Jodid, Thiocyanat, Cyanid und Sulfat verwendet. Einige Thalliumkomplexe werden identifiziert und ihre Assoziationskonstanten geschätzt.

REFERENCES

[1] G. H. MORRISON AND H. FREISER, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957, p. 160, 178, 181–184; *Anal. Chem.*, 32 (1960) 38R, 43R.

[2] G. K. SCHWEITZER AND A. D. NORTON, *Anal. Chim. Acta*, 30 (1964) 119; G. K. SCHWEITZER AND G. T. COCHRAN, *Anal. Chim. Acta*, 30 (1964) 413.

[3] R. P. BELL AND J. H. B. GEORGE, *Trans. Faraday Soc.*, 49 (1953) 619.

[4] G. K. SCHWEITZER, *Anal. Chim. Acta*, 30 (1964) 68.

[5] R. O. NILSSON, *Arkiv Kemi*, 10 (1957) 363.

[6] J. BJERRUM, G. SCHWARZENBACH AND L. G. SILLEN, *Stability Constants. Part II. Inorganic Ligands*, The Chemical Society, London, 1958, p. 16, 42, 85, 92, 106, 116, 122.

SUGAR SEPARATIONS ON ION-EXCHANGE RESINS IN MIXTURE WITH CELITE

BENGT ARWIDI AND OLOF SAMUELSON

Department of Engineering Chemistry, Chalmers Tekniska Högskola, Göteborg (Sweden)

(Received February 28th, 1964)

As demonstrated in earlier papers[1-4], the adsorption of sugars onto ion-exchange resins from mixed solvents can be utilized as a method of quantitatively separating various sugars. Mixtures of ethanol–water, acetone–water or ternary mixtures with water as one component can be used to advantage. One factor which limits the applicability of this technique is that the rate of diffusion inside the resin particles is much lower in mixed solvents than in water[5]. In ethanol–water solutions, the only system studied systematically, the separation factors increase when the ethanol concentration is increased. At the same time the peak elution volumes increase, which gives rise to a broadening of the elution curves (*cf.* ref. 6). An additional broadening occurs because of the fact that the diffusion rate inside the resin is lowered at high ethanol concentration. In separation of sugars with similar properties it is, therefore, important that fine resin particles be used.

Working with very fine particles has the disadvantage that the pressure drop in the column is very high. To avoid excessively high pressures when finely powdered resins are employed the resin in this work was mixed with a filter aid (Celite 545). The separations were restricted to the common monosaccharides formed during the hydrolysis of wood.

EXPERIMENTAL

Jacketed ion-exchange columns were used in this work to permit a study of the influence of the temperature. Most experiments were carried out with Dowex 21 K (crushed and fractionated). Two experiments with an experimental resin of the same type but with spherical particles are also reported. The exchange capacity of this resin was 2.7 mequiv. per gram of oven-dried chloride resin. For Dowex 21 K the corresponding figure was 4.2. In other respects the working conditions were the same as described previously[4].

The eluant concentration was kept constant at 88% ethanol. Unless otherwise mentioned, the amounts of sugar added were: 2.5 mg of arabinose, 5 mg of xylose, 2.5 mg of mannose, 2.5 mg of galactose, and 5 mg of glucose.

The eluate was analyzed automatically by means of a Technicon Autoanalyzer as described in a previous paper[2]. Instead of analyzing the fractions collected in a fraction collector, the eluate was in some experiments fed directly into the monitor. After loading the column and starting the elution, the analysis was in this case automatic and could be run without any attention, for instance during the night.

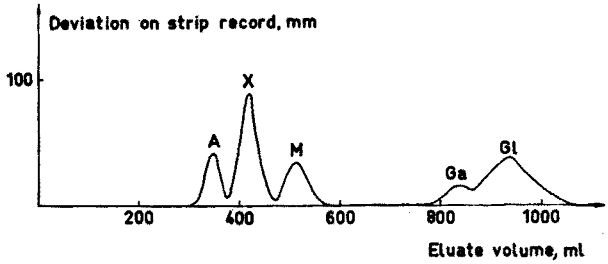


Fig. 1. Separation of monosaccharides in a column (8 × 750 mm) with Dowex 21 K and Celite at 28°. Flow rate: 0.8 ml/cm²/min.

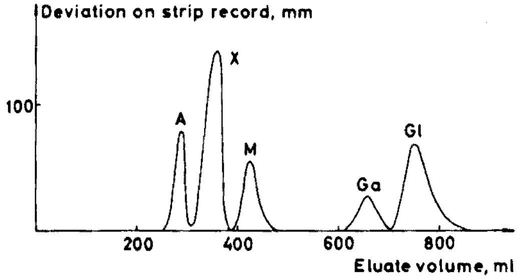


Fig. 2. Separation of monosaccharides in a column (8 × 750 mm) with Dowex 21 K and Celite at 47°. Flow rate: 0.8 ml/cm²/min.

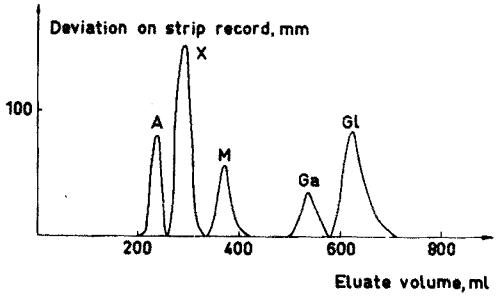


Fig. 3. Separation of monosaccharides in a column (8 × 750 mm) with Dowex 21 K and Celite at 60°. Flow rate: 0.8 ml/cm²/min.

RESULTS AND DISCUSSION

As shown in a previous paper[4], a quantitative separation of the monosaccharides present in hydrolyzates from wood can be achieved in 88% ethanol on a column with anion exchanger in its sulfate form. A crushed resin (Dowex 21 K) with a particle size 15–40 μ was used for this purpose. Experiments with coarser particles gave unsatisfactory results.

In order to study the possibilities of speeding up the separation, a resin of this type with smaller particles (1–16 μ) was used in mixture with an equal volume of Celite 545. The results with a column of the same dimensions as used in the earlier work are given in Fig. 1. As in earlier experiments the sugars appear in the following order: arabinose (A), xylose (X), mannose (M), galactose (Ga), glucose (Gl). The peak elution volumes are only about half as much as those obtained in the earlier work, which is explained by the smaller amount of resin in the column. The separation is not satisfactory under these conditions but can be improved by increasing the column length.

A more attractive method is to increase the temperature. The results reproduced in Fig. 2 were obtained at 47°, whereas those reported in Fig. 1 refer to an experiment at 28° under otherwise constant conditions. It is seen that an increased temperature results in less broadening of the elution curves, which, at least partly, is explained by an increased rate of diffusion inside the resin particles. The overlapping of the curves at 47° is so small that accurate quantitative determinations of all sugars can be obtained from this run. As can be seen in Fig. 3, a further, although less pronounced, improvement is obtained when the experiment is run at 60°. Another advantage of working at high temperature is that the pressure drop in the column is decreased markedly. In these runs the pressure drop was 7 atm in the experiment at 28° and 3 atm at 60°.

A comparison between the peak elution volumes of the monosaccharides at various temperatures shows that the temperature has a great influence. Smaller volumes are obtained at elevated temperature, which means that under otherwise constant conditions less time is required to carry out an experiment. It is well known that the peak elution volume of a given solute is determined by its distribution coefficient (*cf.* ref. 6). Hence, the results given in Figs. 1–3 show that with all monosaccharides the uptake decreases when the temperature is raised.

Experiments with varying flow rates carried out at 60° showed that an increase from 0.8 to 1.1 ml/cm^2/min has only a slight effect upon the chromatogram, whereas a further increase to 1.7 ml/cm^2/min results in overlapping curves.

From the experiments described above, it can be seen that quantitative separations can be achieved using a mixture of fine resin particles and Celite. The time required for a complete separation has been shortened in comparison to that reported in the earlier paper[4]. With the equipment available it has not been possible to run experiments with the crushed Dowex 21 K with the fine particle size (1–16 μ). The improvement resulting from the decrease in particle size is, however, not so great as would be anticipated from experiments with resin of varying particle size carried out without mixing with Celite. It, therefore, seems probable that Celite has a negative effect on the separation.

This assumption was confirmed in experiments using a spherical resin with the particle size 1–10 μ which could be used without mixing with Celite. The upper diagram in Fig. 4 shows the separation of xylose and glucose in a column filled with pure resin.

After this experiment the column was emptied and refilled after mixing the resin with Celite. The results obtained with this mixture under otherwise unchanged conditions are given in the lower diagram in Fig. 4. A broadening of the curve representing glucose is observed as well as a slight overlapping of the elution curves.

The experimental resin used in this run had a lower ion-exchange capacity but was in other respects of the same type as Dowex 21 K. A lower exchange capacity means a less effective uptake of sugar[5] under otherwise constant conditions. This disadvantage can to some extent be compensated for by using a higher ethanol concentration. The ideal situation would be to use a porous high-capacity resin with uniform spherical particles of very small diameter.

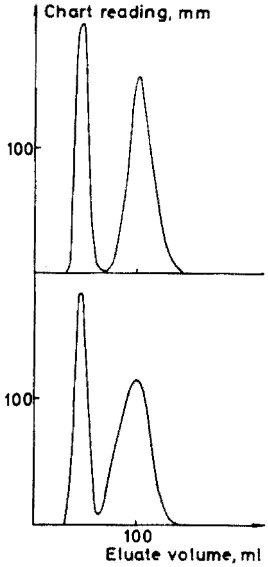


Fig. 4. Separation of xylose (1.5 mg) and glucose (2.7 mg) at 20° in a column with an inner diameter of 4 mm. Flow rate: 2 ml/cm^2/min. Upper diagram: spherical resin (bed height 270 mm); lower diagram: same resin with Celite (bed height 700 mm).

It is hoped that such resins will be commercially available in the near future. In the meantime the method can be applied using a mixture of crushed resin and Celite. The addition of Celite reduces the pressure drop in the column and eliminates the difficulties in running a column filled with fine, irregular resin particles. The presence of Celite in the column has, however, a detrimental effect upon the column efficiency.

The financial support of the Swedish Technical Research Council is gratefully acknowledged. Thanks are also due to Dr. H. W. HOLY, Technicon Instruments Co., Chertsey, Great Britain, for valuable support.

SUMMARY

The chromatographic separation of sugars in ethanol–water solutions by means of anion-exchange resins can be improved markedly by using extremely fine resin particles. To avoid an excessively high pressure drop in the column when crushed resin particles are employed the resin can be used in mixture with Celite. Working at elevated temperature results in improved separations and a considerable saving of time.

RÉSUMÉ

La séparation chromatographique des sucres, dans des solutions éthanol–eau, au moyen de résines échangeuses d'anions, peut être grandement améliorée, en utilisant des particules de résine extrêmement fines. L'emploi d'un mélange résine broyée–celite, à températures élevées, permet d'améliorer les séparations, avec un gain de temps considérable.

ZUSAMMENFASSUNG

Die chromatographische Trennung von Zuckern in Äthanol–Wasser-Lösungen mittels Anionenaustauscherharzen kann durch Verwendung extrem kleiner Harzteilchen merklich verbessert werden. Um bei der Anwendung feinzerteilter Harzpartikelchen einen übermässig hohen Druck in der Kolonne zu vermeiden, kann eine Mischung mit Celite benützt werden. Das Arbeiten bei erhöhter Temperatur ergab verbesserte Trennungen und einen beträchtlichen Zeitgewinn.

REFERENCES

[1] O. Samuelson and B. Swenson, *Acta Chem. Scand.*, 16 (1962) 2056.
[2] O. Samuelson and B. Swenson, *Anal. Chim. Acta*, 28 (1963) 426.
[3] J. Dahlberg and O. Samuelson, *Svensk Kem. Tidskr.*, 75 (1963) 178.
[4] J. Dahlberg and O. Samuelson, *Acta Chem. Scand.*, 17 (1963) 2136.
[5] H. Rückert and O. Samuelson, *Svensk Kem. Tidskr.*, 66 (1954) 337; *Acta Chem. Scand.*, 11 (1957) 315.
[6] O. Samuelson, *Ion Exchange Separations in Analytical Chemistry*, Almqvist and Wiksell, Stockholm; Wiley, New York, 1963.

ANION-EXCHANGE SEPARATION OF URANIUM FROM THE LANTHANIDES

I. HAZAN AND J. KORKISCH

Analytical Institute, University of Vienna, Vienna (Austria)

(Received February 19th, 1964)

The ability of the aliphatic mono- and di-carboxylic acids to form negatively charged complexes with various metal ions has been employed by some investigators for separations by means of anion exchange. ZAKI, SHAKIR AND KHALIFA[1] used buffered solutions of oxalic, succinic or adipic acid as complexing media for the separation of uranium, thorium, zirconium and other elements. Ascorbic acid was employed by KORKISCH *et al.*[2] to develop several methods for the separation of uranium from various elements. KORKISCH AND HAZAN[3] investigated the adsorption behavior in water and methanol media of uranium and other elements in the presence of polyfunctional organic acids, especially of the homologous dicarboxylic acids of the aliphatic series. Buffered solutions of acetic acid were also used in some investigations as complexing medium. HECHT *et al.*[4] carried out a detailed investigation concerning the isolation and determination of extremely small amounts of uranium in river waters and in minerals using an acetate medium. The acetate form of a strongly basic resin was also used by RILEY AND WILLIAMS[5] for the removal of uranium before the spectrophotometric determination of aluminium.

In continuation of previous studies on the adsorption behavior of various elements on Dowex-1 from acetic acid– organic solvent mixtures[6], a detailed investigation of the adsorption characteristics of uranium and the rare-earth elements in presence of acetic acid–organic solvent mixtures using 13 different organic solvents is presented in this paper. As a result of these studies methods for the quantitative separation of the negatively charged acetate complex of uranium from the lanthanides were developed.

EXPERIMENTAL

Reagents and solutions

(a) Ion-exchange resin. The strongly basic anion-exchange resin Dowex 1-×8 (100–200 mesh, chloride form) was used. For the equilibrium and separation experiments in the acetic acid–organic solvent solutions, the resin was transformed to the acetate form by treating its chloride form with an aqueous solution of acetic acid in presence of an excess of ammonium or sodium acetate. This treatment, which should be carried out in an ion-exchange column, was continued until no more chloride ions could be detected in the effluent. Thereafter the resin was thoroughly

washed with distilled water in order to remove the excess of acetic acid and its salt; for the column operations the resin was then treated with the corresponding solution used for pretreatment (see below). Then the resin was washed with methanol and dried in air. Since the acetate form of the resin is not stable for a long time (transformation into the carbonate form) it should be prepared not more than a few days before use.

(b) Standard solutions of uranium and the lanthanides. The reagent-grade nitrates of uranium and the lanthanides (La, Ce, Pr, Sm, Gd, and Yb as representatives of the "light" and "heavy" rare-earth elements) were dissolved in glacial acetic acid to give solutions containing exactly known quantities of these elements.

(c) Organic solvents. The following reagent-grade solvents were employed: methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, acetone, tetrahydrofuran, dioxan, methyl glycol, ethyl glycol, formic acid and glacial acetic acid.

Apparatus

The column operations were carried out in columns of the same type and dimensions as described earlier[2]; the height of the resin bed was 10 cm and its diameter 0.6 cm. The photoelectric fluorimeter employed for the determination of uranium was a Galvanek Morrison Fluorimeter, Mark V[7].

Determination of uranium and the lanthanides

Uranium in the eluates or filtrates (after removal of the resin by filtration) was determined fluorimetrically by means of a procedure described by SCHÖNFELD *et al.*[7]. The rare-earth elements were determined by titration with EDTA in presence of xylenol orange as indicator, in a medium buffered with hexamethylene tetramine.

Determination of distribution coefficients

The weight distribution coefficients given by the equation: distribution coefficient = $K_d = \{\mu g \text{ element/g resin}\}/\{\mu g \text{ element/ml of solution}\}$ were determined by employing the equilibrium (batch) method (KORKISCH AND TERA[2]). For this purpose in each case 1 ml of the standard solution containing 5 mg of the metal ion in question was diluted to 20 ml with the organic solvent. To this solution 1 g of the resin (acetate form) was added and the mixture agitated for 12 h to insure complete attainment of equilibrium. Thereafter the resin was filtered off and the element was determined in an aliquot of the filtrate as described above.

Column operations

(a) Pretreatment of resin bed. The acetate form of the resin was introduced into the ion-exchange column from a suspension of the resin in a solvent mixture of the same composition which was to be used later as the sorption solution. For further pretreatment 50 ml of this solution were passed through the resin bed to establish exactly the same conditions as existing during the sorption process.

(b) Sorption. For the direct separation of uranium from the lanthanides (see Table II), a sorption solution consisting of 100 ml of glacial acetic acid containing known amounts of the elements in question was employed. This solution was passed through the resin bed at a flow rate of 0.3–0.5 ml/min; only uranium was strongly retained

by the resin. To remove the last traces of the rare earths the resin bed was washed with 50 ml of glacial acetic acid.

For the simultaneous adsorption of uranium and the rare earths (see Table III), a sorption solution consisting of 95 ml of tetrahydrofuran and 5 ml of glacial acetic acid containing the elements was passed through the column at a flow rate of 0.3–0.5 ml/min. The effluent in this case contained neither uranium nor the rare-earth elements.

(c) Elution. For the separation of the coadsorbed lanthanides from uranium on the resin the following eluants could be effectively employed: 50 ml of glacial acetic acid, 50 ml of 95% methanol–5% acetic acid or 100 ml of 95% ethanol–5% acetic acid. During this elution process only the lanthanides were removed from the column, uranium being strongly retained. The subsequent elution of the adsorbed uranium was effected by passing 100 ml of 1 *N* hydrochloric or nitric acid through the resin bed.

RESULTS AND DISCUSSION

In Table I the values for the distribution coefficients of uranium and the lanthanides in mixtures of 95% organic solvent–5% acetic acid are shown. From these results it is seen that in methanol, ethanol, formic and acetic acid solutions only uranium is strongly retained by the resin, so that such mixtures can be used as media for an effective separation of uranium from the rare earths.

TABLE I

DISTRIBUTION COEFFICIENTS IN 95% SOLVENT + 5% ACETIC ACID MIXTURES

Solvent	*Element*						
	UO_2^{2+}	La^{3+}	Ce^{3+}	Pr^{3+}	Sm^{3+}	Gd^{3+}	Yb^{3+}
Methanol	50,120.	0.1	0.1	0.1	0.1	0.1	0.1
Ethanol	112,200.	10.	15.	21.	29.	33.	35.
n-Propanol	501,200.	140.	180.	220.	260.	320.	410.
Isopropanol	158,500.	420.	610.	780.	900.	980.	1,100.
n-Butanol	130,000.	180.	340.	450.	560.	620.	670.
Isobutanol	100,000.	160.	200.	220.	620.	650.	870.
Acetone	63,100.	185.	250.	280.	752.	960.	1,420.
Tetrahydrofuran	8,800.	350.	880.	950.	980.	1,050.	1,330.
Dioxan	151,500.	110.	230.	310.	690.	710.	750.
Methyl glycol	160,000.	30.	56.	104.	155.	170.	250.
Ethyl glycol	98,000.	33.	130.	150.	190.	290.	320.
Formic acid	315.	0.1	0.1	0.1	0.1	0.1	0.1
Acetic acid	160,000.	0.1	0.1	0.1	0.1	0.1	0.1

Because of the extremely high distribution coefficient of uranium in 100% acetic acid (see last horizontal column of Table I) this medium was selected to develop a method for the direct separation of uranium from the rare-earth elements (see above under (*b*)) (methanol could be used similarly to acetic acid).

The results of several quantitative separations are shown in Table II. The working

TABLE II

SEPARATION OF URANIUM FROM THE LANTHANIDES IN 100% ACETIC ACID

Separated elements	*Amount of U taken (mg)*	*Amount of lanthanide taken (mg)*	*Amount of U recovered (mg)*	*Amount of lanthanide recovered (mg)*
U + La	40.00.	5.20.	39.90.	5.05.
U + Ce	40.00.	3.65.	40.20.	3.60.
U + Pr	40.00.	3.10.	40.00.	3.02.
U + Sm	40.00.	3.80.	39.85.	3.70.
U + Gd	40.00.	3.55.	39.92.	3.49.
U + Yb	40.00.	1.74.	39.98.	1.80.

capacity of the resin for uranium in this medium was found to be 350 mg of uranium/g of dry resin.

Based on the fact that the rare-earth elements and uranium are very strongly adsorbed from a medium consisting of 95% tetrahydrofuran and 5% acetic acid (see Table I), a method for the simultaneous adsorption of these elements was developed. From the experimental results shown in Table III, it is clear that a quantitative adsorption of uranium and the rare earths can be achieved by means of this procedure.

TABLE III

SEPARATION OF URANIUM FROM THE LANTHANIDES AFTER SIMULTANEOUS ADSORPTION FROM 95% TETRAHYDROFURAN–5% ACETIC ACID MIXTURE

Separated elements	*Amount of U taken (mg)*	*Amount of lanthanide taken (mg)*	*Amount of U recovered (mg)*	*Amount of lanthanide recovered (mg)*
U + La	40.00.	5.20.	40.00.	5.20.
U + Ce	40.00.	3.65.	39.50.	3.62.
U + Pr	40.00.	3.10.	39.65.	3.12.
U + Sm	40.00.	3.80.	39.50.	3.78.
U + Gd	40.00.	3.55.	39.90.	3.56.
U + Yb	40.00.	1.74.	39.28.	1.74.

For the separation of uranium from the rare earths on the column a mixture consisting of 95% methanol–5% acetic acid was employed; the lanthanides thus passed quantitatively into the eluate whereas uranium was retained. The working capacities for uranium in the tetrahydrofuran and methanol media were found to be 70 mg and 100 mg of uranium/g of dry resin respectively.

When a mixture of 95% ethanol–5% acetic acid was employed for the elution of the rare earths, a much larger elution volume (100 ml) was required than if methanol was used; in the latter case less than 50 ml was sufficient to remove the rare earths quantitatively. This is due to the fact that the lanthanides are more strongly adsorbed from ethanol than from methanol medium (see Table I). A study of the elution characteristics of the individual rare-earth elements with 95% ethanol–5% acetic acid as the eluting agent, showed that corresponding to the increase of the K_d values from lanthanum to ytterbium (see Table I), the elution volume has to be increased from 50 ml for lanthanum to 100 ml for ytterbium. This behavior of the lanthanides in the organic solvent–acetic acid mixtures, *i.e.* the stronger adsorption of the heavy rare earths in comparison to that of the light lanthanides, is exceptional and has not been previously observed either in pure aqueous solution or in mixed and non-aqueous solvents; normally the reverse effect can be observed. The reason for this inversion in the media investigated here is not known. Because thorium hydrolyzes in the media employed, no experiments with this element could be performed.

In conclusion, it can be said that the above procedures are well suited to the quantitative separation of relatively large quantities of uranium from the lanthanides, a fact which might be of importance for the removal of rare earths formed by fission of uranium.

The research work described was sponsored by the International Atomic Energy Agency and the U.S. Atomic Energy Commission under contract (AT(30-1)-2623). The generous support from these agencies is gratefully acknowledged.

SUMMARY

The anion-exchange behavior of uranium and the lanthanides in acetic acid–organic solvent mixtures is described. The distribution coefficients of the elements in 13 organic solvents containing acetic acid as the complexing agent were measured, and methods for the quantitative separation of uranium from the rare-earth elements are proposed.

RÉSUMÉ

Les auteurs ont examiné la séparation de l'uranium d'avec les lanthanides, au moyen d'un échangeur d'anions. On a mesuré les coefficients de partage de ces éléments dans 13 solvants organiques, en présence d'acide acétique comme agent complexant. Des méthodes de séparation quantitative de l'uranium d'avec les éléments des terres rares sont proposées.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wird das Anionenaustauschverhalten von Uran und der Lanthanide in essigsauren organischen Lösungsmittelgemischen beschrieben. Basierend auf Messungen der Verteilungskoeffizienten dieser Elemente in 13 essigsäurehaltigen organischen Lösungsmitteln, wurden Methoden zur quantitativen Trennung des Urans von den Seltenen Erdmetallen mittels Anionenaustausches entwickelt.

REFERENCES

[1] M. R. ZAKI AND K. SHAKIR, *Z. Anal. Chem.*, 180 (1961) 188; 185 (1962) 423; H. KHALIFA AND M. R. ZAKI, *Z. Anal. Chem.*, 158 (1957) 1.
[2] J. KORKISCH, A. FARAG AND F. HECHT, *Mikrochim. Acta*, (1958) 415; J. KORKISCH, P. ANTAL AND F. HECHT, *Mikrochim. Acta*, (1959) 693; J. KORKISCH AND F. TERA, *Anal. Chem.*, 33 (1961) 1265.
[3] J. KORKISCH AND I. HAZAN, *Talanta*, 11 (1964) 523.
[4] F. HECHT, J. KORKISCH, R. PATZAK AND A. THIARD, *Mikrochim. Acta*, (1956) 1283; J. KORKISCH, A. THIARD AND F. HECHT, *Mikrochim. Acta*, (1956) 1422.
[5] J. P. RILEY AND H. P. WILLIAMS, *Mikrochim. Acta*, (1959) 825.
[6] J. KORKISCH AND S. URUBAY, *Talanta*, 11 (1964) 721
[7] T. SCHÖNFELD, M. EL GARHI, C. FRIEDMANN AND J. VESELSKY, *Mikrochim. Acta*, (1960) 883

S-BENZYLTHIOURONIUM SALTS OF SOME CARBOXYLIC ACIDS, SULFONIC ACIDS, AND PHENOLS

AAGE JART, ALLAN J. BIGLER AND VIBEKE BITSCH

Organic-Chemical Laboratory, The Technical University, Copenhagen (Denmark)

(Received March 3rd, 1964)

The present paper deals with a great number of S-benzylthiouronium salts, most of which have not been described before. Melting points and analyses of the derivatives are listed in Table I. The order used in this Table is that which is applied to the acids in *Beilstein*; the sulfonic acids and the phenols are placed after the carboxylic acids.

TABLE I

	Acid	*M.P.(°)*	*Equiv. weight or % N*	
			Calculated	*Found*
1	Fluoroacetic acid	158	244	242
2	Trifluoroacetic acid	168–70	280	283
3	Difluorochloroacetic acid	179–80	297	295
4	Dibromoacetic acid	173–74	384	381
5	Iodoacetic acid	123–24	352	348
6	2,2-Dichloropropionic acid	176–77	309	308
7	3-Bromopropionic acid	124–25	319	326
8	3-Iodopropionic acid	133	366	366
9	Heptafluorobutanoic acid	187–88	380	377
10	3-Chlorobutanoic acid	148–49	289	289
11	2-Methyl-2,3-dichloropropionic acid	139	323	322
12	Isovaleric acid	160–61	268	265
13	2-Bromohexanoic acid	136	361	361
14	Isocaproic acid	157	282	282
15	2-Bromo-4-methylpentanoic acid	139–40	361	358
16	2,2-Dimethylbutanoic acid	132–33	282	285
17	3,3-Dimethylbutanoic acid	159	282	283
18	Enanthic acid	146	296	297
19	2,2-Dimethylpentanoic acid	143–44	296	297
20	3,6-Dimethylheptanoic acid	136–37	324	322
21	Hendecanoic acid	149	353	360
22	11-Bromohendecanoic acid	138	431	433
23	Margaric acid	133–34	437	431
24	Behenic acid	135–37	507	500
25	2-Bromocrotonic acid	181	331	331
26	Angelic acid	128–29	266	265
27	3-Methylcrotonic acid	158	266	267
28	2-Methyl-4-pentenoic acid	144	280	278
29	Petroselinic acid	131–32	449	457
30	Oleic acid	132	449	446

TABLE I (Continued)

	Acid	*M.P.(°)*	*Equiv. weight or % N*	
			Calculated	*Found*
31	Elaidic acid	140–41	449	463
32	Erucic acid	142	505	512
33	Stearolic acid	134	447	447
34	2-Methylglutaric acid, disalt	143–44	239	243
35	2,2-Dimethylsuccinic acid, disalt	117	239	244
36	2,3-Dimethylsuccinic acid, disalt	153–54	239	241
37	2,2-Dimethylglutaric acid, monosalt	166	326	321
38	2,4-Dimethylglutaric acid, disalt	140–42	246	245
39	Butylsuccinic acid, disalt	144–45	253	254
40	3-Methyl-3-ethylglutaric acid, monosalt	163	340	343
41	*tert.*-Butylsuccinic acid *sec.*-butyl ester	110	396	398
42	Dipropylmalonic acid, monosalt	156–58	354	352
43	9-Cyanononanoic acid	146–47	349	347
44	Dodecanedioic acid, disalt	150	281	281
45	11-Cyanohendecanoic acid	142	378	387
46	Brassylic acid, disalt	162–63	288	287
47	Tetradecanedioic acid, disalt	176	295	300
48	Mesaconic acid, disalt	160–61	231	236
49	Methylallylmalonic acid, disalt	140–41	245	248
50	Muconic acid, disalt	190	237	240
51	Butane-1,2,3,4-tetracarboxylic acid, tri- and tetrasalt	163	244 225	231
52	Methoxyacetic acid	166–67	256	255
53	Ethoxyacetic acid	161–62	270	269
54	Ricinelaidic acid	129–30	465	462
55	Tartronic acid, disalt	158–59	226	224
56	2-Ketobutanoic acid	155	268	267
57	N,N-Dimethyldithiocarbamic acid carboxymethyl ester	158	345	346
58	Nitrilotriacetic acid, disalt	113–14	13.38%	13.21%
59	Phenylmercaptoacetic acid	171–72	334	333
60	3,5-Dimethylphenoxyacetic acid	181	346	342
61	1-Nitro-2-naphthoxyacetic acid	196	413	418
62	Cyclopropanecarboxylic acid	155–56	252	252
63	Cyclopentanecarboxylic acid	158–59	280	278
64	Cyclohexylacetic acid	159–63	308	306
65	Cyclopenten-2-ylacetic acid	155	292	291
66	*o*-Fluorobenzoic acid	175–76	306	304
67	*m*-Fluorobenzoic acid	154	306	307
68	*p*-Fluorobenzoic acid	180	306	306
69	2-Chloro-4-fluorobenzoic acid	160–61	341	340
70	*p*-Iodobenzoic acid	195–97	414	412
71	4-Bromo-3,5-dinitrobenzoic acid	182–83	457	446
72	Thiobenzoylthioglycolic acid	154–55	378	379
73	*p*-Bromophenylacetic acid	158	381	378
74	*m*-Toluic acid	172	302	299
75	2-Phenylbutanoic acid	162–63	330	327

TABLE I (Continued)

	Acid	*M.P.(°)*	*Equiv. weight or % N*	
			Calculated	*Found*
76	2,4,6-Trimethylbenzoic acid	171–72	330	330
77	2-Naphthylacetic acid	160–62	352	352
78	3,3-Diphenylpropionic acid	150	392	397
79	Cyclobutane-1,1-dicarboxylic acid, disalt	144	238	238
80	Naphthalic acid, disalt	178–79	274	276
81	Hemimellitic acid, disalt	173	271	268
82	Cyclohexanol-2-carboxylic acid	149–50	310	314
83	Thiosalicylic acid	159	320	323
84	2,3′-Thiodibenzoic acid, disalt	170–71	9.24%	9.26%
85	Acetylvanillic acid	126	376	378
86	*o*-Acetylbenzoic acid	140	330	328
87	3-(*p*-Methoxybenzoyl)propionic acid	150	374	375
88	3-(*p*-Ethoxybenzoyl)propionic acid	143	388	387
89	3-(3′-Bromo-4′-methoxybenzoyl)-propionic acid	143	6.18%	6.12%
90	3-(2′,5′-Dimethoxybenzoyl)propionic acid	120–21	404	407
91	*p*-Sulfamidobenzoic acid	178	367	367
92	2-(*p*-Dimethylaminobenzoyl)benzoic acid	168	9.65%	9.74%
93	*p*-Phenylazobenzoic acid	189	14.28%	14.27%
94	Methyl red	105–06	16.08%	15.91%
95	Thiophene-2-carboxylic acid	184–85	294	290
96	Coumarilic acid	212–13	328	332
97	Xanthene-9-carboxylic acid	135–37	392	398
98	2-(2′-Thenoyl)benzoic acid	160–61	398	405
99	Isonicotinic acid	151–52	14.52%	14.28%
100	3-Pyridylacetic acid	138	13.85%	13.61%
101	6-Methylpicolinic acid	169–70	13.07%	13.24%
102	3-(2′-Pyridyl)acrylic acid	165	13.32%	13.34%
103	3-Indolylacetic acid	172–73	12.30%	12.46%
104	Quinaldic acid	188–89	12.38%	12.25%
105	Quinolinic acid, disalt	171	14.02%	13.95%
106	Isocinchomeronic acid, disalt	200–01	14.02%	14.24%
107	Kynurenic acid	211–12	11.25%	11.40%
108	2-Carboxymethylmercapto-4-methylpyrimidine	158–59	15.99%	15.63%
109	8-Bromocinnolone-(4)-carboxylic acid (3)	198	435	432
110	2-Amino-4-carboxy-5-chloropyrimidine	213–14	20.60%	19.86%
111	Diphenyl-4-sulfonic acid	195	7.00%	6.77%
112	8-Hydroxyquinoline-5-sulfonic acid	202	10.74%	10.92%
113	2,4-Dinitrophenol	118	350	345
114	3,5-Dinitro-*o*-cresol	115–17	364	362
115	2,4-Dinitro-1-naphthol	162	400	396
116	Styphnic acid, disalt	167–68	289	284

Among the carboxylic acids investigated many dicarboxylic acids occurred. In these cases, an attempt was always made to prepare the normal salts by neutralizing the acid in question with 2 equivalents of base and adding 2.25 equivalents of S-benzylthiouronium chloride. The procedure often resulted in precipitation of the disalts, but in a few cases the monosalts were isolated. Sometimes the procedure resulted in a mixture of the 2 salts which could be purified only with difficulty, to yield a well-defined compound. In the present work such mixed products are omitted; only in the case of butane-1,2,3,4-tetracarboxylic acid, a mixture of salts (trisalt/tetrasalt) is included.

Hitherto, only a limited number of S-benzylthiouronium salts of heterocyclic carboxylic acids have been described; the present work includes many derivatives of such acids.

In contrast to previous authors[1] we succeeded in obtaining well crystallized and pure derivatives of 3 dinitrophenols; also a disalt of styphnic acid was prepared without difficulties.

The purity of the S-benzylthiouronium salts prepared was checked, if possible, by titration with perchloric acid in glacial acetic acid using crystal violet as an indicator. This procedure was easily performed as a semi-micro method requiring 0.05–0.1 mequiv. of the derivative.

The melting points were determined as described under the heading EXPERIMENTAL; they are of limited value only for the purpose of identifying the acids concerned. As pointed out in a previous article[2], dealing with infrared absorption spectra of S-benzylthiouronium salts, these spectra are much more convenient for identification purposes. The article mentioned[2] contains spectra (625–4000 cm^{-1}) of all the S-benzylthiouronium salts dealt with in the present work as well as of 246 others.

EXPERIMENTAL

Preparation of derivatives

The acid (2–5 mmole) was dissolved or suspended in a few ml of water or ethanol and titrated with an aqueous solution of sodium hydroxide (1 *N*) to a slightly acid reaction (methyl red). The resulting solution was heated to 90–95° and a hot solution of S-benzylthiouronium chloride in water or aqueous ethanol was added (10–15% excess); the mixture was immediately cooled in an ice bath, and in many instances the S-benzylthiouronium salts rapidly began to separate out. If this was not the case, crystallization could generally be effected by allowing the mixture to stand in a refrigerator — in some cases allowing the solvent to evaporate at the same time.

The resulting products were purified by recrystallization from water or dilute ethanol. In order to prevent destruction as far as possible, heating was performed on a water bath. Pure S-benzylthiouronium salts were generally obtained after 2 recrystallizations. Solvent was removed from the end-products *in vacuo* at 45° for 24 h.

Salts of long-chain fatty acids often contained small amounts of free fatty acids, especially when precipitated from concentrated solutions. In such cases it is necessary to work with much more dilute solutions than those mentioned above.

Titration of derivatives

The S-benzylthiouronium salts were titrated with perchloric acid in glacial acetic acid using crystal violet as an indicator[3]. The titration was performed on a semi-micro scale using 0.05–0.1 mequiv. of the derivative. In the case of the salts for which this method was unsuitable (usually indicated by poorly defined end-point), *e.g.* pyridine and quinolinecarboxylic acids, and certain other nitrogen-containing acids as well as salts of sulfonic acids, the total nitrogen was determined by the DUMAS method (by Mr. P. HANSEN, The Microanalytical Laboratory, University of Copenhagen).

Determination of melting points

The sample was introduced into the melting point apparatus (a 50-ml beaker with silicone oil and fitted with a stirrer, electrical heating element and a verified thermometer) at a temperature 10–15° below the anticipated melting point. The rate of heating was carefully adjusted to 2°/min.

Acids

The acids used for the preparation of the derivatives were in most cases commercial products. Some others were prepared by well-known methods, whereas a few have not been described before. Some details concerning the origin of the acids are given below.

Samples 1–7, 10, 11, 13, 14, 16–19, 21, 22, 27, 34, 36–38, 40, 42, 45, 48, 51–53, 55, 59, 60, 62–69, 73–75, 77, 79–82, 85, 86, 91, 95–97, 99–101, 103, 106–108 and 110 were obtained from Fluka in a purum grade; samples 22, 42 and 59 were $\geqslant$ 99% pure. Samples 12, 23, 35, 56, 58, 83, 104 and 105 were obtained from Fluka in a puriss. grade; sample 12 was $>$ 99.5% pure and 105 $\geqslant$ 99%.

Samples 29 and 46 were obtained from Light whereas samples 114 and 115 were obtained from Judex. Details of preparation of samples 24, 30, 31, 32 and 54 are given in ref. 4.

Other samples are mentioned below.

8. *3-Iodopropionic acid* was prepared at the laboratory; m.p. 82–84°.

9. *Heptafluorobutanoic acid* from Fluka (pract., b.p. 117–119°).

15. *2-Bromo-4-methylpentanoic acid* was prepared from isocaproic acid (14) by bromination as in a method for preparation of similar compounds[5] (b.p. 125°/12 mm).

20. *3,6-Dimethylheptanoic acid* was prepared by addition of isoamyl-magnesium bromide to *sec.*-butylcrotonate[6]. The crude ester was distilled *in vacuo* and hydrolysed by refluxing with an aqueous solution of potassium hydroxide; finally the acid was carefully fractionated *in vacuo*, the fraction boiling at 140–142°/20 mm being collected in 25% yield. Although the procedure used may often give by-products which are difficult to remove, the purity of the 3,6-dimethylheptanoic acid was proved by gas chromatography to be $>$ 99%.

25. *2-Bromocrotonic acid* was prepared by bromination of crotonic acid to yield 2,3-dibromobutyric acid[7] giving 2-bromocrotonic acid on treatment with potassium hydroxide[8]; recrystallized from ethanol and sublimed *in vacuo* at 45°, m.p. 80–81°.

26. *Angelic acid* was prepared from tiglic acid through 2,3-dibromo-2-methylbutyric acid and 3-bromoangelic acid[9]; m.p. 44.6–45.2°.

28. *2-Methyl-4-pentenoic acid* was prepared (by Dr. BOLL, The Royal Danish School of Pharmacy) by decarboxylation[10] of methylallylmalonic acid (49).

33. *Stearolic acid* was prepared from propyl oleate (originally synthesized from 30) by a well-known procedure[11]; m.p. 45.2–45.4°.

39. *Butylsuccinic acid*: the synthesis of this compound has been described[12]; m.p. 81°.

41. tert.-*Butylsuccinic acid* sec.-*butyl ester*: the synthesis of this compound has been described[13]; m.p. 57–58°.

43. *9-Cyanononanoic acid* was prepared by reaction between sebacic acid and urea giving sebaconitrile, which on further heating gives 9-cyanononanoic acid[14]; m.p. 48.4–49.0°.

44. *Dodecanedioic acid* was prepared from sebacic acid, the latter at first being esterified with ethanol and reduced to 1,10-decanediol[15]. The diol was in turn converted to the dibromide[16] and by refluxing with excess of potassium cyanide in 50% ethanol, the dinitrile was obtained. This product was hydrolysed to give the acid[17]; m.p. 126.2–126.6°.

47. *Tetradecanedioic acid* was prepared from decamethylenedibromide (*cf.* (44)) and sodium malonic ester[17]; m.p. 120.4–120.8°.

49. *Methylallylmalonic acid* was prepared (by Dr. BOLL, The Royal Danish School of Pharmacy) from methylmalonic acid ethylester and allyl chloride[10]; m.p. 84.2–84.6°.

50. *Muconic acid* was prepared by bromination of adipyl chloride and elimination of hydrogen bromide by treatment of the product obtained with a potassium hydroxide solution[18]. The acid melted at 296° (the *trans–trans* form).

57. *N,N-Dimethyldithiocarbamic acid carboxymethyl ester* was prepared by reacting the sodium salt of N,N-dimethyldithiocarbamic acid (from dimethylamine and carbon disulfide) with sodium chloroacetate[19]; m.p. 142–143°.

61. *1-Nitro-2-naphthoxyacetic acid* was prepared by nitration of 2-naphthoxyacetic acid[20] obtained by reaction between 2-naphthol and chloroacetic acid in sodium hydroxide solution[21]; m.p. 181–183°.

70. p-*Iodobenzoic acid* was prepared by diazotization of *p*-aminobenzoic acid and subsequently reaction with potassium iodide[22]. The product obtained was purified by sublimation and melted at 168–169°.

71. *4-Bromo-3,5-dinitrobenzoic acid* was prepared by nitration of *p*-bromobenzoic acid with a mixture of concentrated nitric and sulphuric acids; m.p. 180° (yield: 58%).

72. *Thiobenzoylthioglycolic acid* was prepared from benzoyl trichloride[23], *i.e.* reaction with potassium hydrogen sulfide and subsequently reaction with sodium chloroacetate; m.p. 126.7–127.3°.

76. *2,4,6-Trimethylbenzoic acid* was prepared from mesitylene by bromination[24] and subsequent reaction of the 2-bromomesitylene with magnesium followed by reaction with dry ice[25]. The resulting acid was recrystallized from methanol and melted at 152.0–152.5°.

78. *3,3-Diphenylpropionic acid* was prepared by reaction of cinnamic acid and benzene in the presence of aluminium chloride[26]; m.p. 155.0–155.8°.

84. *2,3′-Thiodibenzoic acid* was prepared from thiosalicylic acid (83) and *m*-iodobenzoic acid methyl ester (synthesized[27] and subsequently esterified with methanol, m.p. 50–51°), similarly to the 2,2′-isomer already described in the literature[28]; m.p. 180.8–181.6°.

87. *3-(*p*-Methoxybenzoyl)propionic acid* was prepared by reaction of succinic anhydride and aluminium chloride with anisole[29]. The product was recrystallized from ethanol and melted at 135.1–135.7°.

88. *3-(*p*-Ethoxybenzoyl)propionic acid* was prepared by reaction of succinic anhydride and aluminium chloride with phenetole[29]. The product was recrystallized from ethanol and melted at 138.9–139.7°.

89. *3-(3'-Bromo-4'-methoxybenzoyl)propionic acid* was prepared by reaction of succinic anhydride and aluminium chloride with *o*-bromoanisole[29]. The product was recrystallized from ethanol and melted at 191.6–192.0°.

90. *3-(2',5'-Dimethoxybenzoyl)propionic acid* was prepared by reaction of succinic anhydride and aluminium chloride with hydroquinone dimethyl ether[29]. The product was recrystallized from ethanol and melted at 105.8–106.5°.

92. *2-(*p*-Dimethylaminobenzoyl)benzoic acid* was prepared by reaction of dimethylaniline and aluminium chloride with phthalic anhydride[30]. The product was recrystallized from ethanol and melted at 194–195°.

93. p-*Phenylazobenzoic acid* was prepared by reaction between *p*-aminobenzoic acid and nitrosobenzene (obtained from nitrobenzene[31]) as in a previous method[32]; m.p. 245–6°.

94. *Methyl red*: from Merck.

98. *2-(2'-Thenoyl)benzoic acid* was prepared by reaction between phthalic anhydride and thiophene in the presence of aluminium chloride[33]. The product was recrystallized from toluene and melted at 143.1–143.7°.

102. *3-(2'-Pyridyl)acrylic acid* was prepared (by C. BRETTING, M.Sc., in this laboratory) from 1,1,1-trichloro-2-hydroxy-3-(2-pyridyl)-propane (obtained from α-picoline and chloral[34]) as described by KING *et al.*[35]; m.p. 200.1–200.6°.

109. *8-Bromocinnolone-(4)-carboxylic acid (3)* was prepared (by Dr. R. R. SHOUP, University of New Mexico, Albuquerque, N.M.) as described previously[36]; m.p. dec. > 220°.

111. *Diphenyl-4-sulfonic acid* was prepared by sulfonating diphenyl[37]; m.p. 140–142°.

112. *8-Hydroxyquinoline-5-sulfonic acid* was prepared by sulfonating 8-hydroxyquinoline[38]; m.p. 211–212°.

113. *2,4-Dinitrophenol:* from Fluka (pract., 98%).

116. *Styphnic acid* was prepared by sulfonating resorcinol with concentrated sulfuric acid and nitrating the resulting disulfonic acid with nitric acid[39]; m.p. 177.4–177.6°.

A grant from The Danish Council for Scientific and Industrial Research (Det Teknisk-Videnskabelige Forskningsråd) is gratefully acknowledged.

SUMMARY

116 S-Benzylthiouronium salts have been prepared and were, if possible, checked by titration with perchloric acid in glacial acetic acid on a semi-micro scale. Out of these, 110 are salts of carboxylic acids, 2 of sulfonic acids, and 4 of nitrophenols. The melting points determined according to a standard procedure are given.

RÉSUMÉ

116 sels de S-benzylthiouronium (110 sels d'acides carboxyliques, 2 d'acides sulfoniques et 4 de nitrophénols) ont été préparés et contrôlés, à l'échelle semi-micro, par titrage au moyen d'acide perchlorique, en milieu acide acétique glacial. Les points de fusion, déterminés selon un procédé standard, sont donnés.

ZUSAMMENFASSUNG

116 S-Benzylthiouronium-salze (davon 110 Salze von Carboxylsäuren, 2 von Sulfonsäuren und 4 von Nitrophenolen) wurden dargestellt und wenn möglich durch Titration mit Perchlorsäure in Eisessig im Halbmikromassstab geprüft. Die Schmelzpunkte wurden nach einem angegebenen Standardverfahren bestimmt.

REFERENCES

[1] A. FRIEDIGER AND C. PEDERSEN, *Acta Chem. Scand.*, 9 (1955) 1425.
[2] A. JART, *Acta Polytech. Scand., Chem. Met. Ser. No. 24*, 1963.
[3] J. BERGER, *Acta Chem. Scand.*, 8 (1954) 427.
[4] A. JART, *Acta Chem. Scand.*, 14 (1960) 1876.
[5] *Org. Syn.*, Coll. Vol. III (1955) 523.
[6] *Org. Syn.*, 41 (1961) 60.
[7] P. SEIFERT, E. VOGEL, A. ROSSI AND H. SCHINZ, *Helv. Chim. Acta*, 33 (1950) 731.
[8] N. H. CROMWELL AND F. PELLETIER, *J. Org. Chem.*, 15 (1950) 881.
[9] R. E. BUCKLES AND G. V. MOCK, *J. Org. Chem.*, 15 (1950) 682.
[10] S. STÄLLBERG-STENHAGEN, *Arkiv Kemi*, 23A (1946) No. 15.
[11] *Org. Syn.*, Coll. Vol. III (1955) 785.
[12] J. MUNCH-PETERSEN, C. BRETTING, P. M. JØRGENSEN, S. REFN, V. K. ANDERSEN AND A. JART, *Acta Chem. Scand.*, 15 (1961) 291.
[13] V. K. ANDERSEN AND J. MUNCH-PETERSEN, *Acta Chem. Scand.*, 16 (1962) 952; 17 (1963) 1470.
[14] *Org. Syn.*, Coll. Vol. III (1955) 768.
[15] *Org. Syn.*, Coll. Vol. II (1943) 154.
[16] *Org. Syn.*, Coll. Vol. II (1943) 227.
[17] P. CHUIT, *Helv. Chim. Acta*, 9 (1926) 264.
[18] *Org. Syn.*, Coll. Vol. III (1955) 623.
[19] K. A. JENSEN, *J. Prakt. Chem.*, 159 (1941) 189.
[20] F. SPITZER, *Ber.*, 34 (1901) 3192.
[21] F. H. LEES AND F. SHEDDEN, *J. Chem. Soc.*, 83 (1903) 758.
[22] C. WILLGERODT, *Ber.*, 27 (1894) 2331.
[23] *Org. Syn.*, 42 (1962) 100.
[24] *Org. Syn.*, Coll. Vol. II (1943) 95.
[25] *Org. Syn.*, Coll. Vol. III (1955) 553.
[26] P. PFEIFFER AND H. L. DE WAAL, *Ann.*, 520 (1935) 189.
[27] D. H. DERBYSHIRE AND W. A. WATERS, *J. Chem. Soc.*, (1950) 3694.
[28] Á. KUCSMAN AND J. KAPOVITS, *Acta Chim. Acad. Sci. Hung.*, 34 (1962) 72.
[29] J. D. REINHEIMER AND J. C. SMITH, *J. Org. Chem.*, 17 (1952) 1505.
[30] A. HALLER AND A. GUYOT, *Bull. Soc. Chim. France*, [3] 25 (1901) 168.
[31] *Org. Syn.*, Coll. Vol. III (1955) 668.
[32] *Org. Syn.*, Coll. Vol. III (1955) 711.
[33] W. STEINKOPF, *Ann.*, 407 (1915) 99.
[34] C. W. TULLOCK AND S. M. MCELVAIN, *J. Am. Chem. Soc.*, 61 (1939) 963.
[35] J. A. KING, V. HOFMANN AND F. H. MCMILLAN, *J. Org. Chem.*, 16 (1951) 1105.
[36] H. J. BARBER, K. WASHBOURN, W. R. WRAGG AND E. LUNT, *J. Chem. Soc.*, (1961) 2828.
[37] P. LATSCHINOW, ZH., 5 (1873) 50; *cf. Beilstein* XI, 192.
[38] A. CLAUS AND M. POSSELT, *J. Prakt. Chem.*, [2] 41 (1890) 33.
[39] V. MERZ AND G. ZETTER, *Ber.*, 12 (1879) 2035.

SUR UNE METHODE SIMPLIFIEE DE DOSAGE MICROBIOLOGIQUE DU MS-INOSITOL

V. N. PARANJAPYE, J. DESHUSSES ET TH. POSTERNAK

Laboratoires de Chimie biologique et organique spéciale, Université, Genève (Suisse)

(Reçu le 5 mars, 1964)

Le ms-inositol (myo-inositol) est un composant obligatoire de toute cellule vivante, qui présente un caractère vitaminique pour certains organismes. Diverses méthodes de dosage ont été proposées pour cette substance. Certaines sont de caractère chimique et reposent sur une oxydation periodique[1]; elles nécessitent préalablement une purification soigneuse du ms-inositol, *p.ex.* par des techniques chromatographiques. L'avantage des méthodes microbiologiques est, comme on sait, d'être par contre applicables à des mélanges complexes. Pour le dosage du ms-inositol, on a utilisé les microorganismes suivants: *Saccharomyces cerevisiae* Hansen (souche No. 1 de Toronto)[2]; *Saccharomyces cerevisiae* (souche Gebrüder Mayer)[3]; *Saccharomyces carlsbergensis* (ATCC 9080)[4]; *Kloeckera brevis*[5]; *Neurospora crassa* mutant inositolless[6]; *Schizosaccharomyces pombe.*

Dans notre laboratoire, nous avons utilisé pour des dosages de ms-inositol les trois premiers microorganismes mentionnés; les résultats étaient très erratiques et irréguliers ce qui est dû essentiellement au fait que ces levures sont douées d'un certain pouvoir de synthèse du ms-inositol; ce dernier joue ici simplement le rôle de facteur complémentaire.

La levure *Schizosaccharomyces pombe* est, par contre, complètement incapable de synthétiser le ms-inositol dont elle a un besoin absolu. L'emploi de ce microorganisme avait déjà été indiqué par NORTHAM ET NORRIS[7], et par NORRIS ET DARBRE[8]. Ces auteurs employaient des milieux de cultures complexes et difficiles à préparer; d'autre part, le domaine des concentrations utilisables en ms-inositol était relativement étroit. Nous avons élaboré un milieu de culture beaucoup plus simple qui, en outre, a l'avantage de comporter un domaine plus large de concentrations utilisables en ms-inositol. D'autre part, les résultats obtenus sont remarquablement reproductibles, ce qui n'est pas souvent le cas avec les méthodes microbiologiques.

PARTIE EXPÉRIMENTALE

Microorganisme

Le microorganisme employé était *Schizosaccharomyces pombe* souche Lindner var. liquefaciens Osterwalder (Centraalbureau voor Schimmelcultures, Yeast Division, Delft, Pays-Bas).

Conservation de la souche

Les cultures du microorganisme sont repiquées tous les 15 jours (ou tous les mois) sur un milieu contenant par litre d'eau du robinet: extrait de malt Difco 15 g; glucose 5 g; DL-asparagine 0.5 g; agar 25 g. On laisse 24 h à 30°; les cultures sont ensuite conservées à 0–5°.

Mesure de la croissance

La croissance du microorganisme sur milieu liquide a été estimée par turbidimétrie au moyen du colorimètre photoélectrique Klett-Summerson, en employant le filtre No. 54.

Préparation des inoculats

Les cellules sont transferrées du milieu solide agarisé à un milieu liquide intermédiaire contenant par litre d'eau du robinet:

Glucose	100 g	NaCl	0.5 g
Extrait de malt Difco	15 g	$CaCl_2 \cdot 2H_2O$	0.4 g
$(NH_4)_2SO_4$	0.6 g	$FeCl_3$ à 1%	0.5 ml
KH_2PO_4	1.5 g		

Le pH final est d'environ 5.

Après 18–24 h de croissance à 30°, les cellules sont recueillies par centrifugation dans des conditions de stérilité; elles sont lavées 3 fois à l'eau distillée stérile et suspendues dans l'eau distillée stérile. La suspension ainsi obtenue doit donner une lecture turbidimétrique de 50 unités Klett (filtre No. 54).

Milieu pour les dosages

Le milieu de base[9] employé pour les dosages contient par litre d'eau bidistillée:

Glucose	20 g	$CaCl_2 \cdot 2H_2O$	0.5 g
DL-Asparagine	4 g	Hydrolysat de caséine dépourvue de vitamines (Difco)	2 g
$(NH_4)_2SO_4$	4 g		
KH_2PO_4	4 g	Solution de vitamines	2 ml
$MgSO_4 \cdot 7H_2O$	1 g		

Le pH final est d'environ 5.

La solution de vitamines contient par litre d'eau bidistillée stérile:

Chlorhydrate de thiamine	1 g	Nicotinamide	1 g
Chlorhydrate de pyridoxine	1 g	Biotine	1 mg
Pantothénate de calcium	1 g		

Cette solution de vitamines est préparée tous les mois et conservée à −20°.

Technique des dosages

Le milieu de base est réparti à raison de 5 ml dans des erlenmeyers de 50 ml. On introduit, soit des quantités connues d'inositol, soit des volumes déterminés de la solution inconnue, éventuellement diluée, dans laquelle on désire effectuer le dosage. Un certain nombre d'erlenmeyers reçoivent, enfin, à la fois la solution inconnue et des quantités connues d'inositol. Le volume total est complété à 10 ml au moyen d'eau bidistillée. Après stérilisation à 115° durant 15 min, on inocule chaque erlenmeyer au moyen de 4 gouttes de l'inoculat. Après séjour à l'étuve à 30° durant 44 h, la croissance est mesurée par turbidimétrie.

Pour établir la courbe de référence, 10 groupes de 4 erlenmeyers sont additionnés respectivement des quantités suivantes d'inositol (en μg): 0, 0.5, 1, 1.5, 2, 3, 4, 5, 7.5 et 10.

Deux groupes au moins (de 4 erlenmeyers) sont additionnés chacun de volumes différents de la solution inconnue, éventuellement diluée. D'autres groupes d'erlenmeyers reçoivent non seulement la solution à doser, mais encore des quantités connues d'inositol. Pour une précision maximum, la quantité totale d'inositol présente ne doit pas dépasser 4 μg par erlenmeyer, soit 0.4 μg/ml.

RÉSULTATS ET DISCUSSION

Comme le montre la Fig. 1, il existe une relation linéaire entre la croissance exprimée en unités Klett et la quantité d'inositol, tant que celle-ci est comprise entre 0 et 4 μg par erlenmeyer (0–0.4 μg/ml). La courbe de référence est extrêmement reproductible et il serait par conséquent possible d'opérer des dosages à des concentrations plus élevées, avec une précision quelque peu diminuée.

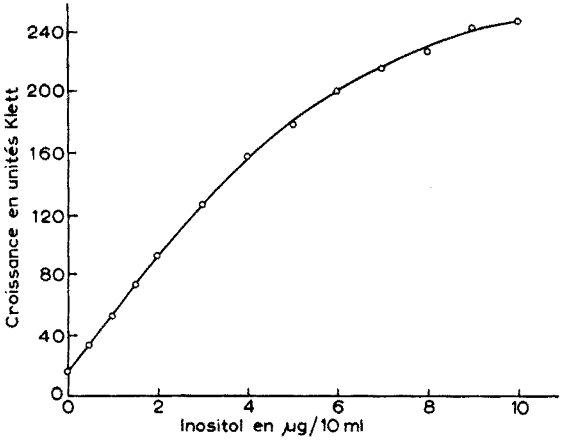


Fig. 1. Croissance de *Schizosaccharomyces pombe* en présence de concentrations en ms-inositol de 0 à 10 μg/10 ml.

La Fig. 2 indique que la croissance optimum est obtenue avec 10 μg d'inositol par erlenmeyer (1 μg/ml). Au-dessus de cette concentration, la courbe de croissance présente un palier; aucune inhibition ne se produit, même lorsque la concentration en inositol s'élève à 10 mg/ml.

Nous avons employé cette méthode avec succès pour doser l'inositol dans des hydrolysats acides de cellules de *Saccharomyces carlsbergensis* et de diverses fractions de phospholipides de *Schizosaccharomyces pombe*[10]. Les écarts observés dans 3 séries de mesures étaient de ±5%. Lorsque l'inositol était ajouté, en même temps que la solution à analyser, à raison de 0.5 μg, 1 μg et 2 μg, nous avons pu retrouver, par le dosage, de 98 à 110% de cet inositol additionnel (en moyenne 102%). Une telle précision peut être considérée comme très satisfaisante lorsqu'il s'agit d'une méthode microbiologique.

Le microorganisme employé possède, répétons-le, un besoin absolu en inositol comme facteur de croissance. C'est la raison pour laquelle la vitamine a un effet considérable et reproductible sur cette croissance. Un autre avantage de la technique est qu'il n'est pas nécessaire d'agiter les récipients durant l'incubation, ce qui simplifie notablement l'appareillage.

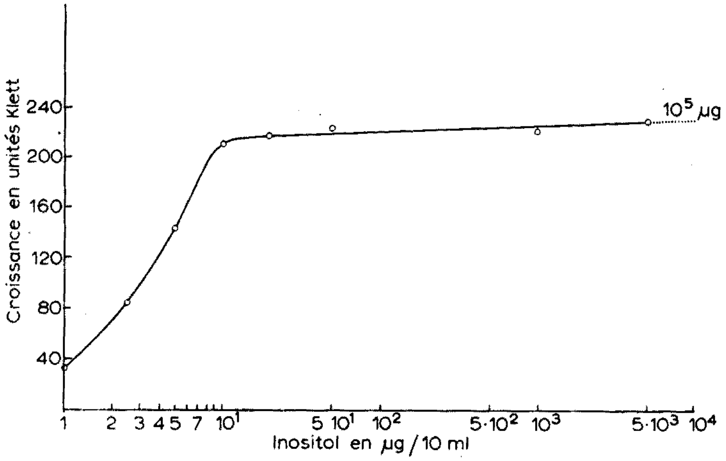


Fig. 2. Croissance de *Schizosaccharomyces pombe* en présence de concentrations en ms-inositol de 0 à 100 mg/10 ml.

RÉSUMÉ

Une méthode microbiologique simple de dosage de l'inositol, basée sur l'emploi de *Schizosaccharomyces pombe* Lindner, a été décrite. Les résultats obtenus sont très reproductibles et les techniques sont simples.

SUMMARY

A simplified microbiological assay for inositol involving the use of *Schizosaccharomyces pombe* Lindner is described. The results are very reproducible and the method is simple to operate.

ZUSAMMENFASSUNG

Beschreibung einer mikrobiologischen Methode zur Bestimmung von Inosit unter Verwendung von *Schizosaccharomyces pombe* Lindner. Die Methode ist einfach und die Ergebnisse sind gut reproduzierbar.

BIBLIOGRAPHIE

[1] P. Fleury et M. Joly, *J. Pharm. Chim.*, 26 (1937) 397; B. S. Platt et G. E. Glock, *Biochem. J.*, 37 (1943) 709; B. W. Agranoff, R. M. Bradley et R. O. Brady, *J. Biol. Chem.*, 233 (1958) 1077.
[2] D. W. Woolley, *J. Biol. Chem.*, 140 (1941) 453.
[3] R. J. Williams, A. K. Stout, H. K. Mitchell et J. R. McMahan, *Texas, Univ. Publ.*, 4137 (1941) 27.
[4] S. Sonne et H. Sobotka, *Arch. Biochem.*, 14 (1947) 93.
[5] P. R. Burkholder, J. McVeigh et D. Moyer, *J. Bacteriol.*, 48 (1944) 385.
[6] G. W. Beadle, *J. Biol. Chem.*, 156 (1944) 683.
[7] B. E. Northam et F. W. Norris, *J. Gen. Microbiol.*, 7 (1952) 245.
[8] F. W. Norris et A. Darbre, *Analyst*, 81 (1956) 394.
[9] D. Pennington, C. H. Sayer et J. Schmidt, *J. Bacteriol.*, 62 (1951) 677.
[10] Th. Posternak, W. H. Schopfer et J. Deshusses, *Arch. Sci. (Geneva)*, 13 (1960) 530.

Short Communications

Effects of sample cell position and dimensions on the fluorescence intensity–concentration curve for "perpendicular-type" fluorimeters

One annoying aspect of quantitative fluorimetry is the non-linear relationship between the measured quantity (fluorescence intensity) and the concentration of the fluorophore. Analytical use of the non-linear portion of this curve can be made provided that a suitable calibration curve is established, but in most cases curvature of the response curve, which is usually due to attenuation of the exciting beam, or so-called "inner filter effect"[1], becomes excessive and the upper concentration limit for analysis is dictated by inversion of the calibration curve. A method to correct data for this effect has been described by PARKER[1] who also pointed out that it would be preferable to avoid working in this region of the curve. Dilution of the test solution often remedies the difficulty, but is not a panacea; *e.g.* the fluorophore concentration may be so small that its emission cannot be detected after dilution; in some work disturbing a system at equilibrium by dilution may be undesirable.

Many authors have considered the factors affecting the measured fluorescence intensity for various arrangements of the components of a fluorimeter and including many complications, *e.g.*, self-absorption, quenching[2-4]. There are, however, two parameters whose effects on the fluorescence intensity–concentration curve have been largely ignored in discussions of "perpendicular" fluorimeters. These terms are often included, but as constants, probably because most instruments lack controls necessary to vary these parameters. The present discussion is concerned with the effects on the response curve of these two parameters: the linear distance within the sample cell over which the exciting radiation travels (*1*) before the fluorescence is "seen" by the detector and (*2*) before it leaves the region viewed by the detector. The exact value of each of these terms is usually fixed in a given instrument (*e.g.*, by baffles); moreover, their magnitudes are usually not known and are often inconvenient or impossible to measure accurately.

Theory

Although variations exist, most sample cells are designed and positioned to provide for measurement of the fluorescence emitted at right angles to the incident beam as shown in Fig. 1. Assuming this geometry and the absence of quenching and of self-absorption of the emitted radiation by the sample solution, it can be shown that[2,5]:

$$I_f = gsA\Phi I_0[\exp(-\varepsilon x_1 c) - \exp(-\varepsilon x_2 c)] \qquad (1)$$

where I_f is the fluorescence intensity read on the meter; s is the correction factor for variations in the detector response with wavelength; g is a geometric term determined usually by the slit-width setting of the fluorescence monochromator or by baffles: it accounts for the fact that only a portion of the radiation (emitted in all directions) is passed to the detector. A is the cross-sectional area of the sample cell irradiated with the exciting beam of intensity I_0; Φ is the energy yield of fluorescence; ε is the absorptivity index of the sample at the exciting wavelength (molar absorptivity/2.303 for a single absorbing species); c is the (molar) concentration of the fluorophore; and x_1 and x_2 are the distance parameters within the sample cell as defined above and shown in Fig. 1.

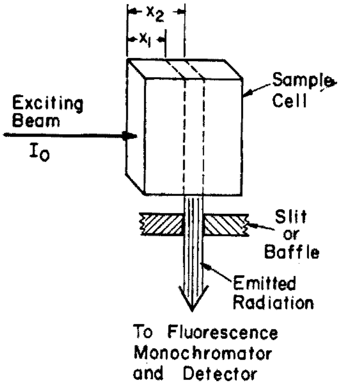


Fig. 1. Sample cell position and geometry for "perpendicular" fluorimeter.

For a given instrument, fluorescent system and operating conditions, equation (1) can be simplified by including all constant terms in K and representing the difference between the exponential terms by the function η:

$$I_t = K\eta \tag{2}$$

The behavior of the function $\eta(c)$ will depend on the values of x_1 and x_2 and will describe the shape of the fluorescence intensity–concentration curve under these conditions.

The curves in Fig. 2 show $\eta(c)$ calculated for several values and combinations of x_1 and x_2 assuming ε to be $2.0 \cdot 10^3$. It is seen that inversion of the response curve will occur at sufficiently high concentrations of the fluorophore whenever the value of x_1 exceeds zero — *i.e.* if the incident beam travels any distance within the sample cell before the excited fluorescence is passed to the detector. Comparison of curves A and B with E, C and D shows that an increase in x_1 will result in decreased sensitivity and in a smaller useful working range, *i.e.* reversal of the response curve occurs at lower concentrations. As shown by comparing curves A and B or D and C, for a fixed x_1 value, an increase in x_2 results in a decreased useful working range, but in increased sensitivity over that range of concentration.

Experimental

A Farrand Model 104243 Spectrofluorimeter was modified as described and used to measure the fluorescence intensity of quinine sulfate solutions in 0.10 M sulfuric acid at 450 mμ excited by radiation from a low-pressure mercury arc ("Mineralight") positioned directly above the sample compartment. The cover for the latter was replaced with one of identical size having a *ca.* 1 cm^2 hole to admit the exciting beam. Slits with a 5-mμ effective band width were used and the instrument was standardized with a 6.0 p.p.m. quinine sulfate solution. A quartz sample cell 10 × 20 × 50 mm deep was used and measurements were made with 2.0, 3.0, 6.0 and 7.0 ml of test solution in the cell. It is estimated that radiation emitted by the sample solution between depths of 8 mm and 28 mm would be passed to the detector. Data obtained with 2.0 ml of solution in the cell were multiplied by 4.7, which was the ratio of the detector reading observed when the cell contained 3.0 ml of 500 p.p.m. quinine sulfate to that observed when 2.0 ml of the same solution were present. The correction was used to compensate in part for the large change in the geometric factor (g) produced when the solution depth was changed over this range.

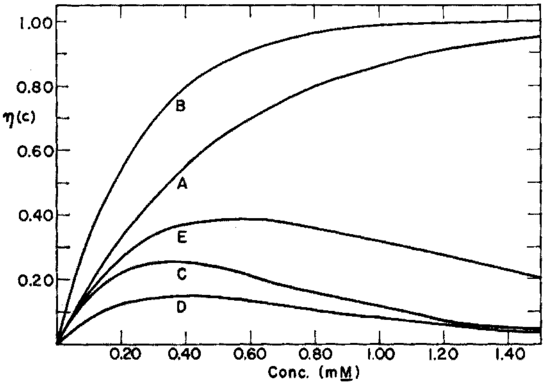


Fig. 2. Variation of $\eta(c)$ for several values of x_1 and x_2. $\varepsilon = 2.0 \cdot 10^3$.

Curve	x_1 *(cm)*	x_2 *(cm)*
A	0	1.00
B	0	2.00
C	1.00	2.00
D	1.00	1.50
E	0.50	1.50

Results and discussion

The effects predicted by eqns. (1) and (2) were confirmed for several values and combinations of the parameters as shown in Fig. 3. Because there is no advantage in theory to having the quantity x_1 other than zero, it is suggested that the entrance slit or baffle to the fluorescence monochromator should have one side fixed and the cell holder positioned to maintain x_1 as near to zero as possible without introducing errors due to physical imperfections or residual fluorescence in the sample cell wall material. The other side, which would determine x_2, should be adjustable and fitted with a calibrated dial so that one could reproduce accurately the optimum value of x_2 for the system and concentrations under investigation. This modification is not feasible for instruments lacking an entrance slit to the emission monochromator. Other alternatives which would permit some selection of the sensitivity and working range (*e.g.*, variability of the incident beam intensity or changing the cross-sectional area of irradiation) are usually not convenient to control, nor would reversal be eliminated. In some cases it may be advantageous to change the excitation wavelength to one which is less strongly absorbed by the sample solution. Because the absorptivity of the solution will be smaller, the effect is the same as decreasing x_1 and also (x_2-x_1), resulting in a greater useful working range of concentrations before reversal occurs, but in reduced sensitivity.

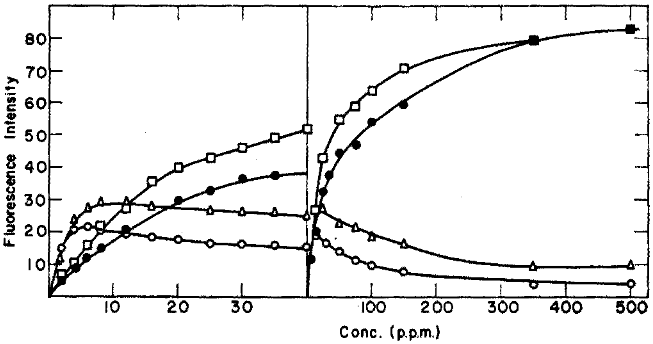


Fig. 3. Fluorescence intensity–concentration curves for quinine sulfate in 0.10 N H_2SO_4.

Curve	*ml Sample*
●	2.0
□	3.0
△	6.0
○	7.0

FLETCHER[6] has advocated and demonstrated the use of a vertical-axis transmission design for fluorimeters and has pointed out certain advantages of such a design. One of these is the possibility of selecting the depth of the sample solution in the cell, permitting measurements to be made on the more linear portions of the response curve where greatest sensitivity is obtained. This is equivalent to having x_1 equal to zero and x_2 variable and reproducible for that particular kind of instrument design.

Department of Chemistry,
University of Rhode Island,
Kingston, R. I. (U.S.A.)

W. E. OHNESORGE

[1] C. A. PARKER AND W. J. BARNES, *Analyst*, 82 (1957) 606.
[2] H. BRAUNSBERG AND S. B. OSBORN, *Anal. Chim. Acta*, 6 (1952) 84.
[3] R. G. MILKEY AND M. H. FLETCHER, *J. Am. Chem. Soc.*, 79 (1957) 5425.
[4] C. A. PARKER AND W. T. REES, *Analyst*, 87 (1962) 83.
[5] W. E. OHNESORGE AND L. B. ROGERS, *Spectrochim. Acta*, 15 (1959) 27.
[6] M. H. FLETCHER, *Anal. Chem.*, 35 (1963) 278, 288.

(Received April 13th, 1964)

Synthesis and spectral characteristics of 4,4′-dimethoxythiobenzophenone

The reaction of elemental sulfur with N-(4,4′-dimethoxybenzohydrilidene)benzylamine, $(CH_3OC_6H_4)_2C{=}NCH_2C_6H_5$, Schonberg's reagent, was reported by SCHONBERG AND URBAN in 1934[1]. This reaction was adapted to the determination of elemental sulfur by ORY, WARREN AND WILLIAMS[2], who showed that the reaction gave reproducible amounts of 4,4′-dimethoxythiobenzophenone. NEELY AND WILLIAMS[3] studied the infrared spectra of the reagent and reaction products and were able to assign most of the observed bands in Schonberg's reagent. Among the products of the reaction were identified hydrogen sulfide, benzonitrile, and 4,4′-dimethoxythiobenzophenone, with indications that other products were also being formed. Since that time, a fourth product, bis(*p*-methoxyphenyl)methylenimine, has been identified[4]. HUDDLESTON's study[5] and further work in this laboratory have shown that the basic reaction between Schonberg's reagent and sulfur is somewhat less straightforward than was first supposed by ORY. However, the determination may be standardized and carried out under controlled conditions to give satisfactory analytical results for sulfur. The highly colored thioketone is easily determined photometrically.

TABLE I

ANALYSES OF 4,4′-DIMETHOXYTHIOBENZOPHENONE

Sample	*C (%)*	*H (%)*	*O (%)*	*S (%)*	*m.p. (°)*
Present work[a]	69.53	5.48	12.33	12.20	116–117
	69.76	5.61	12.36	12.39	
GATTERMAN[6]	—	—	—	—	115
SCHONBERG[7]	70.19	6.03	—	12.13	114–115
LOSACH[8]	—	—	—	—	116
Theoretical	69.74	5.46	12.39	12.41	—

[a] Analyses done by Galbraith Laboratories, Knoxville, Tennessee.

Spectroscopically pure thioketone was required for its satisfactory characterization. The synthesis and purification procedures reported below proved to be particularly convenient because they minimized handling problems due to light sensitivity, air oxidation, and thermal instability of the product.

The purity of the thioketone described here seems the highest yet attained, and the compound analysis (Table I) is the most complete yet reported. The infrared spectrum shown in Fig. 1 is previously unreported. Of particular interest are two absorption bands which are newly assigned to carbon–sulfur bonding in the thioketone. This communication also corrects the assignment of the 773 cm^{-1} band, erroneously attributed by WILLIAMS[4] to N-H bending. The frequency so assigned should have been 750 cm^{-1} whereas 773 cm^{-1} is a methyl band. Extinction coefficients and absorption maxima in the visible range (Table II) for the thioketone are given for two new solvents and for another solvent where our results were not in agreement with the work of previous investigators.

The synthesis is similar to that of LOSACH AND GUILLOUZO[8] with improvements in yield attributable to the utilization of a single solvent at a lower temperature.

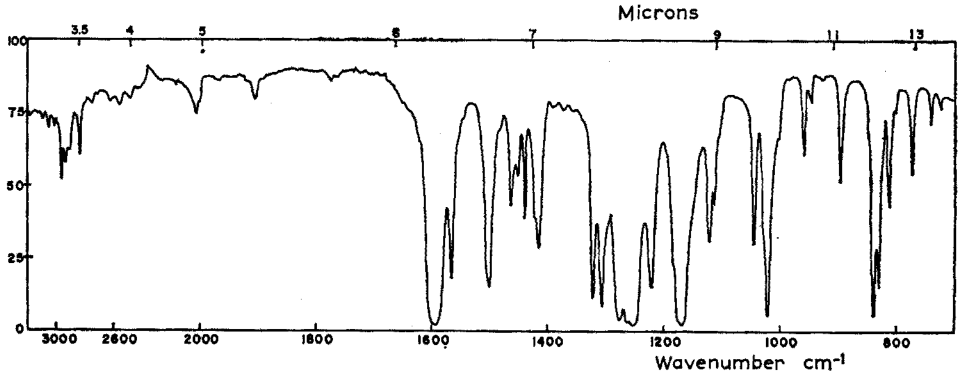


Fig. 1. Infrared spectrum of 4,4′-dimethoxythiobenzophenone (Beckman IR-7, with KBr disk). Comparison of the spectra of 4,4′-dimethoxythiobenzophenone (I), 4,4′-dimethoxybenzophenone (II), and bis(*p*-methoxyphenyl)-methylenimine (III) shows 3 bands in I which are not in II or III: 1221 cm^{-1}, 1045 cm^{-1}, and 740 cm^{-1}. The first 2 are strong bands, and the last is weak. Others[8,9] have reported the 1221 cm^{-1} band at 1224 and 1219 cm^{-1} and made the assignment to carbon–sulfur bonding. This study seems to verify that assignment and to indicate that the 1045 cm^{-1} and 740 cm^{-1} bands are also associated with carbon–sulfur bonding in aromatic thioketones.

TABLE II

λ_{max}(VISIBLE) AND MOLAR EXTINCTION COEFFICIENTS OF 4,4′-DIMETHOXYTHIOBENZOPHENONE IN SEVERAL SOLVENTS (WITH BECKMAN DB)[a]

Solvent	*E (Abs. mole^{-1}cm^{-1})*	λ_{max}	*Reference*
Carbon disulfide	266	593	Present work
Cyclohexane	315	590	Present work
n-Propanol	344	577	Present work
n-Propanol	314	568	10
Ethanol	277	570	11
Ethanol	278	577	12

[a] The Beckman DB spectrophotometer was calibrated using the 546 mercury line.

Experimental

The 4,4′-dimethoxythiobenzophenone was prepared by refluxing 14.35 g (5.75 · 10^{-2} moles) of 4,4′-dimethoxybenzophenone with excess phosphorus pentasulfide in 250 ml of reagent-grade carbon tetrachloride for 30 h. The solution was decanted, washed 3 times with 250-ml portions of saturated aqueous sodium carbonate followed by 3 250-ml distilled water washes, and dried over anhydrous sodium carbonate. The carbon tetrachloride solution was chromatographed through an activated alumina column previously washed with carbon tetrachloride. Unreacted ketone was retained while thioketone was eluted. Center cuts of the thioketone fraction from several chromatograms were collected under nitrogen and stored in the dark. The solvent was evaporated at reduced pressure, and 6.0 g (2.3 · 10^{-2} moles) of crystalline 4,4′-dimethoxythiobenzophenone was obtained and stored under nitrogen in an amber glass bottle. Yield through all operations was 40%.

The very strong 1643 cm^{-1} carbonyl band of the ketone was absent in the spectrum of the thioketone. The melting point of the product, determined in a sealed capillary under one atmosphere of nitrogen (30°), was 116–117°.

Department of Chemistry,
Louisiana State University,
Baton Rouge, La. (U.S.A.)

H. B. WILLIAMS
F. M. HILBURN*
K. YARBROUGH

1 A. SCHONBERG AND W. URBAN, *Ber.*, 67 (1934) 1999.
2 H. A. ORY, V. L. WARREN AND H. B. WILLIAMS, *Analyst*, 82 (1957) 189.
3 W. C. NEELY AND H. B. WILLIAMS, *Anal. Chim. Acta*, 24 (1961) 575.
4 H. B. WILLIAMS, P. E. KOENIG, G. HUDDLESTON, T. COUVILLON AND W. CASTILLE, *J. Org. Chem.*, 28 (1963) 463.
5 G. R. HUDDLESTON, *The Kinetics and Mechanism of the Reaction Between Sulfur and N-(4,4'-Dimethoxybenzohydrilidene)benzylamine*, Dissertation, Louisiana State University, 1960.
6 N. LOSACH AND G. GUILLOUZO, *Bull. Soc. Chim. France*, (1957) 1221.
7 L. GATTERMAN, *Ber.*, 28 (1895) 2869.
8 A. SCHONBERG, O. SCHUTZ AND S. NICKEL, *Ber.*, 61 (1928) 1375.
9 R. MECHE *et al.*, *Z. Naturforsch.*, 10b (1955) 367.
10 H. L. DONLE AND G. VOLKERT, *Z. Physik. Chem.*, *Abt. B*, 8 (1930) 60.
11 G. OSTER, L. CITAREL AND M. GOODMAN, *J. Am. Chem. Soc.*, 84 (1962) 703.
12 P. BROCKLEHUST AND A. BURAWAY, *Tetrahedron*, 10 (1960) 118.

(Received April 24th, 1964)

---

* National Science Foundation College Teacher Research Participant.

Anal. Chim. Acta, 31 (1964) 488–490

The direct polarographic determination of uranium(VI) in nitric acid media

Excellent polarographic waves for the uranium(VI) to (V) step can be obtained in strongly acidic media, such as sulfuric, hydrochloric and perchloric[1-3]. PROPST[4] has described conditions for the "in-line" determination of uranium(VI) in nitric acid and discussed the effect of tri-*n*-butyl phosphate (TBP) and iron(III) on the uranium wave. Generally, when uranium is determined in the presence of corrosion and fission products, uranium is first separated[5] before its polarographic determination in a non-aqueous medium. The present paper describes a rapid method for the direct polarographic determination of uranium in synthetic solutions. The supporting electrolyte is nitric acid saturated with a TBP–odorless kerosene mixture. Potential interferences and methods for their elimination are outlined.

Apparatus

A "Metrohm Polarecord E 216 R" was used to record the polarograms. A 25-ml "Metrohm" cell with 5 ground sockets and provided with a conventional dropping mercury cathode and a saturated calomel electrode (S.C.E.) was employed. The capillary had the following characteristics: $m = 2.2501$ mg/sec and $t = 3.11$ sec in 1.6 *N* nitric acid at an applied potential of 0.35 V *vs.* S.C.E.

Reagents

Standard uranium(VI) solutions (0.183 moles/l) were prepared by dissolving a weighed amount of Baker reagent-grade uranyl nitrate hexahydrate in 1 l of 1 *N* HNO_3. The solution was standardized gravimetrically as U_3O_8.

Supporting electrolyte: 245 ml of Baker reagent-grade nitric acid (68–70%, w/v) and 5 ml of 40% (v/v) TBP in kerosene were diluted with conductivity water to 1 l and shaken for 2 h. After 1 h the separated organic phase was rejected.

Ascorbic acid: E. Merck reagent-grade quality.

Procedure

In a 50-ml volumetric flask, mix 5–20 ml of the sample ($1\text{–}7 \cdot 10^{-4}$ *M* uranium(VI)), 20 ml of 4 *N* nitric acid saturated with TBP–odorless kerosene mixture and 0.5 g of ascorbic acid. Dilute to volume with conductivity water and record the polarogram after deaeration with nitrogen.

A calibration curve was employed for the determination of uranium present in the aliquot taken.

Results and discussion

Uranium(VI) was reduced in 1.6 *N* nitric acid to the pentavalent state, giving a well-defined polarographic wave, with $E_{\frac{1}{2}} = 0.17$ V *vs.* S.C.E. The diffusion current measured at -0.35 V *vs.* S.C.E. was proportional to the uranium(VI) concentration in the range 1 to $7 \cdot 10^{-4}$ *M*.

TBP is a capillary-active substance, being absorbed on the surface of the mercury drop[7]. Polarograms of 1.6 *N* nitric acid saturated with TBP–kerosene showed no reduction waves, but the decomposition potential of nitric acid was shifted by 320 mV to a more negative potential. In 1.6 *N* nitric acid saturated with TBP–kerosene, the diffusion current of uranium(VI) was reduced by 49%. This suppression was constant in the presence of an excess of TBP–kerosene. An excess over the amount required for saturation, was always added in order to allow for possible fluctuations in the TBP–kerosene content of the sample.

The behaviour of various ions and their effects on the polarographic wave of uranium(VI) were investigated. Ions which did not interfere at concentrations of at least tenfold that of the uranium were: NO_3^-, Nb(V), Cr(III), Cr(VI), Ni(II), Ru(IV), La(III), Ce(III), Sc, Nd, Sm, Eu and Zr. The interference of iron(III), nitrite, cerium-(IV) and tungsten(IV) in the concentration limits shown in Table I, could be eliminated by the addition of 0.5 g of ascorbic acid. Copper and lead in concentrations exceeding fivefold that of uranium interfered. Precipitation with N-benzoyl-N-phenylhydroxylamine prevented interference of molybdenum(VI) and vanadium(V); the solid reagent was added to an aliquot of the sample with stirring at 60° and, after deaeration the diffusion current was measured without filtration.

Five synthetic mixtures were analyzed by the method described. Their composition and the analytical results are given in Table II. The method was found to be simple, rapid and suitable for product control. Metal ions, such as copper and lead which interfere, are not liable to be present in process solutions.

TABLE I

BEHAVIOUR OF INTERFERING IONS IN THE POLAROGRAPHIC DETERMINATION OF URANIUM(VI)

($1.83 \cdot 10^{-4}$ *M* U in 1.6 *N* HNO_3 saturated with TBP–odorless kerosene)

Ion added	*Concentration (M)*	*Ion/U molar ratio*	*μA measured*[a]	
			Without ascorbic acid	*With 0.5 g ascorbic acid*
None	—	—	0.61	0.61
Cerium(IV)	$4.00 \cdot 10^{-5}$	0.22	0.49	0.61
	$2.00 \cdot 10^{-4}$	1.09	1.58	0.62
	$4.00 \cdot 10^{-3}$	21.86	30.40	0.61
	$8.00 \cdot 10^{-2}$	437.48	0-s[b]	0.62
	$1.00 \cdot 10^{-1}$	546.43	0-s	0.63
	$1.60 \cdot 10^{-1}$	874.96	0-s	0.84
Iron(III)	$0.90 \cdot 10^{-5}$	0.05	0.62	0.62
	$3.60 \cdot 10^{-5}$	0.20	0.60	0.61
	$1.79 \cdot 10^{-4}$	0.98	0.74	0.62
	$3.60 \cdot 10^{-4}$	1.97	1.29	0.61
	$7.16 \cdot 10^{-4}$	3.91	1.88	0.64
	$1.07 \cdot 10^{-3}$	5.87	1.96	0.71
Nitrite (as $NaNO_2$)	$2.10 \cdot 10^{-5}$	0.12	0.64	0.61
	$2.10 \cdot 10^{-4}$	1.15	0.69	0.61
	$2.10 \cdot 10^{-3}$	11.48	0.93	0.62
	$2.10 \cdot 10^{-2}$	114.75	2.96	0.63
Tungsten(VI)	$5.46 \cdot 10^{-5}$	0.30	0.29	0.61
	$2.18 \cdot 10^{-4}$	1.19	0.13	0.62
	$5.46 \cdot 10^{-4}$	2.98	0.09	0.59
	$1.09 \cdot 10^{-3}$	5.96	0.11	0.49
Copper(II)	$3.24 \cdot 10^{-5}$	0.18	0.46	0.41
Lead(II)	$1.41 \cdot 10^{-4}$	0.77	0.63	0.61
	$1.41 \cdot 10^{-3}$	7.70	6.32	6.19
Molybdenum(VI)	$2.10 \cdot 10^{-5}$	0.12	0.16	0.18
Vanadium(V)	$3.92 \cdot 10^{-5}$	0.21	0.36	0.34

[a] Diffusion current at −0.35 V *vs.* S.C.E.

[b] Off-scale.

TABLE II

ANALYSIS OF SYNTHETIC MIXTURES, SIMILAR IN COMPOSITION TO PLANT SOLUTIONS

U taken (mM/l)	*Components (mmole/l) in mixture with uranium*					*TBP–kerosene*	*U found (mM/l)*	*% Error*
	Nitrate as $NaNO_3$	*Nitrite as $NaNO_2$*	*Fe(III)*	*Ce(III)*	*W(VI)*			
0.183	0.600	0.023	0.179	0.200	0.054	0.740	0.176	−3.8
0.183	1.200	0.234	0.036	2.000	0.108	0.480	0.191	+4.3
0.183	9.600	0.468	0.716	0.800	0.027	0.430	0.185	+1.1
0.366	4.800	0.936	1.070	4.000	0.218	1.480	0.357	−3.3
0.549	2.400	1.304	0.360	8.000	0.162	1.215	0.556	+3.8

The authors wish to thank the management of the Israel Atomic Energy Commission, Dimona Research Establishment, for their kind permission to publish the present work.

Atomic Energy Commission, Hakirya, J. MASHALL
Tel-Aviv (Israel) J. KENDLER

1 W. E. HARRIS AND I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 67 (1945) 1484.
2 P. HERASYMENKO, *Chem. Listy*, 19 (1925) 172.
3 I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part II, Vol. 9, Interscience, 1959.
4 R. C. PROPST, *Report D.P.–572*, June, 1961.
5 D. J. FISHER AND P. F. THOMASON, *Anal. Chem.*, 28 (1956) 1285.
6 H. E. ZITTEL AND L. B. DUNLOP, *Anal. Chem.*, 34 (1962) 1757.
7 C. E. MICHELSON AND K. KOYAMA, *Report Hw–42637*, April, 1956.

(Received April 18th, 1964)

Anal. Chim. Acta, 31 (1964) 490–493

The spectrographic determination of strontium and barium in oxygen and carbon dioxide atmospheres

In the course of the development of a general spectrographic scheme for the analysis of carbonate sediments, it was found necessary to suppress CN emission which seriously interferes with the determination of trace elements such as strontium and barium. The most promising method of accomplishing this is to carry out the determinations in a nitrogen-free atmosphere and various methods have been proposed for surrounding the D.C. arc with controlled atmospheres[1,2], two of which[3,4] incorporate a modified form of the STALLWOOD air-jet[5]. In none of these studies have details been given of such factors as intensity and differences in reproducibility between the various atmospheres. It was therefore decided to investigate the effects of surrounding the D.C. arc with a number of single nitrogen-free gases. Attempts were made to surround the arc with carbon dioxide and argon using both the original and modified versions of the STALLWOOD air-jet,but these gases did not completely displace the air from the arc and the intensity of CN emission was therefore only slightly reduced. This is in agreement with earlier conclusions[3,6] about the behaviour of carbon dioxide. In order to investigate the effects of completely surrounding the arc, a fully enclosed arc chamber was therefore constructed which incorporated a modified STALLWOOD air-jet (Fig. 1).

The chamber which is constructed of brass and Sindanyo consists of 3 parts. The body of the chamber is provided with 3 windows, 2 of which (A and B) allow an image of the electrodes to be projected on to a screen so that their position and separation

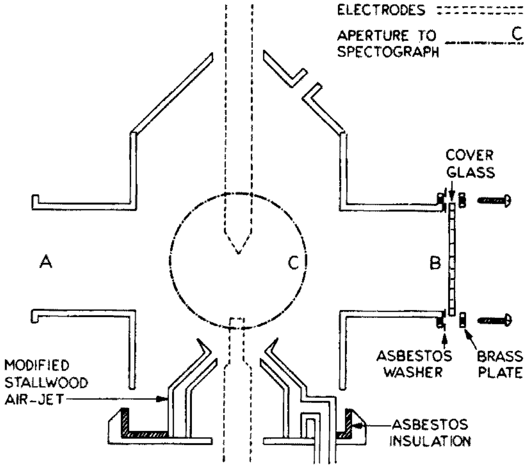


Fig. 1. The totally enclosed arc chamber.

can be controlled, and one, covered with a quartz disc (C), which allows the light from the arc to pass to the condensing mirror of the spectrograph. The top of the chamber has an opening to allow the hot gases to escape and is a truncated cone which fits loosely around the upper electrode. The modified STALLWOOD air-jet is mounted in a circle of Sindanyo in order to insulate it from the body of the chamber. The base is removable to enable the chamber to be cleaned.

Comparison of the spectra produced in oxygen and carbon dioxide

Strontium and barium were selected as test elements because they are of interest in carbonate geochemistry and because they lie in the general area of CN emission (the use of Sr 4077.714 Å is precluded if CN emission is not suppressed[7]). The effects of using oxygen and carbon dioxide in the arc chamber were investigated; the use of argon was not studied as this gas greatly prolonged the time necessary for complete volatilization of the sample. Details of the spectrographic conditions are given in Table I. In this paper attention is confined to the barium 4554.042 Å and the Sr 4077.714 Å lines. The effects of using carbon dioxide and oxygen may be discussed under three headings.

(*a*) *Suppression of CN emission.* CN emission was completely suppressed by the use of oxygen; traces of CN bands were found when carbon dioxide was used and probably resulted from the presence of small amounts of nitrogen in the gas. The approximate times for the complete volatilization of the sample were: in air, 3.5 min; in carbon dioxide, 2.5 min; and in oxygen, 45 sec. Owing to the short volatilization period in oxygen the continuum and therefore the plate background was less pronounced than in carbon dioxide, where the background was also increased by the formation of the C_2 band with a bandhead at 4737.1 Å. The line intensities, measured as element/internal standard ratios, were lower in oxygen than in carbon dioxide (see Fig. 2).

(*b*) *Effect on working curves.* In the log(intensity)–log(concentration) curve for the analysis of barium in air, the line intercepts the concentration axis at an angle of less than 45°. The working curves produced for barium and strontium in both oxygen and

TABLE I

DETAILS OF THE SPECTROGRAPHIC CONDITIONS

Spectrograph	Hilger large quartz spectrograph.
Slit width	25 μ.
Emulsion	Ilford N. 30 Ordinary plates, processed according to the maker's instructions.
Emulsion calibration	A rotating 7-step sector was placed between the condensing lens and the slit and a Joyce-Loebl recording microdensitometer was used for the measurement of spectral line intensities.
Electrodes	Electrodes were machined from 5.5 mm diam. carbon rods (Morgan Crucible Co.) to the following dimensions: *anode*, outer diam. 4 mm, crater internal diam. 2.5 mm, crater depth 7 mm; *cathode*, 5.5-mm carbon rod sharpened to a fine point.
Electrode gap	4 mm.
Current	5 A for 10 sec then to completion at 7 A.
Exposure	To completion.
Gas flow	CO_2 4 l/min; O_2 4 l/min (measured initially by means of a gas meter). Gas pressures were measured with a water manometer and were kept constant at 10 cm of water.
Artificial standard	This was used as a matrix material for all determinations and was prepared from the Johnson Matthey range of Specpure compounds to resemble the composition of an impure limestone. It had the following composition: SiO_2 42%, CaO 36%, Al_2O_3 15%, K_2CO_3 2.4%, total iron 2.5%, MgO 1.0%, TiO_2 0.7%, Na_2CO_3 0.4%.
Trace element lines	Strontium, 4077.714 Å; barium, 4554.042 Å; palladium, 3634.695 Å.
Preparation of samples	Palladium was used as internal standard and artificial standards containing a range of barium and strontium concentrations were mixed mechanically with a mixture of carbon and ammonium chloroplatinate, containing 0.1% palladium, in the proportion of one part of sample to two parts of C–Pd mixture. The samples were packed into the electrodes by hand.

carbon dioxide (Fig. 2) have slopes much closer to unity. Such effects were noted by STALLWOOD[5] and may result from the use of the air-jet rather than from a particular gas. However, STALLWOOD was concerned with extremely volatile elements and suppression of CN emission, which decreases the amount of blackening in this part of the photographic plate, probably affects the slope of the curves.

(*c*) *Reproducibility data.* Eight replicate analyses were made by arcing mixtures of barium and strontium in the synthetic base in carbon dioxide and oxygen atmospheres. The results are given in Table II. Replicate analyses for barium were also carried out in air, without the use of an air-jet, and gave a coefficient of variation of 23.4%.

The best comparison with the present work is provided in the data given by SHAW[8] for the analysis of barium in the diabase (WI). Arcing was carried out in air using a modified STALLWOOD air-jet and although the matrix and operating conditions were somewhat different from those used in the present work, the same barium and internal standard line were employed. It is therefore possible to make a general comparison between the precision of the spectrographic determination of barium in air (without the use of an air-jet) and in oxygen and carbon dioxide, with that in air using an air-jet. The coefficient of variation for the determination of barium calculated from SHAW[3] (Table V, Diabase W-1) is 18.2%. This lies between the value given in the present paper for the replicate analysis of barium using an air-jet in carbon dioxide or oxygen atmospheres and that found using air (without the use of an air-jet).

The reproducibility data indicate that under the conditions used both gases produce

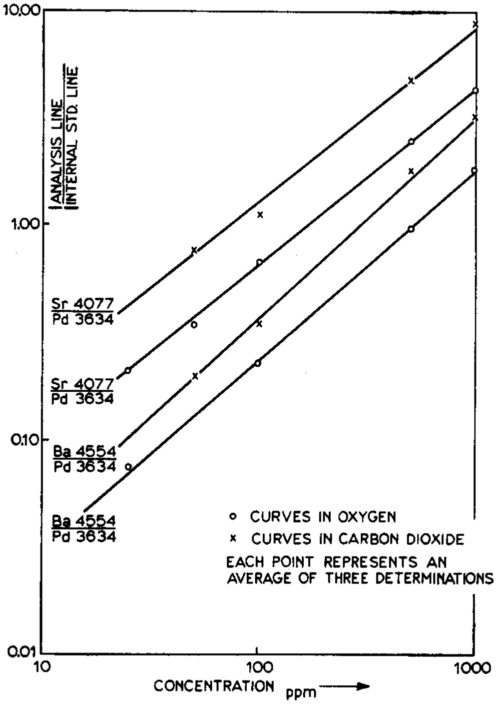


Fig. 2. Working curves for strontium and barium in oxygen and carbon dioxide.

TABLE II

REPRODUCIBILITY DATA FOR BARIUM AND STRONTIUM ANALYSES

1. Strontium 4077.714 Å	*p.p.m. Sr in* CO_2		*p.p.m. Sr in* O_2	
	64	66	61	62
	66	68	65	61
	65	61	63	64
	67	66	65	63
	Mean 66.5		Mean 63	
Coefficient of variation 3.28%			Coefficient of variation 2.54%	
2. Barium 4554.042 Å	*p.p.m. Ba in* CO_2		*p.p.m. Ba in* O_2	
	60	62	43	56
	48	58	48	45
	44	64	58	58
	62	56	53	57
	Mean 56.8		Mean 52.5	
Coefficient of variation 12.9%			Coefficient of variation 11.9%	

very similar coefficients of variation. However, oxygen has the advantage that it cuts down the arcing time and suppresses formation of the C_2 band system at 4737.1 Å. It is probable that the use of oxygen or carbon dioxide could be incorporated with advantage into a general spectrographic scheme for the analysis of carbonate or silicate rocks, particularly for those elements whose sensitive lines cannot be used owing to masking by CN emission.

Department of Oceanography,
The University,
Liverpool (Great Britain)

F. Wilson
R. Chester

[1] L. T. Steadman, *Phys. Rev.*, 38 (1943) 322.
[2] G. W. Marks and M. Gardner, *Rev. Sci. Instr.*, 18 (1947) 370.
[3] D. M. Shaw, O. Wickremasinghe and C. Yip, *Spectrochim. Acta*, 13 (1958) 197.
[4] C. D. Curtis, *Nature*, 96 (1962) 1087.
[5] B. J. Stallwood, *J. Opt. Soc. Am.*, 44 (1954) 171.
[6] D. M. Hirst and G. D. Nicholls, *J. Sediment. Petrol.*, 28 (1958) 461.
[7] L. H. Ahrens, *Spectrochemical Analysis*, Addison–Wesley, Cambridge, Mass., U.S.A.
[8] D. M. Shaw, *Can. Mineralogist*, 6 (1960) 467.

Received April 6th, 1964)

Anal. Chim. Acta, 31 (1964) 493–497

Book Reviews

Kazunobu Kodama, *Methods of Quantitative Inorganic Analysis*, Interscience Publishers–J. Wiley & Sons, Inc., London–New York, 1963, 507 pp., price £ 8.0.0.

The contents of this text are succinctly described in the sub-title: *An Encyclopedia of Gravimetric, Titrimetric and Colorimetric Methods.* As analytical encyclopedias go, this strikes one as a slightly unusual book from the moment one sees its format to the time when its contents have been appraised. Most books of this nature tend to run to several volumes and in a sense are self-defeating with respect to their objective. For chemical analysis in the classical vein is a unified field of closely knit disciplines resting on a common matrix of inorganic reactions which proceed virtually to completion. This sense of unity is preserved in this compact and closely integrated survey and time may well show that it will succeed in its object. This is a book that I would certainly recommend over the next few years to every graduate and undergraduate who wishes to pursue a career in inorganic analysis. Its coverage is genuinely encyclopedic.

The text is divided into three main sections. Part I (41 pp.) deals with general considerations, Part II (107 pp.) with organic reagents and Part III (327 pp.) with the determination of the elements. There are 63 chapters in all, each one a monograph on its own topic with its own references separately listed and numbered. Lastly, there is a comprehensive general index and a most useful organic reagent index. The text is published in a $7^1/_2 \times 10''$ format and a double column presentation is used together with a very effective interplay of small, large and bold typeface.

More than most, this is a true encyclopedia in the real sense of the word and as such I have nothing but praise for it. If criticism had to be made it might be that there is an overweighting in favour of gravimetry and titrimetry as opposed to colorimetry. Thus the introductory chapter on optical methods scarcely does much more than mention the names of various techniques. One might reasonably have expected the author to discuss the Lambert–Beer law and define the ε term used to compare sensitivities subsequently as basic minimum background data. However, be that as it may, this is a really worthwhile text and the author has undoubtedly provided a most valuable addition to the range of genuinely indispensable reference books on analytical chemistry.

T. S. WEST (London)

Anal. Chim. Acta, 31 (1964) 497–498

L. E. ORGEL, *Chimie des Métaux de Transition–Théorie du Champ des Ligandes*, Traduit de *An Introduction to Transition-Metal Chemistry–Ligand-Field Theory* par C. TROYANOWSKY, Dunod, Paris, 1964, 222 pp., prix 19 F.

Ce petit livre de la Collection "Monographies Dunod" s'adresse aux étudiants en chimie minérale, et à ceux qu'intéressent des données générales sur ce domaine assez neuf de la théorie de la valence et de la théorie électronique des complexes. L'auteur a choisi pour sujet, dans le but d'illustrer cette théorie, la chimie des éléments allant du titane au zinc, et des éléments correspondants des periodes supérieures. Ces éléments forment, en effet, un groupe dont l'intérêt réside surtout dans l'existence de plusieurs degrés d'oxydation et de nombreux complexes avec des "ligandes" variés.

Après avoir rappelé l'essentiel de la théorie des orbitales, l'auteur décrit d'une façon détaillée la stéréochimie des complexes des métaux de transition, mettant en évidence, notamment, les phénomènes de coordinence et le rôle de facteurs électroniques, pour déterminer ceux-ci, ainsi que l'importance des rayons ioniques. Il discute également des spectres et diagrammes des niveaux d'énergie, de la vitesse et des mécanismes de réaction, enfin de la distinction entre liaison covalente et liaison ionique. Les divers types de complexes avec les valeurs inférieures (carbonyle, nitrosyle, arsines, phosphines, phénanthroline, hydrocarbures insaturés, etc.) et avec les valences supérieures des métaux considérés (fluorure, oxyde), sont pour terminer décrits et justifiés sous cet aspect de la structure.

En un volume restreint, l'auteur donne ainsi de la théorie dite "du champ des ligandes" une description succincte mais claire, en évitant les discussions mathématiques justificatives mais qui surchargeraient l'exposé. Si, comme l'en prévient lui-même l'auteur, le chimiste théoricien n'y trouvera pas son compte, du moins le chimiste plus classique et en particulier l'analyste y pourront puiser des notions extrêmement utiles à la compréhension des phénomènes réels qu'ils observent avec les complexes en solution.

B. TREMILLON (Paris)

Anal. Chim. Acta, 31 (1964) 498

Methods of Biochemical Analysis, Vol. 11, Edited by D. GLICK, Interscience–Wiley, New York, 1963. vi + 442 pp. Price 110/—.

A science cannot progress more rapidly than its necessary tools permit. In no case has this generalization been more applicable than to the tremendous strides forward which biochemistry has made during the last two decades or so. Biochemists have taken full advantage of the remarkable advances which have taken place both in the development of new experimental techniques and in the refinement of older methods. The working biochemist must now of necessity be familiar with a range of instruments and experimental methods which, not long ago, would have seemed impossibly wide. It is for this reason that this series of annual volumes has been invaluable and that this, the eleventh volume, will be assured of a welcome in biochemical laboratories of all kinds. As in previous volumes the range of methods considered is broad and will be of immediate interest to those working in the fields of steroid metabolism, enzymology, mineral metabolism and proteins and amino acids, while many others will find that the applicability of the techniques discussed can be extended to assist in their problems. It is not reasonable in reviewing such a volume to single out individual articles for individual mention. A brief account of all the chapters will therefore be given.

J. B. WILLIS deals with the analysis of biological materials by atomic absorption spectroscopy, discussing theory, instrumentation and the application of the technique to the determination of 19 metals. In a lengthy chapter on the separation and determination of steroids by gas chromatography, E. C. HORNING, W. J. A. VANDEN HEUVEL AND B. G. GREECH give a most useful account of the fundamental principles upon which gas chromatography is based, including definitions of terms in common use together with details of the essential features of the packed column technique, *e.g.* detection systems, supports and coatings, liquid phases, and of methods of separation, *e.g.* choice of phase and derivatives. In the final sections the separation of various types of steroid, the identification of steroids and preparative separations are dealt with. I. E. BUSH contributes a chapter on advances in direct scanning of paper chromatograms for quantitative estimation, considering at length the chemical, optical and instrumental requirements of such procedures with particular reference to paper chromatography techniques used in the author's laboratory and to an automatic scanner which he has developed. Specific procedures for reducing steroids, 17-ketosteroids, Δ^4-3-ketosteroids, dinitrophenyl derivatives and amino acids are described. M. K. SCHWARTZ AND O. BODANSKY review automated methods for determination of enzymic activity, including various recording instruments and instruments in which the preparation of reaction mixtures is also automated, *e.g.* Robot Chemist, Astra Enzyme Assayer, Auto-Analyser. Computer techniques for calculation of results are also considered. The estimation of magnitudes of alternative metabolic pathways is considered by I. J. KOPIN. In this article a theoretical kinetic section is followed by a consideration of its application to the metabolism of adrenaline and noradrenaline. F. L. CRANE AND R. A. DILLEY deal with the determination of coenzyme Q (ubiquinone), giving an account of its distribution, extraction, purification and measurement by specific assay methods. The paper chromatography of the coenzyme and related terpenoid quinones is described. Biological assay methods and the determination of ubichromanol are also considered. R. P. DAVIS contributes a chapter on the measurement of carbonic anhydrase activity, describing the preparation of the enzyme by salt fractionation and column chromatography and its determination by manometric, indicator, spectrophotometric, electrometric, rapid flow and histochemical methods. In the last article, O. H. MÜLLER discusses polarographic analysis of proteins, amino acids and other compounds by means of the Brdička reaction, the catalytic reaction at a dropping mercury electrode effected by some amino acids, polypeptides and proteins dissolved in a cobalt-containing buffer. The literature on this subject is extensive and widely distributed so that this concise review is of particular value. The author deals with the essentials of the reaction and the "weaknesses and uncertainties" in present knowledge, as well as with possible new uses and the rationalisation of methods of presenting results. It will be clear from this summary of the contents of this volume that it fully maintains the standard set by previous volumes in the series.

H. G. BRAY (Birmingham)

Anal. Chim. Acta, 31 (1964) 499–500

G. A. RECHNITZ, *Controlled-Potential Analysis*, International Series of Monographs on Analytical Chemistry, Vol. 13, Pergamon Press, Oxford–London–New York–Paris, 1963, 85 pp., price 35/—.

"In this monograph", the author claims, "an effort has been made to provide sufficient information about the theoretical background, instrumental considerations, and experimental techniques of controlled-potential coulometry so as to enable the practicing analytical chemist to make use of this method for his own particular requirements". If instead of "to make use of", he had said, "to decide whether it were worth looking further into", then the effort could be acclaimed as reasonably successful. Certainly the bibliography is good and the coverage extends well into 1962. "While this modest monograph", continues the author, "is not intended in any way as a textbook it is hoped that it may serve to stimulate some interest in this interesting and useful technique". In fact, the work is in the nature of an extended and rather individualistic review of basic considerations, the meat of which can be extracted in half-an-hour. Theory is treated in 15 pages, apparatus and techniques in 22 pages, and the remaining 30 pages of text pass in review the determination of the inorganic elements. What is given is sound and useful, and the sins are mostly of omission, which cannot be pressed in view of the author's disclaimer, but which tend to emphasise the cursory and superficial treatment in places and may leave unfortunate lacunae in the reader's grasp of the subject. This is perhaps most noticeable in the section on apparatus and technique. The intriguing and tantalising mentions of kinetic and mechanism studies could profitably have been considerably extended, or else reduced to a passing reference; or is this justification of the author's claim to stimulate interest? There are evidences of hasty preparation—an affliction of modern textbooks—which are frequently irritating, among them the very frequent, inconsistent and annoying use of CL as the symbol for chlorine in the formulation of its compounds throughout the final section. If the purpose of this book be that he who runs may read, then the runner will profit by his reading in measure with his haste.

E. BISHOP (Exeter)

Anal. Chim. Acta, 31 (1964) 500

WHAT'S NEW FROM B.D.H?

ARSENAZO III
A reagent for thorium, uranium, and zirconium

The reagent forms stable complexes with a number of elements but is reported[1] to be most selective for thorium[2], uranium[3], and zirconium[4]. These can be estimated directly after dissolving the sample and selecting the appropriate conditions; the absorbance of the arsenazo III complexes is measured spectrophotometrically.

1. Savvin, S.B., *Talanta*, 1961, **8**, 673-85
2. Nemodruk, A. A. and Kochetkova, N. E., *C.A.*, 1962, **57**, 11855h
3. Luk'yanov, V. F., Savvin, S. B. and Nikol'skaya, I. V., *C.A.*, 1961, **55**, 8174e
4. Goryushina, V. G. and Romanova, E. V., *C.A.*, 1961, **55**, 10210g

---

STYRENE OXIDE

A very reactive and versatile intermediate, readily forming polymers and copolymers. With Grignard reagent 1:2- or 2:2-diphenyl-ethanol is produced[1]. The coloured reaction products from styrene oxide and pyridine or quinoline derivatives provide a method of colorimetric assay for this class of compound[2].

1. Karasch, M. S. and Clapp, M., *J. Org. Chem.*, 1938, **3**, 355
2. Roth, H. J. and Schrimpf, H. O., *Arch. Pharm.*, 1960, **293**, 22-8

SILVER DIETHYL-DITHIOCARBAMATE
A reagent for arsenic

A sensitive colorimetric test for arsenic as arsine depends on the measurement of the red colour formed in a 0.5% solution of silver diethyl-dithiocarbamate in pyridine[1]; the solution is stable for many months. The method has been successfully employed for determining arsenic in technical iron, in germanium dioxide, and in petroleum stocks and catalysts. Parts per billion of As in naphthas may also be determined[2].

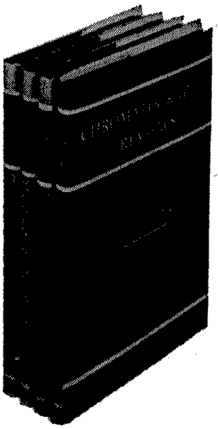
1. Vasak, V. and Sedivec, V., *Chem. Listy*, 1952, **46**, 341-4
2. Powers, C. W., *et al.*, *Analyt. Chem.*, 1959, **31**, 1589-93

B.D.H. LABORATORY CHEMICALS

For academic, analytical and research purposes B.D.H. supply nearly 7,000 organic and inorganic laboratory reagents and biochemical materials of a universally recognised standard of purity which are in everyday use in the foremost laboratories of more than a hundred countries throughout the world.
The B.D.H. Laboratory Chemicals Division gladly gives every assistance in the provision of supplies of B.D.H. chemicals through the most convenient channels. If your own laboratory has no B.D.H. catalogue or does not receive B.D.H. technical literature please let us know.

BDH
THE BRITISH DRUG HOUSES LTD.
B.D.H. LABORATORY CHEMICALS DIVISION POOLE, ENGLAND.

G10c



CHROMATOGRAPHIC REVIEWS

Edited by **M. LEDERER**, Istituto di Chimica Generale ed Inorganica, Rome (Italy)

Presenting an annual account of each year's most significant developments this series has rapidly established itself as the leading guide to current techniques and developments within a dynamic new field of scientific activity.

VOLUME 6 (1963)
Contents: 1. Commercial equipment for gas chromatography (G. S. Learmonth, Birmingham). 2. Centrifugal chromatography (Z. Deyl, J. Rosmus and M. Pavlíček, Prague). 3. Chromatography of free nucleotides (J. J. Saukkonen, Helsinki) with an Addendum: Applications of chromatographic techniques for the study of free nucleotides (J. J. Saukkonen and P. Virkola, Helsinki). 4. Paper chromatography of iodoamino acids and related compounds (L. G. Plaskett, Edinburgh). 5. Chromatographic techniques for pesticide residue analysis (G. Zweig, Davis, Calif.). 6. Liquid ion exchangers: separations on inert supports impregnated with liquid ion exchangers (E. Cerrai, Segrate, Milan). 7. Polymeric coordination compounds. The synthesis and applications of selective ion-exchangers and polymeric chelate compounds (G. Nickless and G. R. Marshall, Bristol). 8. Application of paper ionophoresis and electrochromatography to the study of metal complexes in solution (E. Blasius and W. Preetz, Berlin-Charlottenburg).

viii + 220 pages 32 tables 100 illus. 1085 lit.refs. Dfl. 35.- 70s. $12.75

Other volumes already published in the series:

VOLUME 1 (1958) "...an invaluable reference book" The Analyst
ix + 276 pages 114 tables 64 illus. 952 lit.refs. Dfl. 24.- 48s. $8.75

VOLUME 2 (1959) "...a must for all research libraries" Indian Journal of Scientific Research
viii + 195 pages 29 tables 49 illus. 1177 lit.refs. Dfl. 24.- 48s. $9.00

VOLUME 3 (1960)
viii + 187 pages 32 tables 71 illus. 986 lit.refs. Dfl. 25.- 50s. $10.25

VOLUME 4 (1961) "...should be read by all those with an active interest in physical methods of separation" Nature
viii + 184 pages 39 tables 41 illus. 620 lit.refs. Dfl. 25.- 50s. $9.50

VOLUME 5 (1962) "...extremely valuable and indispensable" Journal of the Indian Medical Profession
ix + 244 pages 51 tables 35 illus. 1145 lit.refs. Dfl. 30.- 60s. $11.00

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

New from Elsevier

COMPREHENSIVE ANALYTICAL CHEMISTRY

VOLUME IIA

Edited by

CECIL L. WILSON, Professor of Inorganic and Analytical Chemistry, University of Belfast, Northern Ireland

and

DAVID W. WILSON, Head of the Chemistry Department, Sir John Cass College, London

All types of analytical determination are being covered in the series COMPREHENSIVE ANALYTICAL CHEMISTRY, which will comprise five volumes, some consisting of several parts. On completion, the series will provide a working manual ideally suited both to the analytical chemist and the research worker regularly encountering analytical problems in his everyday work.

CONTENTS: 1. Introduction. 2. Electrodeposition. 3. Potentiometric titrations. 4. Conductometric titrations. 5. High-frequency conductometric (impedimetric) titrations. Subject Index.

xvi + 268 pages 18 tables 80 illus. 875 lit.refs. 1964
Subscription price: 50s. Non-subscription price: 60s.

TITRATIONS IN NON-AQUEOUS SOLVENTS

by

J. KUCHARSKÝ, Pharmaceutical and Biochemical Research Institute, Prague

and

L. ŠAFAŘÍK, State Institute for Drug Analysis, Prague

A completely revised translation of the 1961 Czech Edition

From reviews of the Czech Edition:
"... recommended as a good handbook for laboratory workers"
Chemicky prumysl
"We recommend the book to all chemists working in organic analysis"
Farmeceutski glasnik
"There remains the wish that this Czechoslovak book be published in a language well known in the world" Fresenius Zeitschrift für analytische Chemie
"... very important for every analyst wishing to be informed of the present state of an outstanding sphere of analytical chemistry" Pharmaceutisch Weekblad

CONTENTS: 1. Acid - base theories. 2. Solvents. 3. Indication of the end-point. 4. Titrants and primary standards. 5. Factors influencing the course of titration. 6. The methodology of titrations. 7. Neutralization titrations. 8. Oxidation - reduction titrations. 9. Determination of equivalents of compounds. Subject Index with synonyms.

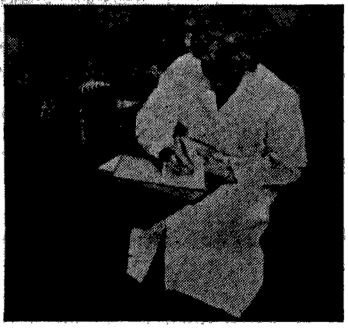
x + 260 pages 33 tables 29 illus. 462 lit.refs. 1964 70s.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

Incidental information

No. 17

Items of interest from our laboratory notebooks



9-(4-Dimethylaminophenyl)-2,3,7-trihydroxy-6-fluorone

A reagent for the spectrophotometric determination of **Ta** in the presence of **Zr, Nb** or **Ti.** (see V. A. Nazarenko and M. B. Shustova, *Zavodskaya Lab.* **2B,** 1283 (1957); C.A. **53,** 13874c (1959)). CODE 3862·3. Price 1g 9/9, 5g 40/-.

1,3-Diphenylpropan-1,3-dione (Dibenzoylmethane)

A reagent for the spectrophotometric determination of **U.** A procedure that includes ion-exchange separation from **Th** is described by H. J. Seim *et al. Anal. Chem.* 31, 957 (1959). CODE 4004·45. Price 5g 7/6, 10g 13/6.

4-(2-Pyridylazo)-resorcinol, sodium salt (PAR)

An extremely sensitive reagent for the colorimetric determination of **Co, Pb** and **U.** (see F. H. Pollard *et al. Anal. Chim. Acta* **20,** 26 (1959)). CODE 7275·5. Price 1g 6/-, 5g 22/9, 10g 44/-.

***o*-(Hydroxymercuri)-benzoic acid**

A titrimetric reagent for S^{2-}, **thiourea, xanthates, mercaptans** and many other organic sulphur compounds. (see M. Wronski *Analyst* **83,** 314 (1958)). CODE 4691. Price 1g, 12/6, 5g 52/6.

Phenyl 2-pyridyl-ketoxime

A colorimetric reagent for the determination of iron in strong alkalis and of **"oxidised" iron** in the presence of metallic iron. (see F. Trusell and H. Diehl *Anal. Chem.* **31,** 1978 (1959)). CODE 6711. Price 1g 30/-, 5g 135/-.

THESE PRODUCTS OF OUR OWN LABORATORIES CAN ALL BE SUPPLIED FROM STOCK

H & W

CHEMICALS

for research, analysis and industry

HOPKIN & WILLIAMS LIMITED, CHADWELL HEATH, ESSEX, ENGLAND

Branches: London, Manchester, Birmingham, Glasgow. *Agents throughout U.K. and all over the world*

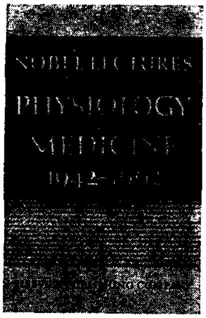
Member of the Derbyshire Stone Group. TAS/HW.20

Vol. **31**, No. 5 ANALYTICA CHIMICA ACTA NOVEMBER 1964

CONTENTS

Short Communications

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH



NOBEL PRIZE LECTURES

PHYSIOLOGY OR MEDICINE

CHEMISTRY

PHYSICS

each category to be contained in three volumes

1901–1921/1922–1941/1942–1962

In the world of science, the history of research and progress in the last sixty years is largely a history of the accomplishments of the Nobel Prize winners. Annually these achievements are placed in perspective at the Nobel Prize ceremonies held each December in Stockholm. Published for the Nobel Foundation, the collected Nobel Lectures are being issued, for the first time in English, by Elsevier. The lectures have been arranged in chronological order according to subject, beginning in 1901 and continuing through 1962. Each lecture is preceded by the presentation address to the prizewinner and followed by his or her biography. Initially, the Nobel Prize Lectures in CHEMISTRY, in PHYSICS, and in PHYSIOLOGY or MEDICINE will be issued, each in three volumes (not separately available), to be completed in about one year.

now published

NOBEL LECTURES CHEMISTRY 1942–1962

Alder – Calvin – Diels – Giauque – Hahn – Hevesy – Heyrovsky – Hinshelwood – Kendrew – Libby – McMillan – Martin – Northrop – Pauling – Perutz – Robinson – Sanger – Seaborg – Semenov – Stanley – Staudinger – Sumner – Synge – Tiselius – Todd – Vigneaud – Virtanen

xiv + 712 pages, 41 tables, 228 illustrations, 481 lit. references, 1964
price per set of three volumes: £ 24.0.0 or Dfl. 240,—

NOBEL LECTURES PHYSICS 1942–1962

Appleton – Bardeen – Blackett – Bloch – Born – Bothe – Brattain – Bridgman – Cerenkov – Chamberlain – Cockcroft – Frank – Glaser – Hofstadter – Kusch – Lamb – Landau – Lee – Mössbauer – Pauli – Powell – Purcell – Rabi – Segrè – Shockley – Stern – Tamm – Walton – Yang – Yukawa – Zernike

xiii + 621 pages, 183 illustrations, 376 lit. references, 1964
price per set of three volumes: £ 24.0.0 or Dfl. 240,—

NOBEL LECTURES PHYSIOLOGY OR MEDICINE 1942–1962

Beadle – Békésy – Bovet – Burnet – Chain – Cori, C. F. – Cori, G. T. – Cournand – Crick – Dam – Doisy – Enders – Erlanger – Fleming – Florey – Forsmann – Gasser – Hench – Hess – Houssay – Kendall – Kornberg – Krebs – Lederberg – Lipmann – Medawar – Moniz – Müller – Muller – Ochoa – Reichstein – Richards – Robbins – Tatum – Theiler – Theorell – Weller – Wilkins – Waksman – Watson

xiv + 839 pages, 33 tables, 200 illustrations, 844 lit. references, 1964
price per set of three volumes: £ 24.0.0 or Dfl. 240,—

EPC

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

272E

QH1 S7a
16 on